2019

JEE ADVANCED

Comprehensive Chemistry

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Comprehensive Chemistry—JEE Advanced

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A Word to the Reader

Comprehensive Chemistry JEE Advanced *is based on the prescribed syllabus.*

Divided into 34 chapters that covers the entire gamut of the subject (Physical Chemistry, Inorganic Chemistry & Organic Chemistry), each chapter begins with a revisit of the important list of definitions, formulae, theorems, etc.

This is followed by MCQs, Linked-Comprehension Type, Assertion-Reason and Matrix-Match type questions.

All questions are fully solved and there is adequate coverage of more difficult concepts.

Some key features

- IUPAC recommendations and SI units used throughout.
- Straight-Objective-type questions are enlarged and classified with their solutions.

What's special?

- Over 3000 MCQs with one correct choice and completely solved
- Around 800 MCQs with more than one correct choice and fully solved
- More than 170 Linked comprehension type questions
- About 370 Assertion- Reason type questions & over 120 matrix-match questions
- Two model test papers with solutions
- JEE Advanced chemistry papers of 2012, 2013, 2014 and 2015 given with complete solutions.

Tips for studying Chemistry

The three branches of Chemistry, viz., Physical, Inorganic and Organic are equally important. Physical Chemistry is less diverse compared to Organic and Inorganic. The applications to different problems in this are also straightforward.

Given below are some important topics of Physical, Organic and Inorganic that require special attention:

Physical:

- Bohr's theory of atomic structure, quantum numbers and orbitals.
- MO approach to diatomic molecules, concepts of hybridization/VSEPR theory.
- Van der Waals equation of state and its application to the behaviour of real gases.
- Crystal systems, packing of atoms, ionic solids, density of crystals and imperfection
- Colligative properties of non-electrolytic and electrolytic solutions.
- Electrolysis, conductance and galvanic cells.
- Rate laws, effect of catalyst and temperature on the rate of reaction.
- pH of salt solutions and solubility product.
- Le-Chatelier principle, relation between K_p and K_c.
- Thermochemical calculations and criterion of spontaneity.
- Radioactive decay.

Organic and Inorganic

- Boron and its compounds.
- Silicates and silicones.

- Oxoacids of P, S and halogens.
- Interhalogens and compounds of noble gases.
- Transition elements, coordination compounds and lanthanides.
- Important compounds such as H_2O_2, $NaHCO_3$, Na_2CO_3, $KMnO_4$ and K_2CrO_7.
- Quantitive analysis of salts.
- Isomerism including optical isomerism.
- Inductance and resonance effects on acidity and basicity of acids and bases.
- Factors affecting S_N1 and S_N2 reactions.
- Reactions involving rearrangement.
- Bromination and hydrogenation of cis- and trans-alkenes, debromination of dibromobutane.
- Characteristic reaction of aldehede, ketones and carboxylic acids derivatives.
- Reactions with Grignard reagent and those of diazonium salt.
- Carbohydrates and polymers.
- Quantitative analysis of organic compounds.

All the above topics are adequately covered in this book, supported by plenty of practice problems.

New Feature

An interactive CD of 10 full length Mock Papers with Answer Key and Complete Solutions.

We wish the aspirants all the best in their endeavours.

THE PUBLISHERS

Syllabus

Physical Chemistry

General topics: Concept of atoms and molecules; Dalton's atomic theory; Mole concept; Chemical formulae; Balanced chemical equations; Calculations (based on mole concept) involving common oxidation-reduction, neutralisation, and displacement reactions; Concentration in terms of mole fraction, molarity, molality and normality.

Gaseous and liquid states: Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waals equation; Kinetic theory of gases; Average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases.

Atomic structure and chemical bonding: Bohr model, spectrum of hydrogen atom, quantum numbers; Wave-particle duality, de Broglie hypothesis; Uncertainty principle; Qualitative quantum mechanical picture of hydrogen atom, shapes of s, p and d orbitals; Electronic configurations of elements (up to atomic number 36); Aufbau principle; Pauli's exclusion principle and Hund's rule; Orbital overlap and covalent bond; Hybridisation (involving s, p and d orbitals only); Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

Energetics: First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity. Chemical equilibrium: Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of ΔG and ΔG^o in chemical equilibrium; Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts. Electrochemistry: Electrochemical cells and cell reactions; Standard electrode potentials; Nernst equation and its relation to ΔG; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's law; Concentration cells.

Chemical kinetics: Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation).

Solid state: Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c, α, β, γ), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects.

Solutions: Raoult's law; Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point.

Surface chemistry: Elementary concepts of adsorption (excluding adsorption isotherms); Colloids: types, methods of preparation and general properties; Elementary ideas of emulsions, surfactants and micelles (only definitions and examples).

Nuclear chemistry: Radioactivity: isotopes and isobars; Properties of α, β and γ rays; Kinetics of radioactive decay (decay series excluded), carbon dating; Stability of nuclei with respect to proton-neutron ratio; Brief discussion on fission and fusion reactions.

Inorganic Chemistry

Isolation/preparation and properties of the following non-metals: Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens; Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur.

Preparation and properties of the following compounds: Oxides, peroxides, hydroxides, carbonates, bicarbonates, chlorides and sulphates of sodium, potassium, magnesium and calcium; Boron: diborane, boric acid and borax; Aluminium: alumina, aluminium chloride and alums; Carbon: oxides and oxyacid (carbonic acid); Silicon: silicones, silicates and silicon carbide; Nitrogen: oxides, oxyacids and ammonia; Phosphorus: oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine; Oxygen: ozone and hydrogen peroxide; Sulphur: hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate; Halogens: hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder; Xenon fluorides.

Transition elements (3d series): Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Coordination compounds: nomenclature of mononuclear coordination compounds, *cis-trans* and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

Preparation and properties of the following compounds: Oxides and chlorides of tin and lead; Oxides, chlorides and sulphates of Fe^{2+}, Cu^{2+} and Zn^{2+}; Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate.

Ores and minerals: Commonly occurring ores and minerals of iron, copper, tin, lead, magnesium, aluminium, zinc and silver.

Extractive metallurgy: Chemical principles and reactions only (industrial details excluded); Carbon reduction method (iron and tin); Self reduction method (copper and lead); Electrolytic reduction method (magnesium and aluminium); Cyanide process (silver and gold).

Principles of qualitative analysis: Groups I to V (only Ag^+, Hg^{2+}, Cu^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+}); Nitrate, halides (excluding fluoride), sulphate and sulphide.

Organic Chemistry

Concepts: Hybridisation of carbon; Sigma and pi-bonds; Shapes of simple organic molecules; Structural and geometrical isomerism; Optical isomerism of compounds containing up to two asymmetric centres, (*R*, *S* and *E*, *Z* nomenclature excluded); IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi-functional compounds); Conformations of ethane and butane (Newman projections); Resonance and hyperconjugation; Keto-enol tautomerism; Determination of empirical and molecular formulae of simple compounds (only combustion method); Hydrogen bonds: definition and their effects on physical properties of alcohols and carboxylic acids; Inductive and resonance effects on acidity and basicity of organic acids and bases; Polarity and inductive effects in alkyl halides; Reactive intermediates produced during homolytic and heterolytic bond cleavage; Formation, structure and stability of carbocations, carbanions and free radicals.

Preparation, properties and reactions of alkanes: Homologous series, physical properties of alkanes (melting points, boiling points and density); Combustion and halogenation of alkanes; Preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Preparation, properties and reactions of alkenes and alkynes: Physical properties of alkenes and alkynes (boiling points, density and dipole moments); Acidity of alkynes; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination); Reactions of alkenes with $KMnO_4$ and ozone; Reduction of alkenes and alkynes; Preparation of alkenes and alkynes by elimination reactions; Electrophilic addition reactions of alkenes with X_2, HX, HOX and H_2O (X=halogen); Addition reactions of alkynes; Metal acetylides.

Reactions of benzene: Structure and aromaticity; Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of *o*-, *m*- and *p*-directing groups in monosubstituted benzenes.

Phenols: Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation); Reimer-Tiemann reaction, Kolbe reaction.

Characteristic reactions of the following (including those mentioned above): Alkyl halides: rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions; Alcohols: esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, $ZnCl_2$/concentrated HCl, conversion of alcohols into aldehydes and ketones; Ethers: Preparation by Williamson's Synthesis; Aldehydes and Ketones: oxidation, reduction, oxime and hydrazone formation; Aldol condensation, Perkin reaction; Cannizzaro reaction; Haloform reaction and nucleophilic addition reactions (Grignard addition); Carboxylic acids: formation of esters, acid chlorides and amides, ester hydrolysis; Amines: basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines, Sandmeyer and related reactions of diazonium salts; carbylamine reaction; Haloarenes: nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and Cine substitution).

Carbohydrates: Classification; mono- and di-saccharides (glucose and sucrose); Oxidation, reduction, glycoside formation and hydrolysis of sucrose.

Amino acids and peptides: General structure (only primary structure for peptides) and physical properties.

Properties and uses of some important polymers: Natural rubber, cellulose, nylon, teflon and PVC.

Practical organic chemistry: Detection of elements (N, S, halogens); Detection and identification of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro; Chemical methods of separation of mono-functional organic compounds from binary mixtures.

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CHAPTER 1

THE CONCEPT OF ATOMS AND MOLECULES

ATOMIC AND MOLECULAR MASSES

The branch of chemistry which deals with mass relationships in chemical reactions is called stoichiometry. Before dealing with this branch, a brief review of the terms recommended by IUPAC in describing the atomic and molecular masses is in order.

Relative Atomic Mass of an Element The ratio of the average mass per atom of the natural isotopic composition of the element to 1/12th of the mass of an atom of nuclide ^{12}C is known as the relative atomic mass (formerly known as atomic weight) of the element.

Relative Molecular Mass of a Compound The ratio of the average mass per molecule of the natural isotopic composition of the compound to 1/12th mass of an atom of nuclide ^{12}C is known as relative molecular mass (formerly known as molecular weight) of the compound.

Atomic Mass Unit The quantity 1/12th mass of an atom of nuclide ^{12}C is known as the atomic mass unit. The value of atomic mass unit can be determined from the fact that 1 mol of ^{12}C has been assigned mass exactly to 0.012 kg. Hence,

$$1\ \text{amu} = \frac{(0.012\ \text{kg mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1})}{12} = 1.6606 \times 10^{-27}\ \text{kg}$$

Atomic Mass The average mass per atom of natural isotopic composition of an element is known as atomic mass. It is given as Atomic mass = (Relative atomic mass) (atomic mass unit).

Molecular Mass The average mass per molecule of natural isotopic composition of a compound is known as molecular mass. It is given as Molecular mass = (Relative molecular mass) (atomic mass unit).

Mole of a Substance One mole (1 mol) of a substance contains as many objects (e.g. atoms, molecules, ions) as there are atoms in exactly 12 g of nuclide ^{12}C. This number is approximately equal to 6.022×10^{23}.

Amount of a Substance If a sample of a substance contians N specified entities, the amount of substance (formerly known as number of mole) is given as $n = N/N_A$, where N_A is Avogadro constant (= 6.022×10^{23} mol^{-1}). The unit of amount of substance is 'mol'.

Molar Mass The average mass per unit amount of a substance (applicable to both elements and compounds) of naturally isotopic composition is known as molar mass. Its unit is g mol^{-1} or kg mol^{-1}.

The molecular (or molar) mass of a compound is equal to the sum of atomic (or molar) masses of its constituent atoms. The atomic (or molecular) mass of an atom (or a compound) expressed in atomic mass unit and the molar mass expressed in g mol^{-1} have the same numerical value. This value is also the same as that of relative atomic (or molecular) mass of the substance.

LAWS OF CHEMICAL COMBINATION

There are three laws of chemical combination. These are as follows.

Law of Conservation of Masses (Lavoisier, 1774) The mass is conserved in a chemical reaction.

Law of Constant Composition (Proust, 1799) All pure samples (drawn from different sources) of the same compound contain the same elements combined in the same proportion by mass.

Law of Multiple Proportion (Dalton, 1803) Two elements, A and B combine to form more than one compound, the masses of A which separately combine with a fixed mass of B (or vice versa) are in the ratio of small whole numbers.

QUANTITATIVE INFORMATION FROM A CHEMICAL EQUATION

A balanced chemical equation provides quantitative information regarding the consumption of reactants and creation of products. The numbers which appear before the chemical symbols and which balance the equation (with the understanding that if no number appears, it is equal to unity) are called the stoichiometric coefficients (or numbers) and are proportional to the number of molecules or the amount of the constituents that change during the progress of the reaction. For a general case

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \tag{1}$$

where ν_A, ν_B, ν_C and ν_D are the stoichiometric coefficients of the species A, B, C and D, respectively. The progress of the reaction is described in terms of a physical parameter, known as *extent of reaction* (symbol; ξ, pronounced as xi). It is expressed as

$$-\frac{\Delta n_A}{\nu_A} = -\frac{\Delta n_B}{\nu_B} = \frac{\Delta n_C}{\nu_C} = \frac{\Delta n_D}{\nu_D} = \xi \tag{2}$$

where Δns represent the changes in the amount (i.e. number of moles) of the species. The negative and positive signs represent decrease and increase in the amount of the species, respectively. The unit of ξ is mol.

Equation (2) is often interpreted as follows.

$$-\nu_A \xi \text{ of A} \equiv -\nu_B \xi \text{ of B} \equiv \nu_C \xi \text{ of C} \equiv \nu_D \xi \text{ of D} \tag{3}$$

where the sign ≡ is used for the term 'equivalent to'.

Equation (3) is often used for a unit extent of reaction where $\xi = 1$ mol. In this case, we have

$$-\nu_A \text{ mol of A} \equiv -\nu_B \text{ mol of B} \equiv \nu_C \text{ mol of C} \equiv \nu_D \text{ mol of D} \tag{4}$$

In other words ν_A mol of A on reacting with ν_B mol of B gives ν_C mol of C and ν_D mol of D.

Since the amount of species is directly proportional to the number of species, Eq. (4) may also be expressed as

$$-\nu_A \text{ molecules of A} \equiv -\nu_B \text{ molecules of B} \equiv \nu_C \text{ molecules of C} \equiv \nu_D \text{ molecules of D} \tag{5}$$

indicating that ν_A molecules of A on reacting with ν_B molecules of B produces ν_C molecules of C and ν_D molecules of D.

The relative changes in the masses of species are obtained by multiplying the terms in Eq. (4) by the respective molar masses, i.e.

$$-\nu_A M_A \text{ mol of A} \equiv -\nu_B M_B \text{ mol of B} \equiv \nu_C M_C \text{ mol of C} \equiv \nu_D M_D \text{ mol of D} \tag{6}$$

Equations (4) to (6) may be illustrated by taking the example of the reaction

$$\begin{array}{lccccccc} & Pb(NO_3)_2 & + & 2\,KI & \rightarrow & PbI_2 & + & 2\,KNO_3 \\ \text{Molar mass:} & 331.2\text{ g mol}^{-1} & & 166.0\text{ g mol}^{-1} & & 461.0\text{ g mol}^{-1} & & 101.1\text{ g mol}^{-1} \end{array}$$

Equation (4) tells that

1 mol of $Pb(NO_3)_2$ on reacting with 2 mol of KI produces 1 mol of PbI_2 and 2 mol of KNO_3.

Equation (5) tells that

1 molecule of $Pb(NO_3)_2$ on reacting with 2 molecules of KI produces 1 molecule of PbI_2 and 2 molecules of KNO_3.

Equation (6) tells that

331.2 g of $PbNO_3$ on reacting with 2 × 166.0 g of KI produces 461.0 g of PbI_2 and 2 × 101.1 g of KNO_3.

EXPRESSING CONCENTRATION OF A SUBSTANCE

The different ways of expressing the concentration of a substance are as follows.

Mass Percentage The defining expression is

$$\text{Mass percentage of A} = \frac{\text{Mass of substance A}}{\text{Total mass of the system}} \times 100$$

Mole Fraction The defining expression is $\text{Mole fraction of A} = \dfrac{\text{Amount (in mol) of substance A}}{\text{Total amount of substances in the system}}$

In symbolic form, $x_A = n_A/n_{\text{total}}$

Molarity The defining expression is $\text{Molarity of A} = \dfrac{\text{Amount (in mol) of substance A}}{\text{Volume of solution expressed in dm}^3}$

In symbolic form, $M = n_2/V$; (V expressed in dm^3)

The unit of molarity is mol dm^{-3}. It is commonly abbreviated by the symbol M and is spelled as molar. The molarity of a substance is temperature-dependent property due to the variation of volume with temperature.

Molality The defining expression is $\text{Molality of A} = \dfrac{\text{Amount (in mol) of substance A}}{\text{Mass of solvent expressed in kg}}$

In symbolic form, $m_A = n_A/m_1$; (m_1 expressed in kg)

The unit of molality is mol kg^{-1} and is spelled as molal. The molality of a substance is independent of temperature of solution.

CONVERSION OF CONCENTRATION UNITS

Representing solvent and solute in a binary solution by subscripts 1 and 2, respectively, the various conversion expressions are as follows.

Mole fraction into molarity $M = \dfrac{x_2\rho}{x_1M_1 + x_2M_2}$ *Molarity into mole fraction* $x_2 = \dfrac{MM_1}{\rho + M(M_1 - M_2)}$

Mole fraction into molality $m = \dfrac{x_2}{x_1M_1}$ *Molality into mole fraction* $x_2 = \dfrac{mM_1}{1 + mM_1}$

Molality into molarity $M = \dfrac{m\rho}{1 + mM_2}$ *Molarity into molality* $m = \dfrac{M}{\rho - MM_2}$

where M_1 and M_2 are the molar masses of solvent and solute, respectively, and ρ is the density of solution (expressed in mass per dm^3 of solution).

CONCEPT OF EQUIVALENT

One equivalent of a substance in a reaction is defined as the amount of substance which reacts or liberates 1 mol of electrons (or H^+ or OH^- ions). In a reaction, a substance always reacts with another substance in equivalent amounts. The equivalent mass of a substance in a reaction is defined as the molar mass divided by the number of equivalents in 1 mol of the substance. The concentration of a solution may be expressed in normality(Symbol: N) which is equal to the amount of solute in equivalents dissolved in 1 dm^3 of the solution. It has the units of equivalent per dm^3 and is abbreviated by the symbol N. The number of equivalents of the substance is given as

$$\text{Amount in equivalents} = \frac{\text{Mass of solute}}{\text{Equivalent mass}}$$

The equivalent mass of a solute (and also the normality of the solution) has to be determined with reference to a reaction since the solute may react in different ways in different reactions. For example, $KMnO_4$ oxidizes a reducing agent in different manners depending upon the medium as described in the following.

Acidic medium : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Weakly acidic or neutral or weakly alkaline medium : $MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O$

Alkaline medium : $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

Hence,

$$\text{Equivalent mass of } KMnO_4 \text{ in acidic medium } = \frac{\text{Molar mass of } KMnO_4}{5 \text{ eq mol}^{-1}}$$

$$\text{Equivalent mass of } KMnO_4 \text{ in weakly acidic, alkaline or neutral medium } = \frac{\text{Molar mass of } KMnO_4}{3 \text{ eq mol}^{-1}}$$

$$\text{Equivalent mass of } KMnO_4 \text{ in alkaline medium } = \text{Molar mass of } KMnO_4/\text{eq mol}^{-1}$$

In volumetric analysis, the expression $N_1V_1 = N_2V_2$ indicates the equality of substances being titrated in equivalents at the equivalence point.

BALANCING CHEMICAL EQUATION

Quite often one has to write a balanced chemical equation while dealing with the problem on stoichiometry. After writing reactants and products, the balancing can be carried out by hit and trial method. However, two systematic methods are available for balancing redox reactions. Before describing these methods, the rules governing the computation of oxidation state of an element are described in the following.

Rules to Compute Oxidation Number The oxidation number of an element is the number assigned to it by following the arbitrary rules given below.

1. A free element (regardless of whether it exists in monatomic or polyatomic form, e.g. Hg, H_2, P_4 and S_8) is assigned an oxidation number of zero.
2. A free monatomic ion is assigned an oxidation number equal to the charge it carries. For example, the oxidation numbers of Al^{3+}, S^{2-} and Cl^- are +3, –2, and –1, respectively.
3. In their compounds, the alkali and alkaline earth metals are assigned oxidation numbers of +1 and +2, respectively.
4. The oxidation number of hydrogen in its compounds is generally +1 except the ionic hydrides such as LiH, $LiAlH_4$, where its oxidation number is –1.
5. The oxidation number of fluorine in all its compounds is –1. The oxidation number of all other halogens is –1 in all compounds except those with oxygen (e.g. ClO_4^-) and halogens having a lower atomic number (e.g. ICl_3^-). The oxidation number of the latter is determined via oxygen and halogen of lower atomic number.
6. The oxidation numbers of both oxygen and sulphur in their normal oxides (e.g. Na_2O) and sulphides (e.g. CS_2) is –2. The exceptions are the peroxides (e.g. H_2O_2 and Na_2O_2), superoxides (e.g. KO_2) and the compound OF_2. Their oxidation numbers are determined by the rules 3, 4 and 5.
7. The algebraic sum of oxidation numbers of atoms in a chemical species (compound or ion) is equal to the net charge on the species.

A few examples of the computation of oxidation number of atoms N in various compounds are as follows. If x is the oxidation number of N, we have

NH_3	$x + 3(+1) = 0$	which gives $x = -3$	HN_3	$+1 + 3(x) = 0$	which gives $x = -\frac{1}{3}$
N_2H_4	$2x + 4(+1) = 0$	which gives $x = -2$	NO_2	$x + 2(-2) = 0$	which gives $x = 4$
N_2O_4	$2x + 4(-2) = 0$	which gives $x = 4$	NO_2^-	$x + 2(-2) = -1$	which gives $x = 3$
NH_2OH	$x + 2(+1) + 1(-2) + 1 = 0$	which gives $x = -1$	NO	$x + 1(-2) = 0$	which gives $x = 2$
HNO_3	$+1 + x + 3(-2) = 0$	which gives $x = 5$	N_2O	$2x + 1(-2) = 0$	which gives $x = 1$
HCN	$+1 + 4 + x = 0$	which gives $x = -5$			

Balancing Redox Reactions via Oxidation Numbers The steps involved in this method are as follows.

1. Identify the elements in the unbalanced equation whose oxidation number are changed.
2. Balance the number of atoms of each element whose oxidation number is changed.
3. Find out the total change in oxidation number for each of oxidant and reductant and make them equal by multiplying by small coefficients.

4. Balance the remainder of atoms by inspection and add, if necessary, H^+ (acidic medium) or OH^- (alkaline medium) or H_2O (to balance oxygen) as the case may be.

Taking the example of $Cu + H^+ + NO_3^- \to Cu^{2+} + H_2O + NO$ we have

Step 1 : $\overset{0}{Cu} + H^+ + \overset{+5}{N}O_3^- \to \overset{+2}{Cu}^{2+} + H_2O + \overset{+2}{N}O$ *Step* 2 : Not required

Step 3 :
$$\begin{array}{c} [1(-3) = -3] \times 2 \\ 3Cu + H^+ + 2NO_3^- \to 3Cu^{2+} + H_2O + 2NO \\ [1(+2) = +2] \times 3 \end{array}$$

Step 4 : $3Cu + 8H^+ + 2NO_3^- \to 3Cu^{2+} + 4H_2O + 2NO$

Balancing Redox Reaction via Ion-Electron (or Half-Equation) Method In this case, the steps involved are:

1. Write the two separate half equations involving the species oxidized along with its oxidation product and the species reduced along with its reduced product.
2. Balance the number of atoms oxidized (or reduced) on both sides of the equation.
3. Depending upon the medium (acidic or alkaline), add H^+ (two H^+ per O atom on the same side of oxygen) or OH^- (two OH^- per O atom on the opposite side of oxygen) so that the oxygen atoms in the equations are converted into water which are also included in the appropriate side of the equation.
4. Now add electrons in the right (or left) hand side of the oxidation (or reduction) reaction for balancing the charges on both sides.
5. Now multiply each resultant equation in step 4 by the smallest possible integer so as to have the same number of electrons in both oxidation and reduction reactions.
6. Add the two equations and cancel the common species appearing on both sides of the equation.

Taking again the example $Cu + H^+ + NO_3^- \to Cu^{2+} + H_2O + NO$ we have

Step 1 :	$Cu \xrightarrow{\text{oxidation}} Cu^{2+}$	$NO_3^- \xrightarrow{\text{reduction}} NO$
Step 2 :	Not required	
Step 3 :	$Cu \to Cu^{2+}$	$NO_3^- + 4H^+ \to NO + 2H_2O$
Step 4 :	$Cu \to Cu^{2+} + 2e^-$	$NO_3^- + 4H^+ + 3e^- \to NO + 2H_2O$
Step 5 :	$[Cu \to Cu^{2+} + 2e^-] \times 3$ $[NO_3^- + 4H^+ + 3e^- \to NO + 2H_2O)] \times 2$	
Step 6 :	$3Cu + 2NO_3^- + 8H^+ \to 3Cu^{2+} + 2NO + 4H_2O$	

Straight Objective Type

Atomic and Molar Masses

1. The atomic mass of an element is measured relative to the mass of
(a) hydrogen atom (b) oxygen atom
(c) carbon-12 (d) isotopic mixture of ^{12}C, ^{13}C and ^{14}C.

2. One atomic mass unit is equivalent to
(a) 1.66×10^{-27} g (b) 1.66×10^{-27} kg (c) 1.66×10^{-27} mg (d) 1.66×10^{-27} cg

3. The numerical value of atomic mass of an element is equal to its relative atomic mass when the former is expressed in
(a) g mol^{-1} (b) kg mol^{-1} (c) mg mol^{-1} (d) cg mol^{-1}

4. The numerical values of molecular mass and molar mass of a substance are identical when
(a) molecular mass is expressed in grams and molar mass in atomic mass unit
(b) both molecular mass and molar mass are expressed in atomic mass unit
(c) molecular mass is expressed in atomic mass unit and molar mass in grams
(d) both molecular mass and molar mass are expressed in grams

5. The value of Avogadro constant is
(a) 6.022×10^{23} (b) 6.022×10^{23} mol^{-1}
(c) 6.022×10^{23} atoms (d) 6.022×10^{13} molecules mol^{-1}

6. The amount of electrons in one kg is
(a) 6.022×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$ (c) $\frac{6.022}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.022} \times 10^{8}$

7. Which of the following has maximum number of atoms?
(a) 24 g of C (M = 12 g mol^{-1}) (b) 23 g of Na (M = 23 g mol^{-1})
(c) 48 g of S (M = 32 g mol^{-1}) (d) 108 g of Ag (M = 108 g mol^{-1}) (2003)

8. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5%, respectively, the relative atomic mass of Fe is
(a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05 (2009)

9. The largest number of molecules is in
(a) 36 g of water (b) 28 g of carbon monoxide
(c) 46 g of ethyl alcohol (d) 54 g of nitrogen pentoxide (1979)

10. A gaseous mixture contains oxygen ans nitrogen in the ratio of 1: 4 by mass. The ratio of their number of molecules is
(a) 1: 4 (b) 1: 8 (c) 7: 32 (d) 3: 16 (1979)

11. Which of the following has highest mass?
(a) 20 g phosphorus (b) 5 mol of water
(c) 2 equivalent of Na_2CO_3 (d) 12×10^{24} atoms of hydrogen (1978)

12. The volume of H_2 evolved at STP when 0.9 g of Al (molar mass: 27 g mol^{-1}) is dissolved in excess of dilute H_2SO_4 is
(a) 0.58 L (b) 1.12 L (c) 2.40 L (d) 2.9 L

Concentrations

13. 40.25 g of Glauber's salt is dissolved in water to obtain 500 mL of solution of density 1077.5 g dm^{-3}. The molality of Na_2SO_4 in solution is about
(a) 0.25 mol kg^{-1} (b) 0.24 mol kg^{-1} (c) 0.26 mol kg^{-1} (d) 0.27 mol kg^{-1}

14. The mass of $NaBrO_3$ required to prepare 150 mL of 0.75 N of a solution based on the reaction $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$ is
(a) 1.42 g (b) 2.83 g (c) 3.85 g (d) 4.25 g

15. Which of the following expressions correctly represent the conversion expression of molality m of a solution in terms of mole fraction x_2 of the solute in the solution?
(a) $x_2 = mM_1/(1 - mM_1)$ (b) $x_2 = mM_1/(1 + mM_1)$ (c) $x_2 = (1 + mM_1)/mM_1$ (d) $x_2 = (1 - mM_1)/mM_1$
where M_1 is the molar mass of solvent.

16. Which of the following expressions correctly represent the conversion of molality m into molarity M of a solution?
(a) $M = m\rho/(1 + mM_2)$ (b) $M = m\rho/(1 + mM_2)$ (c) $M = (1 + m\rho)/mM_2$ (d) $M = (1 - m\rho)/mM_2$
where ρ and M_2 are the density of solution and molar mass of solute, respectively.

17. The mole fraction of ethanol in water is 0.08. Its molality will be
(a) 2.41 mol kg^{-1} (b) 4.83 mol kg^{-1} (c) 3.33 mol kg^{-1} (d) 6.41 mol kg^{-1}

18. The expression converting mole fraction of a solute into molarity of solution is
(a) $M = x_2 M_2 / (x_1 M_1 + x_2 M_2)$ (b) $M = (x_1 M_1 + x_2 M_2) / x_2 M_2$
(c) $M = x_2 \rho / (x_1 M_1 + x_2 M_2)$ (d) $M = x_1 \rho / (x_1 M_1 + x_2 M_2)$
where the various symbols have their usual meanings.

19. The expression converting molarity (M) into mole fraction x_2 of the solute in the solution is
(a) $x_2 = \dfrac{M\,M_2}{\rho + M(M_1 - M_1)}$ (b) $x_2 = \dfrac{M\,M_1}{\rho + M(M_1 - M_2)}$

(c) $x_2 = \dfrac{M\,M_2}{\rho + M\,(M_2 - M_1)}$ (d) $x_2 = \dfrac{M\,M_1}{\rho + M\,(M_2 - M_1)}$

where the various symbols have their usual meanings.

20. The normality of 0.3 M phosphorous acid (H_3PO_3) is,

(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6

21. An aqueous solution of acetic acid has density 1.1 g mol^{-1} and molality 4.6 mol kg^{-1}. The molarity of acetic acid would be

(a) 3.2 M (b) 3.5 M (c) 3.97 M (d) 4.6 M

22. The volume of 82.5 mass percent of H_2SO_4 (density 1.6 g cm^{-3}) to prepare 200 cm^3 of 15 mass per cent of H_2SO_4 (density 1.1 g cm^{-3}) is

(a) 162 cm^3 (b) 173 cm^3 (c) 180 cm^3 (d) 193 cm^3

23. 115 ml of ethanol (density = 0.8 g ml^{-1}) on mixing with 99 mL of water gives 200 mL of solution. The numerical values molarity, molality and mole fraction of ethanol, respectively, are

(a) 10, 20.2, 0.267 (b) 20.2, 10, 0.267 (c) 10, 20.2, 0.733 (d) 20.2, 10, 0.733

Oxidation Number

24. One mole of N_2H_4 loses 10 mol 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 state of hydrogen.)

(a) -1 (b) -3 (c) $+3$ (d) $+5$ (1981)

25. The oxidation number of carbon in CH_2O is

(a) -2 (b) $+2$ (c) 0 (d) $+4$ (1982)

26. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)^+]SO_4$. The oxidation state of iron is

(a) 1 (b) 2 (c) 3 (d) 0 (1984)

27. The equivalent mass of $MnSO_4$ is half its molar mass when it is converted to

(a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-} (1988)

28. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is

(a) $+3$ (b) $+2$ (c) $+1$ (d) -1 (1990)

29. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 are

(a) 0 and -1 (b) -1 and -2 (c) -2 and 0 (d) -2 and $+1$ (1992)

30. For the redox reaction $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$ the correct coefficients of the reactants for the balanced reaction are

	MnO_4^-	$C_2O_4^{2-}$	H^+		MnO_4^-	$C_2O_4^{2-}$	H^+	
(a)	2	5	16	(b)	16	5	2	
(c)	5	16	2	(d)	2	16	5	(1993)

31. 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) oxidation and reduction (d) neutralization (1980)

32. Oxidation state of oxygen atom in potassium superoxide is

(a) $-1/2$ (b) -1 (c) -2 (d) 0

33. The compound having the lowest oxidation state of iron is

(a) $K_4Fe(CN)_6$ (b) K_2FeO_4 (c) Fe_2O (d) $Fe(CO)_5$

34. The oxidation state of nickel in $Ni(CO)_4$ is

(a) 0 (b) $+2$ (c) $+4$ (d) -4

35. The oxidation state of nitrogen in N_3H is

(a) $-1/3$ (b) -1 (c) $+1/2$ (d) $+2$

36. Which of the following reactions is a redox reaction?

(a) $Cr_2O_3 + 6HCl \rightarrow 2CrCl_3 + 3H_2O$ (b) $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$

(c) $2CrO_4^{2-} + H^+ \rightleftharpoons Cr_2O_7^{2-} + OH^-$ (d) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$

37. The compound having +2 as the oxidation state of oxygen is

(a) H_2O_2 (b) CO_2 (c) F_2O (d) MnO_2

38. The oxidation state of oxygen in O_3 is
(a) +1 and –1 (b) +2 and –2 (c) 0.5 and –0.5 (d) zero

39. The anion nitrate can be converted into ammonium ion. The equivalent mass of NO_3^- ion in this reaction would be
(a) 6.20 g eq^{-1} (b) 7.75 g eq^{-1} (c) 10.5 g eq^{-1} (d) 21.0 g eq^{-1}

40. The equivalent mass of $Na_2S_2O_3$ in its reaction with I_2 is equal to
(a) molar mass (b) molar mass/2 (c) molar mass/3 (d) molar mass/4

41. The oxidation numbers of sulphur in S_8, S_2F_2, H_2S respectively, are
(a) 0, +1 and –2 (b) +2, +1 and –2 (c) 0, +1 and +2 (d) –2, +1 and –2 (1999)

42. Amongst the following, identifies the species with an atom in +6 oxidation state
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2 (2000)

43. The correct order of compounds with increasing oxidation number of Ni is
(a) $Ni(CO)_4 < K_2[NiF_6] < K_2[Ni(CN)_4]$ (b) $Ni(CO)_4 < K_2[Ni(CN)_4] < K_2[NiF_6]$
(c) $K_2[Ni(CN)_4] < K_2[NiF_6] < Ni(CO)_4$ (d) $K_2[Ni(CN)_4] < Ni(CO)_4 < K_2[NiF_6]$

44. Which of the following acids has more than one oxidation state of sulphur atoms?
(a) $H_2S_2O_8$ (b) $H_2S_2O_6$ (c) $H_2S_2O_7$ (d) $H_2S_2O_5$

45. The correct order of compounds with increasing oxidation number of phosphorus is
(a) $P_4 < PH_3 < P_2O_3$ (b) $P_4 < P_2O_3 < PH_3$ (c) $P_2O_3 < P_4 < PH_3$ (d) $PH_3 < P_4 < P_2O_3$

46. The oxidation numbers of P in P_4, PH_3 and NaH_2PO_2, respectively, are
(a) 0, –3, +1 (b) 0, –3, –1 (c) 0, +3, –1 (d) 0, +3, +1

47. In the reaction $KSbO_2^- + 2KOH + 2H_2O + 2ClO_2 \rightarrow KSb(OH)_6^- + KClO_2$, the species undergone
(a) oxidation is Cl (b) oxidation is Sb (c) oxidation is O (d) reduction is Sb

48. The pair of the compounds in which both the metals are in the highest possible oxidation state is
(a) $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$, $Ni(CO)^4$
(c) TiO_2, MnO^2 (d) CrO_2Cl_2, MnO_4^- (2004)

Balancing Chemical Equation

49. The stoichiometric numbers of species from left to right in the chemical equation $Cu_2O + NO_3^- + H^+ \rightarrow Cu^{2+} + NO + H_2O$ when balanced respectively are
(a) 1, 1, 6, 2, 1, 3 (b) 2, 1, 8, 4, 1, 4 (c) 2, 2, 12, 4, 2, 6 (d) 3, 2, 14, 6, 2, 7

50. The stoichiometric numbers of species from left to right in the chemical equation

$$Mn^{2+} + PbO_2 + H^+ \rightarrow MnO_4^- + Pb^{2+} + H_2O$$

when balanced respectively are
(a) 1, 4, 8, 1, 4, 4 (b) 1, 3, 4, 1, 3, 2 (c) 2, 5, 4, 2, 5, 2 (d) 2, 7, 12, 2, 7, 6

51. The stoichiometric numbers of species from left to right in the chemical equation $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$ when balanced respectively are
(a) 2, 4, 12, 3, 6 (b) 1, 3, 6, 2, 3 (c) 1, 5, 6, 3, 3 (d) 1, 1, 6, 1, 3

52. The stoichiometric numbers of species from left to right in the chemical equation $Br_2 + NaOH \rightarrow NaBr + NaBrO_3 + H_2O$ when balanced respectively are
(a) 3, 4, 3, 1, 2 (b) 1, 2, 1, 1, 2
(c) 2, 4, 3, 1, 2 (d) 3, 6, 5, 1, 3

53. The stoichiometric number of species from left to right in the chemical equation $P_4 + NaOH + H_2O \rightarrow PH_3 + NaH_2PO_2$ when balanced respectively are
(a) 1, 2, 2, 1, 2 (b) 1, 3, 3, 1, 3 (c) 2, 6, 1, 4, 4 (d) 2, 6, 6, 3, 1

Chemical Reactions

54. If 0.5 mol of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is
(a) 0.70 mol (b) 0.50 mol (c) 0.20 mol (d) 0.10 mol (1981)

55. A certain compound has the molecular formula X_4O_6. If 10.0 g of compound contains 6.06 g of X, the atomic mass of X is
(a) 32 amu (b) 37 amu (c) 42 amu (d) 48 amu

56. The extent of reaction
(a) is unitless (b) has the unit of g (c) has the unit of mol (d) has the unit of mol^{-1}.

57. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is
(a) (2/5) mal (b) (3/5) mal (c) (4/5) mal (d) 1 mal (1997)

58. HBr and HI can reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce
(a) H_2SO_4 (b) $KMnO_4$ (c) $K_2Cr_2O_7$ (d) none of these

59. A solution of sodium metal in liquid ammonia is strongly reducing agent due to the presence of
(a) sodium atoms (b) sodium hydride (c) sodium amide (d) solvated electrons

60. The reaction which proceeds in the forward direction is
(a) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$ (b) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$ (d) $2CuI + I_2 + 4K^+ = 2Cu^{2+} + 4KI$ (1991)

61. The masses of P_4O_6 and P_4O_{10} that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2 respectively are
(a) 3.0 g, 1.0 g (b) 1.5 g, 2.5 g (c) 2.5 g, 1.5 g (d) 2.0 g, 2.0 g

62. Mixing of 50 mL of 0.25 M lead nitrate solution with 25 mL of 0.10 M chromic sulphate solution causes the precipitation of lead sulphate. The molarity of Pb^{2+} and Cr^{3+} ions in the solution respectively are
(a) 0.0667 M, 0.0667 M (b) 0.1 M, 0.2 M (c) 0.125 M, 0.05 M (d) 0.05 M, 0.125 M

63. A mixture weighing 4.08 g of BaO (molar mass of Ba = 138 g mol^{-1}) and unknown carbonate XCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 M HCl. The excess acid required 16 mL of 2.5 M NaOH solution for complete neutralization. The molar mass of M is about
(a) 20 g mol^{-1} (b) 30 g mol^{-1} (c) 40 g mol^{-1} (d) 50 g mol^{-1}

64. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600 °C until the mass of residue was constant. If the loss in mass is 28 per cent, the masses of lead nitrate and sodium nitrate in the mixture respectively were
(a) 3.32 g, 1.68 g (b) 1.68 g, 3.32 g (c) 2.50 g, 2.50 g (d) 3.50 g, 1.50 g

65. A compound $Pb(NO_3)_2$ on strong heating loses 32.6 per cent of its mass. The molar mass of Pb is about
(a) 200 g mol^{-1} (b) 207 g mol^{-1} (c) 214 g mol^{-1} (d) 221 g mol^{-1}

66. The per cent loss in mass of $K_2Cr_2O_7$ (molar mass Cr = 52 g mol^{-1}) on heating will be about
(a) 25% (b) 16% (c) 8% (d) 4%

67. Five millilitre of 0.1 M Pb $(NO_3)_2$ is mixed with 10 mL of 0.02 M KI. The amount of PbI_2 precipitated will be about
(a) 10^{-3} mol (b) 10^{-4} mol (c) 2×10^{-4} mol (d) 4×10^{-3} mol

68. A solution containing Na_2CO_3 and $NaHCO_3$ is titrated against 0.1 M HCl solution using methyl orange indicator. At the equivalence point,
(a) both Na_2CO_3 and $NaHCO_3$ are completely neutralized
(b) only Na_2CO_3 is wholly neutralized
(c) Only $NaHCO_3$ is wholly neutralized
(d) Na_2CO_3 is neutralized upto the stage of $NaHCO_3$

69. A solution containing Na_2CO_3 and $NaHCO_3$ is titrated against 0.1 M HCl solution using phenolphthalein indicator. At the equivalence point,
(a) both Na_2CO_3 and $NaHCO_3$ are completely neutralized
(b) only Na_2CO_3 is wholly neutralized
(c) only $NaHCO_3$ is wholly neutralized
(d) Na_2CO_3 is neutralized upto the stage of $NaHCO_3$

70. A solution containing NaOH and Na_2CO_3 is titrated against 0.1 M HCl solution using phenolphthalein indicator. At the equivalence point,
(a) both NaOH and Na_2CO_3 are completely neutralized
(b) only NaOH is completely neutralized
(c) only Na_2CO_3 is completely neutralized
(d) NaOH completely and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

71. A solution containing NaOH and Na_2CO_3 is titrated against 0.1 M HCl solution using methyl orange indicator. At the equivalence point,

(a) both NaOH and Na_2CO_3 are completely neutralized
(b) only NaOH is completely neutralized
(c) only Na_2CO_3 is completely neutralized
(d) NaOH completely and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

72. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. The value of n is
(a) 1 (b) 2 (c) 3 (d) 4

73. 20 mL of an acidified solution of ferrous sulphate requires 15 mL of 0.1 M solution of $KMnO_4$ for complete oxidation. For the same solution, the volume of 0.1 M $K_2Cr_2O_7$ for complete oxidation would be
(a) 24 mL (b) 18.0 mL (c) 16.67 mL (d) 12.5 mL

74. Twenty millilitre of a solution is 0.1 M in each of Na_2CO_3 and $NaHCO_3$. It is titrated against 0.1 M HCl using phenolphthalein as the indicator. The volume of HCl used at the end point will be
(a) 10 mL (b) 20 mL (c) 30 mL (d) 60 mL

75. Twenty millitre of a solution is 0.1 M in each of Na_2CO_3 and $NaHCO_3$. It is titrated against 0.1 M HCl using methyl orange as the indicator. The volume of HCl used at the end point will be
(a) 10 mL (b) 20 mL (c) 30 mL (d) 60 mL

76. Ten millilitre of 0.01 M iodine solution is titrated against 0.01 M sodium thiosulphate solution using starch solution. The volume of sodium thiosulphate consumed upto the end point is
(a) 10 mL (b) 15 mL (c) 20 mL (d) 30 mL

77. 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 (2001)

78. The reaction, $3ClO_3^-$ (aq) → ClO_3^- (aq) + 2Cl– (aq), is an example of
(a) oxidation reaction (b) reduction reaction
(c) disproportionation reaction (d) decomoposition reaction (2001)

79. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is
(a) (molar mass)/2 (b) (molar mass)/6 (c) (molar mass)/3 (d) same as molar mass

80. Which of the following is not oxidized by O_3?
(a) KI (b) $KMnO_4$ (c) K_2MnO_4 (d) $FeSO_4$

81. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is
(a) 3 (b) 4 (c) 5 (d) 6

82. 2.76 g of silver carbonate, on heating strongly yields a residue of
(a) 2.32 g (b) 2.48 g (c) 2.52 g (d) 2.64 g

83. One gram of $CaCO_3$(s) and Na_2CO_3(s) when heated strongly left a residue weighing 0.56 g. The mass per cent of $CaCO_3$ in the mixture is
(a) 50% (b) 60% (c) 75% (d) 80%

84. 6.0 g of C reacts completely with 12 g of O_2 producing a mixture of CO(g) and CO_2(g). The mass percent of CO(g) in the gaseous mixture will be about
(a) 45% (b) 57% (c) 64% (d) 76%

85. A mixture of CO(g), CH_4(g) and He gases has a volume of 20 cm^3. When exploded in the presence of excess of O_2, a net decrease of 13.0 cm^3 in volume is observed at room temperature. When the remaining mixture is passed through NaOH solution, a further decrease of 14.0 cm^3 in volume is observed. The volume percentages of CO, CH_4 and He in the original mixture, respectively, are
(a) 50, 30, 20 (b) 50, 20, 30 (c) 20, 50, 30 (d) 20, 30, 50

86. A compound $M \cdot xH_2O$ contains 45.5 mass per cent of water. If the molar mass M is 152 g mol^{-1}, the value of x will be
(a) 4 (b) 5 (c) 6 (d) 7

87. 0.5 g of fuming H_2SO_4 is diluted with water. This solution requires 22 mL of 0.5 M NaOH for complete neutralization. The mass per cent of SO_3 in the fuming H_2SO_4 is
(a) 25.1 (b) 30.2 (c) 35.2 (d) 40.1

88. 90 mL of 10 mass percent solution of KI (density: 1.132 g mL^{-1}) is mixed with 90 mL of 20 mass per cent of $Pb(NO_3)_2$ (density : 1.1 g mL, M(Pb) = 208 g mol^{-1}) The amount of PbI_2 precipitated will be
(a) 0.04 mol (b) 0.05 mol (c) 0.06 mol (d) 0.1 mol

89. A mass of 0.355 g of the compound $M_2CO_3 \cdot xH_2O$ (molar mass of M: 23 g mol^{-1}) is dissolved in 100 mL water and titrated against 0.05 M HCl using methyl orange indicator. If the volume of HCl consumed is 100 mL, the value of x is
(a) 2 (b) 5 (c) 7 (d) 10

90. 20 mL of a solution containing 0.34 g of an impure sample of H_2O_2 reacts with 0.465 g of $KMnO_4$ (molar mass: 155 g mol^{-1}) in acidic medium. The per cent purity of H_2O_2 is about
(a) 60% (b) 70% (c) 75% (d) 80%

91. A mixture of Na_2CO_3 and NaOH in a solution requires 20 mL of 0.1M HCl solution for neutralization when phenolphthalein indicator is used. The volume consumed is 25 mL when methyl orange indicator is used. The mass per cent of Na_2CO_3 in the given mixture is about
(a) 47% (b) 57% (c) 67% (d) 75%

92. The mass of AgCl precipitated when 4.68 g of NaCl is added to a solution containing 6.8 g of $AgNO_3$ is
(a) 4.52 g (b) 5.74 g (c) 7.18 g (d) 8.2 g

Multiple Correct Choice Type

1. Which of the following statements are correct?
(a) The reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is not an example of redox reaction.
(b) The reaction $2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2 + 2H^+$ is an example of a redox reaction.
(c) The oxidation number of an oxidant is increased in a redox reaction.
(d) The oxidation number of a reductant is increased in a redox reaction.

2. Which of the following statements are *not* correct?
(a) The increase in oxidation number of an element implies that the element has undergone oxidation.
(b) The increase in oxidation number of an element implies that the elements has undergone reduction.
(c) The oxidation number can never be a fraction. It is always a positive or negative integer.
(d) In a reaction H_2MoO_4 is changed to MoO_2^+. In this case, H_2MoO_4 acts as a reducing agent.

3. Which of the following statements are correct?
(a) The oxidation state of Mo when it undergoes transition from H_2MoO_4 to MoO_2^{2+} is increased by one.
(b) The disproportionation reaction $2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+$ is an example of a redox reaction.
(c) The equivalent mass of $KMnO_4$ in alkaline medium is molar mass divided by five.
(d) The equivalent mass of $KMnO_4$ in weakly acidic or neutral or weakly alkaline medium is molar mass divided by three.

4. Which of the following statements are correct?
(a) The equivalent mass of $KMnO_4$ in strongly alkaline medium is equal to its molar mass.
(b) The equivalent mass of $S_2O_3^{2-}$ in its reaction with I_2 is molar mass divided by two.
(c) A solution of cerium(IV) in sulphuric acid acts as an oxidizing reagent.
(d) The equivalent mass of $K_2Cr_2O_7$ in acidic medium is molar mass divided by five.

5. Which of the following statements are correct?
(a) Potassium bromate, $KBrO_3$, acts as a strong oxidizing agent. It accepts 6 electrons to give KBr.
(b) Potassium bromate can quantitatively convert Br^- to Br_2.
(c) Potassium iodate solution can be kept for a long time without decomposition.
(d) In 3N HCl solution, iodate can oxidize I_2 according to the reaction

$$IO_3^- + 2I_2 + 10Cl^- + 6H^+ \rightarrow 5ICl_2^- + 3H_2O$$

In this reaction, the equivalent mass of IO_3^- is molar mass divided by four.

6. Which of the following statements are correct?
(a) The equivalent mass of a substance can be calculated with out considering the reaction it undergoes.
(b) One mole of $K_4Fe(CN)_6$ produces 17 mol of total species in solution.
(c) The molar mass of N_2 is 28 g mol^{-1}. Its molecular mass will be 28 u.
(d) Hydrogen peroxide can act both as oxidizing as well reducing agent.

7. The reaction between peroxydisulphate ion ($S_2O_8^{2-}$) and chromium in acidic medium produces sulphate and dichromate ions. In this reaction (Choose only the correct ones)
(a) the oxidation state of S changes from +7 to +6.
(b) the oxidation state of Cr changes from 0 to +3.

(c) The equivalent mass of $S_2O_8^{2-}$ would be molar mass divided by two.
(d) The equivalent mass of Cr would be molar mass divided by three.

8. In 2N HCN solution, iodate I_2 according to the reaction

$$IO_3^- + 2I_2 + 10CN^- + 6H^+ \rightarrow 5I(CN)_2^- + 3H_2O$$

In this reaction (choose only the correct ones),
(a) the oxidation state of I in IO_3^- is changed from +5 to +1.
(b) the oxidation state of I in I_2 is changed from +1 to 0.
(c) the equivalent mass of IO_3^- is molar mass divided by four.
(d) the equivalent mass of I_2 is molar mass divided by two.
(e) IO_3^- acts a a/an reducing reagent.
(f) I_2 acts as a/an oxidizing reagent.

9. Which of the following statements are correct?
(a) The oxidation number of iodine in periodic acid (H_5IO_6) is +7.
(b) Hydrazine (N_2H_4) is a reducing agent. In its reaction with I_2, nitrogen is evolved. The equivalent mass of hydrazine in this reaction is molar mass divided by two.
(c) In the reaction $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ the equivalent mass of IO_3^- is molar mass divided by five.
(d) The iodine produced in the reaction $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ is titrated against $S_2O_3^{2-}$ ions. Knowing the normality of $S_2O_3^{2-}$, normality of iodine and hence normality of IO_3^- is determined. To get the strength of IO_3^- in g L^{-1}, the equivalent mass employed for IO_3^- in g L^{-1}, would be molar mass divided by four.

10. Which of the following statements are *not* correct?
(a) IO_4^- is a strong oxidizing agent in acidic medium. In its oxidizing action, it is reduced to I_2. The equivalent mass of IO_4^- will be molar mass divided by seven.
(b) In a oxidation reaction, bromate (BrO_3^-) is converted into Br^-. The equivalent mass of BrO_3^- will be molar mass divided by five.
(c) The oxidation state of S in CNS^- is +1.
(d) In a reaction between IO_3^- and CNS^-, the latter is converted into SO_4^{2-} and HCN. The equivalent mass of CNS^- would be molar mass divided by six.

11. Which of the following statements are correct?
(a) One mole of potash alum contains a total 32 mol of the independent species.
(b) One of mole of $K_3Fe(CN)_6$ contains a total 10 mol of the independent species.
(c) 0.1 M sulphuric acid has a normality of 2 N.
(d) The oxidation number of alkali metal is always taken equal to +1.

12. In the reaction $6OCl^- + 2NH_3 \rightarrow 6Cl_2 + N_2 + 6OH^-$, the species undergone
(a) oxidation is N (b) reduction is N (c) oxidation is Cl (d) reduction is Cl

13. Which of the following concentrations are correct for 13 mass percent of sulphuric acid (dendity : 1.09 g mL^{-1})?
(a) 1.443 M (b) 1.625 M (c) 1.625 mol kg^{-1} (d) 1.525 mol kg^{-1}

14. 1.8 g of Mg in burnt in a closed vessel which contains 0.8 g of oxygen. Which of the following facts are correct for the resultant system?
(a) Amount of MgO formed is 0.05 mol
(b) Mass of Mg left in excess is 0.8 g
(c) Amount of oxygen left is zero.
(d) Volume of 0.25 M H_2SO_4 to dissolve the formed MgO is 200 mL

Linked Comprehension Type

1. 250 mL of a solution contains 0.42 g of oxalic acid. This solution is used in determining molarity of sodium hydroxide solution which, in turn, is used to determine the molarity of sulphuric acid solution. This acid solution is furthur used in determining the masses of Na_2CO_3 and $NaHCO_3$ present in a solution. Based on these experiments, answer correctly the following three questions.
(i) In determining the molarity of sodium hydroxide solution, 9.6 mL of this solution required 10 mL of oxalic acid solution to locate end point with the help of phenolphthalein indicator. For sulphuric acid

solution, 9.0 mL of NaOH solution is used in neutralizing 10 mL of sulphuric acis solution while using phenolphthalein indicator. The molarity of sulphuric acid solution is

(a) 0.01 M (b) 0.0125 M (c) 0.02 M (d) 0.025 M

(ii) 10.0 mL of the solution containing Na_2CO_3 and $NaHCO_3$ requires 4.0 mL of sulphuric acid with phenolphthalein indicator. The mass of Na_2CO_3 present per litre of the solution is

(a) 1.06 g L^{-1} (b) 2.12 g L^{-1} (c) 2.52 g L^{-} (d) 3.18 g L^{-1}

(iii) 10.0 mL of the solution containing Na_2CO_3 and $NaHCO_3$ requires 14.0 mL of suphuric acid with methyl orange indicator. The mass of $NaHCO_3$ present per litre of the solution is

(a) 0.63 g L^{-1} (b) 1.06 g L^{-} (c) 1.26 g L^{-1} (d) 2.52 g L^{-1}

2. 250 mL of a solution contains 0.63 g of oxalic acid. This solution is used in determining molarity of sodium hydroxide solution, which, in turn, is used to determine the molarity of sulphuric acid solution. This acid solution is furthur used in determining the masses of Na_2CO_3 and NaOH present in a solution. Based on these experiments, answer correctly the following three questions.

(i) In determining the molarity of sodium hydroxide solution, 9.6 mL of this solution required 10 mL of oxalic acid solution to locate end point with the help of phenolphthalein indicator. For sulphuric acid solution, 8.4 mL of NaOH solution is used in neutralizing 10 mL of sulphuric acid solution while using phenolphthalein indicator. The mass of sulphuric acid present per litre of the solution is

(a) 1.51 g (b) 1.72 g (c) 1.92 g (d) 2.21 g

(ii) 10.0 mL of the solution containing Na_2CO_3 and NaOH requires 12.0 mL of sulphuric acid with phenolphthalein indicator and 16.0 mL with methyl orange indicator. The mass of Na_2CO_3 present per litre of the solution is

(a) 1.48 g (b) 1.88 g (c) 2.28 g (d) 2.68 g

(iii) From the part (ii), the mass of NaOH present per litre of the solution is

(a) 0.56 g (b) 0.92 g (c) 1.12 g (d) 1.52 g

3. 250 mL of a solution contains 0.63 g of oxalic acid. This solution is used to determine molarities of NaOH solution and $KMnO_4$ solution. These solutions, in turn, are used separately to determine the masses of oxalic acid and sodium oxalate present together in a solution. Based on these experiments, answer correctly the following three questions

(i) In determining the molarty of sodium hydroxide solution, 9.6 mL of this solution is used to locate the end point for 10 mL of oxalic acid solution with phenolphthalein indicator. For $KMnO_4$ solution, 9.8 mL of $KMnO_4$ solution is used to locate the end point for acidified 10 mL of oxalic acid. The molarities of NaOH and $KMnO_4$ solutions, respectively, are

(a) M/24, M/24.5 (b) M/24, M/122.5 (c) M/24.5, M/24 (d) M/122.5, M/24

(ii) 10.0 mL of the solution containing oxalic acid and sodium oxalate together requires 8.5 mL of sodium hydroxide to get end point with phenolphthalein indicator. The mass of oxalic acid present per litre of the solution is

(a) 2.23 g (b) 1.58 g (c) 2.58 g (d) 3.2 g

(iii) 10.0 mL of the acidified solution containing oxalic acid and sodium oxalate required 20.7 mL of $KMnO_4$ solution. The mass of sodium oxalate present per litre of the given solution is

(a) 2.86 g (b) 3.08 g (c) 3.58 g (d) 4.18 g

4. 10 mL of a given hydrogen peroxide sample (density 1.2 g/mL) is titrated with M/50 solution of $KMnO_4$ in acidic medium. The volume of $KMnO_4$ solution used is found to be 28.4 mL. Based on this information, answer the following three questions.

(i) The molatity of H_2O_2 in the given hydrogen peroxide sample is

(a) 0.284 M (b) 0.142 M (c) 0.426 M (d) 0.071 M

(ii) The molality of H_2O_2 in the given hydrogen peroxide sample is

(a) 0.119 mol kg^{-1} (b) 0.238 mol kg^{-1} (c) 0.056 mol kg^{-1} (d) 0.36 mol kg^{-1}

(iii) The volume strength at STP of the given hydrogen peroxide sample is

(a) 2.59 (b) 2.09 (c) 1.59 (d) 0.99

Assertion Reason Type

Below are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code among a, b, c and d which are, defined below.

Code

(a) Both S and E are true, and E is the correct explanation of S.
(b) Both S and E are true but E is not the correct explanation of S.
(c) S is true but E is false.
(d) S is false but E is true

	STATEMENT(S)	EXPLANATION(E)
1.	In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of acid required at the equivalence point is twice that of the acid required using phenolphthalein as the indicator.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
2.	In the titration of Na_2CO_3 with HCl using methyl orange indicator, the equivalent mass of Na_2CO_3 is the molar mass divided by 2.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
3.	In the titration of Na_2CO_3 with HCl using phenolphthalein indicator, the equivalent mass of Na_2CO_3 is the molar mass divided by 2.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
4.	The equivalent mass of $KMnO_4$ in a redox reaction depends on the medium whether it is acidic, basic or neutral.	The oxidation reaction of MnO_4^- is $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. This reaction occurs irrespective of the nature of medium
5.	The $Cr_2O_7^{2-}$ is reduced to CrO_4^{2-} when the medium is made alkaline.	The oxidation states of Cr in $Cr_2O_7^{2-}$ and CrO_4^{2-} are identical.
6.	The atomic mass of an element expressed in amu (atomic mass unit) and its molar mass expressed in g mol^{-1} have the same numerical value.	The numerical value of product of amu in SI unit Avogadro constant is equal to 1
7.	The density of a substance expressed in g cm^{-3} kg dm^{-3} have the same numerical value.	The numerical value of density is same because 1 kg = 10^3 g and 1 cm = 10^{-1} dm.
8.	The atomic mass of most elements have non-integral values.	The atomic mass of an element is the mass of protons and neutrons contained in its nucleus.
9.	Amount of a substance is defined as $n = N/N_A$ where N is the number specified entities of the substance and N_A is Avogadro constant.	The amount of a substance may be expressed in various ways such as parts per million and grams.
10.	If the amount x of A in the reaction $2A \rightarrow B$ is converted into B, then the extent of reaction is x.	The extent of reaction is defined as $\Delta n_A/\nu_A$ where Δn_A is the amount of substance undergone a change and ν_A is its stoichiometric number.
11.	The extent of reaction has the unit of 'mol'.	The unit of amount of substance is 'mol'.
12.	Molarity of a solution is a temperature dependent physical property.	Volume of a solution changes with change in temperature.
13.	In the volumetric analysis, molarity of unknown solution may be determined by using the molarity expression $M_1V_1 = M_2V_2$.	The molarity expression $M_1V_1 = M_2V_2$ cannot be written like the normality expression $N_1V_1 = N_2V_2$.
14.	1 mol (5 Fe^{2+} ions) ≡ 5 mol of Fe^{2+} ions.	A grouping of five Fe^{2+} ions together as a single unit decreases the amount of Fe^{2+} ion to one fifth of the original amount.
15.	Mole fraction of a constituent in a solution is an intensive quantity.	Mole fraction of a constituent is independant of the volume of the solution.

Matrix Match Type

1. Column I lists some of the concentration terms and Column II includes some of their characteristics. Match each entry of Column I with those listed in Column II.

Column I	**Column II**
(a) Molarity	(p) eq dm^{-3}
(b) Molality	(q) mol dm^{-3}
(c) Mole fraction	(r) unit less
(d) Normality	(s) mol kg^{-1}
	(t) Temperature dependent
	(u) Temperature independent

2. Column I lists equivalent masses and Column II lists some of the typical titrations. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Molar mass/ (5 eq mol^{-1})	(p) $KMnO_4$ in Fe^{2+} versus MnO_4^- titration in alkaline medium
(b) Molar mass/ (2 eq mol^{-1})	(q) $KMnO_4$ in oxalic acid vesus MnO_4^- titration in acidic medium
(c) Molar mass/ (6 eq mol^{-1})	(r) $Na_2S_2O_3$ in I_2 versus $S_2O_3^{2-}$ titration
(d) Molar mass/ (1 eq mol^{-1})	(s) $K_2Cr_2O_7$ in Fe^{2+} versus $Cr_2O_7^{2-}$ titration
	(t) Oxalic acid in oxalic acid versus MnO_4^- titration in acidic medium.

3. Column I includes some of the concentration terms and their defining/ equivalent expressions are listed in Column II. In the expressions, the symbols stand for the various physical fquantities as described in the following

x_1 Mole fraction of solvent
x_2 Mole fraction of solute
M_1 Molar mass of solvent
M_2 Molar mass of solute
ρ density of solution
m Molality of solute in solution
M Molarity of solute in solution

Match each entry in Column I with those given in Column II.

Column I	**Column II**
(a) x_1	(p) $x_2\rho/(x_1M_1 + x_2M_2)$
(b) x_2	(q) x_2/x_1M_1
(c) M	(r) $mM_1/(1 + mM_1)$
(d) m	(s) $MM_1/\{\rho + M(M_1 - M_2)\}$
	(t) $m\rho/(1 + mM_2)$
	(u) $M/(\rho - MM_2)$
	(v) $1/(1 + mM_1)$

ANSWERS

Straight Objective Type

1. (c)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (a)
8. (b)	**9.** (a)	**10.** (c)	**11.** (c)	**12.** (b)	**13.** (b)	**14.** (b)
15. (b)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (b)	**20.** (d)	**21.** (c)
22. (d)	**23.** (b)	**24.** (c)	**25.** (c)	**26.** (a)	**27.** (b)	**28.** (c)
29. (b)	**30.** (a)	**31.** (c)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (a)
36. (d)	**37.** (d)	**38.** (d)	**39.** (b)	**40.** (a)	**41.** (a)	**42.** (d)
43. (b)	**44.** (d)	**45.** (d)	**46.** (a)	**47.** (b)	**48.** (d)	**49.** (d)
50. (c)	**51.** (c)	**52.** (d)	**53.** (b)	**54.** (d)	**55.** (b)	**56.** (c)
57. (a)	**58.** (d)	**59.** (d)	**60.** (a)	**61.** (d)	**62.** (a)	**63.** (c)
64. (a)	**65.** (b)	**66.** (c)	**67.** (b)	**68.** (a)	**69.** (d)	**70.** (d)

71. (a) **72.** (b) **73.** (d) **74.** (b) **75.** (d) **76.** (c) **77.** (a)
78. (c) **79.** (b) **80.** (b) **81.** (d) **82.** (a) **83.** (c) **84.** (c)
85. (b) **86.** (d) **87.** (c) **88.** (b) **89.** (a) **90.** (c) **91.** (a)
92. (b)

Multiple Correct Choice Type

1. (b), (d) **2.** (b), (c), (d) **3.** (b), (d) **4.** (a), (c)
5. (a), (b), (c), (d) **6.** (c), (d) **7.** (a), (c) **8.** (a), (c), (d)
9. (a), (c) **10.** (b), (c) **11.** (a), (c), (d) **12.** (a), (d)
13. (a), (d) **14.** (a), (c), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (a) **(iii)** (c) **2.** **(i)** (b) **(ii)** (a) **(iii)** (c)
3. **(i)** (b) **(ii)** (a) **(iii)** (d) **4.** **(i)** (b) **(ii)** (a) **(iii)** (c)

Assertion Reason Type

1. (b) **2.** (a) **3.** (d) **4.** (c) **5.** (d) **6.** (c) **7.** (a)
8. (c) **9.** (c) **10.** (d) **11.** (b) **12.** (a) **13.** (d) **14.** (a)
15. (b)

Matrix Match Type

1. (a) – (q), (t); (b) – (s), (u); (c) – (r), (u); (d) – (p), (t)
2. (a) – (q); (b) – (t); (c) – (s); (d) – (p), (r)
3. (a) – (v); (b) – (r), (s); (c) – (p), (t); (d) – (q), (u)

Hints and Solutions

Straight Objective Type

Atomic and Molar Masses

1. The atomic mass of an element is measured relative to the atomic mass of carbon-12.

2. One atomic mass unit $= \dfrac{(1/12)\text{th of mass of } {}^{12}\text{C}}{\text{Avogadro constant}} = \dfrac{(1/12)\left(12\,\text{g mol}^{-1}\right)}{6.023\times 10^{23}\,\text{mol}^{-1}} = 1.66\times 10^{-24}\,\text{g} = 1.66\times 10^{-27}\ \text{kg}$

6. Mass of a single electron $= 9.108\times 10^{-28}$ g; Number of electrons in 1 kg $= \dfrac{10^3\,\text{g}}{9.108\times 10^{-2}\,\text{g}}$

Amount of electrons in 1 kg $= \dfrac{10^3\,\text{g}}{(9.108\times 10^{-28}\,\text{g})\,(6.022\times 10^{23}\text{mol}^{-1})} = \dfrac{10^8}{9.108\times 6.022}$ mol

7. Amount of C $= \dfrac{24\,\text{g}}{12\,\text{g mol}^{-1}} = 2$ mol   Amount of Na $= \dfrac{23\,\text{g}}{23\,\text{g mol}^{-1}} = 1$ mol

Amount of S $= \dfrac{48\,\text{g}}{32\,\text{g mol}^{-1}} = 1.5$ mol   Amount of Ag $= \dfrac{108\,\text{g}}{108\,\text{g mol}^{-1}} = 1$ mol

Larger the amount of substance, larger the number of molecules.

8. Relative atomic mass Fe is $(0.05\times 54 + 0.9\times 56 + 0.05\times 57) = 55.95$

9. Amount of water, $\dfrac{M}{M} = \dfrac{36\text{ g}}{18\text{ g mol}^{-1}} = 2$ mol; Amount of carbon monoxide = $\dfrac{28\text{ g}}{28\text{ g mol}^{-1}} = 1$ mol

Amount of ethyl alcohol = $\dfrac{46\text{ g}}{46\text{ g mol}^{-1}} = 1$ mol; Amount of nitrogen pentoxide = $\dfrac{54\text{ g}}{108\text{ g mol}^{-1}} = 0.5$ mol

Larger the amount of substance, larger the number of molecules.

11. Mass of water = (5 mol) (18g mol^{-1}) = 90 g; Mass of Na_2CO_3 = (2 eq) (53 g eq^{-1}) = 106 g

Mass of hydrogen = $\left(\dfrac{12 \times 10^{24}}{6.022 \times 10^{23}\text{ mol}^{-1}}\right)$ (2 g mol^{-1}) $\simeq$ 40 g

12. The reaction is $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4) + 3H_2$

Amount of Al = $\left(\dfrac{0.9\text{g}}{27\text{g mol}^{-1}}\right) = \dfrac{1}{30}$ mol; Amount of H_2 evolved = $\left(\dfrac{3}{2}\right)\left(\dfrac{1}{30}\text{mol}\right) = \dfrac{1}{20}$ mol

Volume of H_2 evolved = $\left(\dfrac{1}{20}\text{mol}\right)$ (22.4 L mol^{-1}) = 1.12 L

13. Molar mass of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ = 322 g mol^{-1}

Molar mass of Na_2SO_4 = 142 g mol^{-1}

Mass of Na_2SO_4 in solution = (40.25 g) $\left(\dfrac{142\text{ g mol}^{-1}}{322\text{ g mol}^{-1}}\right)$ = 17.75 g

Mass of solution = (500 mL) (1.0775 g mol^{-1}) = 538.75 g

Mass of water = (538.75 – 17.75) g = 521 g

Amount of Na_2SO_4 = $\dfrac{17.55\text{ g}}{142\text{ g mol}^{-1}}$ = 0.125 mol

Molality of Na_2SO_4 = $\dfrac{0.125\text{ mol}}{0.521\text{ kg}}$ = 0.24 mol kg^{-1}

14. Amount of $NaBrO_3$ in the solution = (0.75 eq dm^{-3}) (0.150 dm^3) = 0.1125 eq

Mass of $NaBrO_3$ required = (0.1125 eq) (151 / 6) g eq^{-1} = 2.83 g

15. Since $m = n_2$ / (1 kg of solvent), we have $n_1 = 1$ kg / M_1

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{(1\text{ kg} / M_1) + n_2} = \frac{(n_2/\text{kg})}{(1/M_1) + n_2/\text{kg}} = \frac{m M_1}{1 + m M_1}$$

16. Since $m = n_2/(1$ kg of solvent), we have $n_1 = 1$ kg$/M_1$

The molarity of solution is $M = \dfrac{n_2}{V} = \dfrac{n_2}{(1\text{ kg} + n_2 M_2)/\rho} = \dfrac{(n_2/1\text{ kg})\,\rho}{1 + (n_2/1\text{ kg})\,M_2} = \dfrac{m\rho}{1 + m M_2}$

17. We have $n_2 = 0.08$ mol, $n_1 = 0.92$ mol; $m = \dfrac{0.08\text{ mol}}{(0.92\text{ mol})(0.018\text{ kg mol}^{-1})}$ = 4.83 mol kg^{-1}

18. We have $x_2 = \dfrac{n_2}{n_1 + n_2}$

Mass of solution = $n_1M_1 + n_2M_2$; Volume of solution, $V = (n_1M_1 + n_2M_2)/\rho$

Hence, $M = \dfrac{n_2}{V} = \dfrac{n_2}{(n_1M_2 + n_2 M_2)/\rho} = \dfrac{n_2\,\rho}{n_1M_2 + n_2 M_2} = \dfrac{x_2}{x_1M_2 + x_2 M_2}$

20. Phosphorous acid is a dibasic acid. Hence 0.3 M will be 0.6 N.

21. Let $m_1 = 1000$ g. Then $n_2 = 4.6$ mol; $m_2 = n_2 M_2 = (4.6 \text{ mol})(60 \text{ g mol}^{-1}) = 276$ g

Mass of solution = 1000 g + 276 g = 1276 g; Volume of solution = $m/\rho = (1276\text{g})/(1.1\text{g mL}^{-1}) = 1160$ mL

$$M_1 = n_2/V = (4.6 \text{ mol})/(1.16 \text{ L}) = 3.97 \text{ M}$$

22. Mass of 200 cm^3 of 15 mass percent of H_2SO_4; $m = \rho V = (1.1\text{g cm}^{-3})(200 \text{ cm}^3) = 220$ g

Mass of H_2SO_4 in this solution = $\left(\frac{15}{100} \times 220\text{g}\right) = 33\text{g}$; Mass of water in this solution = 220g – 33g = 187g

Mass of 82.5% H_2SO_4 containing 33 g H_2SO_4; $M = \frac{100}{82.5} \times 33 \text{ g} = 40$ g

Mass of water in this solution = 40 g – 33 g = 7 g; Volume of water in this solution = 7 cm^3

Thus 7 cm^3 of 84 % H_2SO_4 should be diluted to get 200 cm^3 of 15% H_2SO_4. The volume of water required with be 200 cm^3 – 7 cm^3 = 193 cm^3.

23. Mass of ethanol, $m_2 = V_2\rho = (115 \text{ mL})(0.8 \text{ g mL}^{-1}) = 92.0$ g

Amount of ethanol, $n_2 = \frac{m_2}{M_2} = \frac{92.0\text{g}}{46 \text{ g mol}^{-1}} = 2.0$ mol; Mass of water, $m_1 = 99$ g (since $\rho = 1$ g mL^{-1})

Amount of water, $n_1 = \frac{m_1}{M_1} = \frac{99\text{g}}{18\text{g mol}^{-1}} = 5.5$ mol

Molality of ethanol, $m = \frac{n_2}{m_1} = \frac{2.0 \text{ mol}}{(99 \times 10^{-3} \text{ kg})} = 20.2 \text{ mol kg}^{-1}$

Molarity of ethanol, $M = \frac{n_2}{V} = \frac{2.0 \text{ mol}}{(200 \times 10^{-3} \text{ L})} = 10 \text{ mol L}^{-1}$

Mass fraction of ethanol, $x_2 = \frac{n_2}{n_1 + n_2} = \frac{2}{2 + 5.5} = 0.267$

Oxidation Number

24. $\left(2\overset{-4}{N}\right)$ in $N_2H_4 \xrightarrow{-10e^-} \left(2\overset{+6}{N}\right)$ in Y. Oxidation state of N in Y is +3

25. We have $x + 2(+1) + (-2) = 0$. This gives $x = 0$.

26. The oxidation state of iron in $[Fe(H_2O)_5(NO)^+]^{2+}$ is + 1.

27. The oxidation states of Mn^{2+} are $\overset{+2}{Mn}SO_4$; $\overset{+3}{Mn}_2O_3$; $\overset{+4}{Mn}O_2$; $\overset{+7}{Mn}O_4^-$; $\overset{+6}{Mn}O_4^{2-}$

When $MnSO_4$ is changed to MnO_2, the change in oxidation state is +2. Hence, equivalent mass of $MnSO_4$ will be half of its molar mass.

28. For the species $H_2PO_2^-$, we have $2(+1) + x + 2(-2) = -1 \Rightarrow x = +1$

29. The reaction is $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

The oxidation states of most electronegative atom in the products (which is oxygen) are –2 and –1.

30. The balanced equation can be obtained as follows.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

31. Oxidation and reduction reactions take place simultaneously.

32. Potassium superoxide is KO_2. The oxidation state of oxygen is –1/2.

33. The oxidation states of Fe are $K_4\overset{+2}{Fe}(CN)_6$; $K_2\overset{+6}{Fe}O_4$; $\overset{+1}{Fe_2}O$; $\overset{0}{Fe}(CO)_5$

34. The oxidation state of Ni is zero as the CO ligand is a neutral species.

35. The oxidation of N in N_3H may be computed from the expression $3x + 1 = 0$. This gives $x = -1/3$.

36. Only in the reaction d, oxidation states of Cr and I change. In the other reactions, no change in oxidation state of any of the species occurs.

37. The oxidation states of oxygen are $H_2\overset{-1}{O_2}$; $C\overset{-2}{O_2}$; $F_2\overset{+2}{O}$; $Mn\overset{-2}{O_2}$

38. The oxidation state of oxygen in O_3 is zero.

39. We have $\overset{+5}{N}O_3^- \rightarrow \overset{-3}{N}H_4^+$. The change in oxidation state is –8. The equivalent mass of NO_3^- would be molar mass/8, i.e., 62 g mol^{-1}/8 eq mol^{-1} = 7.75 g eq^{-1}.

40. The reactions are

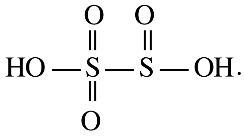
$$\begin{array}{l} 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \\ I_2 + 2e^- \rightarrow 2I^- \\ \hline 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \end{array}$$

For 2 mol of $Na_2S_2O_3$, 2 mol of electrons are involved. Hence, its equivalent mass will be equal to molar mass.

41. The oxidation numbers are $\overset{0}{S_8}$; $\overset{+1}{S_2}F_2$; $H_2\overset{-2}{S}$

42. The oxidation states are $\overset{+7}{Mn}O_4^-$; $\overset{+3}{Cr}(CN)_6^{3-}$; $\overset{+4}{Ni}F_6^{2-}$; $\overset{+6}{Cr}O_2Cl_2$

43. The oxidation number of Ni are as follows. $\overset{0}{Ni}(CO)_4$; $K_2(\overset{+IV}{Ni}F_6)$; $K_2[\overset{+II}{Ni}(CN)_4]$

44. The structure of $H_2S_2O_5$ is  $HO{-}S(=O)_2{-}S(=O){-}OH$. The oxidation states of S are +V and +III.

45. The oxidation number of phosphorus in PH_3, P_4 and P_2O_3 are –3, 0 and +3, respectively.

47. Oxidation implies increase in oxidation number. The oxidation number of Sb in $KSbO_2^-$ and $KSb(OH)_6^-$ are +2 and +4, respectively.

48. The oxidation states are as follows. (a) +2, +3 (b) +3, 0 (c) +4, +4 (d) +6, +7

49. The balanced chemical equation is $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6\,Cu^{2+} + 2NO + 7H_2O$

Not only atoms but also the charges should be balanced on both sides of a balanced chemical equation.

50. The balanced chemical equation is $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

51. The balanced chemical equation is $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

52. The balanced chemical equation is $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

53. The balanced chemical equation is $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

Chemical Reactions

54. The reaction is $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6NaCl$. Hence

3 mol $BaCl_2$ ≡ 2 mol Na_3PO_4 and thus 0.5 mol $BaCl_2$ ≡ (2/3) (0.5 mol Na_3PO_4) ≡ 0.33 mol Na_3PO_4

2 mol Na_3PO_4 ≡ 3 mol $BaCl_2$ and thus 0.2 mol Na_3PO_4 ≡ (3/2) (0.2 mol $BaCl_2$) ≡ 0.1 mol $BaCl_2$

Obviously, Na_3PO_4 is the limiting reagent. Hence

2 mol Na_3PO_4 ≡ 1 mol $Ba_3(PO_4)_2$ and thus 0.2 mol Na_3PO_4 ≡ 0.1 mol $Ba_3(PO_4)_2$

55. If M is the atomic mass of X, we have $\dfrac{4M}{4M + 96\ \text{amu}} = \dfrac{6.06}{10}$

Solving for M, we get $M = 36.9$ amu

56. The unit of extent of reaction is mol.

57. The reactions are

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O\ ] \times 2 \\ \underline{SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5} \\ 2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \end{array}$$

$$2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } S_2O_3^{2-} \quad \text{and hence} \quad (2/5) \text{ mol } MnO_4^- \equiv 1 \text{ mol } S_2O_3^{2-}$$

58. F^- is most stable species amongst Cl^-, Br^- and I^-. It does not reduce none of the three species H_2SO_4, $KMnO_4$ and $K_2Cr_2O_7$.

59. Sodium in liquid ammonia is strongly reducing agent due to the presence of solvated electrons.

60. The reactions b to d have tendencies to proceed from right side to left side. The reaction a proceeds in the forward direction.

61. The reactions are $\underset{n_1}{P_4} + \underset{3n_1}{3O_2} \rightarrow \underset{n_1}{P_4O_6}$ and $\underset{n_2}{P_4} + \underset{5n_2}{5O_2} \rightarrow \underset{n_2}{P_4O_{10}}$

Given: $$n_1 + n_2 = \frac{2\text{ g}}{124\text{ g mol}^{-1}} = \frac{1}{62}\text{ mol} \quad \text{and} \quad 3n_1 + 5n_2 = \frac{2\text{ g}}{124\text{ g mol}^{-1}} = \frac{1}{16}\text{ mol}$$

Solving for n_1 and n_2, we get $n_1 = 0.009$ mol and $n_2 = 0.007$ mol

$$m_1 = (0.009\text{ mol})\ (124 + 96)\text{ g mol}^{-1} \simeq 1.98\text{ g and } m_2 = (0.007\text{ mol})\ (124 + 160)\text{ g mol}^{-1} \simeq 1.99\text{ g.}$$

62. The reaction is $3Pb(NO_3)_2 + Cr_2(SO_4)_3 \rightarrow 3PbSO_4 + 2Cr(NO_3)_3$

$$\text{Amount of } Pb(NO_3)_2 = (0.25\text{ mol dm}^{-3})\ (0.05\text{ dm}^3) = 0.0125\text{ mol}$$

$$\text{Amount of } Cr_2(SO_4)_3 = (0.10\text{ mol dm}^{-3})\ (0.025\text{ dm}^3) = 0.0025\text{ mol}$$

Here, $Cr_2(SO_4)_3$ acts as a limiting reagent.

$$\text{Molarity of } Pb^{2+} \text{ ions} = \frac{(0.0125 - 3 \times 0.0025)\text{ mol}}{0.075\text{ dm}^3} = 0.066\text{ mol dm}^{-3}$$

$$\text{Molarity of } Cr^{3+} \text{ ions} = \frac{2 \times 0.0025\text{ mol}}{0.075\text{ dm}^3} = 0.066\text{ mol dm}^{-3}$$

63. Loss in mass on heating is due to the reaction $XCO_3 \rightarrow XO + CO_2$. Hence

$$\text{Amount of } XCO_3 = \text{Amount of } XO = \text{Amount of } CO_2 = \frac{4.08\text{ g} - 3.64\text{ g}}{44\text{ g mol}^{-1}} = 0.01\text{ mol}$$

The dissolution of BaO and XO consumes HCl due to the processes

$$BaO + 2HCl \rightarrow BaCl_2 + H_2O \quad \text{and} \quad XO + 2HCl \rightarrow XCl_2 + H_2O$$

Amount of excess acid = Amount of NaOH consumed = (2.5 M) (0.016 L) = 0.04 mol

Amount of HCl used in the dissolution processes = (1.0 M) (0.1 L) – 0.04 mol = 0.06 mol

Hence $n_1(BaO) + n_2(XO) = 0.06\text{ mol} / 2 = 0.03$ mol

Amount of BaO in the mixture is $n_1(BaO) = 0.03\text{ mol} - 0.01\text{ mol} = 0.02$ mol

Hence $(0.02\text{ mol})\ (M_{BaO}) + (0.01\text{ mol})\ M_{XCO_3} = 4.08\text{ g}$

that is, $(0.02\text{ mol})\ (154\text{ g mol}^{-1}) + (0.01\text{ mol})\ (M_X + 60\text{ g mol}^{-1}) = 4.08\text{ g}$

This gives $M_X = 40\text{ g mol}^{-1}$

64. Heating of the mixture results into the reactions:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2 \quad \text{and} \quad 2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

We have $M(Pb(NO_3)_2) = 331\text{ g mol}^{-1}$ $\quad M(NaNO_3) = 85\text{ g mol}^{-1}$

$M(PbO) = 223\text{ g mol}^{-1}$ $\quad M(NaNO_2) = 69\text{ g mol}^{-1}$

If x is the mass of $Pb(NO_3)_2$, then $\dfrac{223}{331}x + \dfrac{69}{85}(5.0\text{ g} - x) = (0.72)\ (5.0\text{ g})$

Solving for x, we get $x = 3.32$ g

65. The reaction to be considered is $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$

$$\frac{M_{Pb} + 16\ \text{g mol}^{-1}}{M_{Pb} + 124\ \text{g mol}^{-1}} = \frac{67.4}{100}. \qquad \text{Solving for } M_{Pb}\text{, we get} \quad M_{Pb} = 207\ \text{g mol}^{-1}$$

66. The reaction to be considered is $4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

The loss in mass is due to escape of O_2. For 1 mol of $K_2Cr_2O_7$, (3/4) mol of O_2 is released. Hence

$$\frac{\text{mass of (3/4) mol of } O_2}{\text{mass of 1 mol of } K_2\,Cr_2\,O_7} \times 100 = \frac{24\ \text{g}}{249\ \text{g}} \times 100 = 8\%$$

67. The reaction to be considered is $Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$

Amount of $Pb(NO_3)_2$ = (0.1 M) $(5 \times 10^{-3}$ L) = 5×10^{-4} mol

Amount of KI = (0.02 M) $(10 \times 10^{-3}$ L) = 2×10^{-4} mol

Limiting reagent is KI. The amount of PbI_2 will be 1×10^{-4} mol.

68. With methyl orange indicator, both Na_2CO_3 and $NaHCO_3$ are neutralized.

69. With phenolphthalene indicator, Na_2CO_3 is neutralized upto the stage of $NaHCO_3$.

70. With phenolphthalene, NaOH and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

71. With methyl orange, both NaOH and Na_2CO_3 are completely neutralized.

72. The reactions are $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$$A^{n+} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5 - n)e^-$$

Hence, we will have $(5)(1.61 \times 10^{-3}\ \text{mol}) = (5 - n)(2.68 \times 10^{-3}\ \text{mol})$
which gives $n = 2$

73. Volume of $K_2Cr_2O_7$ required will be (15 mL) $\left(\frac{5}{6}\right)$ = 12.5 mL

where 5 is the number of electrons involved in the oxidation reaction with MnO_4^- and 6 is those involved with $Cr_2O_7^{2-}$. The above expression follows from the normality expression.

$$(15\ \text{mL})\ (0.1 \times 5\ \text{N}\ MnO_4^-) = (V)\ (0.1 \times 6\ \text{N}\ Cr_2O_7^{2-})$$

74. The reaction occurring is $Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$

Since molarity of Na_2CO_3 and HCl are identical, the volume of HCl required in the above reaction will be the same as that of Na_2CO_3.

75. The reactions occurring are $Na_2CO_3 + 2H^+ \rightarrow 2Na^+ + H_2O + CO_2$

$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2$$

Since molarity of Na_2CO_3, $NaHCO_3$ and HCl are identical, the volume of HCl consumed will be 2 × 20 mL + 20 mL (= 60 mL).

76. The reaction to be considered is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Amount of I_2 = $(0.01\ \text{mol L}^{-1})\ (10 \times 10^{-3}\ \text{L}) = (1 \times 10^{-4})$ mol

Amount of $S_2O_3^{2-}$ consumed = 2×10^{-4} mol

$$\text{Volume of } S_2O_3^{2-} \text{ consumed} = \frac{2 \times 10^{-4}\ \text{mol}}{0.01\ \text{mol}^{-1}} = 2 \times 10^{-2}\ \text{L} = 20\ \text{mL}$$

77. Normality of oxalic acid = $\left(\frac{6.3\ \text{g}}{6.3\ \text{g eq}^{-1}}\right)\left(\frac{1}{250 \times 10^{-3}\ \text{L}}\right) = 0.4\ \text{eq L}^{-1}$

$$V_{NaOH} = \frac{(10\ \text{mL})\ (0.4\ \text{N})}{(0.1\ \text{N})} = 40\ \text{mL}$$

78. The changes in oxidation numbers are $\overset{+5}{\text{ClO}_3^-} + 2\overset{+5}{\text{ClO}_3} \rightarrow \overset{+7}{\text{ClO}_4} + \overset{-1}{\text{Cl}^-}$

Chlorine undergoes increase as well decrease in oxidation states. Hence, the reaction is disproportionation reaction.

79. The reaction of $Cr_2O_7^{2-}$ involving the release of I_2 from I^- is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Hence, Equivalent mass of $K_2Cr_2O_7 = \dfrac{\text{Molar mass}}{6}$

80. Mn in $KMnO_4$ is already present in the highest oxidation state.

81. The reaction is $\underset{1\text{ mol}}{Cr_2O_7^{2-}} + 14H^+ + \underset{6\text{ mol}}{6Fe^{2+}} \rightarrow 2Cr^{3+} + 7\,H_2O + 6Fe^{3+}$

82. $Ag_2CO_3 \rightarrow Ag_2O + CO_2$; $\left(\dfrac{2\times108+16}{2\times108+12+48}\times 2.76\,\text{g}\right) = \left(\dfrac{232}{276}\times 2.76\,\text{g}\right) = 2.32\,\text{g}$

83. Only $CaCO_3$ on heating undergoes the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Loss of mass is due to escape of $CO_2(g)$

$$\text{Amount of } CO_2 \text{ escaped} = \frac{1.0\,\text{g} - 0.67\,\text{g}}{44\,\text{g mol}^{-1}} = \frac{3}{4} \times 10^{-2}\text{ mol}$$

Amount of $CaCO_3(s)$ in mixture will be equal to the amount of CO_2 evolved. Hence, mass of $CaCO_3$ will be

$$m = nM = \left(\frac{3}{4}\times10^{-2}\text{ mol}\right)(100\,\text{g mol}^{-1}) = 0.75\,\text{g}$$

$$\text{Mass percent of } CaCO_3 = \frac{0.75\,\text{g}}{1\text{g}}\times100 = 75\%$$

84. The reactions are $\underset{n_1}{C(s)} + \underset{n_1/2}{\frac{1}{2}O_2(g)} \rightarrow \underset{n_1}{CO(g)}$ and $\underset{n_2}{C(s)} + \underset{n_2}{O_2(g)} \rightarrow \underset{n_2}{CO_2(g)}$

Total mass of C in CO and $CO_2 = (n_1 + n_2)\ (12\,\text{g mol}^{-1})$

Total mass of oxygen in CO and $CO_2 = (n_1 + 2n_2)\ (16\,\text{g mol}^{-1})$

Hence $(n_1 + n_2)\ (12\,\text{g mol}^{-1}) = 6.0\,\text{g}$ and $(n_1 + 2n_2)\ (16\,\text{g mol}^{-1}) = 12.0\,\text{g}$

or $n_1 + n_2 = 0.5$ mol and $n_1 + 2n_2 = 0.75$ mol

Solving for n_1 and n_2, we get

$n_1 = 0.25$ mol and $n_2 = 0.25$ mol;

$m_1 = (0.25\text{ mol})\ (28\,\text{g mol}^{-1}) = 7\text{g mol}^{-1}$; $m_2 = (0.25\text{ mol})\ (44\,\text{g mol}^{-1}) = 11\text{g mol}^{-1}$

$$\text{Mass percent of CO} = \frac{7}{10} \times 100 = 63.6$$

85. On explosion, CO and CH_4 is converted to CO_2

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \text{and} \quad CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

Let V_1, V_2 and V_3 be the partial volumes of CO, CH_4 and He in the original 20 cm^3 of the mixture. From the chemical equations given above, we have

$$V_1(CO) \equiv \frac{V_1}{2}\ (O_2) \equiv V_1(CO_2) \quad \text{and} \quad V_2(CH_4) \equiv 2V_2(O_2) = V_2(CO_2)$$

The decrease in volume is due to consumption of O_2 since $V_1(CO)$ and $V_2(CH_4)$ are replaced by equal volumes of $V_1(CO_2)$ and $V_2(CO_2)$, respectively. Hence

$$\frac{V_1}{2} + 2V_2 = 13\ \text{cm}^3$$

On passing through NaOH(aq), CO_2(g) will be absorbed. Hence $V_1 + V_2 = 14\ \text{cm}^3$

These two equations give $V_1 = 10\ \text{cm}^3$ and $V_2 = 4\ \text{cm}^3$

Thus, $V_3(\text{He}) = (20 - 10 - 4)\ \text{cm}^3 = 6\ \text{cm}^3$

Volume percent of CO = (10/20) × 100 = 50%; Volume percent of CH_4 = (4/20) × 100 = 20%

Volume percent of He = (6/20) × 100 = 30%

86. We have $\dfrac{18x}{18x+152} = \dfrac{45.5}{100}$. This gives $x = \dfrac{0.455\times152}{18(1-0.455)} = 6.92$

87. Let n_1 and n_2 be the amounts of SO_3 and H_2SO_4 in the given solution of fuming H_2SO_4. The neutralization reactions are

$$SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O \quad \text{and} \quad H_2SO_4 + 2OH^- \rightarrow SO_4^{2-} + 2H_2O$$

We will have

(1) $n_1M_1 + n_2M_2 = 0.5$ g ; (Given mass of mixture)

(2) $2(n_1 + n_2) = (22 \times 10^{-3}\ \text{L})\ (0.5\ \text{mol L}^{-1}) = 0.011$ mol (Equivalent H_2SO_4 is consumed)

or $n_1 + n_2 = 0.0055$ mol;

Eliminating n_2 from Eqs (1) and (2), we get

$n_1(80\ \text{g mol}^{-1}) + (0.0055\ \text{mol} - n_1)\ (98\ \text{g mol}^{-1}) = 0.5$ g

or $n_1(80- 98)\ \text{g mol}^{-1} = 0.5\ \text{g} - 0.0055 \times 98\ \text{g} = 0.5\ \text{g} - 0.539$ g

$$n_1 = \frac{0.039}{18}\ \text{mol} = 0.0022\ \text{mol}; \quad m_1 = (0.0022\ \text{mol})\ (80\ \text{g mol}^{-1}) = 0.176\ \text{g}$$

Mass percent of $SO_3 = \dfrac{0.176}{0.5} \times 100 = 35.2$

88. Mass of KI in solution = $\left(\dfrac{16}{100}\right)(1.132\ \text{g mL}^{-1})\ (90\ \text{mL}) = 16.30$ g

Amount of KI = $\dfrac{16.30\text{g}}{(39+127)\text{g mol}^{-1}} = 0.10$ mol

Mass of $Pb(NO_3)_2$ in solution = $\left(\dfrac{20}{100}\right)(1.1\ \text{g mL}^{-1})\ (90\ \text{mL}) = 19.8$ g

Amount of $Pb(NO_3)_2$ = $\dfrac{19.8\ \text{g}}{\{208+2(14+48)\}\ \text{g mol}^{-1}} = 0.06$ mol

The precipitation reactionis $\underset{0.06\ \text{mol}}{Pb(NO_3)_2} + \underset{0.1\ \text{mol}}{2KI} \rightarrow PbI_2 + 2KNO_3$

Here KI is the limiting reagent. Thus amount of PbI_2 precipitated will be 0.05 mol

89. The neutralization reaction is $M_2CO_3 + 2HCl \rightarrow 2MCl + CO_2 + H_2O$

Amount of H^+ in 100 mL of 0.05 M HCl solution,

$$n = VM = (100 \times 10^{-3}\ \text{L})\ (0.05\ \text{mol L}^{-1}) = 0.005\ \text{mol}$$

Amount of M_2CO_3 = $\dfrac{n(\text{HCl})}{2} = \dfrac{0.005\ \text{mol}}{2} = 0.0025$ mol

Hence (0.0025 mol) [{106 + x(18)} g mol^{-1}] = 0.355 g

This gives $x = 2$

90. Amount of $KMnO_4$ = $\dfrac{m}{M} = \dfrac{0.465\text{g}}{155\text{g mol}^{-1}} = 0.003$ mol

The reaction between MnO_4^- and H_2O_2 is $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

Amount of H_2O_2 in the given solution = $\frac{5}{2} \times 0.003$ mol = 0.0075 mol

Mass of H_2O_2 = (0.0075 mol) (34 g mol^{-1}) = 0.255 g

Mass percent purity of H_2O_2 = $\frac{0.255\text{ g}}{0.34\text{ g}} \times 100 = 75$

91. The neutralization reactions are

Phenolphthalein		Methyl orange	
	$OH^- + H^+ \rightarrow H_2O$		$OH^- + H^+ \rightarrow H_2O$
	$CO_3^{2-} + H^+ \rightarrow HCO_3^-$		$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

The extra 5 mL of HCl used in the methyl orange indicator corresponds to the neutralization reaction

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Therefore, for the complete neutralization of Na_2CO_3, the volume of HCl used will be 10 mL. The volume used for neutralizing NaOH will be 25 mL – 10 mL = 15 mL.

Amount of HCl in 10 mL HCl solution = $(10 \times 10^{-3}$ L) (0.1 mol L^{-1}) = 10^{-3} mol

Amount of HCl in 15 mL HCl solution = 1.5×10^{-3} mol

Amount of NaOH in the mixture = amount of HCl = 1.5×10^{-3} mol

Amount of Na_2CO_3 in the mixture = $\frac{1}{2}$ (amount of HCl) = 0.5×10^{-3} mol

Mass of NaOH in the mixture = $(1.5 \times 10^{-3}$ mol) (40 g mol^{-1}) = 0.06 g

Mass of Na_2CO_3 in the mixture = $(0.5 \times 10^{-3}$ mol) (106 g mol^{-1}) = 0.053 g

Mass per cent of Na_2CO_3 in the mixture = $\frac{0.053}{0.053+0.06} \times 100 = 47$

92. Amount of NaCl = $\frac{4.68\text{ g}}{58.5\text{ g mol}^{-1}} = 0.08$ mol; Amount of $AgNO_3$ = $\frac{6.8\text{ g}}{170.0\text{ g mol}^{-1}} = 0.04$ mol

Since the amount of $AgNO_3$ is less than that of NaCl, the whole of $AgNO_3$ is precipitated.

Mass of AgCl precipitated = (0.04 mol) (143.5 g mol^{-1}) = 5.74 g

Multiple Correct Choice Type

1. (a) The oxidation state of oxygen in H_2O_2 is –1. It is changed to –2 in water and to zero in O_2.
(b) The oxidation state of S is changed from +7 to +6 whereas that of O is changed from 0 to –2.
(c) An oxidant absorbs electron(s), its oxidation number is decreased.
(d) A reductant releases electron(s), its oxidation number is increased.

2. (a) The element undergoing oxidation causes the release of electron(s). Hence, its oxidation number is increased.
(b) The element undergoing reduction absorbs electron(s). Hence, its oxidation number is decreased.
(d) The oxidation state of Mo is changed from +6 to +5. Thus, H_2MoO_4 is an oxidizing agent.

3. (a) It is decreased by one.
(b) In this case, Mn^{3+} is changed to Mn^{4+} and another Mn^{3+} is changed to Mn^{2+}.
(c) In alkaline medium, the reaction is $MnO_4^- + e^- \rightarrow MnO_4^{2-}$
(d) In neutral medium (or weakly acidic or alkaline), the reaction is

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

4. (a) In strongly alkaline medium, MnO_4^- undergoes the reaction $MnO_4^- + e^- \rightarrow MnO_4^{2-}$. Hence, its equivalent mass is equal to its molar mass.

(b) The reaction is $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

Hence, Equivalent mass = $\frac{2 \times \text{Molar mass}}{2}$ = molar mass

(c) The reaction is $Ce^{4+} + e^- \rightarrow Ce^{3+}$

(d) The reaction is $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Equivalent mass = molar mass/6 eq mol^{-1}

5. (a) The reaction is $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$.

(d) The change in oxidation state of iodine in IO_3^- is from +5 to +1.

6. (a) The equivalent mass of a substance may have different values in different reactions. Thus, the reaction has to be considered before determining its equivalent mass.

(b) One mole of $K_4Fe(CN)_6$ produces 4 mol of K^+ and 1 mol of $Fe(CN)_6^{4-}$ ions.

(d) As an oxidizing reagent, the reaction is $2H^+ + H_2O_2 + 2e^- \rightarrow 2H_2O$.

As a reducing reagent, the reaction is $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$.

7. (b) The oxidation state changes from 0 to +6. (d) The equivalent mass is molar mass divided by six.

8. (b) The oxidation state changes from 0 to +1. (e) IO_3^- is oxidizing agent.

(f) I_2 is reducing agent.

9. (b) The equivalent mass is molar mass divided by four.

(d) The equivalent mass is molar mass divided by five.

10. (b) The equivalent mass is molar mass divided by six. (c) The oxidation state of S is zero.

11. (b) There are four species.

13. The mass of 1000 mL solution will be (1000 mL) (1.09 g mL^{-1}) = 1090 g. The mass of sulphuric acid in the solutionis (13/100) (1090 g) = 141.7 g. Amount of sulphuric is 141.7 g/98 g mol^{-1} = 1.446 mol. Hence,

$$\text{Molarity of } H_2SO_4 = \frac{1.446\ \text{mol}}{1\text{L}} = 1.446\ \text{mol L}^{-1}$$

$$\text{Molality of } H_2SO_4 = \frac{1.446\ \text{mol}}{(1090 - 141.7) \times 10^{-3}\ \text{kg}} = 1.525\ \text{mol kg}^{-1}$$

14. The burning reaction is $2\ Mg + O_2 \rightarrow 2MgO$

Initial amount of Mg = (1.8 g/24g mol^{-1}) = 0.075 mol

Initial amount of O_2 = (0.8 g/32 g mol^{-1}) = 0.025 mol

In the combustion reaction, whole of O_2 will be used

Amount of MgO formed = 2 × 0.025 mol = 0.050 mol

Amount of O_2 left = 0

Mass of Mg left = [(0.075 – 0.050) mol] [24 g mol^{-1}]

From the reaction $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$, we write

$$V(0.25\ \text{M}) = 0.05\ \text{mol} \quad \text{or} \quad V = \frac{0.05}{0.25}\ \text{L} = 0.2\ \text{L or } 200\ \text{mL}$$

Link Comprehension Type

1. Normality of oxalic acid solution is $N_1 = \dfrac{m_2/M_{\text{eq}}}{V_1} = \dfrac{(0.42\ \text{g})/(63\ \text{g eq}^{-1})}{(250 \times 10^{-3}\ \text{L})} = \dfrac{2}{75}\text{N}$

(i) Normality of sodium hydroxide solution is $N_2 = \dfrac{N_2 V_1'}{V_2} = \dfrac{(2\ \text{N}/75)\ (10\ \text{mL})}{(9.6\ \text{mL})} = \dfrac{1}{36}\text{N}$

Normality of sulphuric acid solution is $N_3 = \dfrac{N_2 V_2'}{V_2} = \dfrac{(\text{N}/36)\ (9.0\ \text{mL})}{(10\ \text{mL})} = \dfrac{1}{40}\text{N}$

Molarity of sulphuric acid solution = (1/2) (1/40) M = M/80

(ii) With phenolphthalene, the reaction occurring is $Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$

To neutralize whole of Na_2CO_3, volume of H_2SO_4 solution will be twice of the given volume of 4.0 mL. Hence, the normality of Na_2CO_3 in the solution is $N_4 = \dfrac{(2 \times 4.0\ \text{mL})\ (\text{N}/40)}{(10\ \text{mL})} = \dfrac{\text{N}}{50}\text{N}$

Mass of Na_2CO_3 in 1L of solution is m = (N/50) (53 g eq^{-1}) = 1.06 g L^{-1}

(iii) Volume of sulphuric acid solution used in neutralizing $NaHCO_3$ will be (14.0 – 2 × 4.0) mL = 6.0 mL.

Hence, the normality of $NaHCO_3$ in the solution is $N_5 = \dfrac{(6.0\ \text{mL})\ (\text{N}/40)}{(10\ \text{mL})} = \dfrac{3}{200}\text{N}$

Mass of $NaHCO_3$ in 1 L of solution is m = (3 N/200) (84 g eq^{-1}) = 1.26 g L^{-1}

2. Normality of oxalic acid solution is $N_1 = \dfrac{m_2/M_{\text{eq}}}{V_1} = \dfrac{0.63\ \text{g}/(63\ \text{g eq}^{-1})}{(250 \times 10^{-3}\ \text{L})} = \dfrac{1}{25}\text{N}$

(i) Normality of sodium hydroxide solution is $N_2 = \dfrac{N_1V_1'}{V_2} = \dfrac{(\text{N}/25)\ (10\ \text{mL})}{(9.6\ \text{mL})} = \dfrac{1}{24}\text{N}$

Normality of sulphuric acid solution is $N_3 = \dfrac{N_2V_2'}{V_3} = \dfrac{(\text{N}/24)\ (8.4\ \text{mL})}{(10\ \text{mL})} = \dfrac{7}{200}\text{N}$

Mass of sulphuric acid present in 1 L of solution $m = \left(\dfrac{7}{200}\text{eq L}^{-1}\right)\left(\dfrac{98}{2}\text{g eq}^{-1}\right)$ = 1.715 g L^{-1}

(ii) The reaction occurring are

Phenolphthalein: $CO_3^{2-} + H^+ \rightarrow CO_3^-$; $OH^- + H^+ \rightarrow H_2O$

Methyl orange: $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$; $OH^- + H^+ \rightarrow H_2O$

Volume of sulphuric acid used to neutralize Na_2CO_3 will be 2(16.0 mL – 12.0 mL) = 8.0 mL

Hence, normality of Na_2CO_3 in solution is $N_4 = \dfrac{(8.0\ \text{mL})\ (7\ \text{N}/200)}{(10\ \text{mL})} = \dfrac{7}{250}\text{N}$

Mass of Na_2CO_3 in 1L of solution is m = (7N/250) (53 g eq^{-1}) = 1.484 g L^{-1}

(iii) Volume of sulphuric acid used to neutralize NaOH will be 16.0 mL – 8.0 mL = 8.0 mL

Hence, Normality of $NaHCO_3$ in solution is $N_4 = \dfrac{(8.0\ \text{mL})\ (7\text{N}/200)}{(10\ \text{mL})} = \dfrac{7}{250}\text{N}$

Mass of NaOH in 1 L of solution is m = (7 N/250) (40g eq^{-1}) = 1.12 g L^{-1}

3. Normality of oxalic acid solution is $N_1 = \dfrac{m_2/M_{\text{eq}}}{V_1} = \dfrac{(0.63\ \text{g})\ (63\ \text{g eq}^{-1})}{(250 \times 10^{-3}\ \text{mL})} = \dfrac{1}{25}\text{N}$

(i) Normality of NaOH solution is $N_2 = \dfrac{N_1V_1'}{V_2} = \dfrac{(\text{N}/25)\ (10\ \text{mL})}{(9.8\ \text{mL})} = \dfrac{1}{24}\text{N}$

Since normality of NaOH is its molarity, the molartiy of NaOH is (1/24) M.

Normality of $KmnO_4$ solution is $N_3 = \frac{N_1V_1''}{V_3} = \frac{\text{(N/25) (10 mL)}}{\text{(9.8 mL)}} = \frac{1}{24.5}\text{N}$

In the reaction of MnO_4^- with oxalic acid, it undergoes the reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Molarity of $KMnO_4$ solution $= \frac{N_{KMnO_4}}{5\text{ eq mol}^{-1}} = \frac{(1/24.5)\text{ eq L}^{-1}}{(5\text{ eq mol}^{-1})} = \frac{1}{122.5}$ mol L^{-1}

(ii) Normality of oxalic acid in the solution containing both oxalic acid and sodium oxalate is

$$N = \frac{(8.5\text{ mL})\,(\text{N}/24)}{(10\text{ mL})} = \frac{8.5}{240}\text{ N}$$

Mass of oxalic acid per litre of solution is $m = \left(\frac{8.5}{240}\text{N}\right)$ $(63\text{ g eq}^{-1}) = 2.23$ g

(iii) Normality of sodium oxalate in the solution containing both oxalic acid and sodium oxalate is

$$N = \frac{\{(20.7 - 8.5)\text{ mL}\}\,(\text{N}/24.5)}{(10\text{ mL})} = 0.498\text{ N}$$

Mass of sodium oxalate present per litre of solution is

$m = (0.0498\text{ N})\ (84\text{ g eq}^{-1}) = 4.18\text{ L}^{-1}$

4. (i) The reactions between H_2O_2 and MnO_4^- are as follows

$$\begin{array}{r} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2 \\ H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5 \\ \hline 2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 4H_2O \end{array}$$

Normality of $KMnO_4$ solution = $(5\text{ eq mol}^{-1})\ (\text{mol L}^{-1}/50) = 0.1\text{ eq L}^{-1}$

Normality of H_2O_2 is $N = \frac{(0.1\text{ N})\,(28.4\text{ mL})}{(10\text{ mL})} = 0.284\text{ N}$

Molarity of $H_2O_2 = \left(\frac{1}{2\text{ eq mol}^{-1}}\right)$ $(0.284\text{ eq L}^{-1}) = 0.142\text{ mol L}^{-1}$

(ii) Mass of 1000 mL of H_2O_2 sample = (1000 mL) (1.2 g mL^{-1}) = 1200 g

Mass of H_2O_2 in this solution = (0.142 mol) (34 g mol^{-1}) = 4.83 g

Mass of solvent in this solution = (1200 g – 4.83 g) = 1195.17 g = 1.195 kg

Molality of $H_2O_2 = \frac{0.142\text{ mol}}{1.195\text{ kg}} = 0.119\text{ mol kg}^{-1}$

(iii) The volume strength of H_2O_2 is based on the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$

2 mol of H_2O_2 gives 1 mol of O_2 or 22.414 L of O_2 at STP

Hence, 0.142 mol L^{-1} solution of H_2O_2 will liberate $\frac{22.414}{2\text{ M}}$ (0.142 M) = 1.59

ANNEXURE

Subjective Problems for Practice

Balancing Chemical Equations

1. Balance the following equations.

(i) $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

(ii) $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

(iii) $C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Steps listed in each case are those mentioned earlier in the text.

(i) $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

Step 1 : $Cu_2O \xrightarrow{\text{oxidation}} Cu^{2+}$ $\qquad NO_3^- \xrightarrow{\text{reduction}} NO$

Step 2 : $Cu_2O \rightarrow \underline{2}Cu^{2+}$ $\qquad NO_3^- \rightarrow NO$

Step 3 : $Cu_2O + \underline{2H}^+ \rightarrow 2Cu^{2+} + \underline{H_2O}$ $\qquad NO_3^- + \underline{4H}^+ \rightarrow NO + \underline{2H_2O}$

Step 4 : $Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + \underline{2e^-}$ $\qquad NO_3^- + 4H^+ + \underline{3e^-} \rightarrow NO + 2H_2O$

Step 5 : $[Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e^-] \underline{\times 3}$

$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \underline{\times 2}$

Step 6 : $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6Cu^{2+} + 2NO + 7H_2O$

(ii) $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

Step 1 : $K_4Fe(\overset{+4}{C}\overset{-5}{N})_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (\overset{-3}{N}H_4)_2SO_4 + \overset{+2}{C}O$

Step 2 : $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

Step 3 :

6(+ 2) = + 12

$K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

6(– 2) = – 12

Step 4 : $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(iii) $C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Step 1 : $\overset{-2}{C_2}H_5OH + \overset{0}{I_2} + OH^- \rightarrow \overset{+2}{C}\overset{-1}{HI_3} + H\overset{+2}{C}O_2^- + \overset{-1}{I^-} + H_2O$

Step 2 : $C_2H_5OH + 2I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Step 3 :

+ 3 + 5 = + 8

$C_2H_5OH + 4I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + 5I^- + H_2O$

(– 4) + (– 4) = – 8

Step 4 : $C_2H_5OH + 4I_2 + 6OH^- \rightarrow CHI_3 + HCOO^- + 5I^- + 5H_2O$

2. Complete and balance the following equations.

(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{3+}$

(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$

(iv) $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$

(v) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$

Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Steps listed in each case are those mentioned earlier in the text.

(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

Step 1 : $Zn \xrightarrow{\text{oxidation}} Zn^{2+}$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NH_4^+$

Step 2 : Not required

Step 3 : $Zn \rightarrow Zn^{2+}$ $\qquad$ $NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$

Steps 4 and 5 : $[Zn \rightarrow Zn^{2+} + 2e^-] \times 4$

$[NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O] \times 1$

Step 6 : $4Zn + NO_3^- + 10H^+ \rightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{3+}$

Step 1 : $C_2H_4O \xrightarrow{\text{oxidation}} C_2H_4O_2$ $\qquad$ $Cr_2O_7^{2-} \xrightarrow{\text{reduction}} Cr^{3+}$

Step 2 : $C_2H_4O \rightarrow C_2H_4O_2$ $\qquad$ $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Step 3 : $C_2H_4O + H_2O \rightarrow C_2H_4O_2 + 2H^+$ $\qquad$ $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Steps 4 and 5 : $[C_2H_4O + H_2O \rightarrow C_2H_4O_2 + 2H^+ + 2e^-] \times 3$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Step 6 : $3C_2H_4O + Cr_2O_7^{2-} + 8H^+ \rightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$

Step 1 : $Cl^- \xrightarrow{\text{oxidation}} Cl_2$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NO$

Step 2 : $2Cl^- \rightarrow Cl_2$ $\qquad$ $NO_3^- \rightarrow NO$

Step 3 : $2Cl^- \rightarrow Cl_2$ $\qquad$ $NO_3^- + 4H^+ \rightarrow NO + 2H_2O$

Steps 4 and 5 : $[2Cl^- \rightarrow Cl_2 + 2e^-] \times 3$

$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 2$

Step 6 : $2NO_3^- + 6Cl^- + 8H^+ \rightarrow 3Cl_2 + 2NO + 4H_2O$ $\quad$ or $\quad$ $2HNO_3 + 6HCl \rightarrow 3Cl_2 + 2NO + 4H_2O$

(iv) $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$

Step 1 : $Ce^{3+} \xrightarrow{\text{oxidation}} Ce^{4+}$ $\qquad$ $S_2O_8^{2-} \xrightarrow{\text{reduction}} SO_4^{2-}$

Step 2 : $Ce^{3+} \rightarrow Ce^{4+}$ $\qquad$ $S_2O_8^{2-} \rightarrow 2SO_4^{2-}$

Step 3 : Not required

Steps 4 and 5 : $[Ce^{3+} \rightarrow Ce^{4+} + e^-] \times 2$

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$

Step 6 : $2Ce^{3+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Ce^{4+}$

(v) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$

Step 1 : $Cl_2 \xrightarrow{\text{oxidation}} ClO^-$ $\qquad$ $Cl_2 \xrightarrow{\text{reduction}} Cl^-$

Step 2 : $Cl_2 \rightarrow 2ClO^-$ $\qquad$ $Cl_2 \rightarrow 2Cl^-$

Step 3 : $Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O$ $\qquad$ $Cl_2 \rightarrow 2Cl^-$

Steps 4 and 5 : $Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e^-$

$Cl_2 + 2e^- \rightarrow 2Cl^-$

Step 6 : $2Cl_2 + 4OH^- \rightarrow 2Cl^- + 2ClO^- + 2H_2O$ $\quad$ or $\quad$ $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

3. Complete and balance the following equations.

(i) $Mn^{2+} + PbO_2 \rightarrow MnO_4^- + Pb^{2+} + H_2O$ $\qquad$ (ii) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

(iii) $ClO_3^- + I^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$ $\qquad$ (iv) $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + H^+ + Ag$ $\quad$ (1986)

Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Listed steps are those mentioned earlier in the text.

(i) $Mn^{2+} + PbO_2 \rightarrow MnO_4^- + Pb^{2+} + H_2O$

Step 1 : $Mn^{2+} \xrightarrow{\text{oxidation}} MnO_4^-$ $\qquad$ $PbO_2 \xrightarrow{\text{reduction}} Pb^{2+}$

Step 2 : Not required.

Step 3 : $Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+$ $\qquad$ $PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

Steps 4 and 5 : $[Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-] \times 2$

$[PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O] \times 5$

Step 6 : $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

(ii) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

*Steps*1 and 2 : $2S \xrightarrow{\text{oxidation}} S_2O_3^{2-}$ $\qquad$ $S \xrightarrow{\text{reduction}} S^{2-}$

Step 3 : $2S + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+$ $\qquad$ $S \rightarrow S^{2-}$

Steps 4 and 5 : $2S + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4e^-$

$[S + 2e^- \rightarrow S^{2-}] \times 2$

Step 6 : $4S + 3H_2O \rightarrow 2S^{2-} + S_2O_3^{2-} + 6H^+$ $\qquad$ or $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(iii) $ClO_3^- + I^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

Steps 1 and 2 : $2I^- \xrightarrow{\text{oxidation}} I_2$ $\qquad$ $ClO_3^- \xrightarrow{\text{reduction}} Cl^-$

Step 3 : $2I^- \rightarrow I_2$ $\qquad$ $ClO_3^- + 3H_2SO_4 \rightarrow Cl^- + 3HSO_4^- + 3H_2O$

Steps 4 and 5 : $2I^- \rightarrow I_2 + 2e^-$

$[ClO_3^- + 3H_2SO_4 + e^- \rightarrow Cl^- + 3HSO_4^- + 3H_2O] \times 2$

Step 6 : $2I^- + 2ClO_3^- + 6H_2SO_4 \rightarrow I_2 + 2Cl^- + 6HSO_4^- + 6H_2O$

(iv) $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + H^+ + Ag$

Steps 1 and 2 : $AsH_3 \xrightarrow{\text{oxidation}} H_3AsO_3$ $\qquad$ $Ag^+ \xrightarrow{\text{reduction}} Ag$

Step 3 : $AsH_3 + 3H_2O \rightarrow H_3AsO_3 + 6H^+$ $\qquad$ $Ag^+ \rightarrow Ag$

Steps 4 and 5 : $AsH_3 + 3H_2O \rightarrow H_3AsO_3 + 6H^+ + 6e^-$

$[Ag^+ + e^- \rightarrow Ag] \times 6$

Step 6 : $AsH_3 + 6Ag^+ + 3H_2O \rightarrow H_3AsO_3 + 6Ag + 6H^+$

4. Balance the following equations.

(i) $As_2S_3 + OH^- + H_2O_2 \rightarrow AsO_4^{3-} + SO_4^{2-} + H_2O$

(ii) $CrI_3 + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + H_2O$

(iii) $P_4 + OH^- + H_2O_2 \rightarrow H_2PO_2^- + PH_3$

(iv) $As_2S_3 + NO_3^- + H^+ + H_2O \rightarrow H_3AsO_4 + NO + S$

Solution

We may arrive at the balanced equations as shown in the following.

(i) $As_2S_3 + OH^- + H_2O_2 \rightarrow AsO_4^{3-} + SO_4^{2-} + H_2O$

Steps 1 and 2 : $As_2S_3 \xrightarrow{\text{oxidation}} 2AsO_4^{3-} + 3SO_4^{2-}$ $\qquad$ $H_2O_2 \xrightarrow{\text{reduction}} 2OH^-$

Step 3 : $As_2S_3 + 40OH^- \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$ $\qquad$ $H_2O_2 \rightarrow 2OH^-$

Steps 4 and 5 : $As_2S_3 + 40OH^- \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O + 28e^-$

$[H_2O_2 + 2e^- \rightarrow 2OH^-] \times 14$

Step 6 : $As_2S_3 + 12OH^- + 14H_2O_2 \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$

(ii) $CrI_3 + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + H_2O$

Steps 1 and 2 : $CrI_3 \xrightarrow{\text{oxidation}} CrO_4^{2-} + 3IO_4^-$ $\qquad$ $H_2O_2 \xrightarrow{\text{reduction}} 2OH^-$

Step 3 : $CrI_3 + 32OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O$ $\qquad$ $H_2O_2 \rightarrow 2OH^-$

Steps 4 and 5 : $[CrI_3 + 32OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O + 27e^-] \times 2$

$[H_2O_2 + 2e^- \rightarrow 2OH^-] \times 27$

Step 6 : $2CrI_3 + 10OH^- + 27H_2O_2 \rightarrow 2CrO_4^{2-} + 6IO_4^- + 32H_2O$

(iii) $P_4 + OH^- + H_2O_2 \rightarrow H_2PO_2^- + PH_3$

Steps 1 and 2 : $\frac{1}{4}P_4 \xrightarrow{\text{oxidation}} H_2PO_2^-$ $\qquad$ $\frac{1}{4}P_4 \xrightarrow{\text{reduction}} PH_3$

Step 3 : $\frac{1}{4}P_4 + 2OH^- \rightarrow H_2PO_2^-$ $\qquad$ $\frac{1}{4}P_4 + 3H_2O \rightarrow PH_3 + 3OH^-$

Steps 4 and 5 : $[\frac{1}{4}P_4 + 2OH^- \to H_2PO_2^- + e^-] \times 3$

$\frac{1}{4}P_4 + 3H_2O + 3e^- \to PH_3 + 3OH^-$

Step 6 : $P_4 + 3OH^- + 3H_2O \to 3H_2PO_2^- + PH_3$

(iv) $As_2S_3 + NO_3^- + H^+ + H_2O \to H_3AsO_4 + NO + S$

Steps 1 and 2 : $As_2S_3 \xrightarrow{\text{oxidation}} 2H_3AsO_4 + 3S$ $NO_3^- \xrightarrow{\text{reduction}} NO$

Step 3 : $As_2S_3 + 8H_2O \to 2H_3AsO_4 + 3S + 10H^+$ $NO_3^- + 4H^+ \to NO + 2H_2O$

Steps 4 and 5 : $[As_2S_3 + 8H_2O \to 2H_3AsO_4 + 3S + 10H^+ + 10e^-] \times 3$

$[NO_3^- + 4H^+ + 3e^- \to NO + 2H_2O] \times 10$

Step 6 : $3As_2S_3 + 4H_2O + 10NO_3^- + 10H^+ \to 6H_3AsO_4 + 9S + 10NO$

5. Balance the following equations.

(i) $O_2 + Cr \xrightarrow{\text{alkaline medium}} Cr(OH)_4^-$ (ii) $MnO_4^{2-} + H^+ \to MnO_2 + MnO_4^-$

(iii) $Ag_2O + AsH_3 \xrightarrow{\text{alkaline medium}} Ag + H_2AsO_3^-$ (iv) $IO_3^- + Cl^- \to I_2 + Cl_2$

Solution

(i) $O_2 + Cr \xrightarrow{\text{alkaline medium}} Cr(OH)_4^-$

Steps 1 and 2 : $Cr \xrightarrow{\text{oxidation}} Cr(OH)_4^-$ $2O_2 \xrightarrow{\text{reduction}} Cr(OH)_4^-$

Step 3 : $Cr + 4OH^- \to Cr(OH)_4^-$ $2O_2 + Cr + 4H_2O \to Cr(OH)_4^- + 4OH^-$

Steps 4 and 5 : $[Cr + 4OH^- \to Cr(OH)_4^- + 3e^-] \times 5$

$[2O_2 + Cr + 4H_2O + 5e^- \to Cr(OH)_4^- + 4OH^-] \times 3$

Step 6 : $8Cr + 6O_2 + 8OH^- + 12H_2O \to 8Cr(OH)_4^-$ or $4Cr + 3O_2 + 4OH^- + 6H_2O \to 4Cr(OH)_4^-$

(ii) $MnO_4^{2-} + H^+ \to MnO_2 + MnO_4^-$

Steps 1 and 2 : $MnO_4^{2-} \xrightarrow{\text{oxidation}} MnO_4^-$ $MnO_4^{2-} \xrightarrow{\text{reduction}} MnO_2$

Step 3 : $MnO_4^{2-} \to MnO_4^-$ $MnO_4^{2-} + 4H^+ \to MnO_2 + 2H_2O$

Steps 4 and 5 : $[MnO_4^{2-} \to MnO_4^- + e^-] \times 2$

$MnO_4^{2-} + 4H^+ + 2e^- \to MnO_2 + 2H_2O$

Step 6 : $3MnO_4^{2-} + 4H^+ \to 2MnO_4^- + MnO_2 + 2H_2O$

(iii) $Ag_2O + AsH_3 \xrightarrow{\text{alkaline medium}} Ag + H_2AsO_3^-$

Steps 1 and 2 : $AsH_3 \xrightarrow{\text{oxidation}} H_2AsO_3^-$ $Ag_2O \xrightarrow{\text{reduction}} 2Ag$

Step 3 : $AsH_3 + 7OH^- \to H_2AsO_3^- + 4H_2O$ $Ag_2O + H_2O \to 2Ag + 2OH^-$

Steps 4 and 5 : $AsH_3 + 7OH^- \to H_2AsO_3^- + 4H_2O + 6e^-$

Step 6 : $[Ag_2O + H_2O + 2e^- \to 2Ag + 2OH^-] \times 3$

$AsH_3 + 3Ag_2O + OH^- \to H_2AsO_3^- + 6Ag + H_2O$

(iv) $IO_3^- + Cl^- \to I_2 + Cl_2$

Steps 1 and 2 : $2Cl^- \xrightarrow{\text{oxidation}} Cl_2$ $2IO_3^- \xrightarrow{\text{reduction}} I_2$

Step 3 : $2Cl^- \to Cl_2$ $2IO_3^- + 12H^+ \to I_2 + 6H_2O$

Steps 4 and 5 : $[2Cl^- \to Cl_2 + 2e^-] \times 5$

$2IO_3^- + 12H^+ + 10e^- \to I_2 + 6H_2O$

Step 6 : $10Cl^- + 2IO_3^- + 12H^+ \to 5Cl_2 + I_2 + 6H_2O$

6. Arrange the following in order of increasing oxidation number of

(i) Iodine : I_2, HI, HIO_4, ICl (ii) Manganese : $MnCl_2$, MnO_2, $KMnO_4$

(iii) Nickel : $K_2[Ni(CN)_4]$, $K_2[NiF_6]$, $Ni(CO)_4$ (iv) Sulphur : S_8, $S_2O_8^{2-}$, $S_2O_3^{2-}$, $S_4O_6^{2-}$.

(i) The oxidation numbers of iodine are shown below alongwith the compounds.

$$\overset{0}{I_2}, H\overset{-1}{I}, H\overset{+7}{I}O_4, \overset{+1}{I}Cl$$

Hence, the increasing order of oxidation number of iodine in the compounds is

$$HI < I_2 < ICl < HIO_4$$

(ii) The oxidation numbers of Mn are shown below alongwith the compounds.

$$\overset{+2}{Mn}Cl_2, \overset{+4}{Mn}O_2, K\overset{+7}{Mn}O_4$$

Hence, the order is $MnCl_2 < MnO_2 < KMnO_4$

(iii) The oxidation numbers of Ni are shown below alongwith the compounds.

$$K_2[\overset{+2}{Ni}(CN)_4], K_2[\overset{+4}{Ni}F_6], \overset{0}{Ni}(CO)_4$$

Hence, the order is $Ni(CO)_4 < K_2[Ni(CN)_4] < K_2[NiF_6]$

(iv) The oxidation numbers of S are shown below alongwith the compounds.

$$\overset{0}{S}_8, \overset{+7}{S}_2O_8^{2-}, \overset{+2}{S}_2O_3^{2-} . \overset{+2.5}{S}_4O_6^{2-}$$

Hence, the order is $S_8 < S_2O_3^{2-} < S_4O_6^{2-} < S_2O_8^{2-}$

Unbalanced Chemical Equations

Complete and balance the following equations adding H^+, OH^- or H_2O as required.

(a) $CrO_4^{2-} + Cu_2O \rightarrow Cr(OH)_4^- + Cu(OH)_2$

(b) $Cu_3P + Cr_2O_7^{2-} \rightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$

(c) $Fe^{2+} + UO_2^{2+} \rightarrow Fe^{3+} + U^{4+}$

(d) $Cu_2O + NO_3^- \rightarrow Cu^{2+} + NO$

(e) $P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2$

(f) $Pb_3O_4 + H_2SO_4 \rightarrow PbSO_4 + O_2$

(g) $IO_3^- + I^- \rightarrow I_2$

(h) $HNO_3 + I_2 \rightarrow NO_2 + HIO_3$

(i) $P_4O_{11} + HNO_2 \rightarrow HPO_3 + N_2O_5$

(j) $IO_3^- + H_3AsO_3 + Cl^- \rightarrow ICl_2^- + H_3AsO_4$

(k) $Cr^{3+} + MnO_4^- \rightarrow Cr_2O_7^{2-} + Mn^{2+}$

(l) $Mg + HNO_3 \rightarrow Mg(NO_3)_2 + NH_4NO_3$

(m) $SnS_2 + NaOH \rightarrow Na_2SnS_3 + Na_2SnO_3$

(n) $Cr(OH)_4^- + HO_2^- \rightarrow CrO_4^{2-} + OH^- + H_2O$

(o) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO$

(p) $Ag + O_2 + CN^- \rightarrow Ag(CN)_2^- + OH^-$

(q) $Zn + NaNO_3 + NaOH \rightarrow NH_3 + Na_2ZnO_2$

(r) $Au + HNO_3 + HCl \rightarrow HAuCl_4 + NO$

(s) $BrO_3^- + Br^- \rightarrow Br_2$

(t) $MnO_4^- + As_2O_3 \rightarrow Mn^{2+} + H_3AsO_4$

(u) $Cu + HNO_3 \rightarrow Cu^{2+} + NO_2 + NO_3^-$

(v) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

(w) $I_2 + OH^- \rightarrow I^- + IO_3^-$

(x) $P_4 + OH^- \rightarrow H_2PO_4^- + PH_3$

(y) $KClO_3 + H_2SO_4 \rightarrow HClO_4 + KHSO_4 + ClO_2$

(z) $I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

ANSWERS

(a) $2CrO_4^{2-} + 3Cu_2O + 2H^+ + 9H_2O \rightarrow 2Cr(OH)_4^- + 6Cu(OH)_2$

(b) $6Cu_3P + 11Cr_2O_7^{2-} + 124H^+ \rightarrow 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} + 53H_2O$

(c) $2Fe^{2+} + UO_2^{2+} + 4H^+ \rightarrow 2Fe^{3+} + U^{4+} + 2H_2O$

(d) $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6Cu^{2+} + 2NO + 7H_2O$

(e) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(f) $2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$

(g) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

(h) $10HNO_3 + I_2 \rightarrow 10NO_2 + 2HIO_3 + 4H_2O$

(i) $2P_4O_{11} + 2HNO_2 + 3H_2O \rightarrow 8HPO_3 + N_2O_5$

(j) $IO_3^- + 2Cl^- + 2H^+ + 2H_3AsO_3 \rightarrow ICl_2 + 2H_3AsO_4 + H_2O$

(k) $10Cr^{3+} + 6MnO_4^- + 22OH^- \rightarrow 5Cr_2O_7^{2-} + 11H_2O + 6Mn^{2+}$

(l) $4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

(m) $3SnS_2 + 6NaOH \rightarrow 2Na_2SnS_3 + Na_2SnO_3 + 3H_2O$

(n) $2Cr(OH)_4^- + 3HO_2^- \rightarrow 2CrO_4^{2-} + OH^- + 5H_2O$

(o) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(p) $4Ag + O_2 + 8CN^- + 2H_2O \rightarrow 4[Ag(CN)_2]^- + 4OH^-$

(q) $4Zn + NaNO_3 + 7NaOH \rightarrow NH_3 + 4Na_2ZnO_2 + 2H_2O$

(r) $2Au + 2HNO_3 + 8HCl \rightarrow 2HAuCl_4 + 2NO + 4H_2O$

(s) $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

(t) $4MnO_4^- + 5As_2O_3 + 12H^+ + 9H_2O \rightarrow 4Mn^{2+} + 10H_3AsO_4$

(u) $Cu + 4HNO_3 \rightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$

(v) $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(w) $6I_2 + 12OH^- \rightarrow 10\,I^- + 2IO_3^- + 6H_2O$

(x) $2P_4 + 3OH^- + 9\,H_2O \rightarrow 3H_2PO_4^- + 5PH_3$

(y) $3\,KClO_3 + 3H_2SO_4 \rightarrow HClO_4 + 3KHSO_4 + H_2O + 2ClO_2$

(z) $6I^- + ClO_3^- + 6\,H_2SO_4 \rightarrow Cl^- + 6\,HSO_4^- + 3I_2 + 3H_2O$

Solved Problems

1. A 1.0 g sample of H_2O_2 solution containing $X\%$ H_2O_2 by mass requires X cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution. (1981)

Solution The equations involved are

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2 \\ \underline{H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5} \\ \hline 2\,MnO_4^- + 5H_2O_2 + 6\,H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O \end{array}$$

From this equation, we find that

$$\text{Equivalent mass of } H_2O_2, \quad M_{eq} = \frac{\text{Molar mass of } H_2O_2}{2\text{ eq mol}^{-1}} = \frac{34\text{ g mol}^{-1}}{2\text{ eq mol}^{-1}} = 17\text{ g eq}^{-1}$$

Mass of H_2O_2 in the given 1.0 g sample, $m_{eq} = \dfrac{X}{100} \times 1.0$ g

Amount (in equivalents) of H_2O_2 in the given 1.0 g sample is

$$n_{eq} = \frac{m}{M_{eq}} = \frac{(X/100)\text{ g}}{17\text{ g eq}^{-1}} = \frac{X}{17 \times 100}\text{ eq} \qquad (1)$$

If N_{KMnO_4} is the normality of $KMnO_4$, the amount (in equivalents) of $KMnO_4$ consumed is

$$n'_{eq} = V_{KMnO_4}\,N_{KMnO_4} = \left(\frac{X}{1000}\text{ L}\right) N_{KMnO_4} \qquad (2)$$

Equating Eqs (1) and (2), we get

$$\left(\frac{X}{1000}\text{ L}\right) N_{KMnO_4} = \frac{X}{17 \times 100}\text{ eq} \qquad \text{or} \qquad N_{KMnO_4} = \frac{10}{17}\text{ eq L}^{-1} = 0.588\text{ eq L}^{-1}$$

2. Hydroxylamine reduces iron(III) according to the equation

$$2NH_2OH + 4Fe^{3+} \rightarrow N_2O(g) + H_2O + 4Fe^{2+} + 4H^+$$

Iron(II) thus produced is estimated by titration with a standard permanganate solution. The reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

A 10 mL sample of hydroxylamine solution was diluted to 1 litre. 50 mL of this diluted solution was boiled with excess of iron (III) solution. The resulting solution required 12 mL of 0.02 M $KMnO_4$ solution for complete oxidation of iron (II). Calculate the mass of hydroxylamine in one litre of the original solution. (1982)

Solution From the given chemical equations, we find that

$$2 \text{ mol } NH_2OH \equiv 4 \text{ mol } Fe^{2+} \quad \text{and} \quad 1 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Fe^{2+}$$

Amount of MnO_4^- consumed in the oxidation of iron(II)

$$= VM = (12 \text{ mL})\ (0.02 \text{ M}) = \left(\frac{12}{1000} \text{ L}\right) (0.02 \text{ mol L}^{-1}) = \frac{12 \times 0.02}{1000} \text{ mol}$$

Since 1 mol $MnO_4^- \equiv 5$ mol Fe^{2+}, we have

Amount of Fe^{2+} formed by the reduction of Fe^{3+} by $NH_2OH = (5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Now since 2 mol $NH_2OH \equiv 4$ mol Fe^{2+}, we have

Amount of NH_2OH present in 50 mL of diluted solution $= \left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Amount of NH_2OH present in 1 L of diluted solution $= \left(\frac{1000}{50}\right)\left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Amount of NH_2OH present in 1 L of undiluted solution $= \left(\frac{1000}{10}\right)\left(\frac{1000}{50}\right)\left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol = 1.2 mol

Mass of NH_2OH present in 1 L of undiluted solution = (1.2 mol) (33 g mol^{-1}) = 39.6 g.

3. A mixture weighing 4.08 g of BaO and unknown carbonate XCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralization. Identify the metal M. (1983)

Solution On heating, we have $XCO_3 \rightarrow XO + CO_2$

The loss of mass (= 4.08 g –3.64 g = 0.44 g) is due to the removal of CO_2. Thus

$$\text{Amount of } CO_2 \text{ released} = \frac{0.44 \text{ g}}{44 \text{ g mol}^{-1}} = 10^{-2} \text{ mol}$$

Hence, Amount of XO = 10^{-2} mol

Now Mass of BaO in the mixture after heating

$$\begin{aligned} &= 3.64 \text{ g} - (10^{-2} \text{ mol})\ (M_{XO}) \\ &= 3.64 \text{ g} - (10^{-2} \text{ mol})\ (M_X + 16 \text{ g mol}^{-1}) \\ &= 3.48 \text{ g} - (10^{-2} \text{ mol})\ (M_X) \end{aligned}$$

From the dissolution reactions $BaO + 2HCl \rightarrow BaCl_2 + H_2O$ and $XO + 2HCl \rightarrow XCl_2 + H_2O$ we conclude that

$$\text{Amount of HCl consumed for the dissolution process} = 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\, M_X}{M_{BaO}} + 10^{-2} \text{ mol}\right]$$

$$\text{Amount of HCl taken for the dissolution process} = (100 \text{ mL})\ (0.1 \text{ M}) = \left(\frac{100}{1000} \text{ L}\right)(1 \text{ mol L}^{-1}) = 0.1 \text{ mol}$$

$$\text{Amount of remaining HCl} = 0.1 \text{ mol} - 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\, M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol}\right]$$

Since the remaining HCl required 16 mL of 2.5 M NaOH $\left(= \frac{16}{1000} \times 2.5 \text{ mol}\right)$ for complete neutralization, we would have

$$\frac{16 \times 2.5}{1000} \text{ mol} = 0.1 \text{ mol} - 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\, M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol}\right]$$

This gives $$M_X = \frac{\left(\frac{16\times 2.5}{1000} - 0.1 + 2\times 10^{-2}\right)\left(\frac{154}{2}\right)\text{g} + 3.48\text{ g}}{\left(10^{-2}\text{ mol}\right)} = 40\text{ g mol}^{-1}$$

Hence, the element X is Ca.

4. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n? (1984)

Solution From the chemical equations

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{and} \quad A^{n+} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5-n)e^-$$

we write

Amount of electrons involved in reducing the given amount of MnO_4^- $= 5 \times 1.61 \times 10^{-3}$ mol

Amount of electrons involved in oxidizing the given amount of A^{n+} $= (5-n) \times 2.68 \times 10^{-3}$ mol

Equating these two, we get

$$5 \times 1.61 \times 10^{-3}\text{ mol} = (5-n) \times 2.68 \times 10^{-3}\text{ mol}$$

Hence, $$n = \frac{5\,(2.68 - 1.61)}{2.68} = \frac{5 \times 1.07}{2.68} \simeq 2.$$

5. Five mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. Thirty mL of this acid solution exactly neutralizes 42.9 mL of sodium carbonate solution containing 1 g of $Na_2CO_3 \cdot 10\,H_2O$ in 100 mL of water. Calculate the mass of SO_4 units in the solution. (1985)

Solution Let V be the volume of sulphuric acid taken while mixing the given acids. We will have

Amount of H^+ in 2 L of acids solution

$$= (5\text{ mL})\,(8\text{ M}) + (4.8\text{ mL})\,(5\text{ M}) + (V)\,(2 \times 17\text{ M})$$

$$= \left(\frac{5}{1000}\text{L}\right)(8\text{ mol L}^{-1}) + \left(\frac{4.8}{1000}\text{L}\right)(5\text{ mol L}^{-1}) + (V)\,(2 \times 17\text{ mol L}^{-1})$$

$$= \left(\frac{1}{1000}\right)\left[5\times 8 + 4.8\times 5 + \left(\frac{V}{\text{mL}}\right)(2\times 17)\right]\text{mol} = \left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]\text{mol}$$

Amount of H^+ in 30 mL of acids solution $= \left(\frac{30}{2000}\right)\left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]$ mol (1)

Mass of sodium carbonate neutralized by 30 mL of acids solution $= \left(\frac{1\text{ g}}{100\text{ mL}}\right)(42.9\text{ mL}) = \frac{42.9}{100}$ g

Amount of sodium carbonate neutralized $= \frac{(42.9/100)\text{ g}}{286\text{ g mol}^{-1}} = \frac{42.9}{100 \times 286}$ mol (2)

From the chemical equation $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ we find that $1\text{ mol } CO_3^{2-} \equiv 2\text{ mol } H^+$

Hence, from Eqs. (1) and (2), we write

$$2\left(\frac{42.9}{100 \times 286}\right) = \left(\frac{30}{2000}\right)\left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]$$

which gives $$\frac{V}{\text{mL}} = \frac{1}{34}\left[2\left(\frac{42.9}{100 \times 286}\right)\left(\frac{2000}{30}\right)\left(\frac{1000}{1}\right) - 64\right] = 4 \quad \text{i.e.,} \quad V = 4\text{ mL}$$

Finally,

Mass of SO_4 unit in 4 mL of 17 M H_2SO_4 solution

$$= (4\text{ mL})\,(17\text{ mol L}^{-1})\,(96\text{ g mol}^{-1}) = \left(\frac{4}{1000}\right)(17)\,(96)\text{ g} = 6.528\text{ g.}$$

6. (i) What is the mass of sodium bromate and molarity of solution necessary to prepare 85.5 mL of 0.672 N solution when the half-cell reaction is $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$. (1987)

(ii) What would be the mass as well as molarity if the half-cell reaction is $2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$?

Solution

(i) Since 6 electrons are involved in the half-cell reaction, we would have

$$\text{Molarity of } BrO_3^- = \frac{0.672}{6}\ \text{M}$$

Amount of BrO_3^- in 85.5 mL of bromate solution

$$= VM = (85.5\ \text{mL})\left(\frac{0.672}{6}\ \text{M}\right) = \left(\frac{85.5}{1000}\ \text{L}\right)\left(\frac{0.672}{6}\ \text{mol L}^{-1}\right) = \left(\frac{85.5}{1000}\right)\left(\frac{0.672}{6}\right)\ \text{mol}$$

$$\text{Mass of } NaBrO_3 \text{ in 85.5 mL of solution} = \left(\frac{85.5}{1000}\right)\left(\frac{0.672}{6}\right)(151)\ \text{g} = 1.446\ \text{g}$$

(ii) Since 5 electrons per BrO_3^- ion are involved in the half-cell reaction, we would have

$$\text{Molarity of } BrO_3^- = \frac{0.672}{5}\ \text{M}$$

$$\text{Mass of } NaBrO_3 \text{ in 85.5 mL of solution} = \left(\frac{85.5}{1000}\right)\left(\frac{0.672}{5}\right)(151)\ \text{g} = 1.735\ \text{g}.$$

7. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL of water. 10 mL of this solution was made to react with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of M/50 potassium permanganate solution. Estimate the mass of hydrazine sulphate in one litre of the solution. (1988)

Reactions: $4\ Fe^{3+} + N_2H_4 \rightarrow N_2 + 4Fe^{2+} + 4H^+$

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Solution From the given chemical equations, we find that

$$1\ \text{mol}\ N_2H_4 \equiv 4\ \text{mol}\ Fe^{2+} \quad \text{and} \quad 5\ \text{mol}\ Fe^{2+} \equiv 1\ \text{mol}\ MnO_4^-$$

Amount of $KMnO_4$ in 20 mL of M/50 solution

$$= VM = (20\ \text{mL})\left(\frac{1}{50}\ \text{M}\right) = \left(\frac{20}{1000}\ \text{L}\right)\left(\frac{1}{50}\ \text{mol L}^{-1}\right) = \frac{20}{1000\times 50}\ \text{mol}$$

$$\text{Amount of equivalent } Fe^{2+} \text{ ions} = 5\left(\frac{20}{1000\times 50}\right)\ \text{mol}$$

$$\text{Amount of equivalent } N_2H_4 = \left(\frac{1}{4}\right)(5)\left(\frac{20}{1000\times 50}\right)\ \text{mol}$$

The above amount is present in 10 mL of the solution. Hence,

$$\text{Amount of } N_2H_6SO_4 \text{ present in 1 L solution} = \left(\frac{1000}{10}\right)\left(\frac{1}{4}\right)(5)\left(\frac{20}{1000\times 50}\right)\ \text{mol}$$

$$\text{Mass of } N_2H_6SO_4 \text{ present in 1 L solution} = \left(\frac{1000}{10}\right)\left(\frac{1}{4}\right)(5)\left(\frac{20}{1000\times 50}\right)(130)\ \text{g} = 6.5\ \text{g}$$

8. A mixture of $H_2C_2O_4$ (oxalic acid) and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N $KMnO_4$ solution for complete reaction. Calculate the masses of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture. (1990)

Solution Let x be the mass of oxalic acid in 2.02 g of the mixture. We will have

$$\text{Molarity of oxalic acid} = \frac{n}{V} = \frac{\left(x/90\ \text{g mol}^{-1}\right)}{1\ \text{L}} = \frac{x}{90\ \text{g}}\ \text{mol L}^{-1}$$

$$\text{Molarity of } NaHC_2O_4 = \frac{(2.02\text{ g} - x)/112\text{ g mol}^{-1}}{1\text{ L}} = \frac{(2.02\text{ g} - x)}{(112\text{ g})}\text{ mol L}^{-1}$$

$$\text{Amount of oxalic acid in 10 mL solution} = VM = \left(\frac{10}{1000}\text{ L}\right)\left(\frac{x}{90\text{ g}}\text{ mol L}^{-1}\right) = \left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right)\text{ mol}$$

$$\text{Amount of } NaHC_2O_4 \text{ in 10 mL solution} = \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\text{ mol}$$

Now from the neutralization reactions

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O \quad \text{and} \quad NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$$

we find that $1\text{ mol } H_2C_2O_4 \equiv 2\text{ mol NaOH}$ and $1\text{ mol } NaHC_2O_4 \equiv 1\text{ mol NaOH}$

Hence,

$$\text{Amount of NaOH equivalent to } H_2C_2O_4 = 2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right)\text{ mol}$$

$$\text{Amount of NaOH equivalent to } NaHC_2O_4 = \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\text{ mol}$$

Total amount of NaOH equivalent to 10 mL solution containing $H_2C_2O_4$ and $NaHC_2O_4$

$$= \left[2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right) + \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\right]\text{ mol}$$

This amount will be equal to the amount of NaOH present in 3.0 mL of 0.1 N NaOH solution. Hence,

$$2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right) + \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right) = \left(\frac{3.0}{1000}\right)(0.1)$$

Solving for x, we get $x = 0.9\text{ g}$

Hence, in the original mixture, we have

Mass of oxalic acid = 0.9 g and Mass of $NaHC_2O_4 = 2.02\text{ g} - 0.9\text{ g} = 1.12\text{ g}$.

9. 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 masses of lead nitrate and sodium nitrate in the mixture. (1990)

Solution Let x be the mass of lead nitrate in the mixture. Heating the mixture results into the following reactions.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

Hence,

$$\text{Mass of PbO obtained} = \frac{2\,M_{PbO}}{2\,M_{Pb(NO_3)_2}} \times x = \frac{223}{331}\,x$$

$$\text{Mass of } NaNO_2 \text{ obtained} = \frac{2\,M_{NaNO_2}}{2\,M_{NaNO_3}}\,(5.0\text{ g} - x) = \left(\frac{69}{85}\right)(5.0\text{ g} - x)$$

$$\text{Total mass of residue} = \frac{223}{331}\,x + \frac{69}{85}\,(5.0\text{ g} - x)$$

Since there occurs 28 per cent loss in mass, we would have

$$\frac{223}{331}\,x + \frac{69}{85}\,(5.0\text{ g} - x) = \frac{100 - 28}{100} \times 5.0\text{ g}$$

Solving for x, we get $x = 3.32\text{ g}$

Hence, Mass of lead nitrate = 3.32 g and Mass of sodium nitrate = (5.0 − 3.32) g = 1.68 g.

10. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $C_2O_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titration. (1991)

Solution The chemical equations involved in the titration of $C_2O_4^{2-}$ with MnO_4^- are :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

From this equation, we conclude 2 mol $MnO_4^- \equiv$ 5 mol $C_2O_4^{2-}$. Hence,

$$\text{Amount of } C_2O_4^{2-} \text{ in the solution} = \left(\frac{5}{2}\right)(22.6\text{ mL})(0.02\text{ M}) = \left(\frac{5}{2}\right)\left(\frac{22.6}{1000}\text{ L}\right)(0.02\text{ mol L}^{-1}) = 0.00113\text{ mol}$$

The chemical equations involved during the treatment of KI and the titration with $Na_2S_2O_3$ are

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2 \quad\text{and}\quad I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

From these equations, we conclude

$$2\text{ mol } Cu^{2+} \equiv 4\text{ mol } I^- \equiv 1\text{ mol } I_2 \quad\text{and}\quad 1\text{ mol } I_2 \equiv 2\text{ mol } S_2O_3^{2-}$$

Now,
$$\text{Amount of } S_2O_3^{2-} \text{ consumed} = (11.3\text{ mL})(0.05\text{ M}) = \left(\frac{11.3}{1000}\text{ L}\right)(0.05\text{ mol L}^{-1})$$
$$= \left(\frac{11.3}{1000}\right)(0.05)\text{ mol} = 0.000565\text{ mol}$$

Amount of Cu^{2+} equivalent to the above amount of $S_2O_3^{2-}$ = 0.000 565 mol

Hence,
$$\frac{\text{Amount of } Cu^{2+}}{\text{Amount of } C_2O_4^{2-}} = \frac{0.000565}{0.00113} = \frac{1}{2}$$

11. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991)

Solution We have

$$\text{Mass of } Fe_2O_3 \text{ in the sample} = (1.0\text{ g})\left(\frac{55.2}{100}\right) = 0.552\text{ g};\qquad \text{Molar mass of } Fe_2O_3 = 159.8\text{ g mol}^{-1}$$

$$\text{Amount of } Fe_2O_3 = \frac{0.552\text{ g}}{159.8\text{ g mol}^{-1}} = 3.454 \times 10^{-3}\text{ mol};\qquad \text{Amount of } Fe^{3+} \text{ ions} = 2 \times 3.454 \times 10^{-3}\text{ mol}$$

On reduction, we have

$$\text{Amount of } Fe^{2+} \text{ ions} = 2 \times 3.454 \times 10^{-3}\text{ mol}$$

$$\text{Molarity of } Fe^{2+} \text{ ions} = \frac{2 \times 3.454 \times 10^{-3}\text{ mol}}{100 \times 10^{-3}\text{ L}} = 6.908 \times 10^{-2}\text{ mol L}^{-1}$$

If z is the number of electrons taken by the oxidant, we will have

$$(25.0\text{ mL})(6.908 \times 10^{-2}\text{ mol L}^{-1})(1\text{ eq mol}^{-1}) = (17.0\text{ mL})(0.0167\text{ mol L}^{-1})(z\text{ eq mol}^{-1})$$

which gives
$$z = \frac{25.0 \times 6.908 \times 10^{-2}}{17 \times 0.0167} = 6.$$

12. One gram of commercial $AgNO_3$ is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with M/10 KIO_3 solution in presence of 6 M HCl till all I^- ions are converted into ICl. It requires 50 mL of M/10 KIO_3 solution. Twenty milliliters of the same stock solution of KI requires 30 mL of M/10 KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in the sample. (Reaction: $KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$.) (1992)

Solution It is given that 20 mL of stock solution of KI requires 30 mL of M/10 KIO_3 solution to convert I^- ions into ICl according to the reaction

$$KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$$

For 50 mL of KI solution, the required volume of KIO_3 solution would be

$$\frac{30\ \text{mL of KIO}_3\ \text{solution}}{20\ \text{mL of KI solution}} \times 50\ \text{mL of KI solution} = 75\ \text{mL of KIO}_3\ \text{solution}$$

After treating 50 mL of KI solution with 1 g $AgNO_3$ sample, the volume of KIO_3 solution used is 50 mL. This means KI equivalent to 25 mL of KIO_3 solution is used in precipitating out Ag^+ ions from 50 mL of KI solution.

$$\text{Amount of KIO}_3\ \text{in 25 mL of M/10 KIO}_3\ \text{solution} = (25\ \text{mL})\left(\frac{1}{10}\text{M}\right) = \left(\frac{25}{1000}\text{L}\right)\left(\frac{1}{10}\text{mol L}^{-1}\right) = 0.002\,5\ \text{mol}$$

$$\text{Amount of KI equivalent to this amount} = 2 \times 0.0025\ \text{mol}$$

$$\text{Mass of AgNO}_3\ \text{precipitated out} = 2 \times 0.0025 \times 170\ \text{g} = 0.85\ \text{g}$$

$$\text{Per cent of AgNO}_3\ \text{in the sample} = \frac{0.85\ \text{g}}{1.0\ \text{g}} \times 100 = 85.$$

13. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mmHg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralization. Calculate the percentage composition of the components of the mixture. (1992)

Solution The evolution of CO_2 on heating the mixture is due to the reaction $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

From the liberated volume of CO_2, we calculate

$$\text{Amount of liberated CO}_2 = \frac{pV}{RT} = \frac{\{(750/760)\ \text{atm}\}\,(0.1239\ \text{L})}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\,(298\ \text{K})} = 0.005\ \text{mol.}$$

From the chemical equation given above, we conclude that

$$\text{Amount of NaHCO}_3\ \text{present in 2.0 g sample of the mixture} = 2 \times 0.005\ \text{mol} = 0.01\ \text{mol}$$

$$\text{Mass of NaHCO}_3\ \text{present in the mixture} = (0.01\ \text{mol})\ (84\ \text{g mol}^{-1}) = 0.84\ \text{g}$$

The treatment of the mixture with HCl solution would cause the following neutralization reactions.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O \quad \text{and} \quad NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$$

Now, 1.5 g of the sample required 150 mL of M/10 HCl. For 2.0 g of the sample, volume of HCl required would be 200 mL. Hence,

$$\text{Amount of HCl in 200 mL of M/10 HCl} = (200\ \text{mL})(0.1\ \text{mol L}^{-1}) = \left(\frac{200}{1000}\text{L}\right)(0.1\ \text{mol L}^{-1}) = 0.02\ \text{mol}$$

Since the mixture contains 0.01 mol of $NaHCO_3$, 0.01 mol out of 0.02 mol would be consumed for the neutralization of $NaHCO_3$. The remaining 0.01 mol will used for the neutralization of Na_2CO_3. From the chemical equation given above, we conclude that

$$\text{Amount of Na}_2\text{CO}_3\ \text{present in the 2.0 g sample of the mixture} = \left(\frac{0.01\ \text{mol}}{2}\right) = 0.005\ \text{mol}$$

$$\text{Mass of Na}_2\text{CO}_3\ \text{present in 2.0 g sample of the mixture} = (0.005\ \text{mol})\ (106\ \text{g mol}^{-1}) = 0.53\ \text{g}$$

Hence, $$\text{Mass per cent of Na}_2\text{CO}_3 = \left(\frac{0.53\ \text{g}}{2.0\ \text{g}} \times 100\right) = 26.5;\ \text{Mass per cent of NaHCO}_3 = \left(\frac{0.84\ \text{g}}{2.0\ \text{g}} \times 100\right) = 42.0$$

$$\text{Mass per cent of Na}_2\text{SO}_4 = 100 - (26.5 + 42.0) = 31.5.$$

14. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25.0 mL of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. What amount of lead sulphate is formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993)

Solution To start with, we have

$$\text{Amount of } Pb(NO_3)_2 = MV = (0.25 \text{ mol L}^{-1})(45 \times 10^{-3} \text{ L}) = 11.25 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } Cr_2(SO_4)_3 = (0.1 \text{ mol L}^{-1})(25 \times 10^{-3} \text{ L}) = 2.5 \times 10^{-3} \text{ mol}$$

The reaction occurring is

$$\begin{array}{lccccccc} & 3Pb(NO_3)_2 & + & Cr_2(SO_4)_3 & \rightarrow & 3PbSO_4 \downarrow & + & 2Cr(NO_3)_3 \\ t = 0 & 11.25 \times 10^{-3} \text{ mol} & & 2.5 \times 10^{-3} \text{ mol} & & 0 & & 0 \end{array}$$

In the above reaction, $Cr_2(SO_4)_3$ has the limiting concentration. Hence, it will be consumed completely.

Thus, Amount of $Pb(NO_3)_2$ left $= 11.25 \times 10^{-3}$ mol $- 3 \times 2.5 \times 10^{-3}$ mol $= 3.75 \times 10^{-3}$ mol

Amount of $PbSO_4$ precipitated $= 3 \times 2.5 \times 10^{-3}$ mol $= 7.5 \times 10^{-3}$ mol

Amount of $Cr(NO_3)_3$ formed $= 2 \times 2.5 \times 10^{-3}$ mol $= 5.0 \times 10^{-3}$ mol

Now the volume of the system after mixing $Pb(NO_3)_2$ and $Cr_2(SO_4)_3$ solutions becomes 70.0 mL (= 45.0 mL + 25.0 mL). Hence,

$$[Pb(NO_3)_2] = \frac{3.75 \times 10^{-3} \text{mol}}{70 \times 10^{-3} \text{L}} = 0.053\,6 \text{ M} \quad \text{and} \quad [Cr(NO_3)_3] = \frac{5.0 \times 10^{-3} \text{mol}}{70 \times 10^{-3} \text{L}} = 0.0714 \text{ M}$$

Assuming $Pb(NO_3)_2$ and $Cr(NO_3)_3$ completely dissociated, we will have

$$[Pb^{2+}] = 0.0536 \text{ M}; \quad [Cr^{3+}] = 0.0714 \text{ M}; \quad [NO_3^-] = (2 \times 0.0536 + 3 \times 0.0714) \text{ M} = 0.3214 \text{ M}$$

Amount of $PbSO_4$ formed $= 7.5 \times 10^{-3}$ mol.

15. A 20.0 cm^3 mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm^3. A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of gaseous mixture in terms of volume percentage. (1995)

Solution Let V_1, V_2 and V_3 be the respective partial volumes of CO, CH_4 and He in the given 20.0 cm^3 of the mixture.

Hence, $V_1 + V_2 + V_3 = 20.0 \text{ cm}^3$ (1)

The combustion reactions are $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ and $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Hence, V_1 volume CO $\equiv \frac{V_1}{2}$ volume $O_2 \equiv V_1$ volume CO_2

V_2 volume $CH_4 \equiv 2V_2$ volume $O_2 \equiv V_2$ volume CO_2

Since there is no volume change due to the replacement of CO into CO_2 and CH_4 into CO_2, the volume change is due to the consumption of O_2. Hence,

$$\frac{V_1}{2} + 2\,V_2 = 13.0 \text{ cm}^3 \qquad (2)$$

The treatment of residual gases with KOH solution would cause the absorption of $CO_2(g)$. Hence,

$$V_1 + V_2 = 14.0 \text{ cm}^3 \qquad (3)$$

Solving V_1, V_2 and V_3 from Eqs (1) to (3), we get $V_1 = 10.0 \text{ cm}^3$, $V_2 = 4.0 \text{ cm}^3$, and $V_3 = 6.0 \text{ cm}^3$

Hence, Volume percentage of CO $= \frac{10.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 50$; Volume percentage of $CH_4 = \frac{4.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 20$

Volume percentage of He = 100 − (50 + 20) = 30.

16. A 20.0 g of mixture Cu_2S and CuS was treated with 400 cm^3 of 0.75 M $KMnO_4$ solution in acidic medium, producing SO_2, Cu^{2+} and Mn^{2+}. The SO_2 was boiled off and the excess MnO_4^- was titrated against 1.0 M Fe^{2+} solution. The volume consumed of the latter was found to be 350 cm^3. Compute the per cent of Cu_2S in the original mixture.

The chemical equations involved are:

(i)
$$\begin{array}{l} \mathrm{MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O]} \times 8 \\ \mathrm{Cu_2S + 2H_2O \rightarrow 2Cu^{2+} + SO_2 + 4H^+ + 8e^-]} \times 5 \\ \hline \mathrm{8MnO_4^- + 5Cu_2S + 44H^+ \rightarrow 8Mn^{2+} + 10Cu^{2+} + 5SO_2 + 22H_2O} \end{array}$$

(ii)
$$\begin{array}{l} \mathrm{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O]} \times 6 \\ \mathrm{CuS + 2H_2O \rightarrow Cu^{2+} + SO_2 + 4H^+ + 6e^-]} \times 5 \\ \hline \mathrm{6MnO_4^- + 5CuS + 28H^+ \rightarrow 6Mn^{2+} + 5Cu^{2+} + 5SO_2 + 14H_2O} \end{array}$$

(iii)
$$\begin{array}{l} \mathrm{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O} \\ \mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-]} \times 5 \\ \hline \mathrm{MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O} \end{array}$$

From the above equations, we conclude that

$$8 \text{ mol MnO}_4^- \equiv 5 \text{ mol Cu}_2\text{S} \ ; \quad 6 \text{ mol MnO}_4^- \equiv 5 \text{ mol CuS} \quad \text{and} \quad 1 \text{ mol MnO}_4^- \equiv 5 \text{ mol Fe}^{2+}$$

Let n_1 and n_2 be the respective amounts of Cu_2S and CuS in 20.0 g mixture. The amount of MnO_4^- used in the oxidation of Cu_2S and CuS will be given as

$$n_3 = \frac{8}{5} n_1 + \frac{6}{5} n_2$$

This amount will also be given as

$$n_3 = \text{Total amount of MnO}_4^- - \text{amount of MnO}_4^- \text{ used in oxidation of Fe}^{2+}$$

$$= (400 \text{ cm}^3)\,(0.75 \text{ M}) - \frac{1}{5}\,[(350 \text{ cm}^3)\,(1.0 \text{ M})]$$

$$= \left(\frac{400}{1000}\text{dm}^3\right)(0.75 \text{ mol dm}^{-3}) - \frac{1}{5}\left[\left(\frac{350}{1000}\text{dm}^3\right)(1.0 \text{ mol dm}^{-3})\right] = 0.230 \text{ mol}$$

Hence, $\quad \frac{8}{5}n_1 + \frac{6}{5}n_2 = 0.230 \text{ mol} \qquad (1)$

Moreover, $\quad n_1M_1 + n_2M_2 = 20.0 \text{ g} \quad \text{i.e.} \quad n_1(159.2 \text{ g mol}^{-1}) + n_2(95.6 \text{ g mol}^{-1}) = 20.0 \text{ g}$

or $\quad 159.2\, n_1 + 95.6\, n_2 = 20.0 \text{ mol} \qquad (2)$

Solving n_1 and n_2 from Eqs (1) and (2), we get

$$n_1 = 0.0529 \text{ mol} \qquad \text{and} \qquad n_2 = 0.1212 \text{ mol}$$

$$\text{Per cent of Cu}_2\text{S in the mixture} = \frac{(0.0529 \text{ mol})\,(159.2 \text{ g mol}^{-1})}{20.0 \text{ g}} \times 100 = 42.1.$$

17. A 8.0 g sample contained Fe_3O_4, Fe_2O_3 and inert materials. It was treated with an excess of aqueous KI solution in acidic medium, which reduced all the iron to Fe^{2+} ions. The resulting solution was diluted to 50.0 cm^3 and a 10.0 cm^3 of it was taken. The liberated iodine in this solution required 7.2 cm^3 of 1.0 M $Na_2S_2O_3$ for reduction to iodide. The iodine from another 25.0 cm^3 sample was extracted, after which the Fe^{2+} ions was titrated against 1.0 M MnO_4^- in acidic medium. The volume of $KMnO_4$ solution used was found to be 4.2 cm^3. Calculate the mass percentages of Fe_3O_4 and of Fe_2O_3 in the original mixture. (Given: Molar mass of Fe = 56 g mol^{-1}.)

Solution The reactions with KI solution in acidic medium are

$$\mathrm{Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3\ Fe^{2+} + 4\ H_2O + I_2} \qquad (1)$$

$$\mathrm{Fe_2O_3 + 2I^- + 6H^+ \rightarrow 2\ Fe^{2+} + 3\ H_2O + I_2} \qquad (2)$$

The reaction involving I_2 and $S_2O_3^{2-}$ is $\ 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$

From this equation, we conclude $\ 2 \text{ mol } S_2O_3^{2-} \equiv 1 \text{ mol } I_2$

Amount of $S_2O_3^{2-}$ in 7.2 cm^3 of 1.0 M $Na_2S_2O_3$ solution

$$= (7.2\ \text{cm}^3)\ (1.0\ \text{M}) = \left(\frac{7.2}{1000}\text{L}\right)\ (1.0\ \text{mol L}^{-1}) = \frac{7.2}{1000}\ \text{mol}$$

Amount of I_2 equivalent to the above amount of $S_2O_3^{2-}$ $= \frac{1}{2}\left(\frac{7.2}{1000}\right)$ mol $= 3.6 \times 10^{-3}$ mol

The above iodine is present in 10.0 cm^3 of the solution. Hence

Amount of I_2 liberated in 50.0 cm^3 solution $= 5 \times 3.6 \times 10^{-3}$ mol $= 18.0 \times 10^{-3}$ mol

If n_1 and n_2 are the respective amounts of Fe_3O_4 and Fe_2O_3 present in the given 8.0 g sample, from Eqs (1) and (2), we can write $n_1 + n_2 = 18.0 \times 10^{-3}$ mol (3)

Now from the chemical equation $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

we can write 1 mol $MnO_4^- \equiv 5$ mol Fe^{2+}

Amount of MnO_4^- in 4.2 cm^3 of 1.0 M $KMnO_4$ solution

$$= (4.2\ \text{cm}^3)\ (1.0\ \text{M}) = \left(\frac{4.2}{1000}\text{L}\right)\ (1.0\ \text{mol L}^{-1}) = 4.2 \times 10^{-3}\ \text{mol}$$

Amount of Fe^{2+} ions equivalent to the above amount of MnO_4^- ions

$= 5 \times 4.2 \times 10^{-3}$ mol $= 21.0 \times 10^{-3}$ mol

This amount of Fe^{2+} ions is present in 25.0 cm^3 of the solution. Hence,

Amount of Fe^{2+} ions in 50.0 cm^3 solution $= 2 \times 21.0 \times 10^{-3}$ mol $= 42.0 \times 10^{-3}$ mol

From Eqs (1) and (2), we can now write

$3n_1 + 2n_2 = 42.0 \times 10^{-3}$ mol (4)

Solving for n_1 and n_2 from Eqs (3) and (4), we get

$n_1 = 6 \times 10^{-3}$ mol and $n_2 = 12 \times 10^{-3}$ mol

Hence, Mass of Fe_3O_4 in 8.0 g sample $= (6 \times 10^{-3}\ \text{mol})\ (232.0\ \text{g mol}^{-1}) = 1.392$ g.

Mass of Fe_2O_3 in 8.0 g sample $= (12 \times 10^{-3}\ \text{mol})\ (160\ \text{g mol}^{-1}) = 1.92$ g.

$$\text{Mass per cent of } Fe_3O_4 \text{ in the sample} = \frac{1.392}{8.0} \times 100 = 17.4$$

$$\text{Mass per cent of } Fe_2O_3 \text{ in the sample} = \frac{1.92}{8.0} \times 100 = 24.0$$

18. 25.0 cm^3 of a solution containing Na_2CO_3 and NaOH required 10 cm^3 of 1.0 M H_2SO_4 for neutralization when phenolphthalein was used as the indicator. Whereas when methyl orange was used, it required 15 cm^3 of the same acid for neutralization. Calculate the masses of Na_2CO_3 and NaOH per dm^3 of the solution.

Solution The neutralization reactions are as follows.

Phenolphthalein indicator $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ and $OH^- + H^+ \rightarrow H_2O$

Methyl orange indicator $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$ and $OH^- + H^+ \rightarrow H_2O$

Let n_1 and n_2 be the respective amounts of Na_2CO_3 and NaOH in 25.0 cm^3 of the solution. From the chemical equations given above, we obtain the following equations.

$n_1 + n_2 =$ Amount of H^+ in 10 cm^3 of 1.0 M H_2SO_4

$2n_1 + n_2 =$ Amount of H^+ in 15 cm^3 of 1.0 M H_2SO_4

As each molecule of H_2SO_4 provides $2H^+$ ions, we have

$$n_1 + n_2 = 2\ (10\ \text{cm}^3)\ (1.0\ \text{M}) = 2\left(\frac{10}{1000}\text{dm}^3\right)\ (1.0\ \text{mol dm}^{-3}) = 2 \times 10^{-2}\ \text{mol}$$

$$2n_1 + n_2 = 2\ (15\ \text{cm}^3)\ (1.0\ \text{M}) = 2\left(\frac{15}{1000}\text{dm}^3\right)\ (1.0\ \text{mol dm}^{-3}) = 3 \times 10^{-2}\ \text{mol}$$

Solving for n_1 and n_2 from the above two equations, we get

$n_1 = 10^{-2}$ mol and $n_2 = 10^{-2}$ mol

The above amounts is present in 25.0 cm^3 solution. Hence, for 1 dm^3 solution, we have

Amount of $Na_2CO_3 = 40 \times 10^{-2}$ mol

Amount of NaOH = 40×10^{-2} mol

Hence, Mass of $Na_2CO_3 = (40 \times 10^{-2}\ \text{mol})\ (106\ \text{g mol}^{-1}) = 42.4$ g

Mass of NaOH = $(40 \times 10^{-2}\ \text{mol})\ (40\ \text{g mol}^{-1}) = 16.0$ g

19. A solution contains Na_2CO_3 and $NaHCO_3$. Twenty cm^3 of this solution requires 5.0 cm^3 of 0.1 M H_2SO_4 solution for neutralization using phenolphthalein as the indicator. Methyl orange is then added when a further 5.0 cm^3 of 0.2 M H_2SO_4 was required. Calculate the masses of Na_2CO_3 and $NaHCO_3$ in one litre of this solution.

Solution The reaction occurring are as follows.

$$CO_3^{2-} + H^+ \xrightarrow{\text{Phenolphthalein}} HCO_3^- \quad \text{and} \quad HCO_3^- + H^+ \xrightarrow{\text{Methyl orange}} CO_2 + H_2O$$

Let n_1 and n_2 be the respective amounts of Na_2CO_3 and $NaHCO_3$ present in 20 cm^3 of solution. We will have

n_1 = Amount of H^+ in 5.0 cm^3 of 0.1 M H_2SO_4

$n_1 + n_2$ = Amount of H^+ in 5.0 cm^3 of 0.2 M H_2SO_4

That is
$$n_1 = 2\left(\frac{5.0}{1000}\text{dm}^3\right)(0.1\ \text{mol dm}^{-3}) = 10^{-3}\ \text{mol}$$

$$n_1 + n_2 = 2\left(\frac{5.0}{1000}\text{dm}^3\right)(0.2\ \text{mol dm}^{-3}) = 2 \times 10^{-3}\ \text{mol}$$

which gives $n_1 = 10^{-3}$ mol and $n_2 = 10^{-3}$ mol

The above amounts are present in 20 cm^3 of the solution. Hence, for 1 L of the solution, we have

Amount of $Na_2CO_3 = 50 \times 10^{-3}$ mol and Amount of $NaHCO_3 = 50 \times 10^{-3}$ mol

Hence, Mass of $Na_2CO_3 = (50 \times 10^{-3}\ \text{mol})\ (106\ \text{g mol}^{-1}) = 5.3$ g

Mass of $NaHCO_3 = (50 \times 10^{-3}\ \text{mol})\ (84\ \text{g mol}^{-1}) = 4.2$ g.

20. A 50.0 cm^3 portion of a mixture of H_2SO_4 and $H_2C_2O_4$ required 48.9 cm^3 of 0.15 M NaOH solution for titration. Another 50 cm^3 required 38.9 cm^3 of 0.10 N $KMnO_4$ solution for titration. Calculate the masses of H_2SO_4 and $H_2C_2O_4$ present per dm^3 of the solution.

Solution Let N_1 and N_2 be the respective normalities of H_2SO_4 and $H_2C_2O_4$ in the same soution. Applying the normality equation, we get

$(N_1 + N_2)\ (50.0\ \text{cm}^3) = (0.15\ \text{N})\ (48.9\ \text{cm}^3)$

$N_2\ (50.0\ \text{cm}^3) = (0.10\ \text{N})\ (38.9\ \text{cm}^3)$

Hence,
$$N_2 = \frac{0.10 \times 38.9}{50.0}\ \text{N} = 0.0778\ \text{N} \quad \text{and} \quad N_1 + N_2 = \frac{0.15 \times 48.9}{50.0}\ \text{N} = 0.1467\ \text{N}$$

or $N_1 = 0.1467\ \text{N} - 0.0778\ \text{N} = 0.0689\ \text{N}$

$$\text{Mass of } H_2SO_4 \text{ per dm}^3 \text{ solution} = (0.0689)\left(\frac{98}{2}\text{g}\right) = 3.376\ \text{g}$$

$$\text{Mass of } H_2C_2O_4 \text{ per dm}^3 \text{ solution} = (0.0778)\left(\frac{90}{2}\text{g}\right) = 3.501\ \text{g}$$

Alternatively, we may proceed as follows.

The involved chemical equations are :

(i) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

(ii) $H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

(iii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-\ ] \times 5$

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

From these equations, we conclude

$$1 \text{ mol } H_2SO_4 \equiv 2 \text{ mol NaOH} \ ; \quad 1 \text{ mol } H_2C_2O_4 \equiv 2 \text{ mol NaOH} \ ;$$

$$2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } C_2O_4^{2-} \ ; \quad \text{and} \quad 1 \text{ mol } MnO_4^- \equiv 5 \text{ equivalents } MnO_4^-$$

Let n_1 and n_2 be the respective amounts of H_2SO_4 and $H_2C_2O_4$ present in 50.0 cm^3 of the solution. We will have

$$2n_1 + 2n_2 = \frac{48.9}{1000} \times 0.15 \text{ mol} \quad \text{and} \quad \frac{2}{5}\, n_2 = \frac{38.9}{1000} \times \frac{0.10}{5} \text{ mol}$$

Hence, $$n_2 = \frac{1}{2}\left(\frac{38.9}{1000}\times 0.10\right) \text{ mol} \quad \text{and} \quad n_1 = \frac{1}{2}\left[\frac{48.9}{1000}\times 0.15 - \frac{38.9}{1000}\times 0.10\right] \text{ mol.}$$

The above amounts are present in 50.0 cm^3 of the solution. Hence, in 1 dm^3 of the solution we have

$$\text{Amount of } H_2SO_4 = \frac{1}{2}\left[\frac{48.9}{1000}\times 0.15 - \frac{38.9}{1000}\times 0.10\right]\left(\frac{1000}{50}\right) \text{ mol}$$

$$\text{Amount of } H_2C_2O_4 = \frac{1}{2}\left(\frac{38.9}{1000}\times 0.10\right)\left(\frac{1000}{50}\right) \text{ mol}$$

Hence, $$\text{Mass of } H_2SO_4 = \frac{1}{2}\left[\frac{48.9}{1000}\times 0.15 - \frac{38.9}{1000}\times 0.10\right]\left(\frac{1000}{50}\right)(98 \text{ g}) = 3.376 \text{ g}$$

$$\text{Mass of } H_2C_2O_4 = \frac{1}{2}\left(\frac{38.9}{1000}\times 0.10\right)\left(\frac{1000}{50}\right)(90 \text{ g}) = 3.501 \text{ g.}$$

21. What are the masses of P_4O_6 and P_4O_{10} that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2?

Solution The equations to be considered are $P_4 + 3O_2 \rightarrow P_4O_6$ and $P_4 + 5O_2 \rightarrow P_4O_{10}$

Let x be the mass of P_4 that is converted into P_4O_6 and rest (= 2.0 g – x) into P_4O_{10}. The mass of oxygen required for these conversions will be $\dfrac{x}{4\times 31} \times 96 + \dfrac{2.0\text{ g} - x}{4\times 31} \times 160$ and this will be equal to 2.0 g. Hence, we get

$$\frac{96\,x}{124} + \frac{320.0}{124}\text{ g} - \frac{160\,x}{124} = 2.0 \text{ g}$$

or $$x\,(160 - 96) = (320.0 - 2 \times 124) \text{ g} \quad \text{or} \quad x = \frac{320 - 2\times 124}{160 - 96}\text{ g} = \frac{72}{64}\text{ g} = 1.125 \text{ g.}$$

Hence, $$\text{Mass of } P_4O_6 \text{ obtained} = \frac{\text{Mass of } P_4}{\text{Molar mass of } P_4} \times \text{Molar mass of } P_4O_6$$

$$= \left(\frac{1.125 \text{ g}}{124 \text{ g mol}^{-1}}\right)(220 \text{ g mol}^{-1}) = 1.996 \text{ g}$$

$$\text{Mass of } P_4O_{10} \text{ obtained} = (4.0 - 1.996) \text{ g} = 2.004 \text{ g.}$$

22. One gram of a moist sample of a mixture of $KClO_3$ and KCl was dissolved in water and made up to 250 mL. 25 mL of this solution was treated with SO_2 to reduce chlorate into chloride and the excess SO_2 was boiled off. When the total chloride was precipitated, 0.1435 g of AgCl was obtained. In another experiment 25 mL of the original solution was heated with 30 mL of 0.2 N solution of $FeSO_4$ and unreacted $FeSO_4$ required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the molar ratio of chlorate and chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the equation

$$ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O.$$

Also calculate the mass per cent of moisture present in the moist sample.

Solution Let n_1 and n_2 be the respective amounts of $KClO_3$ and KCl present in the 25 mL of the solution obtained by dissolving the given one gram sample in 250 mL water. The reduction reaction of ClO_3^- with SO_2 is

$$ClO_3^- + 3SO_2 + 3H_2O \rightarrow Cl^- + 3H_2SO_4$$

Thus, the amount of Cl^- obtained by the reduction of ClO_3^- will also be equal to n_1. From the mass of silver chloride obtained, we can write

$$n_1 + n_2 = \frac{0.1435\text{ g}}{M_{\text{AgCl}}} = \frac{0.1435\text{ g}}{143.5\text{ g mol}^{-1}} = 10^{-3}\text{ mol}$$

In the second experiment, the amount of Fe^{2+} ions (in equivalents which will also be equal to the amounts in mol) unreacted will be equal to the amount (in equivalent) of the oxidizing agent in 37.5 mL of 0.08 N solution, i.e.

Amount of unreacted Fe^{2+} ions = (37.5 mL) (0.08 N)

$$= \left(\frac{37.5}{1000}\text{ L}\right)(0.08\text{ eq L}^{-1}) = \frac{37.5 \times 0.08}{1000}\text{ eq} \equiv \frac{37.5 \times 0.08}{1000}\text{ mol}$$

Amount of Fe^{2+} ions added in the beginning = (30 mL) (0.2 N) $\equiv \left(\frac{30}{1000}\text{ L}\right)(0.2\text{ mol L}^{-1}) = \frac{30 \times 0.2}{1000}$ mol

Amount of Fe^{2+} ions used in reducing ClO_3^- to Cl^- = $\left(\frac{30 \times 0.2}{1000} - \frac{37.5 \times 0.08}{1000}\right)$ mol

From the chemical equation $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$, we conclude that

Amount of ClO_3^- ions in 25.0 mL solution, $n_1 = \frac{1}{6}\left(\frac{30 \times 0.2}{1000} - \frac{37.5 \times 0.08}{1000}\right)\text{ mol} = 5 \times 10^{-4}\text{ mol}$

Hence, Amount of Cl^- ions in 25.0 mL solution, $n_2 = (10^{-3} - 5 \times 10^{-4})\text{ mol} = 5 \times 10^{-4}\text{ mol}$

Now, in the 250 mL of the solution, we will have

Amount of ClO_3^- ions = 5×10^{-3} mol and Amount of Cl^- ions = 5×10^{-3} mol

Hence, $$\frac{\text{Amount of } ClO_3^- \text{ ions}}{\text{Amount of } Cl^-} = \frac{5 \times 10^{-3}\text{ mol}}{5 \times 10^{-3}\text{ mol}} = \frac{1}{1}$$

Now
Mass of $KClO_3$ = $(5 \times 10^{-3}\text{ mol})(122\text{ g mol}^{-1}) = 0.61$ g
Mass of KCl = $(5 \times 10^{-3}\text{ mol})(74.5\text{ g mol}^{-1})\ 0.3725\text{ g}$
Total mass of $KClO_3$ and KCl = (0.61 + 0.3725) g = 0.9825 g
Mass of moisture in 1 g sample = (1 − 0.9825) g = 0.0175 g

$$\text{Mass per cent of moisture} = \frac{0.0175\text{ g}}{1\text{ g}} \times 100 = 1.75.$$

23. A precipitate of AgBr and AgCNS weighing 1.002 g was dissolved in 60.0 cm^3 of 0.25 M KCN solution. The excess cyanide required 16.7 cm^3 of 0.1 M $AgNO_3$ for titration to the turbid end point. Calculate the percentage of AgCNS in the original precipitate.

Solution Let n_1 and n_2 be the respective amounts of AgBr and AgCNS present in the given precipitate. We will have

$$n_1 M_{\text{AgBr}} + n_2 M_{\text{AgCNS}} = 1.002\text{ g} \quad \text{i.e.} \quad 187.8\, n_1 + 165.9\, n_2 = 1.002\text{ mol} \qquad (1)$$

The dissolution process is due to the reactions

$$AgBr + 2CN^- \rightarrow Ag(CN)_2^- + Br^- \quad \text{and} \quad AgCNS + 2CN^- \rightarrow Ag(CN)_2^- + CNS^-$$

Hence, Amount of CN^- used in the dissolution process = $2n_1 + 2n_2$ (2)

The titration of CN^- versus Ag^+ involves the reaction $Ag^+ + 2\,CN^- \rightarrow Ag(CN)_2^-$

Hence, Amount of excess CN^- = $2(16.7\text{ cm}^3)(0.1\text{ M})$

$$= 2\left(\frac{16.7}{1000}\text{ dm}^3\right)(0.1\text{ mol dm}^{-3}) = \frac{2 \times 16.7}{1000} \times 0.1\text{ mol}$$

Amount of CN^- used during dissolution process = $(60.0\ cm^3)\ (0.25\ M) = \dfrac{60.0}{1000} \times 0.25$ mol

Amount of CN^- used in the dissolution process = $\left(\dfrac{60}{1000} \times 0.25 - \dfrac{2 \times 16.7}{1000} \times 0.1\right)$ mol = 11.66×10^{-3} mol (3)

Equating Eqs (2) and (3), we get

$$2n_1 + 2n_2 = 11.66 \times 10^{-3}\ \text{mol} \quad \text{or} \quad n_1 + n_2 = 5.83 \times 10^{-3}\ \text{mol} \qquad (4)$$

Solving n_1 and n_2 from Eqs (1) and (4), we get $n_1 = 0.00159$ mol and $n_2 = 0.00424$ mol

$$\text{Mass per cent of AgCNS} = \frac{0.00424 \times 165.9}{0.00424 \times 165.9 + 0.00159 \times 187.8} \times 100 = \frac{0.7034}{0.7034 + 0.2986} \times 100 = 70.2.$$

24. 1.5 g pyrolusite ore was treated with 10 g of Mohr's salt and dilute sulphuric acid resulting into the following equation

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

After the reaction is over, the solution was made up to 250 mL. When 50 mL of this solution was titrated against N/10 $K_2Cr_2O_7$ solution, the volume of the latter consumed was found to be 10 mL. Calculate the percentage of MnO_2 in the given pyrolusite sample.

Solution Normality of the solution prepared after the reaction is over can be computed by using the expression

$$N_1V_1 = N_2V_2.$$

Hence, $(N)\ (50\ \text{mL}) = \left(\dfrac{\text{N}}{10}\right)(10\ \text{mL})$ i.e. $N = 1/50$ N

The normality of Fe^{2+} ions will be same as its molarity. Hence,

$M = 1/50$ M

Amount of Fe^{2+} ions in 250 mL solution

$$= (250\ \text{mL})\left(\frac{1}{50}\text{M}\right) = \left(\frac{250}{1000}\text{L}\right)\left(\frac{1}{50}\text{mol L}^{-1}\right) = \frac{1}{200}\ \text{mol} = 0.005\ \text{mol}$$

$$\text{Amount of Fe}^{2+}\text{ ions taken to start with} = \frac{10\ \text{g}}{392\ \text{g mol}^{-1}} = 0.0255\ \text{mol}$$

Amount of Fe^{2+} ions used in reducing MnO_2 = (0.0255 − 0.005) mol = 0.0205 mol

$$\text{Amount of MnO}_2\text{ reduced} = \frac{0.0205}{2}\ \text{mol} = 0.01025\ \text{mol}$$

Mass of MnO_2 reduced = (0.01025 mol) (86.9 mol^{-1}) = 0.8907 g

$$\text{Per cent of MnO}_2\text{ in the given sample of pyrolusite} = \frac{0.8907\ \text{g}}{1.5\ \text{g}} \times 100 = 59.4.$$

25. Ten grams of a sample of bleaching powder were extracted with water and the solution made upto one litre. 25 mL of this solution was added to 50 mL of N/14 Mohr's salt solution containing enough sulphuric acid. After the reaction was completed, the whole solution required 22 mL of $KMnO_4$ solution containing 2.2571 g of $KMnO_4$ per litre for complete oxidation. Calculate the percentage of available chlorine in the sample of bleaching powder.

Solution The reactions to be considered are :

(i) $Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$

(ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Amount of Fe^{2+} ions added in the beginning

$$= (50\ \text{mL})\left(\frac{1}{14}\text{M}\right) = \left(\frac{50}{1000}\text{L}\right)\left(\frac{1}{14}\text{mol L}^{-1}\right) = \left(\frac{50}{1000}\right)\left(\frac{1}{14}\right)\ \text{mol}$$

$$\text{Amount of Fe}^{2+}\text{ ions oxidized by MnO}_4^- = 5\ (22\text{ mL})\left(\frac{2.2571}{M_{\text{KMnO}_4}}\text{ mol L}^{-1}\right) = 5\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)\text{ mol}$$

$$\text{Amount of Fe}^{2+}\text{ ions oxidized by Cl}_2 = \left[\left(\frac{50}{1000}\right)\left(\frac{1}{14}\right) - 5\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)\right]\text{ mol}$$

$$\text{Amount of Cl}_2\text{ gas available} = \frac{1}{2}\left[\left(\frac{50}{1000}\right)\left(\frac{1}{14}\right) - 5\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)\right]\text{ mol} = 10^{-3}\text{ mol.}$$

This amount is present in 25 mL of the solution. Hence,

Amount of Cl_2 gas available in 1 L solution = 40×10^{-3} mol

Mass of Cl_2 gas available in 1 L solution = $71 \times 40 \times 10^{-3}$ g = 2.84 g

$$\text{Percentage of available Cl}_2 = \frac{2.84\text{ g}}{10\text{ g}} \times 100 = 28.4.$$

26. One gram of a mixture of anhydrous Na_2CO_3 and K_2CO_3 was dissolved in water and volume of the solution was made upto 250 mL. 25 mL of this solution required 26.25 mL of HCl of unknown concentration for complete neutralization. The neutral solution so obtained required 16.25 mL of 0.1 M $AgNO_3$ for complete precipitation. Calculate (a) the percentage of K_2CO_3 in the mixture and (b) the concentration of HCl in grams per litre.

Solution Let x be the mass Na_2CO_3 present in one gram of the given mixture. Then

$$\text{Total amount of CO}_3^{2-}\text{ ions} = \frac{x}{M_{\text{Na}_2\text{CO}_3}} + \frac{1.0\text{ g} - x}{M_{\text{K}_2\text{CO}_3}} = \frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}$$

$$\text{Total amount of CO}_3^{2-}\text{ ions in 25 mL solution} = \frac{1}{10}\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right]$$

Total amounts of H^+ ions required for complete neutralization (or amount of Cl^- ions produced in the complete neutralization)

$$= (2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right]$$

This amount of Cl^- ions must be equal to the amount of Ag^+ ions in 16.25 mL of 0.1 M $AgNO_3$ solution. Hence

$$(2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right] = (16.25\text{ mL})\ (0.1\text{ M})$$

or

$$(2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g})} + \frac{1.0\text{ g} - x}{(138\text{ g})}\right] = \frac{16.25}{1000} \times 0.1$$

Solving for x, we get

$$x = \frac{1}{32}\left[\left(\frac{1}{2}\right)(10)\left(\frac{16.25 \times 0.1}{1000}\right)(138)\ (106) - 106\right]\text{ g} = 0.4016\text{ g}$$

Hence, $\quad$ Mass per cent of K_2CO_3 = $\dfrac{0.5984\text{ g}}{1\text{ g}} \times 100 = 59.84$

Molarity of HCl solution used = $\dfrac{16.25}{26.25} \times 0.1\text{ M} = 0.0619\text{ M}$

Mass of HCl per litre of solution = 0.0619×36.5 g = 2.26 g.

27. Pure $Na_2C_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ are mixed in such a proportion that each gram of the mixture reacts separately with equal volumes of 0.1 M $KMnO_4$ and 0.1 M NaOH. What is the proportion?

Solution The constituent $KHC_2O_4 \cdot H_2C_2O_4$, which contains three replaceable hydrogen atoms, only reacts with NaOH whereas both the constituents react with $KMnO_4$. The reactions are

(i) $H^+ + OH^- \rightarrow H_2O$

(ii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Hence, it follows that $1 \text{ mol } H^+ \equiv 1 \text{ mol } OH^-$ and $2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } C_2O_4^{2-}$.

Let x and $1.0 \text{ g} - x$ be the respective masses of $Na_2C_2O_4$ (molar mass 134 g mol^{-1}) and $KHC_2O_4 \cdot H_2C_2O_4$ (molar mass 218 g mol^{-1}) in one gram of the mixture and let the volume V of $KMnO_4$ solution or NaOH solution that react with one gram of the mixture. We have

$$\text{Amount of } H^+ \text{ in the mixture} = 3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right); \quad \text{Amount of } OH^- \text{ reacted} = V\,(0.1\text{ M})$$

Equating these two, we get

$$3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right) = V\,(0.1\text{ M}) \tag{1}$$

Now $$\text{Amount of } C_2O_4^{2-} \text{ in the mixture} = \frac{x}{134\text{ g mol}^{-1}} + 2 \times \left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)$$

$$\text{Amount of } MnO_4^- \text{ reacted} = V\,(0.1\text{ M})$$

Now since $2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } C_2O_4^{2-}$, we will have

$$\frac{2}{5}\left[\frac{x}{134\text{ g mol}^{-1}} + 2\times\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)\right] = V\,(0.1\text{ M}) \tag{2}$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{2}{5}\left[\frac{x}{134\text{ g mol}^{-1}} + 2\times\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)\right] = 3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)$$

Solving for x, we get

$$x = \frac{134 \times 11}{134 \times 11 + 2 \times 218}\text{ g} = \frac{1474}{1910}\text{ g} \quad \text{and} \quad 1.0\text{ g} - x = \frac{436}{1910}\text{ g}$$

Hence, the ratio of two masses in 1.0 g mixture is

$$\frac{\text{Mass of } Na_2C_2O_4}{\text{Mass of } KHC_2O_4 \cdot H_2C_2O_4} = \frac{1474}{436} = \frac{3.38}{1}.$$

28. A 0.2 g sample of pyrolusite is analyzed as follows. Add 50.0 mL of a 0.10 M solution of ferrous ammonium sulphate to reduce the MnO_2 to Mn^{2+}. After the reduction is complete, the excess ferrous ion is titrated in acid solution with 0.02 M $KMnO_4$, requiring 15.0 mL. Calculate the percentage of manganese in the sample as MnO_2.

Solution The reactions involved are

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$
$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Hence, $1 \text{ mol } MnO_2 \equiv 2 \text{ mol } Fe^{2+}$ and $1 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Fe^{2+}$

To start with, amount of Fe^{2+} ions added = $(50.0 \times 10^{-3}\text{ L})\,(0.10\text{ mol L}^{-1}) = 50.0 \times 10^{-4}$ mol

Amount of MnO_4^- used in oxidizing excess of Fe^{2+} ions = $(15.0 \times 10^{-3}\text{ L})\,(0.02\text{ mol L}^{-1}) = 3 \times 10^{-4}$ mol

Since $1 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Fe^{2+}$, we have

$$\text{Amount of excess } Fe^{2+} \text{ ions} = 5 \times (3 \times 10^{-4}\text{ mol})$$

Amount of Fe^{2+} ions used in the reduction of $MnO_2 = 50 \times 10^{-4}\text{ mol} - 15 \times 10^{-4}\text{ mol} = 35 \times 10^{-4}$ mol

Now since $1 \text{ mol } MnO_2 \equiv 2 \text{ mol } Fe^{2+}$, we will have

$$\text{Amount of } MnO_2 \text{ in 0.2 g sample of pyrolusite} = \frac{1}{2}\,(35 \times 10^{-4}\text{ mol})$$

$$\text{Mass of MnO}_2\text{ in the sample} = \frac{1}{2}\ (35 \times 10^{-4}\text{ mol})\ (86.9\text{ g mol}^{-1}) = 0.152\text{ g}$$

$$\text{Percentage of MnO}_2\text{ in the sample} = \frac{0.152\text{ g}}{0.2\text{ g}} \times 100 = 76.0\ \%.$$

29. A mixture containing only $FeCl_3$ and $AlCl_3$ weights 5.95 g. The chlorides are converted into the hydrous oxides and ignited to Fe_2O_3 and Al_2O_3. The oxide mixture weighs 2.62 g. Calculate the percent of Fe and Al in the original mixture.

Solution Let x and y be the masses of $FeCl_3$ and $AlCl_3$ in the 5.95 g mixture, respectively. Thus,

$$x + y = 5.95\text{ g} \qquad (1)$$

$$\text{Mass of Fe}_2\text{O}_3\text{ obtained from the mass } x \text{ of FeCl}_3 = \frac{x}{M_{\text{FeCl}_3}}\left(\frac{1}{2} M_{\text{Fe}_2\text{O}_3}\right) = x\left(\frac{159.6}{2 \times 162.3}\right) = 0.492\ x$$

$$\text{Mass of Al}_2\text{O}_3\text{ obtained from the mass } y \text{ of AlCl}_3 = \frac{y}{M_{\text{AlCl}_3}}\left(\frac{1}{2} M_{\text{Al}_2\text{O}_3}\right) = y\left(\frac{102}{2 \times 133.5}\right) = 0.382\ y$$

Hence, $0.492\ x + 0.382\ y = 2.62\text{ g}$ (2)

Solving x and y from Eqs (1) and (2), we get

$$x = \frac{5.95 \times 0.382 - 2.62}{0.492 - 0.382}\text{ g} = 3.155\text{ g} \quad \text{and} \quad y = 5.95\text{ g} - 3.155\text{ g} = 2.795\text{ g}$$

Now

$$\text{Mass of Fe in the mixture} = x\left(\frac{M_{\text{Fe}}}{M_{\text{FeCl}_3}}\right) = (3.155\text{ g})\left(\frac{55.8}{162.3}\right) = 1.085\text{ g}$$

$$\text{Mass percent of Fe in the mixture} = \frac{1.085\text{ g}}{5.95\text{ g}} \times 100 = 18.24$$

$$\text{Mass of Al in the mixture} = y\left(\frac{M_{\text{Al}}}{M_{\text{AlCl}_3}}\right) = (2.795\text{ g})\left(\frac{27}{133.5}\right) = 0.565\text{ g}$$

$$\text{Mass percent of Al in the mixture} = \frac{0.565\text{ g}}{5.95\text{ g}} \times 100 = 9.50.$$

30. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution.

Solution Glauber's salt is $NaSO_4 \cdot 10H_2O$.

$$\text{Molar mass of Glauber's salt} = \{2 \times 23.00 + 32.10 + 4 \times 16.00 + 10\,(2 \times 1.01 + 16.00)\}\text{ g mol}^{-1}$$
$$= 322.3\text{ g mol}^{-1}$$

$$\text{Amount of Glauber's salt dissolved, } n_2 = \frac{m}{M} = \frac{8.0575 \times 10^{-2}\text{ kg}}{322.3 \times 10^{-3}\text{ kg mol}^{-1}} = 0.25\text{ mol}$$

$$\text{Mass of 1 dm}^3\text{ solution} = \rho V = (1077.2\text{ kg m}^{-3})\ (10^{-3}\text{ m}^3) = 1.0772\text{ kg}$$

$$\text{Mass of Na}_2\text{SO}_4\text{ in 1 dm}^3\text{ solution,} = n_2\, M_{\text{Na}_2\text{SO}_4} = (0.25\text{ mol})\ (2 \times 23 + 32.10 + 4 \times 16.00)\text{ g mol}^{-1}$$
$$= 35.525\text{ g} = 3.5525 \times 10^{-2}\text{ kg}$$

$$\text{Mass of solvent in 1 dm}^3\text{ solution} = (1.0772 - 3.5525 \times 10^{-2})\text{ kg} = 1.0417\text{ kg}$$

$$\text{Molarity of solution} = \frac{n_2}{V} = \frac{0.25\text{ mol}}{1\text{ dm}^3} = 0.25\text{ mol dm}^{-3}$$

$$\text{Molality of solution} = \frac{n_2}{m_{\text{solvent}}} = \frac{0.25\ \text{mol}}{1.0417\ \text{kg}} = 0.24\ \text{mol kg}^{-1}$$

$$\text{Amount of solvent in 1 dm}^3\text{ solution, } n_1 = \frac{1.0417 \times 10^3\ \text{g}}{18\ \text{g mol}^{-1}} = 57.87\ \text{mol}$$

$$\text{Mole fraction of Na}_2\text{SO}_4\text{ in solution } \frac{n_1}{n_1 + n_2} = \frac{0.25}{0.25 + 57.87} = 0.0043$$

31. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions? (Assume $CaCO_3$ to be completely insoluble in water.) If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million part of water, mass/mass.)

Solution In 10^6 g (= 1000 kg) of the given hard water, we will have

Mass of SO_4^{2-} ions = 96 g; Mass of HCO_3^- ions = 183 g

Thus $$\text{Amount of SO}_4^{2-}\text{ ions} = \frac{96\ \text{g}}{96\ \text{g mol}^{-1}} = 1\ \text{mol};\qquad \text{Amount of HCO}_3^-\text{ ions} = \frac{183\ \text{g}}{61\ \text{g mol}^{-1}} = 3\ \text{mol}$$

These ions are present as $CaSO_4$ and $Ca(HCO_3)_2$. Hence, Amount of Ca^{2+} ions = (1 + 1.5) mol = 2.5 mol.

The addition of CaO causes the following reaction: $CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$

To remove 1.5 mol of $Ca(HCO_3)_2$, 1.5 mol of CaO will be required in the treated water. After this, the solution contains only $CaSO_4$. Thus, 1 mol of Ca^{2+} ions will be present in 10^6 g of water. Hence, its concentration will be 40 ppm.

Molarity of Ca^{2+} ions in the treated water will be 10^{-3} mol L^{-1}. If the Ca^{2+} ions are exchanged by H^+ ions, then

Molarity of H^+ in the treated water = 2×10^{-3} M.

Thus, $\text{pH} = -\log(2 \times 10^{-3}) = 2.7$

32. One litre of a mixture of O_2 and O_3 at STP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the mass per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assume that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? (1997)

Solution The reaction of O_3 with I^- in acidic medium is $O_3 + 2I^- + 2H^+ \rightarrow I_2 + O_2 + H_2O$

Hence, 1 mol O_3 = 1 mol I_2

The reaction of I_2 with $S_2O_3^{2-}$ is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Hence, 2 mol $S_2O_3^{2-} \equiv 1$ mol I_2

$$\text{Amount of S}_2\text{O}_3^{2-}\text{ consumed} = (40 \times 10^{-3}\ \text{L})\left(\frac{1}{10}\ \text{mol L}^{-1}\right) = 40 \times 10^{-4}\ \text{mol}$$

Thus 40×10^{-4} mol $S_2O_3^{2-} \equiv 20 \times 10^{-4}$ mol $I_2 \equiv 20 \times 10^{-4}$ mol O_3

Mass of O_3 present in 1 L of mixture = $(20 \times 10^{-4}\ \text{mol})(48\ \text{g mol}^{-1}) = 9.6 \times 10^{-2}$ g

Total amount of O_2 and O_3 present in 1 L of mixture at STP is

$$n_{\text{total}} = \frac{pV}{RT} = \frac{(1\ \text{atm})(1\ \text{L})}{(0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})(273\ \text{K})} = 4.462 \times 10^{-2}\ \text{mol}$$

Hence,

Amount of O_2 present in 1 L of mixture = $(4.462 \times 10^{-2} - 20 \times 10^{-4})$ mol = 4.262×10^{-2} mol

Mass of O_2 present in 1 L of mixture = $(4.262 \times 10^{-2}\ \text{mol})(32\ \text{g mol}^{-1}) = 1.364$ g

Mass percent of O_3 in the mixture = $\dfrac{9.6\times10^{-2}}{9.6\times10^{-2}+1.364}\times 100 = 6.575$

Amount of photons required to decompose O_3 = Amount of O_3 = 20×10^{-4} mol

Number of photons required = $(20 \times 10^{-4}\text{ mol})(6.023 \times 10^{23}\text{ mol}^{-1}) = 1.205 \times 10^{21}$

33. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

Solution The reaction between KIO_3 and KI is $KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3H_2O + 3I_2$

The reaction of I_2 with thiosulphate ion is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

From these reactions, we can write 1 mol $KIO_3 \cong 3$ mol I_2 and 1 mol $I_2 \cong 2$ mol $S_2O_3^{2-}$

From the given mass of KIO_3, we get Amount of $KIO_3 = \dfrac{0.10\text{ g}}{214.0\text{ g mol}^{-1}} = 4.6729 \times 10^{-4}$ mol

Amount of I_2 generated = $3 \times 4.6729 \times 10^{-4}$ mol

Amount of $S_2O_3^{2-}$ consumed = $2(3 \times 4.6729 \times 10^{-4}\text{ mol})$ (1)

Let M be the molarity of thiosulphate solution. From the given volume of thiosulphate solution, we get

Amount of $S_2O_3^{2-}$ consumed = $MV = M(45.0 \times 10^{-3}\text{ L})$ (2)

Equating Eqs (1) and (2), we get

$$M(45.0 \times 10^{-3}\text{ L}) = 2\,(3 \times 4.6729 \times 10^{-4}\text{ mol})$$

$$M = \frac{2(3\times 4.6729\times10^{-4}\text{ mol})}{45.0\times10^{-3}\text{ L}} = 0.0623\text{ mol L}^{-1}$$

34. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M $KmnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. (1996)

Solution The reactions with KI solution in acidic medium are

$$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + I_2 \quad (1)$$

$$Fe_2O_3 + 2I^- + 6H^+ \rightarrow 2Fe^{2+} + 3H_2O + I_2 \quad (2)$$

The reaction involving I_2 and $S_2O_3^{2-}$ is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

From this equation, we conclude 2 mol $S_2O_3^{2-} \equiv 1$ mol I_2

Amount of $S_2O_3^{2-}$ in 11.0 mL of 0.5 M $Na_2S_2O_3$ solution = $(11.0 \times 10^{-3}\text{ L})(0.5\text{ mol L}^{-1}) = 5.5 \times 10^{-3}$ mol

Amount of I_2 equivalent to the above amount of $S_2O_3^{2-} = \dfrac{1}{2}(5.5 \times 10^{-3}\text{ mol}) = 2.75 \times 10^{-3}$ mol

The above iodine is present in 20 mL of the solution. Hence

Amount of I_2 liberated in 100 mL solution = $5 \times 2.75 \times 10^{-3}$ mol = 13.75×10^{-3} mol

If n_1 and n_2 are the respective amounts of Fe_3O_4 and Fe_2O_3 present in the given 3.00 g sample, then from Eqs (1) and (2), we can write $n_1 + n_2 = 13.75 \times 10^{-3}$ mol (3)

Now from the chemical equation $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

We can write 1 mol $MnO^{-4} \equiv 5$ mol Fe^{2+}

Amount of MnO_4^- in 12.80 mL of 0.25 M $KmnO_4$ solution

= $(12.80 \times 10^{-3}\text{ L})(0.25\text{ mol L}^{-1}) = 3.2 \times 10^{-3}$ mol

Amount of Fe^{2+} equivalent to the above amount of MnO_4^- ions

= $5 \times 3.2 \times 10^{-3}$ mol = 16.0×10^{-3} mol

This amount of Fe^{2+} ions is present in 50 mL of the solution. Hence

Amount of Fe^{2+} ions in 100 mL solution = $2 \times 16.0 \times 10^{-3}$ mol

From Eqs. (1) and (2), we can now write

$$3n_1 + 2n_2 = 32.0 \times 10^{-3} \text{ mol} \qquad (4)$$

Solving for n_1 and n_2 from Eqs (3) and (4), we get

$$n_1 = 4.5 \times 10^{-3} \text{ mol and } n_2 = 9.25 \times 10^{-3} \text{ mol}$$

Mass of Fe_3O_4 in 3.00 g sample = $(4.5 \times 10^{-3}$ mol) (232 g mol^{-1}) = 1.044 g

Mass of Fe_2O_3 in 3.00 g sample = $(9.25 \times 10^{-3}$ mol) (160 g mol^{-1}) = 1.48 g

Mass per cent of Fe_3O_4 in the sample = $\dfrac{1.044}{3} \times 100 = 34.8$

Mass per cent of Fe_2O_3 in the sample = $\dfrac{1.048}{3} \times 100 = 49.3$

35. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. (1995)

Solution The involved reaction is $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$

Hence 1 mol $H_2O_2 \equiv 1$ mol I_2

Amount of I_2 liberated = $\dfrac{0.508\,\text{g}}{(2 \times 127)\,\text{g mol}^{-1}} = 2x\ 10^{-3}$ mol

Thus Amount of H_2O_2 in 5.0 cm^3 solution = 2×10^{-3} mol

Molar concentration of H_2O_2 = $\dfrac{2 \times 10^{-3}\ \text{mol}}{5 \times 10^{3}\ \text{L}} = 0.4\ \text{mol L}^{-1}$

The volume strength of H_2O_2 is based on the reaction $2H_2O \times 2H_2O + O_2$

Thus 2 mol $H_2O_2 \equiv 1$ mol $O_2 \equiv 22.4$ L O_{2s} at STP

Now 2 molar solution of H_2O_2 has volume strength of 22.4.

Hence, 0.4 molar solution of H_2O_2 has volume strength of $\dfrac{22.4}{2\text{M}}$ x 0.4 M = 4.48

36. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper(II) carbonate? (1999)

Solution Molar mass of $CuCO_3$ = $(63.5 + 12 + 3 \times 16)$ g mol^{-1} = 123.58 g mol^{-1}

Amount of given $CuCO_3$ = $\dfrac{0.5\ \text{g}}{123.5\ \text{g mol}^{-1}} = 4.05 \times 10^{-3}$ mol

The dissolution reaction is $CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + CO_2 + H_2O$

From the stoichiometric coefficients, we can write

Amount of H_2SO_4 required for dissolution of the given mass of $CuCO_3$, $n = 4.05 \times 10^{-3}$ mol

Volume of 0.5 M H_2SO_4 solution containing 4.05×10^{-3} mol of H_2SO_4

$$= \frac{n}{M} = \frac{4.05 \times 10^{-3}\ \text{mol}}{0.5\ \text{mol L}^{-1}} = 8.1 \times 10^{-3}\ \text{L} = 8.1\ \text{mL}$$

37. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molar mass. (1999)

Solution Radius of the cylindrical particle is $r = \dfrac{150 \times 10^{-8}\ \text{cm}}{2} = 75 \times 10^{-8}$ cm

Length of the cylindrical particle is $l = 5000 \times 10^{-8}$ cm

Volume of the cylindrical particle is $V = \pi r^2 l = (3.14)\,(75 \times 10^{-8}\ \text{cm})^2\,(500 \times 10^{-8}\ \text{cm}) = 8.83 \times 10^{-17}\ \text{cm}^3$

Mass of the cylindrical particle is $m = \dfrac{V}{\rho} = \dfrac{8.83 \times 10^{-17}\ \text{cm}^3}{0.75\ \text{cm}^3/\text{g}} = 1.18 \times 10^{-16}$ g

Molar mass of the cylindrical particle is $m = m\,N_A = (1.18 \times 10^{-16}\ \text{g})\,(6.022 \times 10^{23}\ \text{mol}^{-1}) = 7.1 \times 10^{7}\ \text{g mol}^{-1}$

38. 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 lmedium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2. (2001)

Solution In acidic medium, MnO_4^- oxidizes H_2O_2 to O_2. The involved reactions are

$$\begin{array}{r} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2 \\ H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn_2^+ + 5O_2 + 8H_2O \end{array}$$

In neutral medium, the reactions of MnO_4^- with Mn^{2+} are as follows.

$$\begin{array}{c} MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2 \\ Mn^{2+}\ 4OH^- \rightarrow MnO_2 + 2H_2O + 2e^-] \times 3 \\ \hline 2MnO_4^- + 3Mn^{2+} + 4OH^- \rightarrow 5MnO_2 + 2H_2O \end{array}$$

The dissolution of MnO_2 in sodium oxalate in acidic medium involves the following reactions.

$$\begin{array}{c} MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O] \\ C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \\ \hline MnO_2 + C_2O_4^{2-} + 4H^+ \rightarrow Mn^{2+} + 2CO_{2+}\ 2H_2O \end{array}$$

Amount of oxalate used in dissolving MnO_2 is

$$n_1 = V_1M_1 = (10\ \text{mL})\ (0.2\ \text{M}) = (10\ \text{mL}) \left(\frac{0.2\ \text{mol}}{1000\ \text{mL}}\right) = 2 \times 10^{-3}\ \text{mol}$$

From the reactions given above, we conclude that

1 mol $C_2O_4^{2-}$ $\equiv$ 1 mol MnO_2; 5 mol $MnO_2 \equiv$ 2 mol MnO_4^-; 2 mol $MnO_4^- \equiv$ 5 mol H_2O_2

Hence, 2×10^{-3} mol $C_2O_4^{2-} \equiv 2 \times 10^{-3}$ mol MnO_2 $\frac{2}{5}$ $(2 \times 10^{-3}$ mol $MnO_4^-)$

$$= \frac{5}{2}\left[\frac{2}{5}(2 \times 10^{-3}\ \text{mol}\, H_2O_2)\right]$$

that is,

2×10^{-3} mol of H_2O_2 was present in 20 mL of hydrogen peroxide solution. Hence, its molarity is

$$M = \frac{n}{V} = \frac{2 \times 10^{-3}}{20 \times 10^{-3}\ \text{L}} = 0.1\ \text{mol L}^{-1}$$

39. What is molarity of water at 4 °C? (2002)

Solution By definition, molarity is the amount of substance (i.e. number of moles) per litre of the solution. To calculate molarity of water, we take 1 L of water and find out the amount of water in this volume. We know that the density of water at 4 °C is 1 g mL^{-1}. Hence, the mass of 1 L of water is

$$m = \rho V = (1\ \text{g mL}^{-1})\ (1000\ \text{mL}) = 1000\ \text{g}$$

The amount of water in this mass is

$$n = \frac{m}{M} = \frac{1000\ \text{g}}{18\ \text{g mol}^{-1}} = 55.56\ \text{mol}$$

Hence, the molarity of water at 4 °C is 55.56 mol L^{-1}.

40. On dissolving 2.0 g of a metal in sulphuric acid, 4.51 g of the metal sulphate was formed. The specific heat capacity of the metal is 0.057 cal g^{-1}. What is the valency of the metal and its exact relative atomic mass. (2003)

Solution Since the product of relative atomic mass and specific heat capacity is approximate 6.4 cal g^{-1},we have

Approximate relative atomic mass of element = $\dfrac{6.4\,\text{cal g}^{-1}}{0.057\,\text{cal g}^{-1}}$ = 112.28

Let x be the valency of M in the metal sulphate, its reaction with H_2SO_4 may be written as

$$2M + xH_2SO_4 \rightarrow M_2(SO_4)x + xH_2$$

We will have $$\frac{2M_r + x(96)}{2M_r} = \frac{4.51}{2} \quad \text{i.e.} \quad \frac{2\times 112.28 + 96x}{2\times 112.28} = \frac{4.51}{2}$$

Solving for x, we get $$x = \frac{4.51\times 2\times 112.28 - 2\times 2\times 112.28}{2\times 96} = 2.94$$

Hence, the correct valency of M is 3 and its correct relative atomic mass is

$$M_r = \left(\frac{3}{2.94}\right)(112.28) = 114.57$$

UNSOLVED PROBLEMS

1. A mixture of FeO and Fe_3O_4 when heated in air to a constant mass gains 5 per cent in its mass. Find the composition of the initial mixture.
2. In the analysis of a 0.5 g sample of feldspar, a mixture of NaCl and KCl is obtained which weighs 0.118 g. Subsequent treatment of the mixed chlorides with $AgNO_3$ gives 0.2451 g of AgCl. What are the percentages of Na_2O and K_2O in feldspar?
3. 2.8 g of an ammonium salt when heated with excess of NaOH solution and the gas evolved was passed into 150 cm^3 of 0.25 M H_2SO_4. The residual acid required 63.0 cm^3 of 0.5 M NaOH for complete neutralization. Calculate the percentage of ammonia in the ammonium salt.
4. In a sample of dolomitic limestone containing 5 mass % silica, 3.5 mass % of combined oxides principally of iron and aluminium, and showing 43.0 % loss on ignition, what are the percentages of CaO and MgO, assuming that the loss is entirely due to carbon dioxide from carbonates of calcium and magnesium?
5. A mixture of pure $K_2Cr_2O_7$ and pure $KMnO_4$ weighing 0.561 g was treated with excess of KI in acidic medium. Iodine liberated required 100 mL of 0.15 M of sodium thiosulphate solution for exact oxidation. What is the percentage of each in the mixture?
6. 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.
7. A solution contains a mixture of sulphuric acid and oxalic acid, 25 mL of the solution requires 35.5 mL of 0.1 M NaOH for neutralization and 23.45 mL of 0.02 M $KMnO_4$ for oxidation. Calculate the molarity of solution with respect to sulphuric acid and oxalic acid.
8. A 0.527 g sample of a mixture containing Na_2CO_3, $NaHCO_3$, and inert impurities is titrated with 0.109 M HCl, requiring 15.7 mL to reach the phenolphthalein end point and a total of 43.8 mL to reach the modified methyl orange end point. What is the per cent each of Na_2CO_3 and $NaHCO_3$ in the mixture?
9. A sample containing amino acid alanine, $CH_3CH(NH_2)COOH$ plus inert matter is analyzed by the Kjeldahl method. A 2.00 g sample is digested, the NH_3 is distilled and collected in 50.0 mL of 0.150 M H_2SO_4, and a volume of 9.0 mL of 0.100 M NaOH is required for back titration. Calculate the per cent alanine in the sample.
10. A 2.50 g sample containing As_2O_5 and Na_2HAsO_3, and inert material is dissolved and the pH is adjusted to neutral with excess $NaHCO_3$. The As(III) is titrated with 0.150 M I_2 solution, requiring 11.3 mL to just reach the end point. Then, the solution (all the arsenic in the +5 state now) is acidified with HCl, excess KI is added,

and the liberated I_2 is titrated with 0.120 M $Na_2S_2O_3$, requiring 41.2 mL. Calculate the per cent As_2O_5 and Na_2HAsO_3 in the sample?

11. A 0.224 g sample that contained only $BaCl_2$ and KBr required 19.7 mL of 0.100 M $AgNO_3$ to reach the end point. Calculate the per cent of each compound present in the sample?

12. The elemental Se, dispersed in a 5.0 mL sample of detergent for dandruff control, was determined by suspending the sample in a warm, ammoniacal solution that contained 45.0 mL of 0.020 M $AgNO_3$:

$$6Ag^+ + 3Se(s) + 6NH_3 + 3H_2O \rightarrow 2Ag_2Se(s) + Ag_2SeO_3(s) + 6NH_4^+$$

The mixture was next treated with excess nitric acid which dissolved the Ag_2SeO_3 but not the Ag_2Se. The Ag^+ from the Ag_2SeO_3 and the excess $AgNO_3$ consumed 16.74 mL of 0.0137 N KSCN in a Volhard titration. How many milligrams of Se were contained per millilitre of sample?

13. A 0.510 g sample of a pesticide was decomposed by fusion with sodium carbonate and leaching the residue with hot water. The fluoride present in the sample was then precipitated as PbClF by addition of HCl and $Pb(NO_3)_2$. The precipitate was filtered, washed, and dissolved in 5% HNO_3. The Cl^- was precipitated by addition of 50.0 mL of 0.20 M $AgNO_3$. After coating the AgCl with nitrobenzene, the excess Ag^+ was back-titrated with 7.42 mL of 0.176 M NH_4SCN. Calculate the per cent F and the per cent Na_2SeF_6 in the sample.

14. A 0.141 g sample of a phosphorus containing compound was digested in a mixture of HNO_3 and H_2SO_4 which resulted in formation of CO_2, H_2O and H_3PO_4. Addition of ammonium molybdate yielded a solid having the composition $(NH_4)_3PO_4 \cdot 12\,MoO_3$. The precipitate was filtered, washed, and dissolved in 50.0 mL of 0.20 M NaOH :

$$(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$$

After boiling the solution to remove the NH_3, the excess NaOH was titrated with 14.1 mL of 0.174 M HCl. Calculate the per cent of phosphorus in the sample.

15. A 1.21 g sample of commercial KOH, which was contaminated by K_2CO_3, was dissolved in water, and the resulting solution was diluted to 500 mL. A 50.0 mL aliquot of this solution was treated with 40.0 mL of 0.053 M HCl and boiled to remove CO_2. The excess acid consumed 4.74 mL of 0.0498 M NaOH using phenolphthalein as the indicator. An excess of neutral $BaCl_2$ was added to another 50.0 mL aliquot to precipitate carbonate as $BaCO_3$. The solution was then titrated with 28.3 mL of the acid to a phenolphthalein end point. Calculate the per cent KOH, K_2CO_3 and water in the sample, assuming that these are the only compounds present.

16. A 0.646 g sample containing $BaCl_2 \cdot 2H_2O$ was dissolved and an excess of a K_2CrO_4 solution added. After a suitable period, the $BaCrO_4$ was filtered, washed, and redissolved in HCl to convert CrO_4^{2-} to $Cr_2O_7^{2-}$. An excess of KI was added, and the liberated iodine was titrated with 84.7 mL of 0.137 M sodium thiosulphate. Calculate the per cent of $BaCl_2 \cdot 2H_2O$.

17. A 0.517 g sample containing $Ba(SCN)_2$ was dissolved in a bicarbonate solution. 50.0 mL of 0.107 N iodine was added, and the mixture was allowed to stand for 5 min. The solution was then acidified, and the excess I_2 was titrated with 16.3 mL of 0.0965 M sodium thiosulphate. Write a balanced equation for the oxidation of SCN^- by I_2; given that the product obtained from SCN^- are SO_4^{2-} and HCN. Calculate the per cent $Ba(SCN)_2$ in the sample.

18. The chromium in a 1.87 g sample of chromite ($FeO \cdot Cr_2O_3$) was oxidized to the +6 state by fusion with sodium peroxide. The fused mass was treated with water and boiled to destroy the excess peroxide. After acidification, the sample was treated with 50.0 mL of 0.160 M Fe^{2+}. A back titration of 2.97 mL of 0.05 N $K_2Cr_2O_7$ was required to oxidize the excess iron(II). What is the percentage of chromite in the sample?

19. In the presence of fluoride ion, Mn^{2+} can be titrated with MnO_4^-, both reactants being converted to a complex of Mn(III). A 0.545 g sample containing Mn_3O_4 was dissolved, and all manganese was converted to Mn^{2+}. Titration in the presence of fluoride ion consumed 31.1 mL of $KMnO_4$ that was 0.117 N against oxalate. (a) Write a balanced equation for the reaction, assuming that the complex is MnF_4^-. (b) What is the normality of the $KMnO_4$ in the titration? (c) What was the per cent Mn_3O_4 in the sample?

20. The H_2S and SO_2 concentrations of a gas were determined by passage through three absorber solutions connected in series. The first contained an ammoniacal solution of Cd^{2+} to trap the sulphide as CdS. The second contained 10.0 mL of 0.0396 N I_2 to oxidize SO_2 to SO_4^{2-}. The third contained 10.0 mL 0.0345 N thiosulphate solution to retain any I_2 carried over from the second absorber. A 25.0 litre gas sample was passed through the apparatus followed by an additional amount of pure N_2 to sweep the last traces of SO_2

from the first and second absorber. The soultion from the first absorber was made acidic, and 20.0 mL of the 0.0396 N I_2 were added. The excess I_2 was back-titrated with 7.45 mL of the thiosulphate solution. The solutions in the second and third absorbers were combined and the resultant iodine was titrated with 2.44 mL of the thiosulphate solution. Calculate the concentrations of SO_2 and H_2S in mg/L of the sample.

21. A 1.850 g sample of a mixture of $CuCl_2$ and $CuBr_2$ was dissolved in water and mixed thoroughly with a 1.80 g portion of AgCl. After the reaction, the solid, which now considered a mixture of AgCl and AgBr, was filtered, washed, and dried. Its mass was found to be 2.052 g. What per cent by mass of the original mixture was $CuBr_2$?

22. A mixture of two monoprotic acids, lactic acid ($HC_3H_5O_3$) and caporic acid ($HC_6H_{11}O_2$), was titrated with 0.05 M NaOH. A 0.10 g sample of the mixture required 20.4 mL of the base. What was the mass of each acid in the sample?

23. A mixture of $CaCl_2$ and NaCl weighing 2.385 g was dissolved in water and treated with a solution of sodium oxalate which produced a precipitate of calcium oxalate. The precipitate was filtered from the mixtrue and then dissolved in HCl to give oxalic acid which when titrated against 0.2 M $KMnO_4$ consumed 19.64 mL of the latter. What was percentage by mass of $CaCl_2$ in the original sample?

24. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample.

ANSWERS

1. 20.12 mass % FeO and 79.88 mass % Fe_3O_4
2. 3.58 mass % Na_2O and 10.62 mass % K_2O
3. 26.4 mass %
4. 32.37 mass % CaO and 16.08 mass % MgO
5. 43.67 mass % $K_2Cr_2O_7$ and 56.33 mass % $KMnO_4$
6. 52.02 mass % $MgCO_3$ and 47.98 mass % $CaCO_3$
7. 0.0241 M H_2SO_4 and 0.0469 M oxalic acid
8. 34.42% Na_2CO_3 and 21.54% $NaHCO_3$
9. 62.8
10. 3.57 mass % As_2O_5 and 11.52 mass % Na_2HAsO_3
11. 32.4 % $BaCl_2$ and 67.7% KBr
12. 7.94 mg/mL
13. 32.4 % F and 67.9 % Na_2SeF_6
14. 6.38%
15. 69.5 % KOH, 22% K_2CO_3, 8.5% H_2O
16. 84%
17. $SCN^- + 3I_2 + 4H_2O \rightleftharpoons SO_4^{2-} + HCN + 7H^+ + 6I^-$ 15.4 %
18. 15.7%
19. (a) $4\,Mn^{2+} + MnO_4^- + 20\,F^- + 8H^+ \rightleftharpoons 5\,MnF_4^- + 4H_2O$
(b) 0.0936 N
(c) 40.8 %
20. 0.365 H_2S mg/L and 0.311 mg SO_2/L
21. 34.2
22. 0.064 g lactic acid and 0.036 g caporic acid
23. 45.70% $CaCl_2$
24. 34.8% Fe_3O_4 and 49.33% Fe_2O_3

CHAPTER 2

GASEOUS, LIQUID AND SOLID STATES

SECTION I GASEOUS STATE

The gaseous state of a matter is characterized by sensitivity of volume change with change in pressure and temperature. This characteristic is due to the larger distance between molecules as compared to their own dimensions. There exists weak intermolecular forces (called van der Waals forces) and the molecules move practically independent of each other with a very large speed (of the order of about 400 m s^{-1}). There exists no boundary surface in the gaseous state and thus molecules try to occupy whole of the volume available for their movement. Experiments and theory have established definite relations between the mass, pressure, volume, density and temperature of the gaseous state. An equation relating pressure, volume, temperature and amount of a gas is known as the *equation of state*.

A few experimentally established expressions relating to the characteristics of gaseous phase are described in the following.

Boyle's Law At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure. Mathematically, it is expressed as

$$V \propto 1/p \qquad \text{or} \qquad pV = \text{constant} \tag{1}$$

Charles Law At constant pressure, the volume of a given mass of a gas varies linearly with temperature in degree Celsius. Mathematically, it is written as

$$V_t = a + bt \tag{2}$$

It is found experimentally that $b = \dfrac{V_0/273.15}{1\,°\mathrm{C}}$

where V_0 is the volume of gas at 0 °C. The constant a will also be equal to V_0. With these, Eq. (2) becomes

$$V_t = V_0\left(1+\frac{t/°\mathrm{C}}{273.15}\right) = V_0\left(\frac{273.15+t/°\mathrm{C}}{273.15}\right) = V_0\left(\frac{T/\mathrm{K}}{273.15}\right) = \left(\frac{V_0}{273.15\,\mathrm{K}}\right)T \tag{3}$$

where the symbol T stands for kelvin temperature. Equation (2) is also expressed as

$$V_t = (\text{constant})\ T \qquad \text{or} \qquad V_t \propto T \tag{4}$$

that is, the volume of a gas is directly proportional to its kelvin temperature.

Gay Lussac's Law An expression similar to Charles law exists between pressure and temperature of the gas at a fixed volume. This law can be expressed as

$$p \propto T \qquad \text{or} \qquad p/T = \text{constant} \tag{5}$$

Equation of State The combination of Boyle's law and Charles law leads to the expression

$$pV = nRT \tag{6}$$

where n is the amount of gas and R is universal gas constant whose value in different units are given below.

$$\begin{aligned} R &= 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ MPa cm}^3 \text{ K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Graham's Law of Diffusion The rate of diffusion of a gas is inversely proportional to the square root of its density or molar mass. Mathematically, it is expressed as

$$r \propto \frac{1}{\sqrt{\rho}} \qquad \text{or} \qquad r \propto \frac{1}{\sqrt{M}}$$

Comparison of the rate of diffusion of two gases under identical conditions provides the relation

$$\frac{r_2}{r_1} = \sqrt{\frac{\rho_1}{\rho_2}} \qquad \text{or} \qquad \frac{r_2}{r_1} = \sqrt{\frac{M_1}{M_2}} \tag{7}$$

If the concentrations (or pressures) of two gases are not identical, the rates of diffusion are related to each other through the expression

$$\frac{r_2}{r_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_2}\right)^{1/2}$$

Dalton's Law of Partial Pressures The total pressure of a mixture of noninteracting gases is equal to the sum of partial pressures of the constituent gases. Mathematically, it is expressed as

$$p_{\text{total}} = p_1 + p_2 + \cdots \tag{8}$$

By definition, the partial pressure of a gas in a mixture of gases is the pressure which the gas would exert if it is allowed to occupy the whole volume of the mixture at the same temperature. It is also given as

$$p_\text{i} = \frac{n_\text{i}}{\sum\limits_\text{i} n_\text{i}}\, p \tag{9}$$

where n_i is the amount of ith constituent in the mixture of the gases containing total amount equal to $\sum\limits_\text{i} n_\text{i}$.

The pressure of a gas collected over volatile liquid such as water will be expressed as

$$p_{\text{total}} = p_{\text{air}} + p_{\text{water}} \tag{10}$$

where p_{air} is the partial pressure of dry air and p_{water} is the vapour pressure (i.e. aqueous tension) of water.

Avogadro's Law Equal volume of all gases under identical conditions of temperature and pressure contains equal number of molecules. 1 mol of any gas (assumed to be ideal) occupies 22.414 L of volume under standard conditions (1 atm and 0 °C) and contains atoms/molecules equal to 6.022×10^{23}. This number is represented by the physical quantity known as *Avogadro constant* (= 6.022×10^{23} mol^{-1}).

KINETIC THEORY OF GASES

Based on certain postulates regarding the characteristics of an ideal gas, kinetic theory of gases provides a theoretical expression of equation of state of an ideal gas. The postulates are

1. All gases are made up of tiny spherical particles called molecules. For a given gas, the size, shape and mass of molecules are completely identical.
2. The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
3. There exists no forces of attraction and repulsion amongst the molecules of a gas.
4. The molecules are perfectly elastic. Thus, no loss of energy occurs during the molecular collisions.
5. The motions of molecules are completely random.
6. The pressure of a gas is due to the collision of molecules with sides of the vessel.
7. Newton's laws of the motion hold good for the movement of molecules.
8. At any instant, a given molecule may have energy ranging from a small value to a large value, but the average kinetic energy of molecules is directly proportional to kelvin temperature.

The equation obtained on the basis of above postulates is known as *kinetic gas equation* and is expressed as

$$pV = \frac{1}{3}\ mN\,\overline{u^2}$$

where m is the mass of each molecule, N is the number of molecules and $\overline{u^2}$ is the mean square speed defined as

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$$

The various gasesous laws (such as Boyle, Charles, etc.) can be derived from the kinetic gas equation.

EXPRESSIONS OF SOME USEFUL PHYSICAL QUANTITIES

The expressions of some useful physical quantities are given in the following.

Root Mean Square Speed This speed is defined as $\sqrt{\overline{u^2}} = \left(\dfrac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}\right)^{1/2}$

and is given by the expression

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

An alternative form of the above equation can be derived. For an ideal gas, $RT = pV/n$. With this, the above expression becomes

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3pV}{nM}} = \sqrt{\frac{3p}{m/V}} = \sqrt{\frac{3p}{\rho}}$$

where m is the mass of the given quantity of the gas and ρ is the density of the gas. It may be mentioned that the root mean square speed depends only on the temperature of the gas, i.e. it is independent of pressure and volume variations at constant temperature, since the product pV and the quantity p/ρ are constant at a given temperature.

Average Speed This speed is defined as $\bar{u} = \dfrac{u_1 + u_2 + \cdots + u_N}{N}$

and is given by the expression

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}\ .$$

Most Probable Speed This is the the speed corresponding to the maximum fraction of the molecules of a gas. Its expression is

$$u_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}}$$

Comparing the three speeds listed above, we find that

$$u_{\mathrm{rms}} : u_{\mathrm{av}} : u_{\mathrm{mp}} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2} \qquad \text{that is} \qquad u_{\mathrm{rms}} > u_{\mathrm{av}} > u_{\mathrm{mp}}$$

Average Kinetic Energy The average kinetic energy of gaseous molecules is defined as $(1/2)m\overline{u^2}$. From the kinetic gas equation, we find that

$$pV = \frac{1}{3}\ mN\,\overline{u^2} = \frac{2}{3}\ N\left(\frac{1}{2}m\,\overline{u^2}\right) \qquad \text{or} \qquad \overline{\mathrm{KE}} = \frac{1}{2}\ m\ \overline{u^2} = \frac{3pV}{2N}$$

For one mole of a gas, $V = V_{\mathrm{m}}$, $N = N_{\mathrm{A}}$. Hence,

$$\overline{\mathrm{KE}} = \frac{3pV_{\mathrm{m}}}{2N_{\mathrm{A}}} = \frac{3RT}{2N_{\mathrm{A}}} = \frac{3}{2}kT$$

where $k = R/N_{\mathrm{A}}$ and is known as *Boltzmann constant.*

VAN DER WAALS EQUATION OF STATE

All the gaseous laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real gases show deviations from these gaseous laws, especially when temperature is low and pressure is high. Real gases follow ideal gas laws under the condition of low pressure and high temperature. Van der Waals pointed out that the deviations shown by real gases are due to the following two facts.

1. The volume occupied by the molecules is not negligible in comparison to the total volume of the gas.
2. There exist forces of attraction between the molecules.

Van der Waals systematically corrected the ideal gas equation in the light of the above two facts. The corrected equation is

$$\left(p + n^2 \frac{a}{V^2}\right)(V - nb) = nRT$$

where a and b are two constants, known as van der Waals constants. The units of a and b are $\mathrm{L^2\ atm\ mol^{-2}}$ and $\mathrm{L\ mol^{-1}}$, respectively. In SI units, a and b are expressed in $\mathrm{Pa\ m^6\ mol^{-2}}$ and $\mathrm{m^3\ mol^{-1}}$, respectively. The constants a and b are characteristic of the given gas. The constant a is a measure of the forces of attraction between gaseous molecules and the constant b is a measure of effective volume occupied by the molecules of 1 mol of a gas. The numerical value of b is four times the actual volume occupied by the molecules in 1 mole of the gas, i.e.

$$b = N_A\,[4(4\pi r^3/3)]$$

where r is the radius of molecule of the gas.

Van der Waals equation accounts for the behaviour of real gases. At low pressures, the gas equation can be written as

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \qquad \text{or} \qquad Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT}$$

where Z is known as *compression factor*. Its value at low pressures is less than one and it decreases with increase in pressure. For a given value of V_m, Z has more value at higher temperature.

At high pressures, the gas equation can be written as

$$p(V_m - b) = RT \qquad \text{or} \qquad Z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT}$$

Here, the compression factor increases with increase in pressure at constant temperature and it decreases with increase in temperature at constant pressure. For the gases H_2 and He, the above behaviour is observed even at low pressures, since for these gases, the value of a is extremely small.

Reduction of Van Der Waals Gas to Virial Equation

For one mole of a gas, the virial equation of state has the following form

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

where B, C, … are known as second, third, etc., virial coefficients.

For one mole of a gas, the van der Waals equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad \text{or} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

or

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT} = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT} = \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots\right] - \frac{a}{V_m RT}$$

$$= 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \ldots$$

The second virial coefficient is given by $B = b - \dfrac{a}{RT}$

At Boyle temperature, the second virial coefficient is zero. Hence, $T_B = \dfrac{a}{Rb}$

At Boyle temperature, the real gas behaves ideally over a wide range of pressure. This is due to the fact that the effects of size of molecules and intermolecular forces roughly compensate each other.

SOME DEFINITIONS

Critical temperature (T_c) It is the maximum temperature at which a gas can be liquefied, i.e., the temperature above which a liquid cannot exist.

Critical pressure (p_c) It is the minimum pressure required to cause liquefaction at critical temperature.

Critical volume (V_c) It is the volume occupied by one mole of a gas at critical temperature and critical pressure.

Critical state A gas having critical temperature, critical pressure and critical volume is said to be in the critical state.

For a van der Waals gas, we have

$$T_c = 8a/(27Rb); \qquad p_c = a/(27b^2); \qquad V_c = 3b; \qquad \text{and} \qquad p_cV_c/RT_c = 3/8$$

Inversion Temperature (T_i) The temperature at which a real gas does not exhibit cooling or heating when it is passed through a throttling device. If the temperature of the gas is lower than its inversion temperature, it exhibits cooling. At higher temperature, it exhibits heating. For a van der Waals gas, $T_i = 2a/Rb$.

Heat Capacity of Gases Heat capacity of a system is defined as the amount of heat required to increase its temperature by 1 degree Celsius. For a gaseous system, two heat capacities may be defined. These are (i) heat capacity at constant volume (C_V) and (ii) heat capacity at constant pressure (C_p). The molar heat capacity is defined for 1 mol of the substance. One can write

$$C_{V,\mathrm{m}} = \text{contribution from (translational + rotational + vibrational) modes}$$

At low temperatures, vibrational modes do not contribute towards heat capacity, its contribution increases with increase in temperature. It is only at higher temperature, it is effective in contributing its full share.

The contributions towards heat capacity are as follows.

$$C_{V,\mathrm{m}} = \text{(Translational + Rotational + Vibrational) contributions}$$

Monatomic Gas $C_{V,\mathrm{m}} = \dfrac{3}{2}R + 0 + 0 = \dfrac{3}{2}R$

Polyatomic Gas *Linear* $C_{V,\mathrm{m}} = \dfrac{3}{2}R + R + (3N - 5)R$

Non-linear $C_{V,\mathrm{m}} = \dfrac{3}{2}R + R + (3N - 6)R$

where N is the number of atoms in the molecule of the gas.

For an ideal gas, $C_{p,\mathrm{m}} = C_{V,\mathrm{m}} - R$

The ratio of $C_{p,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ is represented by the symbol γ. We have

Monatomic gas $\gamma = \dfrac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \dfrac{(5/2)R}{(3/2)R} = \dfrac{5}{3} = 1.667$

Diatomic gas $\gamma = \dfrac{(9/2)R}{(7/2)R} = \dfrac{9}{7} \simeq 1.286$

Triatomic gas, Linear $\gamma = \dfrac{(15/2)R}{(13/2)R} = \dfrac{15}{13} \simeq 1.154$

Nonlinear $\gamma = \dfrac{7R}{6R} = \dfrac{7}{6} \simeq 1.167$

The value of γ decreases with increase in atomicity of the molecule.

Mean Free Path The mean free path is the average distance travelled by a molecule between two succesive collisions. it is given by the expression $\lambda = 1/\sqrt{2}\,\pi\,\sigma^2 N^*$, where σ is molecular diameter and N^* is the number of molecules per unit volume of the gas.

Viscosity of Gases The gases also exhibit viscosity due to the migration of momentum from one layer to nearby layers. It is given by the expression $\eta = (m\,k\,T)^{1/2}\,\pi^{3/2}\,\sigma^2$. The viscosity gases unlike liquids increases with increase in temperature.

Straight Objective Type

Gaseous Laws

1. 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
(a) 1/3 (b) 1/2 (c) 2/3 (d) (1/3) (273/298) (1981)

2. Equal masses of ethane and hydrogen are mixed in an empty container at 25 °C. The fraction of the total pressure exerted by hydrogen is
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16 (1993)

3. Which of the following expressions correctly represents the variation of density of an ideal gas with change in temperature from T_1 to T_2?
(a) $\rho_2 = \rho_1 (T_1 p_2/T_2 p_1)$ (b) $\rho_2 = \rho_1 (T_1 p_1/T_2 p_2)$
(c) $\rho_2 = \rho_1 (T_2 p_2/T_1 p_1)$ (d) $\rho_2 = \rho_1 (T_2 p_1/T_1 p_2)$

4. 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

5. The volume of a gas
(a) is directly proportional to temperature expressed in Celsius scale
(b) is zero at 0 °C
(c) is inversely proportional to kelvin temperature
(d) changes by $V_0/273.15$ for every 1 °C rise in temperature, where V_0 is the temperature at 0 °C

6. For a fixed mass of a gas,
(a) the plot of volume versus Celsius temperature is linear with zero intercept
(b) the plot of volume versus kelvin temperature is linear with a negative slope
(c) the plot of V/T versus T is linear with a positive slope
(d) the plot of V/T versus T is linear with zero slope

7. The dimensionally correct expression for the conversion of kelvin temperature to Celsius temperature is
(a) $t = T + 273.15$ (b) $t = T - 273.15$
(c) $t/°\text{C} = T/\text{K} + 273.15$ (d) $t/°\text{C} = T/\text{K} - 273.15$

8. Which of the following is the value of R expressed in SI units?
(a) 8.314 J mol^{-1} (b) 8.314 J K^{-1} mol^{-1}
(c) 8.314 J K^{-1} (d) 8.314×10^7 ergs K^{-1} mol^{-1}

9. The value of the Boltzmann constant is
(a) 6.023×10^{23} mol^{-1} (b) 1.36×10^{-23} J K^{-1} molecule^{-1}
(c) 1.36×10^{-23} J K^{-1} mol^{-1} (d) 1.36×10^{-23} J K^{-1}

10. The value of Avogadro constant is
(a) 6.022×10^{23} (b) 6.022×10^{13} (c) $6.022 \times 10^{23}\ \text{mol}^{-1}$ (d) $6.022 \times 10^{13}\ \text{mol}^{-1}$

11. At which of the following four conditions, the density of nitrogen will be largest?
(a) STP (b) 273 K and 2 atm (c) 546 K and 1 atm (d) 546 K and 2 atm

12. The temperature of a given mass of a gas is increased from 19 °C to 20 °C at constant pressure. The volume V of the gas is increased
(a) to $V(20/19)$ (b) by 1/273.15 of its volume at 0 °C.
(c) by 1/273.15 of its volume at 0 K. (d) by a factor of 1/273.15.

13. At a given temperature if $\rho(\text{X}) = 3\,\rho(\text{Y})$ and $M(\text{Y}) = 2\,M(\text{X})$, where ρ and M, respectively, stand for density and molar mass of the gases X and Y, then the ratio of their pressures would be
(a) $p(\text{X})/p(\text{Y}) = 1/4$ (b) $p(\text{X})/p(\text{Y}) = 4$ (c) $p(\text{X})/p(\text{Y}) = 6$ (d) $p(\text{X})/p(\text{Y}) = 1/6$

14. The compression factor for an ideal gas is
(a) 1.5 (b) 1.0 (c) 2.0 (d) ∞ (1997)

15. The degree of dissociation of the reaction $AB_2 \rightleftharpoons A + B_2$ is found to be 0.4 at 400 K and 1 atm pressure. If the molar mass of AB_2 is 200 g mol^{-1}, the density of the system at equilibrium would be
(a) 4.35 g dm^{-3} (b) 4.85 g dm^{-3} (c) 5.35 g dm^{-3} (d) 5.85 g dm^{-3}

16. The ratio of densities of a gas at two conditions of temperature and pressure is given by

(a) $\dfrac{\rho_2}{\rho_1} = \left(\dfrac{p_2}{p_1}\right)\left(\dfrac{T_2}{T_1}\right)$ (b) $\dfrac{\rho_2}{\rho_1} = \left(\dfrac{p_2}{p_1}\right)\left(\dfrac{T_1}{T_2}\right)$ (c) $\dfrac{\rho_2}{\rho_1} = \left(\dfrac{p_1}{p_2}\right)\left(\dfrac{T_1}{T_2}\right)$ (d) $\dfrac{\rho_2}{\rho_1} = \left(\dfrac{p_1}{p_2}\right)\left(\dfrac{T_2}{T_1}\right)$

17. A gaseous mixture of helium and oxygen is found to have a density of 0.5 g dm^{-3} at 300 K and 760 Torr. The mass per cent of helium in the mixture is about
(a) 22% (b) 35% (c) 40% (d) 50%

18. The density of a gas is 1.5 g L^{-1} at STP. Its density at 27 °C and 1000 Torr would be
(a) 1.8 g L^{-1} (b) 2.8 g L^{-1} (c) 3.8 g L^{-1} (d) 4.8 g L^{-1}

19. The density of a gas at STP is 1.5 g L^{-1}. Pressure remaining constant, the temperature at which its density is 0.5 g L^{-1} is
(a) 273 °C (b) 546 °C (c) 819 °C (d) 1000 °C

20. A mixture of NH_3(g) and N_2H_4(g) is placed in a sealed container at 300 K. The pressure within the container is 0.6 atm. The container is heated to 1000 K where the two gases undergo decomposition reactions

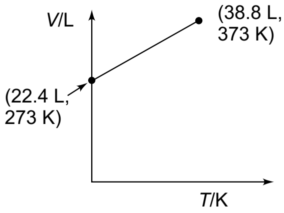
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad \text{and} \quad N_2H_4(g) \rightarrow N_2(g) + 2H_2(g).$$

The pressure of the container at this stage becomes 4.8 atm. The mole per cent of NH_3(g) in the original mixture was
(a) 40 (b) 50 (c) 60 (d) 70

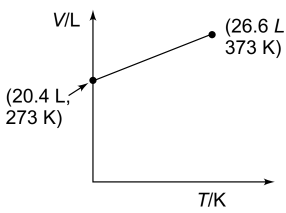
21. The compression factor of an ideal gas.
(a) increases with increase in temperature.
(b) decreases with increase in temperature.
(c) remains constant with change in temperature.
(d) increases with change in temperature in the lower temperature range while it decreases in the higher temperature range.

22. At 100 °C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at this temperature is
(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3 (2000)

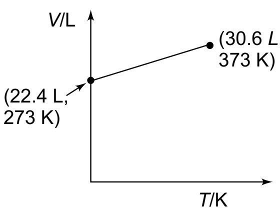
23. Which of the following volume (V)–temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?



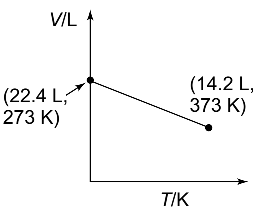
(a)



(b)



(c)



(d)

(2002)

Diffusion of Gases

24. Rate of diffusion of a gas is
(a) directly proportional to its density
(b) directly proportional to its molar mass
(c) directly proportional to the square root of its molar mass
(d) inversely proportional to the square root of its molar mass (1985)

25. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammounium 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.

26. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molar mass of X is
(a) 64.0 g mol^{-1} (b) 32.0 g mol^{-1} (c) 4.0 g mol^{-1} (d) 8.0 g mol^{-1} (1990)

27. Three grams of helium diffuses from a container in 15 min. The mass of sulphur dioxide diffusing from the same container over the same time interval will be
(a) 3 g (b) 6 g (c) 9 g (d) 12 g

28. The volume X of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the specified gas under identical conditions is
(a) 10 seconds : He (b) 20 seconds : O_2 (c) 25 seconds : CO (d) 55 seconds : CO_2
(1996)

29. According to Graham's law, at a given temperature the ratio of the rates of diffusion r_A/r_B of gases A and B is given by
(a) $(p_A/p_B)\,(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)\,(p_A/p_B)^{1/2}$ (c) $(p_A/p_B)\,(M_B/M_A)^{1/2}$ (d) $(M_AM_B)\,(p_B/p_A)^{1/2}$
(1998)

30. The degree of dissociation (α) of the reaction $A_2(g) \rightleftharpoons 2A(g)$ in terms of rate of diffusion (r_{mix}) of equilibrium mixture and that of a reference gas X is given by

(a) $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_{mix}}{r_X}\right)^2 - 1$ (b) $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_X}{r_{mix}}\right)^2 - 1$

(c) $\alpha = \left(\frac{M_X}{M_{A_2}}\right)\left(\frac{r_X}{r_{mix}}\right)^2 - 1$ (d) $\alpha = \left(\frac{M_X}{M_{A_2}}\right)\left(\frac{r_{mix}}{r_X}\right)^2 - 1$

where M stands for the respective molar masses.

31. A 4:1 mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. The composition of the mixture, effusing out initially is about
(a) He : CH_4 :: 1 : 1 (b) He : CH_4 :: 2 : 1 (c) He : CH_4 :: 4 : 1 (d) He : CH_4 :: 8 : 1

32. If methane and helium are allowed to diffuse out of a container under identical conditions of temperature and pressure, the ratio of rate of diffusion of methane to helium is
(a) 4.0 (b) 2.0 (c) 1.0 (d) 0.5

Kinetic Theory of Gases

33. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
(a) are above the inversion temperature (b) exert no attractive forces on each other
(c) do work equal to the loss in kinetic energy (d) collide without loss of energy

34. According to the kinetic theory of gases, for a diatomic molecule
(a) the pressure exerted by the gas is proportional to the mean 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 of the molecules is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecules is proportional to the absolute temperature
(1991)

35. At constant volume, for a fixed amount of a gas the pressure of the gas increases with rise of temperature due to
(a) increase in average molecular speed (b) increased rate of collision amongst molecules
(c) increase in molecular attraction (d) decrease in mean free path

36. Which of the following expressions does not represent an ideal gas?
(a) $p = nRT/V$ (b) $p = \rho RT/M$ (c) $pV = \frac{1}{3}\, m N \overline{u^2}$ (d) $p = \frac{2}{3}\, N\,(\mathrm{KE})$

37. Which of the following statements is not a postulate of the kinetic theory of gases?
(a) Gases are made up of tiny particles called molecules
(b) All molecules move with the same speed and have random motion
(c) The molecules are perfectly elastic
(d) There exists no forces of attraction and repulsion amongst gaseous molecules

38. The value of $(pV_m)_{p \to 0}$ at 0 °C for an ideal gas is
(a) 22.414 bar dm^3 (b) 22.71 bar dm^3 (c) 23.414 bar dm^3 (d) 25.0 bar dm^3

39. Which of the following expressions is correct for an ideal gas?
(a) $p = \frac{2}{3}\frac{V}{N}\bar{E}$ (b) $p = \frac{3}{2}\frac{V}{N}\bar{E}$ (c) $p = \frac{2}{3}\frac{N}{V}\bar{E}$ (d) $p = \frac{3}{2}\frac{N}{V}\bar{E}$

Speeds of Gaseous Molecules

40. The ratio of root mean square speed to average speed of a gas molecule at a particluar temperature is
(a) 1.086 : 1 (b) 1 : 1.086 (c) 2 : 1.086 (d) 1.086 : 2 (1981)

41. The average speed of an ideal gas molecules at 27 °C is 0.3 m s^{-1}. The average speed at 927 °C will be
(a) 0.6 m s^{-1} (b) 0.3 m s^{-1} (c) 0.9 m s^{-1} (d) 3.0 m s^{-1} (1986)

42. The expression of root mean square speed of molecules of a gas is given as
(a) $u_{rms} = \sqrt{\frac{3RT}{M}}$ (b) $u_{rms} = \sqrt{\frac{3RT}{m}}$ (c) $u_{rms} = \sqrt{\frac{3kT}{M}}$ (d) $u_{rms} = \sqrt{\frac{8RT}{\pi M}}$

43. The expression of average speed of molecules of a gas is given as
(a) $u_{av} = \sqrt{\frac{8RT}{\pi m}}$ (b) $u_{av} = \sqrt{\frac{8RT}{\pi M}}$ (c) $u_{av} = \sqrt{\frac{8kT}{\pi M}}$ (d) $u_{av} = \sqrt{\frac{8RT}{M}}$

44. The expression of most probable speed of molecules of a gas is given as
(a) $u_{mp} = \sqrt{\frac{2RT}{M}}$ (b) $u_{mp} = \sqrt{\frac{3RT}{M}}$ (c) $u_{mp} = \sqrt{\frac{8RT}{\pi M}}$ (d) $u_{mp} = \sqrt{\frac{8RT}{M}}$

45. For a given gas, which of the following relationships is correct at a given temperature?
(a) $u_{rms} > u_{av} > u_{mp}$ (b) $u_{rms} < u_{av} < u_{mp}$ (c) $u_{rms} > u_{av} < u_{mp}$ (d) $u_{rms} < u_{av} > u_{mp}$

46. The relative ratio of $u_{rms} : u_{av} : u_{mp}$ at a given temperature is
(a) $\sqrt{3} : \sqrt{56/22} : \sqrt{2}$ (b) $\sqrt{56/22} : \sqrt{2} : \sqrt{3}$ (c) $\sqrt{3} : \sqrt{2} : \sqrt{56/22}$ (d) $\sqrt{2} : \sqrt{56/22} : \sqrt{3}$

47. Which of the following gases will have maximum average speed at a given temperature?
(a) Nitrogen (b) Oxygen (c) Helium (d) Carbon dioxide

48. The most probable speed of an ideal gaseous molecules at 27 °C is 0.3 m s^{-1}. The average speed at 927 °C would be
(a) 0.3 m s^{-1} (b) 0.6 m s^{-1} (c) 0.9 m s^{-1} (d) 1.2 m s^{-1}

49. The root mean square speeds of gaseous molecules changes with change in the
(a) temperature of the gas (b) pressure of the gas
(c) volume of the gas (d) density of the gas

50. The root mean square speed of a gaseous molecules is given as $u_{rms} = \sqrt{3p/\rho}$. This shows that at a given temperature
(a) $u_{rms} \propto \sqrt{p}$ (b) $u_{rms} \propto \sqrt{1/\rho}$ (c) $u_{rms} \propto \sqrt{pV_m}$ (d) $u_{rms} \propto \sqrt{p/V_m}$

51. Which of the following is expected to possess the largest root mean square speed at the same temperature?
(a) H_2S (b) NH_3 (c) SO_2 (d) CO_2

52. The temperature at which root mean square speed of oxygen gas becomes equal to that of SO_2 at 327 °C is
(a) 163.5 °C (b) 654 °C (c) 27 °C (d) 327 °C

53. The ratio between the root means square speed of H_2 at 50 K and that of O_2 at 800 K is
(a) 4 (b) 2 (c) 1 (d) 1/4 (1996)

54. 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) $T(H_2) = \sqrt{7}\,T(N_2)$
(2000)

55. The root mean square speed of a gas at 300 K is 490 m s^{-1}. Its average speed at 300 K would be
(a) 451.3 m s^{-1} (b) 475.2 m s^{-1} (c) 502.0 m s^{-1} (d) 520.1 m s^{-1}

56. The average speed of a gas at 300 K is 475 m s^{-1}. Its most probable speed would be
(a) 520.1 m s^{-1} (b) 501.0 m s^{-1} (c) 450 m s^{-1} (d) 420.9 m s^{-1}

57. The temperature at which the average speed of oxygen becomes equal to that of methane at 327 °C is
(a) 627 ºC (b) 927 ºC (c) 1200 ºC (d) 654 ºC

58. 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) same as that of a hydrogen molecule
(c) four times that of a hydrogen molecule (d) half that of a hydrogen molecule (1982)

59. Which of the following expressions correctly represents the relationship between the average kinetic energy of CO and N_2 molecules at the same temperature?
(a) $\overline{E}(CO) > \overline{E}(N_2)$
(b) $\overline{E}(CO) < \overline{E}(N_2)$
(c) $\overline{E}(CO) = \overline{E}(N_2)$
(d) Cannot be predicted unless volumes of the gases are given

60. The total energy of a given mass of a gas at a given temperature depends on its
(a) pressure (b) volume (c) density (d) temperature

61. The average kinetic energy of gaseous molecules is
(a) $(1/2)kT$ (b) kT (c) $(3/2)kT$ (d) $(3/2)RT$

62. A molecule of SO_2 is two times heavier than O_2 molecule. At 298 K, the average kinetic energy of SO_2 molecules is
(a) two times that of O_2 molecules (b) half that of O_2 molecules
(c) four times that of O_2 molecules (d) same as that of O_2 molecules

63. The root mean square speed of gaseous molecules (molar mass : M) in terms of their molar kinetic energy (E) is
(a) $u_{rms} = \sqrt{3E/2M}$ (b) $u_{rms} = \sqrt{2E/3M}$ (c) $u_{rms} = \sqrt{2E/M}$ (d) $u_{rms} = \sqrt{E/3M}$ (2004)

64. The root mean square speed of an ideal gas at constant pressure varies (ρ) with density as
(a) ρ^2 (b) ρ (c) $\sqrt{\rho}$ (d) $1/\sqrt{\rho}$ (2001)

Real Gases

65. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is
(a) critical temperature (b) Boyle temperature
(c) inversion temperature (d) reduced temperature (1981)

66. In van der Waals equation of state for a nonideal gas the term that accounts for intermolecular forces is
(a) $(V - b)$ (b) $\left(p+\frac{a}{V^2}\right)$ (c) RT (d) $(RT)^{-1}$ (1988)

67. The values of van der Waals constant a for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2}, respectively. The gas which can most easily be liquefied is
(a) O_2 (b) N_2 (c) NH_3 (d) CH_4 (1989)

68. The van der Waals equation for a real gas is
(a) $(p + a/V^2)(V - b) = nRT$ (b) $(p + a/V^2)(V - nb) = nRT$
(c) $(p + na/V^2)(V - nb) = nRT$ (d) $(p + n^2 a/V^2)(V - nb) = nRT$

69. The unit of van der Waals constant *a* is
(a) atm (b) atm L^2 (c) atm L^2 mol^{-1} (d) atm L^2 mol^{-2}

70. The unit of van der Waals constant *b* is
(a) cm^3 (b) cm^3 mol^{-1} (c) cm^3 mol^{-2} (d) $(cm^3\ mol^{-1})^2$

71. In van der Waals equation of state for a nonideal gas, the term that accounts for the molecular volume is
(a) $V - b$ (b) $p + a/V_m^2$ (c) RT (d) $V - nb$

72. The van der Waals constant *b* is equal to
(a) the molecular volume of 1 mol of the gas
(b) two times the molecular volume of 1 mol of the gas
(c) three times the molecular volume of 1 mol of the gas
(d) four times the molecular volume of 1 mol of the gas

73. The values of van der Waals constant *a* for the gases O_2, N_2, CO_2 and CH_4 are 1.360, 1.390, 3.640 and 2.253 L^2 atm mol^{-2}, respectively. The gas which can be most easily be liquefied is
(a) O_2 (b) N_2 (c) CO_2 (d) CH_4

74. The temperature above which a real gas cannot be liquefied is known as
(a) critical temperature (b) consolute temperature
(c) Boyle temperature (d) inversion temperature.

75. The behaviour of a real gas is usually depicted by plotting compression factor $Z\ (= pV_m/RT = V_{real}/V_{ideal})$ versus p at a constant temperature. At low temperature and low pressure, Z is usually less than one. This fact can be explained by van der Waals equation when
(a) the constant *a* is negligible and not *b* (b) the constant *b* is negligible and not *a*
(c) both the constants *a* and *b* are negligible (d) both the constants *a* and *b* are not negligible

76. The behaviour of a real gas is usually depicted by plotting compression factor $Z\ (= pV_m/RT = V_{real}/V_{ideal})$ versus p at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals equation when
(a) the constant *a* is negligible and not *b* (b) the constant *b* is negligible and not *a*
(c) both the constants *a* and *b* are negligible (d) both the constants *a* and *b* are not negligible

77. At Boyle temperature, the value of compression factor $Z\ (= pV_m/RT = V_{real}/V_{ideal})$ has a value of one over a wide range of pressure. This is due to the fact that in the van der Waals equation
(a) the constant *a* is negligible and not *b* (b) the constant *b* is negligible and not *a*
(c) both the constants *a* and *b* are negligible (d) the effect produced due to the molecular attraction compensates the effect produced due to the molecular volume

78. A real gas is expected to bahave more or less ideally at
(a) low temperature and low pressure (b) low temperature and high pressure
(c) high temperature and low pressure (d) high temperature and high pressure (1999)

79. A real gas is expected to behave nonideally at
(a) low temperature and low pressure (b) low temperature and high pressure
(c) high temperature and low pressure (d) high temperature and high pressure

80. The most favourable conditions for a real gas to liquefy are
(a) high temperature and low pressure (B) high temperature and high pressure
(c) low temperature and low pressure (d) low temperature and high pressure

81. The compression factor of a gas is less than unity at STP. Therefore
(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L (c) $V_m = 22.4$ L (d) $V_m > = 44.8$ L (2000)

82. The unit of second virial coefficient is
(a) m^3 (b) m^3 mol^{-1} (c) Pa (d) Pa m^3

83. At Boyle temperature, the compression factor of a gas is
(a) equal to one over wide range of low pressure
(b) equal to one over wide range of high pressure
(c) more than one and it decreases
(d) less than one and it increases with increase in pressure.

84. Which of the following expressions between the van der Waals constant b and the radius r of spherical molecules is correct?

(a) $b = \left(\frac{4}{3}\pi r^3\right) N_A$ (b) $b = 2\left(\frac{4}{3}\pi r^3\right) N_A$ (c) $b = 3\left(\frac{4}{3}\pi r^3\right) N_A$ (d) $b = 4\left(\frac{4}{3}\pi r^3\right) N_A$

85. The value of compression factor of a van der Waals gas at critical point is
(a) 8/27 (b) 27/8 (c) 3/8 (d) 8/3

86. Which of the following statements is correct?
(a) Molecular attractions make the pressure of a van der Waals gas smaller than that of an ideal gas.
(b) Molecular attractions makes the pressure of a van der waals gas larger than that of an ideal gas
(c) Molecular size makes the pressure of a van der Waals gas smaller than that of an ideal gas
(d) Molecular attractions and molecular size have no significant effects on the pressure of a van der Waals gas.

87. Which of the following statements is correct?
(a) Molecular size has an effect of increasing the value of volume of a van der Waals gas as compared to that of an ideal gas
(b) Molecular size has an effect of decreasing the value of volume of van der waals gas as compared to that of an ideal gas
(c) Molecular size has no effect on the volume of a van der Waals gas as compared to an ideal gas
(d) Molecular size effects on the volume of a van der Waals gas depends on its temperature and is independent of nature of the gas

88. Negative deviation from ideal behaviour is due to the fact that
(a) there exist molecular interactions and $pV/nRT > 1$
(b) there exist molecular interactions and $pV/nRT < 1$
(c) atoms have finite size and $pV/nRT > 1$
(d) atoms have finite size and $pV/nRT < 1$ (2003)

89. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is
(a) nb (b) n^2a/V^2 (c) $-n^2a/V^2$ (d) $-nb$ (2009)

90. Positive deviation from ideal behaviour is due to the fact that
(a) molecular attractions play dominant role
(b) molecular volume plays dominant role
(c) both molecular attractions and volume play dominant role
(d) molecular attractions cancel the effect of molecular volume

Additional Problems

91. A gas undergoing expansion through a porous plug exhibits heating if its temperature is
(a) more than inversion temperature (b) less than inversion temperature
(c) more than critical temperature (d) more than Boyle temperature

92. A gas undergoing expansion through a porous plug exhibits cooling if its temperature is
(a) more than inversion temperature (b) less than inversion temperature
(c) less than critical temperature (d) less than Boyle temperature

93. A gas undergoing expansion through a porous plug exhibits neither heating nor cooling if its temperature is equal to
(a) Boyle temperature (b) critical temperature
(c) inversion temperature (d) consolute temperature

94. For a monatomic gas,
(a) molar heat capacity at constant volume, $C_{V,\text{m}} = \frac{3}{2}R$
(b) molar heat capacity at constant pressure $C_{p,\text{m}} = \frac{3}{2}R$
(c) the ratio of $C_{p,\text{m}}$ and $C_{V,\text{m}}$ is 3/5
(d) the difference between $C_{p,\text{m}}$ and $C_{V,\text{m}}$ is $2R$

95. The critical temperature of water is higher than that of O_2 because the H_2O molecule has
(a) few electrons than O_2 (b) two covalent bonds
(c) V-shape (d) dipole moment (1997)

96. For a diatomic gas at low temperatures
(a) molar heat capacity at constant volume, $C_{V,\mathrm{m}} < 3.5R$
(b) molar heat capacity at constant pressure, $C_{p,\mathrm{m}} = 4.5R$
(c) the ratio of $C_{p,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ is 7/9
(d) the difference between $C_{p,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ is $2R$

97. The mean for path of a gas is given by $\lambda = 1/(\sqrt{2}\pi\,\sigma^2 N^*)$ where σ is the molecular diameter and N^* is the number of molecules per unit volume. It implies that
(a) $\lambda \propto p/T$ (b) $\lambda \propto (p/T)^2$
(c) $\lambda \propto T/p$ (d) λ is independent of T and p

98. Let f_1 and f_2 be the fractions of molecules in the range c and $c + \mathrm{d}c$ for SO_2 at $2T$ and O_2 at T, respectively. Which of the following expressions is correct?
(a) $f_1 > f_2$ (b) $f_1 < f_2$
(c) $f_1 = f_2$ (d) f_1 and f_2 cannot be correlated

99. The critical volume is related to van der Waals constant b by the expression
(a) $V_c = b$ (b) $V_c = 2b$ (c) $V_c = 3b$ (d) $V_c = 4b$

100. Which of the following expressions between critical constants and van der Waals constants is not correct?
(a) $T_c = 8a/(27Rb)$ (b) $p_c = a(3b^2)$ (c) $p_cV_c = (3/8)\,RT_c$ (d) $V_c = 3b$

101. The total number of bimolecular collisions Z_{11} per unit volume per unit time is given by $Z_{11} = \left(1/\sqrt{2}\right)\pi\,\sigma^2\,\bar{u}\,N^{*2}$ where σ is molecular diameter, $\bar{u}$ is the average speed and N^* is the number of molecules per unit volume. Which of the following facts is correct?
(a) $Z_{11} \propto p/T$ (b) $Z_{11} \propto p^2/T^{3/2}$ (c) $Z_{11} \propto T^{3/2}/p^2$ (d) $Z_{11} \propto p^2\,T^{3/2}$

102. Which of the following facts regarding the viscosity of a gas is correct?
(a) Viscosity of a gas decreases with increasing temperature
(b) Viscosity of a gas is independent of pressure
(c) Viscosity of a gas is due to the intermolecular interactions
(d) Viscosity of a gas is independent of molecular mass

103. For a van der Waals gas, the inversion temperature is given by the expression
(a) $T_i = 2aR / \mathrm{b}$ (b) $T_i = a / 2Rb$ (c) $T_i = ab / 2R$ (d) $T_i = 2a / Rb$

104. Heat capacity of a diatomic gas in the low temperature range
(a) is independent of its temperature
(b) decreases with increase in temperature
(c) increases with increase in temperature
(d) increases followed by a decrease with increase in temperature.

105. The fraction of molecules having speed in the range c and $c + \mathrm{d}c$ follows the pattern
(a) decreases with increase in the value of c at constant temperature
(b) increases with increase in the value of c at constant temperature
(c) increases with increase in the value of c at low speed range while it decreases at high speed range at constant temperature
(d) decreases with increases in the value of c at low speeds while it increases at high speed range at constant temperature.

106. The critical temperature of a gas is related to its Boyle temperature by the expression
(a) $T_c = (8 / 27)\,T_B$ (b) $T_c = (27 / 8)\,T_B$ (c) $T_c = (3 / 8)\,T_B$ (d) $T_c = (8 / 3)\,T_B$

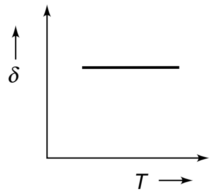
107. The Boyle temperature of a van der Waals gas is given by
(a) $T_B = a/b$ (b) $T_B = a/Rb$ (c) $T_B = Ra/b$ (d) $T_B = Rb/a$

108. At Boyle temperature, the second virial coefficient has a value of
(a) zero (b) positive
(c) negative (d) positive dependent on pressure

109. Which of the following gases is exhibited to have minimum value of van der Constant *a*?
(a) H_2 (b) He (c) N_2 (d) O_2

110. Which of the following gases is expected to have maximum value of critical temperature ?
(a) H_2 (b) He (c) O_2 (d) CO_2

111. An ideal gas is initially at temperature *T* and volume *V*. Its volume is increased due to an increase in temperature ΔT, pressure remaining constant. The quantity $\delta = \Delta V/(V\,\Delta T)$ varies with temperature as

(a)


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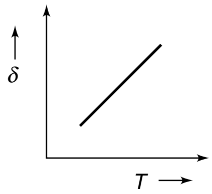

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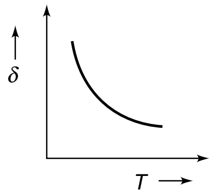
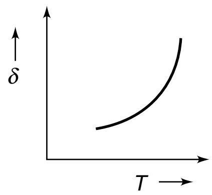


(d)


112. Which of the following statements regarding mean free path of gaseous molecules is correct ?
(a) Directly proportional to the number of molecules per unit volume
(b) Directly proportional to the average speed of molecules
(c) Inversely proportional to the square of molecular diameter
(d) Inversely proportional to the temperature of the gas

Multiple Correct Choice Type

1. Equations of state of an ideal gas is/are
(a) $pV = (1/3)mN$ (b) $pV = nRT$ (c) $p = \rho RT/M$ (d) $p = 3Nk/2V$.

2. The value(s) of universal gas constant is/are
(a) $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ (b) $R = 8.314\ \text{kPa cm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$
(c) $R = 8.314\ \text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ (d) $R = 0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$

3. For a fixed mass of a gas at constant pressure, which of the following statements is/are not correct?
(a) Plot of volume versus Celsius temperature is linear with intercept zero.
(b) Plot of volume versus kelvin temperature is linear with a non-zero intercept.
(c) Plot of *V/T* versus *T* is linear with a positive slope.
(d) Plot of *V/T* versus *T* is linear with a zero slope.

4. Which of the following facts regarding mean free path of gaseous molecules is/are correct?
(a) Mean free path is derectly proportional to kelvin temperature provided pressure of the gas is held constant.
(b) Mean free path is derectly proportional to pressure provided temperature of the gas is held constant.
(c) Mean free path is inversely proportional to the molecular diameter.
(d) Mean free path is inversely proportional to the number of molecules per unit volume of the gas.

5. Which of the following facts regarding an ideal gas is/are correct?
(a) The mean square speed of gaseous molecules is directly proportional to the square root of kelvin temperature.
(b) The mean square speed is inversely proportional to the molecular mass.
(c) The viscosity of a gas increases with increase in temperature.
(d) The viscosity of a gas independent of its density.

6. Two flasks A and B have equal volumes. Flask A contains hydrogen at 300 K while B contains equal mass of methane at 600 K. Which of the following facts is/are correct if the gases follow ideal behaviour ?
(a) Flask A contains greater number of molecules.
(b) The average speed of molecules in flask B is twice that of molecules in flask A.
(c) Both the gases have the same compression factor
(d) Total kinetic energy of molecules in flask A is greater than that of molecules in flask B.

7. Which of the following statements regarding an ideal gas is/are correct?
(a) The product of pressure and volume of a fixed amount of a gas is independent of temperature.
(b) The increase in the compression factor of a gas with increase of pressure is due to the van der Waals constant *b*.

(c) A gas can be liquefied provided its temperature is less than its critical temperature and pressure is more than its critical pressure.
(d) Average speed of molecules of a gas in a container moving only in one dimension is zero.

8. Which of the following statements is/are correct?
(a) The compression factor less than one is due to the van der Waals constant a of a real gas.
(b) The compression factor more than one is due to the excluded volume of the gas.
(c) The excluded volume, which is represented by the van der Waals constant b, is equal to the volume occupied by the molecules of 1 mol of a gas.
(d) At Boyle temperature, the effects caused by the van der Waals constants a and b compensate each other causing the gas to behave ideally over a wide range of pressure.

9. Which of the following statements is/are correct?
(a) The average kinetic energy of oxygen molecules is smaller than that of nitrogen molecules at 298 K.
(b) The average speed of oxygen molecules is smaller than that of nitrogen molecules.
(c) The unit of Boltzman constant is $\mathrm{J\ K^{-1}\ molecule^{-1}}$.
(d) The negative deviation of a real gas from ideal behaviour is due to the molecular attractions.

10. Which of the following statements is/are correct ?
(a) The value of $C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$ (where C stands for heat capacity) of gaseous molecules decreases with increase in the number of atoms in the gaseous molecule.
(b) The molar heat capacity of diatomic molecules at low temperature is about $3.5R$.
(c) The molar average energy of helium gas is $1.5RT$.
(d) The average vibrational energy of a diatomic molecule is $(1/2)kT$.

11. Which of the following facts stated along with the given characteristics of two identical gases is/are correct?
(a) Equal p, V, T ; $m_1 > m_2$ $\Rightarrow \overline{\mathrm{KE}}_1 = \overline{\mathrm{KE}}_2$
(b) Equal p, V, T ; $m_1 > m_2$ $\Rightarrow n_1 > n_2$
(c) Equal p, V, T ; $n_1 > n_2$ $\Rightarrow T_1 < T_2$
(d) Equal V, N, T ; $m_1 > m_2$ $\Rightarrow p_1 > p_2$

12. Which of the following statements are correct?
(a) The unit of K in the expression $V = KT$ is $\mathrm{m^3\ K^{-1}}$.
(b) A gas is heated at constant pressure from 25 °C to 50 °C, it expands to twice its initial volume.
(c) The volume occupied by 32 g of oxygen is greater than that occupied by 16 g of methane, both being at the same T and p.
(d) All real gases can be liquefied and solidified.

13. Which of the following statements are correct?
(a) A real gas can be liquefied if its temperature is greater than its critical temperature.
(b) A real gas is expected to behave ideally at high temperature and low pressure.
(c) The increase in volume per degree rise in Celsius temperature at constant pressure is $V_0/273.15$, where V_0 is the volume of gas at 0 K.
(d) The rate of diffusion is directly proportional to the square root of its kelvin temperature and also inversely proportional to the square root of its molar mass.

14. Which of the following statements are correct?
(a) The molar mass of a gas may be calculated through the expression $M = (\rho/p)RT$.
(b) The value of ρ/p of an ideal gas at a constant temperature is independent of the pressure of the gas.
(c) The Avogadro constant has a value of $6.626 \times 10^{26}\ \mathrm{mol^{-1}}$.
(d) The volume of a fixed mass of gas at constant pressure varies nonlinearly with temperature expressed in Celsius whereas it varies linearly when expressed in kelvin.

15. Which of the following statements are correct?
(a) Equal masses of all gases occupy the same volume at STP.
(b) An ideal gas cannot be liquefied.
(c) Kinetic energy of gaseous molecules is zero at 0 °C.
(d) Gases having very low critical temperatures often show near ideal behaviour at room temperature.

16. Which of the following statements are **not** correct?
(a) The expression of kinetic gas equation is $pV = \frac{1}{3}\ mN\overline{u^2}$.
(b) The symbols $\overline{u^2}$ and $\bar{u}^2$ represent one and the same physical quantity.
(c) The density of an ideal gas increases with increase in temperature provided its pressure is constant.
(d) The average kinetic energy of gaseous molecules depends only on temperature and nature of gaseous molecules.

17. Which of the following statements are **not** correct?
(a) At low pressure the molecules of an ideal gas move with slower speed as compared to the gas at high pressure.
(b) The value of gas constant R is 8.314 J K^{-1}.
(c) The value of Boltzmann constant k is 1.38×10^{-23} J K^{-1} molecule^{-1}.
(d) The van der Waals constant a is a measure of forces of attraction between gaseous molecules of a gas.

18. Which of the following statements are correct?
(a) The van der Waals constant b is four times the volume occupied by molecules in one mole of a gas.
(b) A gas having comparatively higher value of van der Waals constant a can be liquefied more easily.
(c) The term $V_m - b$ in van der Waals equation represents the available volume where molecules of the gas can move.
(d) The compression factor of an ideal gas is independent of temperature and pressure of the gas.

19. Which of the following statements are correct?
(a) The compression factor of a real gas is equal to one over a wide range of pressure provided the gas is at Boyle temperature.
(b) The mean square speed of a gas is defined as $\left(\frac{u_1 + u_2 + u_3 + \cdots + u_N}{N}\right)^2$
(c) The most probable speed of gaseous molecules is the speed possessed by the maximum fraction of the molecules of a gas.
(d) The average speed of a gas varies linearly with increase of temperature.

20. Which of the following statements are **not** correct?
(a) The kinetic energy of 1 mol of a gas is equal to (3/2)RT.
(b) All gases irrespective of their nature have $C_p/C_V = 5/3$.
(c) A real gas obeys $pV = (1/3)\ mN\overline{u^2}$ under all conditions of temperature and pressure.
(d) The ratio of u_{av} and u_{mp} is $\sqrt{56/22} : \sqrt{3}$.

21. Which of the following statements are **not** correct ?
(a) The ratio of u_{av} and u_{mp} is 2 : 3.
(b) The unit of van der Waals constant a is L^2 atm mol^{-1}.
(c) The mean square speed of a gas varies linearly with kelvin temperature.
(d) The increasing order of average, most probable and root mean square speeds is $u_{rms} < u_{av} < u_{mp}$.

22. Which of the following statements are **not** correct?
(a) The product pV has the dimensions of energy.
(b) In the van der Waals equation $\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$, the constant a reflects the actual volume of the gas molecules. (1993)
(c) A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution.
(d) The heat capacity of a monatomic gas is independent of temperature.

23. If a gas is expanded at constant temperature
(a) the pressure decreases
(b) the kinetic energy of the molecules remains the same
(c) the kinetic energy of the molecules decreases
(d) the number of molecules of the gas increases

24. Which of the following statements are **not** correct?

(a) The rate of diffusion of a gas is inversely proportional to the square of density or molar mass.

(b) The value of pV for 5.6 L of an ideal gas is 0.25 RT at STP.

(c) Eight grams each of oxygen and hydrogen at 27 °C will have the total kinetic energy in the ratio of 1 : 8.

(d) The proportionality constant K in $V = KT$ is given as $V_0/273.15$ K where V_0 is the volume of the gas at 0 K.

25. Which of the following statements are **not** correct?

(a) In SI units, the value of gas constant R is 8.314 J K^{-1} mol^{-1}.

(b) In SI units, the value of Boltzmann constant k is 1.38×10^{-23} J K^{-1} mol^{-1}.

(c) The aqueous tension of water at a given temperature is the vapour pressure of water at the given temperature.

(d) The volume occupied by 22 g of carbon dioxide at STP would be 22.414 L.

26. Which of the following statements are **not** correct ?

(a) The abbreviation STP stands for standard temperature and pressure where temperature is 25 °C and pressure is 1 atm.

(b) Two grams of hydrogen contains as many molecules as in 44 g of carbon dioxide.

(c) For an ideal gas at constant temperature, the ratio ρ/p is dependent on pressure.

(d) For an ideal gas at constant volume, the plot of p/T versus T is linear with slope having a nonzero.

27. Which of the following statements are **not** correct?

(a) For an ideal gas at constant temperature, the plot of pV versus p is linear with slope having a zero value.

(b) The density of an ideal gas increases with increase in temperature of the gas, provided the pressure remains constant.

(c) According to the kinetic theory of gases, the average kinetic energy of gaseous molecules is directly proportional to kelvin temperature.

(d) For a given gas, the expression of mean square speed of its molecules in terms of pressure and density is $2p/\rho$.

28. Which of the following statements are correct?

(a) The average kinetic energy of a gas is independent of the molar mass of the gas.

(b) For a given gas at a constant temperature, the root means square speed of its molecules is greater than their average speed.

(c) For a given gas at a constant temperature, the root mean square speed of its molecules is greater than their most probable speed.

(d) For a given gas at a constant temperature, the average speed of its molecules is greater than their most probable speed.

29. Which of the following statements are correct?

(a) The temperature at which a real gas exhibits ideal behaviour over a wide range of pressure is known as Boyle temperature.

(b) The temperature above which a gas cannot be liquefied is known as critical temperature.

(c) The temperature at which a real gas exhibits neither cooling nor heating when passed through a porous plug is known as inversion temperature.

(d) A real gas is expected to behave ideally at low temperature and high pressure.

30. Which of the following statements are not correct?

(a) A real gas is expected to deviate from ideal behaviour at high temperature and low pressure.

(b) The unit of van der Waals constant a in SI units is Pa m^3 mol^{-1}.

(c) The unit of van der Waals constant b in SI units is m^3 mol^{-1}.

(d) The van der Waals constant b is two times the actual volume occupied by molecules of 1 mol of a gas.

31. Which of the following statements are correct?

(a) For a real gas, the compression factor Z is defined as $V_{\text{real}}/V_{\text{ideal}}$.

(b) At low pressure, the variation of compression factor with pressure can be explained from van der Waals equation when the term b is ignored in comparison to the term.V_m.

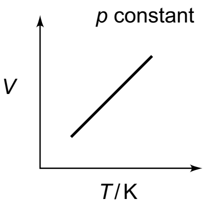
(c) At high pressure, the variation of compression factor with pressure can be explained from the van der Waals equation when the term *a* is ignored in comparison to the term V_m.
(d) The value 6.022×10^{23} mol^{-1} is assigned to Avogadro constant.

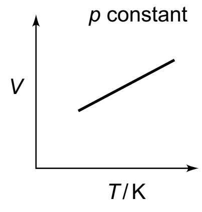
32. Which of the following statements are **not** correct?
(a) The value of $C_p - C_V$ for one mole of an ideal gas is equal to *R*.
(b) The value of C_p/C_V for one mole of an ideal (monatomic) gas is equal to 7/5.
(c) The value of $C_{V,m}$ for a monatomic gases is (3/2)*R*.
(d) The value of γ(= ratio of heat capacities) of gases increases with increases in the atomicity of gaseous molecule.

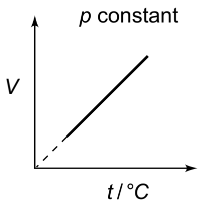
33. Which of the following statements are **not** correct?
(a) The rate of diffusion of helium is about twice that of methane gas.
(b) 0.5 L of a certain gas at STP weighs 0.58 g. Its molar mass is 44 g mol^{-1}.
(c) The root mean square speed of nitrogen gas at 3 atm will be same as that at 1 atm.
(d) The root mean square speed of methane gas will be twice that of helium gas both having the same temperature and pressure.

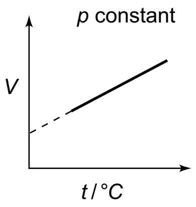
34. Which of the following statements are correct?
(a) The average kinetic energy of a gas at temperature *T* is given as (3/2) *kT*.
(b) The molar kinetic energy of a gas at a temperature *T* is given as (3/2) *RT*.
(c) Of the gases, H_2 and N_2, the larger value of van der Waals constant *a* would be of H_2 gas.
(d) Of the gases, H_2 and N_2, the larger value of van der Waals constant *b* would be of N_2 gas.

35. Which of the following graphs represent the behaviour of an ideal gas?

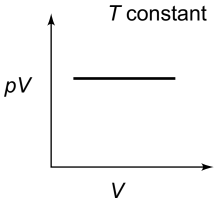
(a) 

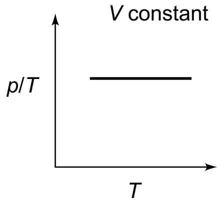
(b) 

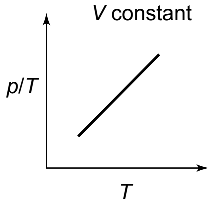
(c) 

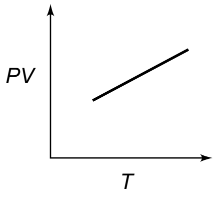
(d) 

36. Which of the following graphs represent the behaviour of an ideal gas?

(a) 

(b) 

(c) 

(d) 

37. Let u_{av}, u_{rms} and u_{mp} respectively denote the average speed, root mean square average speed and most probable speed in an ideal monatomic gas at kelvin temperature *T*. The mass of an atom is *m*. Then
(a) no atom can have a speed greater that $\sqrt{2}\ u_{rms}$.
(b) no atom can have a speed less than $u_{mp}/\sqrt{2}$.
(c) $u_{mp} < u_{av} < u_{rms}$
(d) the average kinetic energy of an atom is (3/4) mu^2_{mp}.

Linked Comprehension Type

1. The behaviour of a real gas is usually depicted by plotting compression factor Z (= pV_m/RT) versus *p* at a constant temperature. These plots are explained on the basis of van der Waals equation $(p + a/V^2_m)(V_m - b) = RT$.

(i) The value of $Z < 1$ is observed provided
(a) *p* is low and $T > T_B$ (Boyle temperature) (b) *p* is low and $T < T_B$
(c) *p* is low and $T = T_B$ (d) *p* is high and $T < T_B$

(ii) The value of $Z > 1$ is observed provided
  (a) p is low and $T < T_c$ (critical temperature) (b) p is low and $T < T_B$
  (c) p is low and $T = T_B$ (d) p is high and $T < T_B$

(iii) The value of $Z = 1$ is observed provided
  (a) p is low and $T > T_B$ (b) p is low and $T < T_B$
  (c) p is low and $T = T_B$ (d) p is high and $T < T_B$

2. The behaviour of a real gas is usually depicted by plotting compression factor Z $(= pV_m/RT)$ versus p at a constant temperature. These plots are explainable on the basis of van der Waals equation of state $(p + a/V^2_m)(V_m - b) = RT$.

(i) The value of $Z > 1$ is explained on
  (a) ignoring the constant a (b) ignoring the constant b
  (c) ignoring both the constants a and b (d) retaining both the constants a and b

(ii) The value of $Z < 1$ is explained on
  (a) ignoring the constant a (b) ignoring the constant b
  (c) ignoring both the constants a and b (d) retaining both the constants a and b

(iii) The value of $Z = 1$ over wide range of low pressure at Boyle temperature is explained on the basis of
  (a) ignoring the constant a (b) ignoring the constant b
  (c) ignoring both the constants a and b (d) retaining both the constants a and b

3. The molar heat capacity of a gas may be computed from the average energy of molecules obtained on the basis of law of equipartion of energy.

(i) Which of the following statements for a monatomic gases is not correct?
  (a) Molar heat capacity at constant volume, $C_{V,m}$, is $(3/2)R$
  (b) Molar heat capacity at constant pressure, $C_{p,m}$, is $(5/2)R$
  (c) The ratio of $C_{p,m}/C_{V,m}$ is $(5/3)$
  (d) The ratio of $C_{p,m}/C_{V,m}$ varies with temperature

(ii) Which of the following statements for a diatomic gases is not correct ?
  (a) $C_{V,m} = (5/2)R$ and $C_{p,m} = (7/2)R$ at low temperatures
  (b) $C_{V,m} = (7/2)R$ and $C_{p,m} = (9/2)R$ at high temperatures
  (c) The value of $C_{V,m}$ varies linearly with temperature for smaller change in temperature
  (d) The value of $C_{V,m}$ varies nonlinearly with temperature for smaller change in temperature

(iii) Which of the following facts is correct for a triatomic gas?
  (a) $C_{V,m}$ is $(13/2)R$ for linear molecules and is $6R$ for non-linear molecules
  (b) $C_{V,m}$ is $6R$ for linear molecules and is $(13/2)$ for non-linear molecules
  (c) The ratio $C_{p,m}/C_{V,m}$ has the same value for linear and non-linear molecules
  (d) The ratio $C_{p,m}/C_{V,m}$ does not vary with temperature

4. The behaviour of a real gas may be represented by Berthelot's equation

$$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

Based on this equation, answer the following three questions.

(i) The unit of constant a is
  (a) Pa m^6 mol^{-2} (b) Pa m^3 mol^{-1} (c) Pa m^6 K mol^{-2} (d) atm L^2 mol^{-2}

(ii) If the Berthelot's equation is transformed into the virial equation in V_m, the second virial coefficient will be given by the expression
  (a) $B = b - \dfrac{a}{RT}$ (b) $B = b - \dfrac{a}{RT^2}$ (c) $B = a - \dfrac{b}{RT}$ (d) $B = a - \dfrac{b}{RT^2}$

(iii) The Boyle temperature for the Berthelot's equation is given by the expression
  (a) $T_B = a/Rb$ (b) $T_B = a/\sqrt{Rb}$ (c) $T_B = \sqrt{a/Rb}$ (d) $T_B = b/Ra$

5. The fraction of gaseous molecules having speed in between u and u + du as governed by Maxwell distribution of speeds is given by

$$\frac{\mathrm{d}N_u}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\exp(-Mu^2/2RT)\,u^2\,\mathrm{d}u$$

Graphically this distribution is shown in Fig. 2.1.

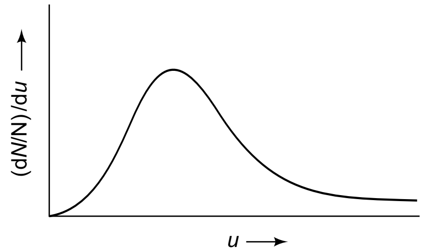


Fig. 2.1

Based on this distribution, answer the following three questions.

(i) With increase in temperature, the quantity (dN/N)/du in the low speed range

(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

(ii) With increase in temperature, the quantity (dN/N)/du in the high speed range

(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

(iii) The maximum value of (dN/N)/du corresponds to most probable speed. With increase in temperature, this maximum fraction

(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

6. At critical temperature and pressure, the van der Waals equation may be written as

$$V_\mathrm{m}^3 - \left(b + \frac{RT_\mathrm{c}}{p_\mathrm{c}}\right)V_\mathrm{m}^2 + \frac{a}{p_\mathrm{c}}V_\mathrm{m} - \frac{ab}{p_\mathrm{c}} = 0$$

At these conditions, the above expression yields three identical and real roots. Thus, the above expression is equivalent to $(V_\mathrm{m} - V_\mathrm{c})^3 = 0$

Based on the identity of the above expressions, answer the following three questions.

(i) The expression of b in terms of V_c is

(a) $b = V_\mathrm{c}/2$ (b) $b = V_\mathrm{c}/3$ (c) $b = V_\mathrm{c}/4$ (d) $b = V_\mathrm{c}/6$

(ii) The expression of a in terms of p_c and T_c is

(a) $a = 27(RT_\mathrm{c})^2/64p_\mathrm{c}$ (b) $a = 27RT_\mathrm{c}/16p_\mathrm{c}$ (c) $a = 64(RT_\mathrm{c})^2/p_\mathrm{c}$ (d) $a = 27p_\mathrm{c}/(RT_\mathrm{c})^2$

(iii) The value of $p_\mathrm{c}V_\mathrm{c}/RT_\mathrm{c}$ is

(a) 1/2 (b) 3/4 (c) 3/8 (d) 3/16

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement –1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explanation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	Statement–2
1.	The value of van der Waals constant a is larger for ammonia than for hydrogen.	Hydrogen bonding is present in ammonia. (1994)
2.	The pressure of a fixed amount of an ideal gas is proportional to the square root of temperature.	Frequency of collision and their impact both increase in proportional to its temperature. (2000)

3.	Heat capacity of a diatomic gas varies with temperature and attains a constant value at high temperature.	The vibrational contribution to heat capacity varies with temperature.
4.	The compression factor of helium is always greater than one irrespective of its temperature.	The critical temperature of helium is very small.
5.	The fraction of molecules having speed in the range c and $c + \mathrm{d}c$ depends on the value of M/T of the gas.	The speed of molecules of a gas depends on the value of M/T of the gas.
6.	The average kinetic energy of gaseous molecules at a fixed temperature is independent of the mass of molecules of the gas.	The mean square speed of gaseous molecules depends inversely on the mass of molecule of a gas.
7.	A real gas behaves ideally over a wide range of pressure at its Boyle temperature.	At Boyle temperature, second virial coefficient of the gas a zero value.
8.	The value of $(pV_\mathrm{m})_{p\to 0}$ of a real gas is independent of its nature.	As $p \to 0$, a real gas behaves as if there exists no molecular attractions and the volume occupied by gaseous molecules is negligible in comparison to its volume.
9.	Pressure of a gas at constant volume increases with increase in temperature.	The speeds of molecules increase causing larger number of collisions with the sides of the vessel.

Matrix Match Type

1. Column II gives the values of van der Waals constant a of a few gases which are shown in Column I. Identify the gas with the corresponding a value.

Column I	**Column II**
(a) H_2	(p) 137.8 kPa $\mathrm{dm}^6\ \mathrm{mol}^{-2}$
(b) He	(q) 21.8 kPa $\mathrm{dm}^6\ \mathrm{mol}^{-2}$
(c) O_2	(r) 364.0 kPa $\mathrm{dm}^6\ \mathrm{mol}^{-2}$
(d) CO_2	(s) 1304 kPa $\mathrm{dm}^6\ \mathrm{mol}^{-2}$
	(t) 3.5 kPa $\mathrm{dm}^6\ \mathrm{mol}^{-2}$

2. Column II gives the values of critical temperatures of a few gases which are shown in Column I. Identify the gas with the corresponding T_e value

Column I	**Column II**
(a) H_2	(p) 33.3 K
(b) He	(q) 304 K
(c) O_2	(r) 5.3 K
(d) CO_2	(s) 154 K
	(t) 647 K

3. Column II gives the values of $\gamma\,(= C_{p,\,\mathrm{m}}/C_{V,\,\mathrm{m}})$ at high temperature of gases which are shown in **Column I**. Identify the gas with the corresponding γ value.

Column I	**Column II**
(a) Monatomic	(p) 1.154
(b) Diatomic	(q) 1.286
(c) Linear Triatomic	(r) 1.167
(d) Nonlinear Triatomic	(s) 1.407
	(t) 1.667

4. For a van der Waals gas, match the entries mentioned in Column I with the correct choice given in Column II.

Column I	**Column II**
(a) Critical temperature	(p) $2a/Rb$
(b) Inversion temperature	(q) a/Rb
(c) Boyle temperature	(r) T/T_c
(d) Reduced temperature	(s) $8a/(27Rb)$

ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (d)	**6.** (d)	**7.** (d)
8. (b)	**9.** (d)	**10.** (c)	**11.** (b)	**12.** (b)	**13.** (c)	**14.** (b)
15. (a)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (b)	**20.** (c)	**21.** (c)
22. (c)	**23.** (c)	**24.** (d)	**25.** (b)	**26.** (a)	**27.** (d)	**28.** (b)
29. (c)	**30.** (a)	**31.** (d)	**32.** (d)	**33.** (b)	**34.** (d)	**35.** (a)
36. (d)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (a)	**41.** (a)	**42.** (a)
43. (b)	**44.** (a)	**45.** (a)	**46.** (a)	**47.** (c)	**48.** (b)	**49.** (a)
50. (c)	**51.** (b)	**52.** (c)	**53.** (c)	**54.** (c)	**55.** (a)	**56.** (d)
57. (b)	**58.** (b)	**59.** (c)	**60.** (d)	**61.** (c)	**62.** (d)	**63.** (d)
64. (d)	**65.** (b)	**66.** (b)	**67.** (c)	**68.** (d)	**69.** (d)	**70.** (b)
71. (d)	**72.** (d)	**73.** (c)	**74.** (a)	**75.** (b)	**76.** (a)	**77.** (d)
78. (c)	**79.** (b)	**80.** (d)	**81.** (b)	**82.** (b)	**83.** (a)	**84.** (d)
85. (c)	**86.** (a)	**87.** (a)	**88.** (b)	**89.** (b)	**90.** (b)	**91.** (a)
92. (b)	**93.** (c)	**94.** (a)	**95.** (d)	**96.** (a)	**97.** (c)	**98.** (c)
99. (c)	**100.** (b)	**101.** (b)	**102.** (b)	**103.** (d)	**104.** (c)	**105.** (c)
106. (a)	**107.** (b)	**108.** (a)	**109.** (b)	**110.** (d)	**111.** (c)	**112.** (c)

Multiple Correct Choice Type

1. (a), (b), (c)	**2.** (a), (c), (d)	**3.** (a), (b), (c)	**4.** (a), (d)
5. (b), (c), (d)	**6.** (a), (c), (d)	**7.** (b), (c), (d)	**8.** (a), (b), (d)
9. (b), (d)	**10.** (a), (c)	**11.** (a), (c)	**12.** (a), (d)
13. (b), (d)	**14.** (a), (b)	**15**. (b), (d)	**16.** (a), (b), (c)
17. (a), (b), (c)	**18.** (a), (b), (c), (d)	**19.** (a), (c)	**20.** (b), (c), (d)
21. (a), (b), (d)	**22.** (b), (c)	**23.** (a), (b)	**24.** (a), (c), (d)
25. (b), (d)	**26.** (a), (c), (d)	**27.** (b), (d)	**28.** (a), (b)
29. (a), (b), (c)	**30.** (a), (b), (d)	**31.** (a), (b), (d)	**32.** (b), (d)
33. (b), (d)	**34.** (a), (b), (d)	**35.** (a), (d)	**36.** (a), (b)
37. (c), (d)			

Linked Comprehension Type

1. **(i)** (b)	**(ii)** (d)	**(iii)** (c)
2. **(i)** (a)	**(ii)** (b)	**(iii)** (d)
3. **(i)** (d)	**(ii)** (c)	**(iii)** (a)
4. **(i)** (c)	**(ii)** (b)	**(iii)** (c)
5. **(i)** (b)	**(ii)** (a)	**(iii)** (b)
6. **(i)** (b)	**(ii)** (a)	**(iii)** (c)

Assertion and Reason Type

1. (c)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (a)
8. (a)	**9.** (b)					

Matrix Match Type

1. (a) – (q); (b) – (t); (c) – (p); (d) – (r)

2. (a) – (p); (b) – (r); (c) – (s); (d) – (q)

3. (a) – (t); (b) – (q); (c) – (p); (d) – (r)

4. (a) – (s); (b) – (p); (c) – (q); (d) – (r)

Hints and Solutions

Straight Objective Type

1. $n(\mathrm{CH_4}) = m/(16\ \mathrm{g\ mol^{-1}})$; $n(\mathrm{O_2}) = m/(32\ \mathrm{g\ mol^{-1}})$

$$\frac{p_{\mathrm{O_2}}}{P} = \frac{(m/32\ \mathrm{g\ mol^{-1}})}{(m/16\ \mathrm{g\ mol^{-1}}) + (m/32\ \mathrm{g\ mol^{-1}})} = \frac{(1/32)}{(1/16)+(1/32)} = \frac{16}{32+16} = \frac{1}{3}$$

2. $n(\mathrm{C_2H_6}) = m/(30\ \mathrm{g\ mol^{-1}})$; $n(\mathrm{H_2}) = m/(2\ \mathrm{g\ mol^{-1}})$

$$\frac{p(\mathrm{H_2})}{p(\mathrm{H_2})+p(\mathrm{C_2H_6})} = \frac{n(\mathrm{H_2})}{n(\mathrm{H_2})+n(\mathrm{C_2H_6})} = \frac{m/2}{(m/2)+(m/30)} = \left(\frac{1}{2}\right)\left(\frac{60}{32}\right) = \frac{30}{32} = \frac{15}{16}$$

3. $pV = nRT = (m/M)\ RT \Rightarrow pM = \rho RT$. Hence, $\rho_2/\rho_1, = (p_2/T_2)/(p_1/T_1) = T_1p_2/T_2p_1$

4. For an ideal gas $pV = nRT = (m/M)RT \Rightarrow pM = \rho RT$, i.e. $\rho = pM/RT$.

Hence $\rho_{(A)} = (M/R)\ (1\ \mathrm{atm}/273\ \mathrm{K})$; $\rho_{(B)} = (M/R)\ (2\ \mathrm{atm}/273\ \mathrm{K})$; $\rho_{(C)} = (M/R)\ (1\ \mathrm{atm}/546\ \mathrm{K})$
$\rho_{(D)} = (M/R)\ (2\ \mathrm{atm}/546\ \mathrm{K})$

The density will be highest for the choice B.

5. The volume of a gas changes by $V_0/273.15$ for every 1 °C increase in temperature, where V_0 is the volume of the gas at 0 °C.

6. The value of V/T remains constant with change in temperature of a gas. Hence, the plot of V/T versus T is linear with zero slope.

7. The dimensionally correct expression is $t/°\mathrm{C} = T/\mathrm{K} + 273.15$

8. The value of R expressed in SI units is $8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

9. The value of Boltzmann constant is $k = \dfrac{R}{N_A} = \dfrac{8.134\ \mathrm{J\ K^{-1}\ mol^{-1}}}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}} = 1.36 \times 10^{-23}\ \mathrm{J\ K^{-1}}$

10. The value of Avogadro constant is $6.022 \times 10^{23}\ \mathrm{mol^{-1}}$.

11. $pV = nRT = (m/M)RT$ i.e $pM = \rho RT$ i.e. $\rho = pM/RT$.

Larger the value of p/T, larger the density of a gas. For choice B, p/T has the largest value.

12. The volume of a gas increases by $V_0/273.15$ with an increase of 1°C, where V_0 is the volume of gas at 0 °C.

13. We have $p = \rho RT/M$.

$$\frac{p(\mathrm{X})}{p(\mathrm{Y})} = \frac{\rho(\mathrm{X})}{\rho(\mathrm{Y})}\frac{M(\mathrm{Y})}{M(\mathrm{X})} = (3)\ (2) = 6$$

14. For an ideal gas, the compression factor is equal to one.

15. We have $\underset{n(1-\alpha)}{\mathrm{AB_2}} \rightleftharpoons \underset{n\alpha}{\mathrm{A}} + \underset{n\alpha}{\mathrm{B_2}}$; total amount of gases = $n(1 + \alpha)$

Since $pV = nRT$, we have $(1\ \mathrm{atm})\ V = n(1 + \alpha)\ RT = n(1.4)\ (0.082\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}})\ 400\ \mathrm{K}$

or $$\frac{n}{V} = \frac{1\ \mathrm{atm}}{(1.4)(0.082)\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}})(400\ \mathrm{K})} = 0.0218\ \mathrm{mol\ L^{-1}}$$

$$\rho = \frac{m}{V} = \frac{(nM)}{V} = \left(\frac{n}{V}\right)M = (0.0218\ \mathrm{mol\ L^{-1}})\ (200\ \mathrm{g\ mol^{-1}}) = 4.35\ \mathrm{g\ L^{-1}}$$

16. Since $pV = nRT = (m\ /\ M)RT$, we have $\rho = \left(\dfrac{m}{V}\right) = \dfrac{pM}{RT}$

This gives $$\frac{\rho_2}{\rho_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{T_1}{T_2}\right)$$

17. Since $\rho = pM/RT$, we get

$$M_{av} = \frac{\rho RT}{p} = \frac{(0.5\ \mathrm{g\ L^{-1}})(0.082\ \mathrm{L\ atm\ K^{-1}mol^{-1}})(300\ \mathrm{K})}{1\ \mathrm{atm}} = 12.3\ \mathrm{g\ mol^{-1}}$$

Since $M_{av} = x_1M_1 + x_2M_2 = M_1 + x_2(M_2 - M_1)$, we get

$$x_2 = \frac{M_{av} - M_1}{M_2 - M_1} = \frac{12.3 - 32}{4 - 32} = 0.70$$

$$m_1 = n_1M_1 = (0.30\ \mathrm{mol})\ (32\ \mathrm{g\ mol^{-1}}) = 9.6\ \mathrm{g}$$

$$m_2 = n_2M_2 = (0.70\ \mathrm{mol})\ (4\ \mathrm{g\ mol^{-1}}) = 2.8\ \mathrm{g}.$$

$$\text{Mass per cent of He} = \frac{m_2}{m_1 + m_2} \times 100 = \frac{2.8}{12.4} \times 100 = 22.6$$

18. We have $\rho_2 = \rho_1\left(\frac{p_2}{p_1}\right)\left(\frac{T_1}{T_2}\right) = (1.5\ \mathrm{g\ L^{-1}})\left(\frac{1000}{760}\right)\left(\frac{273}{760}\right) = 1.8\ \mathrm{g\ L^{-1}}$

19. We have $T_2 = \left(\frac{\rho_1}{\rho_2}\right)T_1 = \left(\frac{1.5}{0.5}\right)(273\ \mathrm{K}) = 819\ \mathrm{K} \equiv 546\ °\mathrm{C}$

20. Let x be the mole fraction of NH_3 in the original mixture.

Amount of gas to start with = 1 mol

Amount of gas at the end = $2x$ mol + $3(1 - x)$ mol = $(3 - x)$ mol

Since $pV = nRT$, we have $\frac{n_1T_1}{n_2T_2} = \frac{p_1}{p_2} \Rightarrow \left(\frac{1}{3-x}\right)\left(\frac{300}{1000}\right) = \frac{0.6}{4.8} = \frac{1}{8}$

Hence $x = 0.6$. Mole per cent of NH_3 = 60%

21. The value of compression factor (= pV_m/RT) is equal to one.

22. By definition, $\rho = m/V$. Hence,

$$\frac{\rho_1}{\rho_V} = \frac{V_V}{V_1} \quad \text{(for the same mass of the substance)}$$

or $$V_1 = \left(\frac{\rho_V}{\rho_1}\right)V_V = \left(\frac{0.0006}{1}\right)(10^3\ \mathrm{cm^3}) = 0.6\ \mathrm{cm^3}$$

23. $V_2 = \left(\frac{V_1}{T_1}\right)T_2 = \left(\frac{22.4\ \mathrm{L}}{273\ \mathrm{K}}\right)(373\ \mathrm{K}) = 30.6\ \mathrm{L}$

24. Rate of diffusion of a gas is inversely proportional to the square root of its molar mass.

25. Since $c_{rms} = \sqrt{3RT/M}$, larger the molar mass, lesser the speed and hence lesser the distance covered. Since $M(\mathrm{HCl}) < M(\mathrm{NH_3})$, the ammonium chloride ring will be formed near the hydrogen chloride end.

26. $\frac{r(\mathrm{CH_4})}{r(\mathrm{X})} = 2 = \sqrt{\frac{M(\mathrm{X})}{M(\mathrm{CH_4})}}$. Hence $M(\mathrm{X}) = 4\ M(\mathrm{CH_4}) = 4 \times 16\ \mathrm{g\ mol^{-1}} = 64\ \mathrm{g\ mol^{-1}}$.

27. We have $r_2 = \left(\frac{M_1}{M_2}\right)^{1/2} r_1 = \left(\frac{4}{64}\right)^{1/2} r_1 = \frac{r_1}{4}$

Since $r = n/t$, we get $r_2/r_1 = n_2/n_1$ i.e. $n_2 = (r_2/r_1)n_1$

$$n_2 = (1/4)(3\text{g}/4\text{g mol}^{-1}) = \frac{3}{16}\text{ mol}; \qquad m_2 = \left(\frac{3}{16}\text{ mol}\right)(64\text{ g mol}^{-1}) = 12\text{ g}.$$

28. $\dfrac{t_2}{t_1} = \left(\dfrac{M_2}{M_1}\right)^{1/2}$. For the choice a, $t_2/t_1 = \sqrt{2}$, for the choice b, $t_2/t_1 = 4$. For the choice c, $t_2/t_1 = \sqrt{14}$. For the choice d, $t_2/t_1 = \sqrt{22}$. Thus, the choice b is correct.

29. $\dfrac{r_A}{r_B} = \left(\dfrac{p_A}{p_B}\right)\left(\dfrac{M_B}{M_A}\right)^{1/2}$. The first term is measure of its concentration and the second term is due to Graham's law of diffusion.

30. We have $\underset{n(1-\alpha)}{A_2(g)} = \underset{2n\alpha}{2A(g)}$

Total amount of gases $= n(1 - \alpha) + 2n\alpha = n(1 + \alpha)$

Average molar mass of gases $= \dfrac{n(1-\alpha)}{n(1+\alpha)}M_{A_2} + \dfrac{2n\alpha}{n(1+\alpha)}M_A = \dfrac{M_{A_2}}{1+\alpha}$

According to Graham's law $\dfrac{r_{\text{mix}}}{r_X} = \left(\dfrac{M_X}{M_{\text{av}}}\right)^{1/2} = \left[\dfrac{M_X}{M_{A_2}/(1+\alpha)}\right]^{1/2}$

which gives $\alpha = \left(\dfrac{M_{A_2}}{M_X}\right)\left(\dfrac{r_{\text{mix}}}{r_X}\right)^2 - 1$

31. We have Partial pressure of He = 16 bar Partial pressure of CH_4 = 4 bar

$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{p_{He}}{p_{CH_4}}\right)\left(\frac{M_{CH_4}}{M_{He}}\right)^{1/2} = \left(\frac{16}{4}\right)\left(\frac{16}{4}\right)^{1/2} = 8$$

32. The relative molar masses of methane and helium are 16 and 4, respectively. Hence

$$\frac{r_{CH_4}}{r_{He}} = \sqrt{\frac{M_{He}}{M_{CH_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

33. The molecules of an ideal gas do not exert force of attraction on each other.

34. The mean kinetic energy of the molecules is proportional to the kelvin temperature.

35. The pressure of a gas increases with increase in temperature. This is due to increase in molecular speeds of gaseous molecules, as this results into increase in molecular collisions with sides of the vessel.

36. For an ideal gas, $pV = nRT = (m/M)\,RT$. Hence, $p = \rho RT/M$.

Also $pV = \dfrac{1}{3}\,mN\,\overline{u^2} = \dfrac{2}{3}N\left(\dfrac{1}{2}m\overline{u^2}\right) = \dfrac{2}{3}N(\overline{\text{KE}})$

37. Molecules in a gas move with all possible speeds.

38. We known that $(pV_m)_{p\to 0}$ = 22.414 L atm = (22.414) (1.01325 bar) L = 22.711 L bar

39. We have $pV = \dfrac{1}{3}\,mN\overline{u^2} = \dfrac{2}{3}N\left(\dfrac{1}{2}m\overline{u^2}\right) = \dfrac{2}{3}N\bar{E}$

40. $c_{\text{rms}} = \sqrt{3RT/M}$ and $c_{\text{av}} = \sqrt{8RT/\pi M}$. Hence

$$\frac{c_{\text{rms}}}{c_{\text{av}}} = \sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3\times 3.14}{8}} = \sqrt{\frac{9.42}{8}} = \sqrt{1.165} = 1.086$$

41. The expression of average speed is $c_{\mathrm{av}} = \sqrt{8RT/\pi M}$. For two temperatures, we have

$$\frac{c_2}{c_1} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{927+273}{27+273}} = \sqrt{\frac{1200}{300}} = 2 \quad \Rightarrow \quad c_2 = 2c_1 = 2\ (0.3\ \mathrm{m\ s^{-1}}) = 0.6\ \mathrm{m\ s^{-1}}$$

42. The root mean square speeds of gaseous molecule is given by $u_{\mathrm{rms}} = \sqrt{3RT/M}$.

43. The average speed of gaseous molecules is given by $u_{\mathrm{av}} = \sqrt{8RT/\pi M}$.

44. The most probable speed of gaseous molecules is given by $u_{\mathrm{mp}} = \sqrt{2RT/M}$.

45. $u_{\mathrm{rms}} : u_{\mathrm{av}} : u_{\mathrm{mp}} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2} :: 1.732 : 1.60 : 1.414$

46. See Q.45

47. Smaller the molar mass, larger the average speed.

48. $u_{\mathrm{mp}} = \sqrt{2RT/M} \quad \Rightarrow \quad \sqrt{2R/M} = u_{\mathrm{mp}}/\sqrt{T} = (0.3\ \mathrm{m\ s^{-1}})/(300\ \mathrm{K})^{1/2}$

$$u_{\mathrm{av}} = \sqrt{8RT/\pi M} = \left(\sqrt{2R/M}\right)\left(2\sqrt{T/\pi}\right) = [(0.3\ \mathrm{m\ s^{-1}})/(300\ \mathrm{K})^{1/2}]\ [2(1200\mathrm{K}/3.14)^{1/2}]$$

$$= (0.3\ \mathrm{m\ s^{-1}})\ \left(4/\sqrt{3.14}\right) = 0.68\ \mathrm{m\ s^{-1}}$$

49. The root mean square speed varies with change in temperature, but not with changes in pressure, volume and density of the gas.

50. The root mean square speed of gaseous molecules is given by $u_{\mathrm{rms}} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3pV_{\mathrm{m}}}{M}}$.

The choice c is correct. The root mean square speed varies as $\sqrt{p/\rho}$ and not on $\sqrt{p}$ and $\sqrt{1/\rho}$ as the ratio p/ρ remains constant at a given temperature.

51. Since $u_{\mathrm{rms}} = \sqrt{3RT/M}$, smaller the value of M, larger the root mean square speed. NH_3 has the least value of molar mass.

52. Since $u_{\mathrm{rms}} = \sqrt{3RT/M}$, we have

$$\frac{T(O_2)}{M(O_2)} = \frac{T(SO_2)}{M(SO_2)}; \qquad T(O_2) = \frac{T(SO_2)}{M(SO_2)}\ M(O_2) = \left(\frac{600\ \mathrm{K}}{64}\right)(32) = 300\ \mathrm{K} \equiv 27\ ^\circ\mathrm{C}$$

53. $$\frac{u_{\mathrm{rms}}(H_2)}{u_{\mathrm{rms}}(O_2)} = \left[\frac{T(H_2)}{M(H_2)}\,\frac{M(O_2)}{T(O_2)}\right]^{1/2} = \left[\left(\frac{50}{2}\right)\left(\frac{32}{800}\right)\right]^{1/2} = 1$$

54. $$\frac{u_{\mathrm{rms}}(H_2)}{u_{\mathrm{rms}}(N_2)} = \sqrt{7} \quad \Rightarrow \quad \left[\frac{T(H_2)}{M(H_2)}\,\frac{M(N_2)}{T(N_2)}\right]^{1/2} = \sqrt{7}. \quad \text{Hence,} \quad \frac{T(H_2)}{T(N_2)} = 7\,\frac{M(H_2)}{M(N_2)} = 7\left(\frac{2}{28}\right) = \frac{1}{2}$$

55. We have $u_{\mathrm{rms}} = \sqrt{3RT/M}$ and $u_{\mathrm{av}} = \sqrt{8RT/\pi M}$

Hence $u_{\mathrm{av}} = \sqrt{8/3\pi}\ u_{\mathrm{rms}} = \sqrt{8/(3\times 3.14)}\ (490\ \mathrm{m\ s^{-1}}) = 451.6\ \mathrm{m\ s^{-1}}$

56. We have $u_{\mathrm{av}} = \sqrt{8RT/\pi M}$ and $u_{\mathrm{mp}} = \sqrt{2RT/M}$

Hence $u_{\mathrm{mp}} = \sqrt{\pi/4}\ u_{\mathrm{av}} = (3.14/4)^{1/2}\ (475\ \mathrm{m\ s^{-1}}) = 420.9\ \mathrm{m\ s^{-1}}$

57. Since $u_{\mathrm{av}} = \sqrt{8RT/\pi M}$, we have $\dfrac{T}{(32)} = \dfrac{\{(327+273)\mathrm{K}\}}{(16)} \Rightarrow T = 600 \times 2\ \mathrm{K} = 1200\ \mathrm{K} \equiv 927\ ^\circ\mathrm{C}$

58. The average molar kinetic energy of a gas is given by $(3/2)RT$. It is independent of the molar mass of the gas.

59. The average kinetic energy of gaseous molecules is independent of the nature of the gas.

60. The total energy of gaseous molecules is given by $E = (3/2)nRT$. It varies with temperature only.

61. The average kinetic energy is given by $\overline{E} = (3/2)kT$,

62. The average kinetic energy of gaseous molecules depends only on temperature and not on the nature of the gas.

63. The expressions are $u_{\text{rms}} = \sqrt{3RT/M}$ and $E = 3RT/2$

Hence, $$u_{\text{rms}} = \left[\left(\frac{3RT}{2}\right)\left(\frac{2}{M}\right)\right]^{1/2} = \sqrt{\frac{2E}{M}}$$

64. The expression of root mean square speed is $u_{\text{rms}} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3pV_{\text{m}}}{M}} = \sqrt{\dfrac{3p}{M/V_{\text{m}}}} = \sqrt{\dfrac{3p}{\rho}}$

65. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is known as Boyle temperature.

66. The intermolecular forces between gaseous molecules is taken care by the van der Waals constant a.

67. Larger the value of van der Waals constant a, more easily the liquefaction of gas occurs.

68. For the amount n of a real gas, the van der Waals equation is expressed as $(p + n^2a/V^2)(V - nb) = nRT$.

69. The unit of n^2a/V^2 is the same as that of pressure. Hence, the unit of a is L^2 atm mol^{-2}.

70. The unit of nb is the same as that of volume. hence, the unit of b is cm^3 mol^{-1}.

71. The term that accounts for the molecular volume is $V - nb$.

72. The van der Waals constant b is four times the volume occupied by 1 mol of molecules.

73. Larger the value of van der Waals constant a, more easily the gas liquefiable.

74. If the temperature of a gas is more than its critical temperature, it cannot be liquefied.

75. The van der Waals equation of state is $\left(p + \dfrac{a}{V_{\text{m}}^2}\right)(V_{\text{m}} - b) = RT$

If we neglect b in comparison to V_{m}, we get

$$\left(p + \frac{a}{V_{\text{m}}^2}\right)(V_{\text{m}}) = RT \quad \text{or} \quad Z = \frac{pV_{\text{m}}}{RT} = 1 - \frac{a}{V_{\text{m}}RT}, \quad \text{that is,} \quad Z < 1.$$

76. The van der Waals equation of state is $\left(p + \dfrac{a}{V_{\text{m}}^2}\right)(V_{\text{m}} - b) = RT$

If we ignore a/V^2 in comparison to p, we get

$$p\,(V_{\text{m}} - b) = RT \quad \text{or} \quad Z = \frac{pV_{\text{m}}}{RT} = 1 + \frac{pb}{RT}, \quad \text{that is,} \quad Z > 1.$$

77. At Boyle temperature, $Z = 1$ over wide range of pressure. This is due to the fact that effects produced by constants a and b compensate each other.

78. High temperature and low pressure conditions favour a gas to behave ideally.

79. Low temperature and high pressure conditions make the gas to behave nonideally.

80. The most favourable conditions for a gas to liquefy is low temperature and high pressure.

81. The compression factor of a real gas is defined as $Z = V_{\text{m, real}}/V_{\text{m, ideal}}$. Hence, $V_{\text{m, real}} < V_{\text{m, ideal}}$.

82. The second virial coefficient is $B = b - a / RT$. Its unit is the same as that b, that is, m^3 mol^{-1}

83. $Z = 1$ over a wide range of pressure.

84. The van der Waals constant b is four times the molecular volume of one mole of a gas.

85. The value of $p_{\text{c}}V_{\text{c}} / RT_{\text{c}}$ is 3/8.

86. We have $p_{\text{ideal}} = p_{\text{real}} + a/V_{\text{m}}^2$

87. We have $V_{\text{ideal}} = V_{\text{real}} - b$

88. Negative deviation means $pV/nRT < 1$. This is possible when the term nb is negligible in comparison to the volume of the gas. In this situation, van der Waals equation is reduced to

$$\left(p + \frac{n^2a}{V^2}\right)(V) = nRT \quad \text{or} \quad \frac{pV}{nRT} = 1 - \frac{na}{VRT}$$

Hence, the constant a (which measures the attraction between molecules) is responsible for making $pV/nRT < 1$.

89. The van der Waals constants a and b accounts for the forces of attraction amongst gaseous molecules and volume occupied by 1 mol of gaseous molecules, respectively. The van der Waals equation is

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb) = nRT$$

The terms n^2a/V^2 accounts for the pressure effects due to molecular attractions.

90. Positive deviation means $pV/nRT > 1$. This is possible when the term n^2a/V^2 is negligible in comparison to the pressure of the gas. In this situation, van der Waals equation is reduced to

$$p(V-nb) = nRT \text{ or } \frac{pV}{nRT} = 1 + \frac{pb}{RT}.$$

91. If the temperature of a gas is greater than its inversion temperature, heating is observed.

92. If the temperature of a gas is lower than its inversion temperature, cooling is observed.

93. If a gas exhibits neither heating nor cooling if its temperature is equal to its inversion temperature.

94. For a monatomic gas, we have $C_{V,\mathrm{m}} = (3/2)R$; $C_{p,\mathrm{m}} = (5/2)R$

95. Water has dipole moment. Because of hydrogen bonding, its T_c is larger.

96. At low temperatures, vibrational modes do not contribute towards heat capacity.

$$C_{V,\mathrm{m}} = \text{contribution from (translational + rotational) modes}$$
$$= 3\left(\frac{1}{2}R\right) + 2\left(\frac{1}{2}R\right) = \frac{5}{2}R$$

97. We have $\lambda = \dfrac{1}{\sqrt{2}\,\pi\sigma^2 N^*}$, where $N^* = \dfrac{N}{V} = \dfrac{N/N_\mathrm{A}}{V/N_\mathrm{A}} = \dfrac{n}{V/N_\mathrm{A}} = \dfrac{pV/RT}{V/N_\mathrm{A}} = \dfrac{p}{kT}$

Hence $\lambda \infty T/p$

98. The fraction of molecules having speeds in the range c and $c + \mathrm{d}c$ is

$$f = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\exp\left(-Mc^2/2RT\right)c^2\,\mathrm{d}c$$

Since f depends on M/T, both SO_2 at $2T$ and O_2 at T will have the same fracton.

99. The critical volume is three times the van der Waals constant b.

100. The correct expression is $p_\mathrm{c} = a/(27/b^2)$

101. Since $N^* = p/kT$ and $\bar{u} = \sqrt{8RT/\pi M}$, we have

$$z_1 \propto \bar{u}\ N^{*2} \propto \sqrt{T}\ (p/T)^2 = p^2/T^{3/2}$$

102. Viscosity of a gas increases with increase in temperature. It is due to the transfer of momentum from one layer to another.

103. The inversion temperature of a van der Waals gas is given by the expression $T_\mathrm{i} = 2a/Rb$.

104. Heat capacity variation follows the pattern shown in Fig. 2.2.

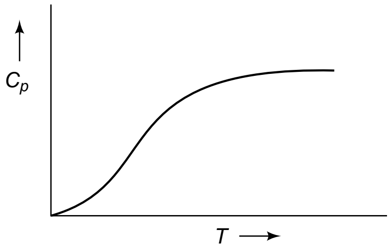


Fig. 2.2

105. Fraction of molecules follows the pattern is shown in Fig. 2.3.

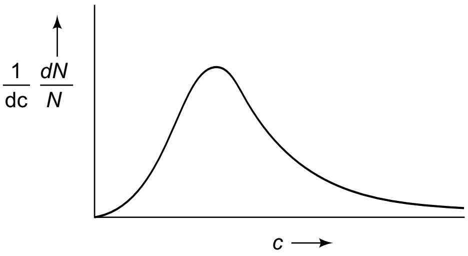


Fig. 2.3

106. We have $T_\mathrm{c} = \dfrac{8a}{27\,R\mathrm{b}}$ and $T_\mathrm{B} = \dfrac{a}{R\mathrm{b}}$. Hence $T_\mathrm{c} = \dfrac{8}{27}T_\mathrm{B}$

107. The Boyle temperature is given by $T_\mathrm{B} = a/Rb$.

108. The second virial coefficient $B(= b - a/RT)$ is zero at Boyle temperature.

109. Helium gas will have minimum a, since it is not easily liquefiable as compared to other given gases.

110. Carbon dioxide is easily liquefiable, hence its critical temperature must be higher than those of the given gases.

111. For an ideal gas $pV = nRT$ Thus $p\Delta V = nR\Delta T$

$$\text{or} \quad \frac{\Delta V}{\Delta T} = \frac{nR}{p} = \frac{nR}{nRT/V} \qquad \text{or} \quad \frac{1}{V}\,\frac{\Delta V}{\Delta T} = \frac{1}{T}$$

With increase in temperature, the value of $(1/V)(\Delta V/\Delta T)$ decreases.

112. The expression of mean free path is $\lambda = \dfrac{1}{\sqrt{2}\,\pi N^{*}\sigma^{2}}$

where N^* is the number of molecules per unit volume and σ is the molecular diameter.

Multiple Correct Choice Type

1. The equations of an ideal gas are

$$pV = nRT$$
$$pV = nRT = (m/M)RT;\ p = (m/V)RT/M = \rho RT/M$$
$$pV = (1/3)\ mN\ \overline{u^2}$$

3. (a) $V_t = V_0 + \dfrac{t/°\text{C}}{273} V_0$; intercept is not zero

(b) $V_T = KT$; intercept is zero

(c) $V = KT$; slope is K

4. The expression of mean free path is $\lambda = 1/\sqrt{2}\ \pi\ \sigma^2 N^*$ where $N^* = \pi/kT$. Hence, $\lambda = kT/\sqrt{2}\ \pi\ \sigma^2 p$.

5. (a) Mean square speed is given by $\overline{u^2} = 3RT/M = 3kT/M$

(c) The expression of viscosity is $\eta = (mkT)^{1/2}/\pi^{3/2}\sigma^2$.

6. (a) $n(H_2) = m/2\ \text{g mol}^{-1}$; $n(CH_4) = m/16\ \text{g mol}^{-1}$. Since $n(H_2) > n(CH_4)$, it follows that $N(H_2) > N(CH_4)$

(b) Average speed depends upon $\sqrt{T/M}$.

$$\frac{u(H_2)}{u(CH_4)} = \left[\frac{T(H_2)}{M(H_2)}\,\frac{M(CH_4)}{T(CH_4)}\right]^{1/2} = \left[\left(\frac{300\,\text{K}}{2\,\text{g mol}^{-1}}\right)\left(\frac{16\,\text{g mol}^{-1}}{600\,\text{K}}\right)\right]^{1/2} = 2$$

(c) For an ideal gas, compression factor is equal to 1.

(d) $(\text{KE})_{\text{total}} = n(\text{KE}) = n(1.5\ RT)$

$$\frac{\text{KE}(H_2)}{\text{KE}(CH_4)} = \frac{\left(m/2\,\text{g mol}^{-1}\right)(1.5\text{R})(300\,\text{K})}{(m/16\,\text{g mol}^{-1})(1.5\text{R})(600\,\text{K})} = 4$$

7. (a) Since $pV = nRT$, the term pV is dependent on temperature.

(c) If na/V^2 is neglected in the van der Waals equation, we get

$$p(V - nb) = nRT \;\Rightarrow\; Z = \frac{pV}{nRT} = 1 + \frac{pp}{RT}$$

8. (a) If nb is neglected in the van der Waals equation, we get

$$(p + n^2a/V^2)V = nRT \;\Rightarrow\; Z = pV/nRT = 1 - na/VRT$$

(b) see, Q. 7

(c) The excluded volume is four times the volumes of molecules of 1 mol of a gas.

9. (a) Average energy $(= 1.5kT)$ depends only on temperature

(b) $\bar{u}\ \left(=\sqrt{8RT/\pi M}\right)$ is inversely proportional to the square root of molar mass

(c) The unit of Boltzmann constant is J K^{-1}

(d) see Q.8

10. (b) The molar heat capacity of diatomic molecules is $2.5R$, there is no contribution from vibrational motion

(d) The average vibrational energy of a diatomic molecule is kT, because both kinetic energy and potential energy contribute.

11. (a) Average energy depends only on temperature of the gas.

(b) For $m_1 > m_2$, we will have $n_1 > n_2$.

(c) Since $pV = nRT$, we will have $T_1 < T_2$ for $n_1 > n_2$.

(d) Since $pV = nRT = (m/M)\ RT$, we will have $p_1 > p_2$ for $m_1 > m_2$.

12. (a) The unit of $K = \dfrac{\text{unit of volume}}{\text{unit of temperature}} = \dfrac{\text{m}^3}{\text{K}}$

(b) We have

$$V_2 = V_1\left(\frac{T_2}{T_1}\right) = V_1\left(\frac{273+50}{273+25}\right) = V_1\left(\frac{323}{298}\right) \neq 2\ V_1$$

(c) 32 g of O_2 and 16 g of CH_4, each is equal to 1 mol. Hence, they occupy the same volume.

(b) A real gas can be liquefied provided its temperature is less than its critical temperature.

13. (a) The gas can be liquefied if its temperature is less than its critical temperature.

(b) At high temperature, the effect of intermolecular attractions become insignificant. At low pressue, volume of the gas will be large and thus the volume occupied by gaseous molecules will be negligible.

(c) V_0 is the volume at 0 °C and not at 0 K.

(d) The rate of diffusion will be directly proportional to the average speed (or any other speed such as root mean square speed) of its gaseous molecules which is given as

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi M}} \qquad \text{Hence, } u_{\text{av}} \propto \sqrt{T} \text{ and } u_{\text{av}} \propto \sqrt{1/M}.$$

14. (a) Assming gas to be ideal, we have

$$pV = n\ RT = \left(\frac{m}{M}\right) RT \qquad \text{or} \qquad M = \left(\frac{m}{V}\right)\frac{RT}{p} = \left(\frac{\rho}{p}\right) RT$$

(b) Since $M = \left(\dfrac{\rho}{p}\right) RT$ or $\left(\dfrac{\rho}{p}\right) = \dfrac{M}{RT}$, the term ρ/p is independent of p at constant T.

(c) The value of Avogadro constant is 6.022×10^{23} mol^{-1}.

(d) The relevant expressions are $V_t = at + b$ and $V_T = KT$

15. (a) It is not equal masses but equal amounts of gases.

(b) An ideal gas does not involve molecular attractions.

(c) It is zero kelvin and not 0 °C.

(d) The room temperatrure is much larger than the critical temperature.

16. (a) The correct expression is $pV = (1/3)\ mN\overline{u^2}$ that is, it involves mean square speed and not square of mean speed.

(b) $\overline{u^2}$ stands for mean square speed whereas $\bar{u}^2$ stands for square of mean speed.

(c) The expression of density is $\rho = Mp/RT$

Thus, density decreases with increase in temperature at constant pressure. The qualitative explanation is that increase in temperature causes increase in volume hence decrease in density (= mass/volume).

(d) According to kinetic theory of gases. $\overline{\text{KE}} = (3/2)\ RT$

17. (a) The speed of molecules depend on the temperature and not on the pressure.

(b) The given value does not carry correct units. The value is 8.314 J K^{-1} mol^{-1}.

(c) The given value does not carry correct units. The value is 1.38×10^{-23} J K^{-1}.

19. (b) The correct expression is $\overline{u^2} = \dfrac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$

(d) The expression $u_{\text{av}} = \sqrt{8RT/\pi M}$ suggests that $u_{\text{av}} \propto \sqrt{T}$.

20. (a) Since $pV = (1/3)\ mN\overline{u^2}$, we get KE = $N_A\left(\frac{1}{2}m\overline{u^2}\right) = \frac{3}{2}pV_m = \frac{3}{2}RT$

(b) It is only monatomic gases which have $C_{p,m}/C_{V,m} = 5/3$ as $C_{p,m} = (5/2)R$ and $C_{V,m} = (3/2)R$.

(c) The expression $pV = (1/3)\ mN\ \overline{u^2}$ is applicable to an ideal gas.

(d) The expression is $\frac{u_{av}}{u_{mp}} = \frac{\sqrt{8RT/\pi M}}{\sqrt{2RT/M}} = \frac{\sqrt{8/\pi}}{\sqrt{2}}$.

21. (a) $u_{av}/u_{mp} = \sqrt{8RT/\pi M}/\sqrt{2RT/M} = 4/\pi$

(b) The unit is L^2 atm mol^{-2}.

(c) $\overline{u^2} = 3RT/M$

(d) The correct order is $u_{mp} < u_{av} < u_{rms}$.

22. (b) The constant a reflects the intermolecular attractions between gaseous molecules. The constant b reflects four times the actual volume occupied by 1 mol of gaseous molecules.

(c) An ideal gas cannot be liquefied as there exists no intermolecular attractions.

(d) The heat capacity of a monatomic gas is due to the contribution from translational motion for which energy levels are very close to each other.

23. The pressure of a gas decreases with increase in volume at constant temperature. The average kinetic energy of the molecules also remains constant at a constant temperature.

37. The expressions of u_{av}, u_{rms} and u_{mp} are

$$u_{av} = \sqrt{\frac{8RT}{\pi m}}\ ; \quad u_{rms} = \sqrt{\frac{3RT}{m}}\ ; \quad u_{mp} = \sqrt{\frac{2RT}{m}}$$

From these, it follows that $u_{mp} < u_{av} < u_{rms}$

The average kinetic energy of gaseous atom is

$$\overline{E} = \frac{1}{2}\ mu^2_{rms} = \frac{1}{2}\ m\left(\frac{3}{2}u^2_{mp}\right) = \frac{3}{4}\ mu^2_{mp}$$

Linked Comprehension Type

1. The variation of Z with p for a van der Waals gas is shown in Fig. 2.4.

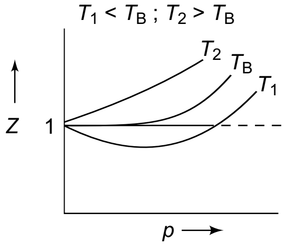


Fig. 2.4

(i) The value is $Z < 1$ provided $T < T_B$ and pressure is low.

(ii) The value is $Z > 1$ provided $T > T_B$ and pressure is high.

(iii) The value is $Z = 1$ provided $T = T_B$ and pressure is low.

2. **(i)** Ignoring a in the van der Waals equation gives

$$Z = \frac{pV_m}{RT} = 1 + \frac{bp}{RT} \quad \Rightarrow \quad Z > 1$$

(ii) Ignoring b in the van der Waals equation gives

$$Z = \frac{pV_\mathrm{m}}{RT} = 1 - \frac{a}{V_\mathrm{m}RT} \quad \Rightarrow \quad Z < 1$$

(iii) At Boyle temperature, the constants satisfy the expression $T_\mathrm{B} = a/Rb$.

3. (i) Both $C_{p,\,\mathrm{m}}$ and $C_{V,\,\mathrm{m}}$ vary with temperature

(iii) For triatomic molecules, $N = 3$ in the following expressions

Linear $\quad C_{V,\,\mathrm{m}} = \frac{3}{2}R + R + (3N - 5)R = \frac{13}{2}R$

Nonlinear $\quad C_{V,\,\mathrm{m}} = \frac{3}{2}R + R + (3N - 6)R = 6R$

4. (i) The unit of a is the same as that of the expression pTV_m^2, *i.e.* Pa K m^6 mol^{-2}

(ii) The Berthelot's equation is $\quad p = \dfrac{RT}{V_\mathrm{m} - b} - \dfrac{a}{TV_\mathrm{m}^2}$

This gives $\dfrac{pV_\mathrm{m}}{RT} = \dfrac{V_\mathrm{m}}{V_\mathrm{m} - b} - \dfrac{a}{V_\mathrm{m}RT^2} = \left(1 - \dfrac{b}{V_\mathrm{m}}\right)^{-1} - \dfrac{a}{V_\mathrm{m}RT^2}$

$$= 1 + \frac{b}{V_\mathrm{m}} + \left(\frac{b}{V_\mathrm{m}}\right)^2 + \cdots - \frac{a}{V_\mathrm{m}RT^2} = 1 + \frac{1}{V_\mathrm{m}}\left(b - \frac{a}{RT^2}\right)^2 + \left(\frac{b}{V_\mathrm{m}}\right)^2 + \cdots$$

The second virial coefficient is $B = b - \dfrac{a}{RT^2}$

(iii) At Boyle temperature $B = 0$. This gives $T_\mathrm{B} = \sqrt{a/Rb}$

5. (i) In the Maxwell relation, the term $M/(2\pi RT)$ decreases while $\exp(-Mu^2/2RT)$ increases with increase in temperature. In the low speed range, the former is larger than the latter, consequently, the fraction decreases.

(ii) In the high speed range, the reverse of the effects discussd in (i) is observed, consequently, the fraction increases.

(iii) Here, also fraction decreases.

6. Comparing the coefficients of V_m's in the expressions

$$V_\mathrm{m}^3 - \left(b + \frac{RT_\mathrm{c}}{p_\mathrm{c}}\right)V_\mathrm{m}^2 + \frac{a}{p_\mathrm{c}}V_\mathrm{m} - \frac{ab}{p_\mathrm{c}} = 0 \quad \text{and} \quad V_\mathrm{m}^3 - 3V_\mathrm{c}V_\mathrm{m}^2 + 3V_\mathrm{c}^2V_\mathrm{m} - V_\mathrm{c}^3 = 0$$

we find that

(i) $b = V_\mathrm{c}/3$; **(ii)** $a = 27\,(RT_\mathrm{c})^2/64p_\mathrm{c}$; **(iii)** $p_\mathrm{c}V_\mathrm{c}/RT_\mathrm{c} = 3/8$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The pressure in a bulb dropped from 2000 to 1500 mmHg in 47 min, when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molar mass 79 g mol^{-1} in the molar ratio 1:1 at a total pressure of 4000 mmHg, was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min. (1981)

Solution Since the mixture contains 1:1 molar ratio of oxygen and another gas, partial pressures of oxygen and the second gas would be 2000 mmHg and 2000 mmHg, respectively. Now in 74 min, the decrease in partial pressure of oxygen would be

$$-\Delta p_{O2} = \frac{(2000-1500)\,\text{mmHg}}{47\,\text{min}} \times 74\ \text{min} = 787.2\ \text{mmHg}$$

Hence, Partial pressure of oxygen at the end of 74 min = (2000 – 787.2) mmHg = 1212.8 mmHg

Now, the ratio of rate of diffusion would be $\frac{r_2}{r_1} = \sqrt{\frac{32}{79}} = 0.6364$

Thus $-\Delta p_{\text{unknown gas}} = (0.6364)\ (787.2\ \text{mmHg}) = 501\ \text{mmHg}$

Partial pressure of unknown gas at the end of 74 min = (2000 – 501) mmHg = 1499 mmHg

Now since the amount of the gas remaining will be directly proportional to its partial pressure, we would have

$$\frac{n_2}{n_1} = \frac{1499}{1212.8} = \frac{1.236}{1}.$$

2. Calculate the average kinetic energy, in joules, of the molecules in 8.0 g of methane at 27 °C. (1982)

Solution We have

$$\text{Average kinetic energy of the gas} = \frac{3}{2}\,RT = \left(\frac{3}{2}\right)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300.15\ \text{K}) = 3743\ \text{J mol}^{-1}.$$

3. The density of mercury is 13.6 g cm^{-3}. Calculate approximately the diameter of an atom of mercury assuming that each atom occupying a cube of edge length equal to the diameter of the mercury atom.

Solution Volume of one atom of Hg is

$$v = \frac{\text{mass of one atom}}{\text{density}} = \frac{(200\ \text{g mol}^{-1})/(6.022\times10^{23}\ \text{mol}^{-1})}{13.6\ \text{g cm}^{-3}} = 2.44\times10^{-23}\ \text{cm}^3$$

As each atom occupies a cube of edge length equal to the diameter of the Hg atom, we will have

$$d^3 = 2.44\times10^{-23}\ \text{cm}^3 \quad \text{or} \quad d = (2.44\times10^{-23}\ \text{cm}^3)^{1/3} = 2.90\times10^{-8}\ \text{cm}.$$

4. Oxygen is present in 1-litre flask at a pressure of 7.6 × 10^{-10} mmHg. Calculate the number of oxygen molecules in the flask at 0 °C. (1983)

Solution Using the expression $pV = nRT$, we have

$$n = \frac{pV}{RT} = \frac{\{(7.6\times10^{-10}/760)\,\text{atm}\}\,(1\,\text{L})}{(0.0821\,\text{atm L K}^{-1}\ \text{mol}^{-1})(273.15\ \text{K})} = 4.459\times10^{-14}\ \text{mol}$$

$$N = nN_A = (4.459\times10^{-14}\ \text{mol})\ (6.023\times10^{23}\ \text{mol}^{-1}) = 2.686\times10^{10}.$$

5. When 2 g of a gas A is introduced into an evacuated flask kept at 25 °C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molar masses $M_A : M_B$. (1983)

Solution Since $pV = n\,RT$, we have

$$pV = \frac{m}{M}\,RT \quad \text{or} \quad M = \frac{mRT}{pV}$$

Hence, $M_A = \frac{(2\,\text{g})RT}{(1\,\text{atm})\,V}$ and $M_B = \frac{(3\,\text{g})RT}{(0.5\,\text{atm})\,V}$. Thus, $\frac{M_A}{M_B} = \left(\frac{2}{1}\right)\left(\frac{0.5}{3}\right) = \frac{1}{3}$.

6. Calculate the root mean square speed of ozone kept in a closed vessel at 20°C and 82 cmHg pressure. (1985)

Solution We have

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(293.15\ \text{K})}{(0.048\ \text{kg mol}^{-1})}\right]^{1/2} = 390.3\ \text{m s}^{-1}.$$

7. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm at 27 °C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up. (1987)

Solution We have,

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \left(\frac{4}{3}\right)\left(\frac{22}{7}\right)\left(\frac{21\,\text{cm}}{2}\right)^3 = 4851\ \text{cm}^3$$

Total volume of the gas available at STP conditions is

$$V = \frac{p_1 V_1}{T_1}\frac{T_0}{p_0} = \frac{(20\,\text{atm})\,(2.82\,\text{L})}{(300\,\text{K})}\left(\frac{273\,\text{K}}{1\,\text{atm}}\right) = 51.324\ \text{L} = 51324\ \text{cm}^3$$

When the balloons are being filled, the pressure in the cylinder will decrease. We can continue filling from the cylinder till the pressure within the cylinder is also 1 atm. At this stage, the volume of 2820 cm^3 of the gas will remain within the cylinder.

Hence, Volume of the gas which can be transferred to balloons will be = 51324 cm^3 – 2820 cm^3 = 48504 cm^3

$$\text{Number of balloons that can be filled up} = \frac{48504\ \text{cm}^3}{4851\,\text{cm}^3/\text{balloon}} = 10\ \text{balloons.}$$

8. The average speed at T_1 (in kelvin) and the most probable speed at T_2 (in kelvin) of CO_2 gas is 9.0×10^4 cm s^{-1}. Calculate the values of T_1 and T_2. (1990)

Solution We have $u_{\text{av}} = \sqrt{\dfrac{8RT}{\pi M}}$

Hence, $$\sqrt{\frac{8RT_1}{\pi M}} = 9.0 \times 10^4\ \text{cm s}^{-1}$$

or $$T_1 = (9.0 \times 10^2\ \text{m s}^{-1})^2\left(\frac{\pi M}{8R}\right) = (9.0 \times 10^2\ \text{m s}^{-1})^2\left[\frac{(3.14)(44\times 10^{-3}\ \text{kg mol}^{-1})}{(8)(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})}\right] = 1682.5\ \text{K}$$

For most probable speed, we have

$$\sqrt{\frac{2RT_2}{M}} = 9.0 \times 10^2\ \text{m s}^{-1}$$

Hence, $$T_2 = (9.0 \times 10^2\ \text{m s}^{-1})^2\left(\frac{M}{2R}\right) = (9.0 \times 10^2\ \text{m s}^{-1})^2\left[\frac{44\times 10^{-3}\ \text{kg mol}^{-1}}{(2)\,(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})}\right] = 2143.4\ \text{K}$$

9. At room temperature the following reactions proceed nearly to completion:

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$$

The dimer N_2O_4 solidified at 262 K. A 250 mL flask and a 100 mL flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to be have ideally.) (1992)

Solution To start with, we have

$$\text{Amount of nitric oxide} = \frac{pV}{RT} = \frac{(1.053\ \text{atm})(0.250\ \text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})(300\,\text{K})} = 0.01069\ \text{mol}$$

$$\text{Amount of oxygen} = \frac{pV}{RT} = \frac{(0.789\ \text{atm})(0.100\ \text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})(300\ \text{K})} = 3.203 \times 10^{-3}\ \text{mol}$$

According to the reaction $2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$, 1 mol of O_2 reacts with 2 mol of NO. Thus, after the reaction, we will have

Amount of oxygen = 0

Amount of nitric oxide = (0.01069 – 2 × 0.0032) mol = 4.283×10^{-3} mol
Amount of N_2O_4 formed =3.203×10^{-3} mol

Now on cooling, N_2O_4(g) is condensed. Thus, only nitric oxide will be present in the entire volume of 0.350 L. Hence,

$$\text{Pressure of the gas} = \frac{nRT}{V} = \frac{(4.283\times10^{-3}\ \text{mol}^{-1})\,(0.0821\ \text{atm L K}^{-1}\ \text{mol}^{-1})\,(220\ \text{K})}{(0.350\ \text{L})} = 0.221\ \text{atm.}$$

10. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 N m^{-2}. Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.84, calculate the most probable speed for these molecules at this temperature. (1993)

Solution We are given that

$$V = 1\ \text{L} \equiv 1\ \text{dm}^3 \equiv 10^{-3}\ \text{m}^3; \quad N = 2.0 \times 10^{21}$$
$$p = 7.57 \times 10^3\ \text{N m}^{-2}$$
$$T = ?; \quad c_{\text{rms}} = ?; \quad c_{\text{mp}}/C_{\text{rms}} = 0.84; \quad c_{\text{mp}} = ?$$

Now $$\text{Amount of gas} = \frac{2.0\times10^{21}}{6.022\times10^{23}\ \text{mol}^{-1}}$$

Using ideal gas equation, we get

$$T = \frac{pV}{nR} = \frac{(7.57\times10^3\ \text{N m}^{-2})\,(10^{-3}\ \text{m}^3)}{(2.0\times10^{21}/6.022\times10^{23}\ \text{mol}^{-1})\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})} = 274.2\ \text{K}$$

Now $$c_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(274.2\ \text{K})}{28\times10^{-3}\,\text{kg mol}^{-1})}\right]^{1/2} = 494.22\ \text{m s}^{-1}$$

$$c_{\text{mp}} = (0.84)\ (494.22\ \text{ms}^{-1}) = 415.14\ \text{m s}^{-1}.$$

11. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weights 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 °C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0 °C. (1994)

Solution Mass of gas used up = (29.0 – 23.2) kg = 5.8 kg

Molar mass of *n*-butane(C_4H_{10}) = 58 g mol^{-1}

$$\text{Amount of gas used up} = \frac{5.8\times10^3\ \text{g}}{58\text{g mol}^{-1}} = 10^2\ \text{mol}$$

Using ideal gas equation, $V= nRT/p$, we get

$$V = \frac{(10^2\ \text{mol})\,(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})\,(300\text{K})}{1\ \text{atm}} \qquad \text{(For normal usuage, } p = 1\ \text{atm)}$$
$$= 2463\ \text{L} = 2463\ \text{dm}^3 = 2.463\ \text{m}^3.$$

Final Pressure Inside the Cylinder The cylinder contains liquefied pertroleum gas in equilibrium with its vapours. So long liquid remains present, the pressure inside the cylinder remains constant. Since the cylinder contains 8.4 kg (= 23.2 kg – 14.8 kg) of the remaining LPG, the pressure inside the cylinder would be 2.5 atm.

12. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2\ Cl$), which is attained at 1200 °C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mmHg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Relative atomic mass of Kr = 84.) (1995)

Solution Let the initial amount of Cl_2 be *n*. If α is the fraction of Cl_2 dissociated at equilibrium, we will have

$$\underset{n(1-\alpha)}{Cl_2} \rightleftharpoons \underset{n(2\alpha)}{2\ Cl}$$

Total amount of species at equilibrium, $n_{\text{total}} = n_{Cl_2} + n_{Cl} = n(1 - \alpha) + n(2\alpha) = n(1 + \alpha)$

Average molar mass of the mixture at equilibrium, $(M_{\text{av}})_{\text{mix}} = \dfrac{nM_{Cl_2}}{n(1+\alpha)} = \dfrac{M_{Cl_2}}{1+\alpha}$

Accordng to Graham's law of diffusion, we get

$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \left[\frac{M_{\text{Kr}}}{(M_{\text{av}})_{\text{mix}}}\right]^{1/2} = \left[\frac{M_{\text{Kr}}(1+\alpha)}{M_{Cl_2}}\right]^{1/2}$$

or
$$\alpha = \left(\frac{M_{Cl_2}}{M_{\text{Kr}}}\right)\left(\frac{r_{\text{mix}}}{r_{\text{Kr}}}\right)^2 - 1 = \left(\frac{71}{84}\right)(1.16)^2 - 1 = 1.1374 - 1 = 0.1374.$$

13. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.00 atm and 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. (1995)

Solution Total amount of the mixture, $n = \dfrac{pV}{RT} = \dfrac{(1.00\,\text{atm})(4.0\,\text{L})}{(0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1})(400\,\text{K})} = 1.295\ \text{mol}$

The combustion reactions are

$$C_2H_6 + \tfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad \text{and} \quad C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Let x be the amount of C_2H_6 in the mixture. As per the above equations, the amount of oxygen consumed would be

$$n(O_2) = \frac{7}{2}x + 3(1.295\ \text{mol} - x)$$

This will be equal to the given amount which is 130 g/32 g mol^{-1}, i.e. (130/32) mol. Hence

$$\frac{7}{2}x + 3(1.295\ \text{mol} - x) = \frac{130}{32}\ \text{mol} \quad \text{or} \quad \frac{7}{2}x - 3x = \left(\frac{130}{32} - 3 \times 1.295\right)\ \text{mol}$$

or
$$x = 2(4.0625 - 3.885)\ \text{mol} = 0.355\ \text{mol}$$

$$\text{Mole fraction of } C_2H_6 = \frac{0.355}{1.295} = 0.274 \quad \text{and} \quad \text{Mole fraction of } C_2H_4 = 1.0 - 0.274 = 0.726$$

14. The relative humidity in a room (4 m × 4 m × 3 m) is 65%. Assuming ideal gas behaviour, what mass of water vapour is present in the room at 25 °C. Given : Vapour pressure of water = 23.8 Torr at 25°C.
Solution We have

$$p(H_2O) = 0.65 \times 23.8\ \text{Torr} = \left(\frac{0.65 \times 23.8}{760} \times 101\,325\right)\text{Pa} = 2062.5\ \text{Pa}$$

Now
$$n_{H_2O} = \frac{p_{H_2O}V}{RT} = \frac{(2062.5\,\text{Pa})(4 \times 4 \times 3\,\text{m}^3)}{(8.314\,\text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1})(298\,\text{K})} = 39.96\ \text{mol}$$

$$m_{H_2O} = n_{H_2O}M_{H_2O} = (39.96\ \text{mol})(18\ \text{g mol}^{-1}) = 719.3\ \text{g}.$$

15. The radius of an Xe atom is 1.3×10^{-8} cm. A 100 cm^3 container is filled with Xe at a pressure of 1.0 atm and a temperature of 273 K. Calculate the fraction of the volume that is occupied by Xe atoms.
Solution We have

$$\text{Amount of Xe atoms, } n = \frac{pV}{RT} = \frac{(1\,\text{atm})(100 \times 10^{-3}\,\text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})(273\,\text{K})} = 4.467 \times 10^{-3}\ \text{mol}$$

Number of Xe atoms, $N = nN_A = (4.467 \times 10^{-3}\ \text{mol})\ (6.022 \times 10^{23}\ \text{mol}^{-1}) = 2.69 \times 10^{21}$

$$\text{Volume occupied by Xe atoms} = N\left(\frac{4}{3}\pi r^3\right) = (2.69 \times 10^{21})\left[\frac{4}{3} \times 3.14 \times (1.38 \times 10^{-8}\ \text{cm})^3\right]$$

$$= 2.47 \times 10^{-2}\ \text{cm}^3$$

$$\text{Fraction of volume occupied by Xe atoms} = \frac{(2.47 \times 10^{-2}\ \text{cm}^3)}{(100\ \text{cm}^3)} = 2.47 \times 10^{-4}.$$

16. Calculate the density of hydrogen chloride gas at 30 °C and 5 atm pressure.

Solution Since $pV = nRT = \dfrac{m}{M}RT$, we have $\rho = \dfrac{m}{V} = \dfrac{pM}{RT}$

Hence, $$\rho = \frac{(5\ \text{atm})\ (36.5\ \text{g mol}^{-1})}{(0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})\ (303.15\ \text{K})} = 7.34\ \text{g L}^{-1}.$$

17. The density of a given gas is 3.41 g L^{-1} at STP. Determine its density at 27 °C and 700 Torr.

Solution Since $\rho = pM/RT$, we have

$$\rho_2 = \left(\frac{p_2}{T_2}\right)\left(\frac{T_1}{p_1}\right)\rho_1 = \left(\frac{700\ \text{Torr}}{300\ \text{K}}\right)\left(\frac{273\ \text{K}}{760\ \text{Torr}}\right)(3.41\ \text{g L}^{-1}) = 2.86\ \text{g L}^{-1}.$$

18. The density of phosphorus vapour at 310 °C and 775 Torr is 2.64 g dm^{-3}. What is the molecular formula of phosphorus?

Solution Since $pV = nRT$, we have

$$pV = \frac{m}{M}RT \qquad \text{or} \qquad M = \left(\frac{m}{V}\right)\frac{RT}{p} = \rho\frac{RT}{p}$$

Substituting the given values, we get

$$M = \frac{(2.64\ \text{g dm}^{-3})\ (8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\ (583\ \text{K})}{(775/760) \times 101.325\ \text{kPa}} = 123.8\ \text{g mol}^{-1}$$

Now since molar mass of P is 31 g mol^{-1}, we have

$$\text{Number of P atoms in a molelcule of phosphorus} = \frac{123.8}{31} = 4$$

Hence, Molecular formula of phosphorus is P_4.

19. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupied 35.5 L at 1.0 bar and 405 K. The mixture reacted completely with 110.3 g of O_2 to produce CO_2 and H_2O. What was the composition of the original mixture? Assume ideal gas behaviour.

Solution We have

$$\text{Total amount of the original mixture, } n = \frac{(1.0\ \text{bar})\ (35.5\ \text{L})}{(0.08314\ \text{bar L K}^{-1}\ \text{mol}^{-1})(405\ \text{K})} = 1.054\ \text{mol}$$

$$\text{Amount of } O_2 \text{ used in combustion} = \frac{110.3\ \text{g}}{32\ \text{g mol}^{-1}} = 3.447\ \text{mol}$$

The combustion reactions are

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2\,(g) + 2H_2O(g) \qquad \text{and} \qquad C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

If n_1 and n_2 are the amounts of $C_2H_4(g)$ and $C_2H_6(g)$ in the given mixture, we will have

$$n_1 + n_2 = 1.054\ \text{mol} \qquad \text{and} \qquad 3n_1 + \frac{7}{2}n_2 = 3.447\ \text{mol}$$

Solving for n_1 and n_2, we get

$$n_1 = 0.484\ \text{mol} \qquad \text{and} \qquad n_2 = 0.57\ \text{mol}$$

20. A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25 °C and 720 Torr. What is the per cent by mass of helium in this mixture?

Solution We have

$$M_{av} = \frac{\rho RT}{p} = \frac{(0.518\ \text{g dm}^{-3})(0.082\ \text{atm dm}^{-3}\ \text{K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{(720/760)\ \text{atm}} = 13.36\ \text{g mol}^{-1}$$

If x is the mole fraction of helium in the mixture, we will have

$$M_{av} = x\,M_{He} + (1-x)\,M_{O2} \quad \text{i.e.} \quad 13.36\ \text{g mol}^{-1} = x\,(4\ \text{g mol}^{-1}) + (1-x)\,(32\ \text{g mol}^{-1})$$

Solving for x, we get $x = \dfrac{32 - 13.36}{28} = 0.666$

Hence, Mass per cent of helium = $\dfrac{0.666 \times 4}{0.666 \times 4 + 0.334 \times 32} \times 100 = 19.95$

21. A mixture of NH_3(g) and N_2H_4(g) is placed in a sealed container at 300 K. The total pressure is 0.5 atm. The container is heated to 1200 K, at which time both substances decompose completely according to the equations

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \qquad \text{and} \qquad N_2H_4(g) \rightarrow N_2(g) + 2H_2(g)$$

After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. Find the amount per cent of N_2H_4(g) in the original mixture.

Solution Let the original mixture contain the amounts n_1 and n_2 of NH_3 and N_2H_4, respectively.

Total amount of gases originally present = $n_1 + n_2$

From the given decomposition reactions, we find that

2 mol NH_3 produces a total of 4 mol of N_2 and H_2

1 mol N_2H_4 produces a total of 3 mol of N_2 and H_2

Hence, Total amount of gases after decomposition of gases = $2n_1 + 3n_2$

Now, using ideal gas law, $pV = nRT$, we get

$$(0.5\ \text{atm})\,V = (n_1 + n_2)\,R\,(300\ \text{K}) \quad \text{and} \quad (4.5\ \text{atm})\,V = (2n_1 + 3n_2)\,R\,(1200\ \text{K})$$

where V is the volume of the container. Dividing the two expressions, we get

$$\left(\frac{2n_1 + 3n_2}{n_1 + n_2}\right)\left(\frac{1200\ \text{K}}{300\ \text{K}}\right) = \frac{4.5\ \text{atm}}{0.5\ \text{atm}}$$

or

$$\frac{2n_1 + 3n_2}{n_1 + n_2} = \frac{9}{4} \quad \text{or} \quad \frac{2(n_1 + n_2) + n_2}{n_1 + n_2} = \frac{9}{4} \quad \text{or} \quad \frac{n_2}{n_1 + n_2} = \frac{9}{4} - 2 = \frac{1}{4}$$

Hence, per cent amount of N_2H_4 is $\dfrac{n_2}{n_1 + n_2} \times 100 = 25.$

22. The total pressure of a mixture of H_2 and O_2 is 1.00 bar. The mixture is allowed to react to form water, which is completely removed to leave only pure H_2 at a pressure of 0.35 bar. Assuming ideal gas behaviour and that all pressure measurements were made under the same temperature and volume conditions, calculate the composition of the original mixture.

Solution For the original mixture, we have $n_1 = \dfrac{(1.00\ \text{bar})\,V}{RT}$

After the reaction, the amount of excess H_2 is given as $n_2 = \dfrac{(0.35\ \text{bar})\,V}{RT}$

The total amount of O_2 and H_2 that have undergone reaction to give water is $n = n_1 - n_2 = \dfrac{(0.65\ \text{bar})\,V}{RT}$

From the chemical equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ we conclude that the amounts of H_2(g) and O_2(g) that have reacted are

$$n(H_2) = \left(\frac{2}{3}\right)\left[\frac{(0.65\ \text{bar})\,V}{RT}\right] \qquad \text{and} \qquad n(O_2) = \left(\frac{1}{3}\right)\left[\frac{(0.65\ \text{bar})\,V}{RT}\right]$$

Now $$n_{\text{total}}(H_2) = \left[(0.35\ \text{bar}) + \frac{2}{3}(0.65\ \text{bar})\right]\left(\frac{V}{RT}\right)$$

Hence, $$x(H_2) = \frac{n_{\text{total}}(H_2)}{n_{\text{total}}(H_2) + n(O_2)} = \frac{0.35 + \frac{2}{3}(0.65)}{\left[0.35 + \frac{2}{3}(0.65) + \frac{1}{3}(0.65)\right]} = 0.35 + \frac{2}{3}(0.65) = 0.78$$

$$x(O_2) = 1 - x(H_2) = 0.22.$$

23. Calculate the root mean square, average and most probable speeds of oxygen molecules at 300 K.

Solution We have

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{32\times10^{-3}\ \text{kg mol}^{-1}}\right]^{1/2} = 483.6\ \text{m s}^{-1}$$

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi M}} = \left[\frac{8(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{(3.14)(32\times10^{-3}\ \text{kg mol}^{-1})}\right]^{1/2} = 445.6\ \text{m s}^{-1}$$

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \left[\frac{2(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{(32\times10^{-3}\ \text{kg mol}^{-1})}\right]^{1/2} = 394.8\ \text{m s}^{-1}.$$

24. The escape velocity, the velocity required by an object to escape from the gravitational field of a body, is given by

$$v_e = \sqrt{2gr}$$

where $r = 6.37 \times 10^6$ m for earth. At what temperature will the v_{rms} of an H_2 molecule attain escape velocity?

Solution Equating v_e with v_{rms}, we get

$$\sqrt{2gr} = \sqrt{\frac{3RT}{M}}$$

or $$T = \frac{2Mgr}{3R} = \frac{2(2.0\times10^3\ \text{kg mol}^{-1})(9.81\ \text{m s}^{-2})(6.37\times10^6\ \text{m})}{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})} = 1.02\times10^4\ \text{K}.$$

25. Calculate the pressure exerted by 2 mol of $CO_2(g)$ confined to 855 cm^3 volume at 300 K using (a) ideal gas equation, and (b) van der Waals equation. Given: $b(CO_2) = 42.8\ \text{cm}^3\ \text{mol}^{-1}$ and $a(CO_2) = 3.61\ \text{L}^2\ \text{atm mol}^{-2}$.

Solution We have

(a) $$p = \frac{nRT}{V} = \frac{(2\ \text{mol})(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{(0.855\ \text{L})} = 57.61\ \text{atm}$$

(b) $$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} = \frac{(2\ \text{mol})(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})(300\text{K})}{(0.855\ \text{L}) - (2\ \text{mol})(0.0428\ \text{L mol}^{-1})} - \frac{(2\ \text{mol})^2(3.61\ \text{L}^2\ \text{atm mol}^{-2})}{(0.855\ \text{L})^2}$$
$$= 64.02\ \text{atm} - 19.75\ \text{atm} = 44.27\ \text{atm}.$$

26. Calculate the pressure exerted by 10^{23} gaseous particles each of mass 10^{-22} g in a container of volume 1 dm^3. The root mean square speed of gaseous molecules is $10^5\ \text{cm s}^{-1}$. What are the average and total kinetic energies of gaseous molecules? What will be its temperature?

Solution We have

$$N = 10^{23}\ \text{molecules};\quad m = 10^{-22}\ \text{g} = 10^{-25}\ \text{kg};\quad V = 1\ \text{dm}^3 = 10^{-3}\ \text{m}^3;\quad u_{\text{rms}} = 10^5\ \text{cm s}^{-1} = 10^3\ \text{m s}^{-1}$$

From the kinetic gas equation, we get

$$p = \frac{1}{3}\frac{mN\overline{u^2}}{V} = \frac{1}{3}\frac{(10^{-25}\ \text{kg})(10^{23})(10^3\ \text{m s}^{-1})^2}{(10^{-3}\ \text{m}^3)} = \frac{1}{3}\times10^7\ \text{Pa}$$

Average energy is

$$\overline{\text{KE}} = \frac{1}{2}m\overline{u^2} = \frac{1}{2}(10^{-25}\ \text{kg})(10^3\ \text{m s}^{-1})^2 = \frac{1}{2}\times10^{-19}\ \text{J}$$

Total kinetic energy is

$$\text{KE} = N(\overline{\text{KE}}) = (10^{23})\left(\frac{1}{2}\times 10^{-19}\ \text{J}\right) = \frac{1}{2}\times 10^{4}\ \text{J}$$

Now since $\overline{\text{KE}} = (3/2)kT$, we get

$$T = \frac{2}{3k}\,(\overline{\text{KE}}) = \frac{2(0.5\times 10^{-19}\ \text{J})}{3(1.38\times 10^{-23}\ \text{J K}^{-1})} = \frac{1}{4.14}\times 10^{4}\ \text{K} = 2415\ \text{K}$$

Alternatively, we may proceed as follows.

Since $u_{\text{rms}} = \sqrt{3RT/M}$, we get

$$T = \frac{M}{3R}\,u^2_{\text{rms}} = \frac{N_A\,m}{3R}\,u^2_{\text{rms}} = \frac{(6.022\times 10^{23}\ \text{mol}^{-1})\,(10^{-25}\ \text{kg})}{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})}\,(10^{3}\ \text{m s}^{-1})^2 = 2415\ \text{K}$$

$$\overline{\text{KE}} = \frac{3}{2}\,kT = \frac{3}{2}\,(1.38\times 10^{-23}\ \text{J K}^{-1})\,(2415\ \text{K}) = 0.5\times 10^{-19}\ \text{J}$$

$$\text{KE} = N\,(\overline{\text{KE}}) = (10^{23})\,(0.5\times 10^{-19}\ \text{J}) = 0.5\times 10^{4}\ \text{J}$$

Finally, $$p = \frac{nRT}{V} = \frac{(10^{23}/6.022\times 10^{23}\ \text{mol}^{-1})\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(2415\ \text{K})}{(10^{-3}\ \text{m}^3)} = 3.334\times 10^{6}\ \text{Pa}.$$

27. A litre gas bulb contains 1.03×10^{23} hydrogen molecules and the pressure exerted by these molecules is 101.325 kPa. Calculate the average square molecular speed of molecules.

Solution We have

$$V = 1\ \text{L} = 1\ \text{dm}^3;\quad p = 101.325\ \text{kPa};\quad N = 1.03\times 10^{23}$$

Hence, $$n = \frac{N}{N_A} = \frac{1.03\times 10^{23}}{6.022\times 10^{23}\ \text{mol}^{-1}} = 0.171\ \text{mol}$$

$$T = \frac{pV}{nR} = \frac{(101.325\ \text{kPa})\,(1\ \text{dm}^3)}{(0.171\ \text{mol})\,(8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})} = 71.27\ \text{K}$$

$$\overline{u^2} = \frac{3RT}{M} = \frac{3\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(71.27\ \text{K})}{(2\times 10^{-3}\ \text{kg mol}^{-1})} = 8.888\times 10^{5}\ (\text{m s}^{-1})^2.$$

28. Calculate molecular diameter of helium from its van der Waals constant $b = 24\ \text{mL mol}^{-1}$.

Solution Since $b = 4\times$ volume occupied by molecules of 1 mol of a gas, we have

$$b = 4\,N_A\left(\frac{4}{3}\pi r^3\right)$$

Therefore, $$r = \left(\frac{3b}{16\,N_A\pi}\right)^{1/3} = \left[\frac{3\times 24\ \text{cm}^3\ \text{mol}^{-1}}{16\,(6.023\times 10^{23}\ \text{mol}^{-1})\,(3.14)}\right]^{1/3} = 1.335\times 10^{-8}\ \text{cm} = 133.5\ \text{pm}$$

Now Molecular diameter, $d = 2r = 267$ pm.

29. The molar volume of helium at 10.1325 MPa and 273 K is 0.011 075 of its molar volume at 101.325 kPa at 273 K. Calculate the radius of helium atom. The value of a may be neglected.

Solution The van der Waals equation after neglecting a reduces to

$$p(V_m - b) = RT$$

Substituting the given data, we get

At 10.1325 MPa: $(10.1325\ \text{MPa})\,(0.011\,075\ V_m - b) = (8.314\ \text{MPa cm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\,(273\ \text{K})$

$$0.011075\ V_m - b = 224.00\ \text{cm}^3\ \text{mol}^{-1} \qquad (1)$$

At 101.325 kPa: $(101.325 \text{ kPa})(V_m - b) = (8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(273 \text{ K})$

i.e. $V_m - b = 22.4 \text{ dm}^3 \text{ mol}^{-1} = 22.4 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ (2)

Multiplying Eq. (2) by 0.011 075 and then subtracting Eq. (1) from it, we get

$$b - 0.011\,075\, b = (248.08 - 224) \text{ cm}^3 \text{ mol}^{-1}$$

or $$b = \frac{24.08 \text{ cm}^3 \text{ mol}^{-1}}{0.988925} = 24.35 \text{ cm}^3 \text{ mol}^{-1}$$

Hence, from the expression

$$b = \left(\frac{4}{3}\pi r^3\right)(4\, N_A)$$

we get $$r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} = \left(\frac{3 \times 24.35 \text{ cm}^3 \text{ mol}^{-1}}{16 \times 3.14 \times 6.023 \times 10^{23} \text{ mol}^{-1}}\right)^{1/3} = 1.34 \times 10^{-8} \text{ cm} = 134 \text{ pm}$$

30. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (1994)

Solution Partial pressure of He $= \dfrac{4 \text{ mol}}{(4+1) \text{ mol}} \times 20 \text{ bar} = 16 \text{ bar}$

Partial pressure of CH_4 = 20 bar – 16 bar = 4 bar

If r_{He} and r_{CH_4} are the rates of effusion of He and CH_4, respectively, then

$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{p_{He}}{p_{CH_4}}\right)\left(\frac{M_{CH_4}}{M_{He}}\right)^{1/2} = \left(\frac{16}{4}\right)\left(\frac{16}{4}\right)^{1/2} = 8$$

Since the rate of effusion of He is eight times more than that of CH_4, the initial mixture issuing out will contain He and CH_4 in the molar ratio of 8 : 1.

31. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mmHg at 300 K. Determine the molar mass or the gas. (1998)

Solution Mass of water filled in the glass vessel, $m_1 = (148.0 - 50.0) \text{ g} = 98.0 \text{ g}$

Volume of glass vessel, $V = \dfrac{m_1}{\rho} = \dfrac{98.0 \text{ g}}{0.98 \text{ g mol}^{-1}} = 100 \text{ mL} = 0.1 \text{ dm}^3$

Mass of gas filled in the vessel, $m = (50.5 - 50.0)\text{g} = 0.5 \text{ g}$

If M is the molar mass of the gas, we will have

$$pV = nRT = \frac{m}{M}RT$$

or $$M = \frac{mRT}{pV} = \frac{(0.5 \text{ g})(8.314 \text{ J K}^{-1}\text{mol}^{-1})(300 \text{ K})}{(101.325 \text{ kPa})(0.1 \text{ dm}^3)} = 123 \text{ g mol}^{-1}$$

32. Using van der Waals equation, calculate the constant a when two moles of a gas confined in a four-litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of b is 0.05 L mol^{-1}. (1998)

Solution Substituting the given data in the van der Waals equation of state

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

we get $$\left[11 \text{ atm} + \frac{(2 \text{ mol})^2 a}{(4 \text{ L})^2}\right][4 \text{ L} - (2 \text{ mol})(0.05 \text{ L mol}^{-1})] = (2 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})$$

or $$\left(11 \text{ atm} + \frac{a}{4} \text{ mol}^2 \text{ L}^{-2}\right)(4 \text{ L} - 0.1 \text{ L}) = 49.2 \text{ L atm}$$

or $$a = 4\left(\frac{49.2}{3.9} \text{ atm} - 11 \text{ atm}\right) \text{L}^2 \text{ mol}^{-2} = 4(12.615 - 11) \text{ L}^2 \text{ atm mol}^{-2} = 6.46 \text{ L}^2 \text{ atm mol}^{-2}$$

33. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1 atm. (Relative atomic mass of P = 31.0 and that of Cl = 35.5.) (1998)

Solution If we start with 1 mol of PCl_5, we will have

$$\underset{(1\ \text{mol})\,(1-\alpha)}{PCl_5} \rightleftharpoons \underset{(1\ \text{mol})\,\alpha}{PCl_3} + \underset{(1\ \text{mol})\,\alpha}{Cl_2}$$

Total amount of gases = (1 mol) $(1 + \alpha)$ = 1.4 mol (since $\alpha = 0.4$)

Volume of gaseous mixture would be

$$V = \frac{nRT}{p} = \frac{(1.4\ \text{mol})\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(400\ \text{K})}{(101.325\ \text{kPa})} = 45.95\ \text{dm}^3$$

Molar mass of PCl_5 = (31.0 + 5 × 35.5) g = 208.5 g

$$\text{Density of equilibrium mixture} = \frac{208.5\ \text{g}}{45.95\ \text{dm}^3} = 4.54\ \text{g dm}^{-3}$$

34. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound. (1999)

Solution The rate of diffusion depends on the following factors.

$$r \propto p \quad \text{and} \quad r \propto \sqrt{1/M}$$

Taking these together, we get

$$\frac{r_2}{r_1} = \frac{p_2}{p_1}\left(\frac{M_1}{M_2}\right)^{1/2}$$

Since $r \propto 1/t$, we can write

$$\frac{t_1}{t_2} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_2}\right)^{1/2} \qquad \text{or} \qquad M_2 = \left(\frac{p_2}{p_1}\frac{t_2}{t_1}\right)^2 M_1$$

Identifying the script 1 with nitrogen and 2 with unknown gas, we get

$$M_2 = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^2 (28\ \text{g mol}^{-1}) = 252\ \text{g mol}^{-1}$$

Let the molecular formula of the unknown compound be XeF_n. We will have

$$M_{\text{xe}} + nM_{\text{F}} = 252\ \text{g mol}^{-1} \qquad \text{i.e.} \quad [131 + n(19)]\text{g mol}^{-1} = 252\ \text{g mol}^{-1}$$

$$n = \frac{252 - 131}{19} = 6.36 \simeq 6$$

Hence, the molecular formula of the gas is XeF_6.

35. The pressure exerted by 12 g of an ideal gas at temperature t (expressed in °C) in a vessel of volume V (expressed in litre) is one atm. When the temperature is increased by 10 degree Celsius at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas = 120.) (1999)

Solution From the expression $pV = nRT$, we can write

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \qquad \text{(since } V \text{ and } n \text{ are constant)}$$

From the given data, we get

$$\frac{1\ \text{atm}}{1.1\ \text{atm}} = \frac{(273 + t/°\text{C})\ \text{K}}{(273 + t/°\text{C} + 10)\,\text{K}} \qquad \text{or} \qquad 283 + t/°\text{C} = 1.1\ (273 + t/°\text{C})$$

or

$$t/°\text{C} = \frac{283 - 1.1 \times 273}{0.1} = -173 \qquad \text{or} \qquad t = -173\ °\text{C}$$

For the given system,

$$n = \frac{12 \text{ g}}{120 \text{ g mol}^{-1}} = 0.1 \text{ mol} \quad \text{and} \quad T = (273 - 173)\text{K} = 100 \text{ K}$$

Hence, $$V = \frac{nRT}{p} = \frac{(0.1 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(100 \text{ K})}{1 \text{ atm}} = 0.82 \text{ L}$$

UNSOLVED PROBLEMS

1. Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 300 K and contain 0.7 mol of H_2 at 0.5 atm. One flask is immersed into a bath kept at 400 K while the other remains at 300 K. Calculate the final pressure and the amount of H_2 in each flask.

2. Calculate the root mean speed of H_2 molecules. Given that the density of gas at 1 atm is 0.09 g dm^{-3}.

3. The density of a gas is 1 g cm^{-3} at 63 K and 0.5 atm. What will be its density at STP?

4. Find the molar mass of Freon-11 (a chlorofluoromethane) from the fact that 8.29 dm^3 of its vapour at 200 °C and 790 Torr has a mass of 30.5 g.

5. The density of a gas X is 2.194 g dm^{-3} at 850 Torr and 298 K. Calculate its molar mass.

6. Calculate the relative rate of diffusion at a given pressure of carbon dioxide at 0 °C and at 100 °C.

7. Calculate the value of R in the units of cm^3 atm mol^{-1} K^{-1}.

8. A sample of nitrogen, collected over water at 25 °C and 752 Torr occupies 53.5 mL. What is the volume of dry gas at standard conditions? Given: Aqueous tension of water at 25 °C is 23.8 Torr.

9. What is the value of R when pressure is expressed in dyn m^{-2} and volume in mm^3?

10. One mole of a gas in a 10 L vessel exerts a pressure of 185.6 cmHg at 298 K. Calculate the value of van der Waals constant a. Given: b = 39.1 cm^3 mol^{-1}.

11. A mixture of CH_4(g) and C_2H_6(g) has a total pressure of 0.53 atm. Just enough O_2(g) is introduced in the mixture to bring its complete combustion to CO_2(g) and H_2O(g). The total pressure of these two gases is found to be 2.2 atm. Assuming constant volume and temperature, find the fraction of CH_4 in the mixture.

12. A sample of C_2H_2(g) has a pressure of 7.8 kPa. After some time a portion of it reacts to form C_6H_6(g). The pressure of the mixtrue of gases is then 3.9 kPa. Assuming constant volume and temperature, find the fraction of C_2H_2, that has undergone reaction.

13. Two moles of NH_3 are encolsed in a 5 dm^3 vessel at 300 K. Calculate the pressure exerted by this gas by using van der Waals equation. Given: $a(NH_3)$ = 422.5 kPa dm^6 mol^{-2} and $b(NH_3)$ = 37.1 cm^3 mol^{-1}.

14. A mixture of H_2 and N_2 weighing 0.116 g is collected over water at 50 °C and occupies a volume of 275 cm^3 when the total pressure is 1 atm. Calculate the composition of dry mixture in mole per cent. The vapour pressure of water at 50 °C is 0.122 atm.

15. Flask A contains a mixture of O_2, SO_2 and He in the volume ratio of 32 : 64 : 4. Flask B contains a mixture of the same gases in the mass ratio 32 : 64 : 4. Each flask is at 1.0 atm and 0 °C. Predict which of the two alternatives is true.

(a) Partial pressures of three gases are same/different in flask A.
(b) Partial pressures of three gases are same/different in flask B.
(c) Partial pressure of O_2 in flask A is greater/smaller than that in flask B.
(d) Partial pressure of SO_2 in flask A is greater/smaller than that in flask B.
(e) Partial pressure of He in flask A is greater/smaller than that in flask B.
(f) The average kinetic energy of gases in flask A will be greater/smaller than or equal to that in flask B.

16. One of the best rocket fuels is dimethylhydrazine. When mixed with dinitrogentetroxide, N_2O_4, it reacts according to the equation

$$(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \rightarrow 3N_2(g) + 4H_2O(g) + 2CO_2(g)$$

If 2.5 mol of dimethylhydrazine reacts completely with N_2O_4 and if the product gases are collected at 20 °C in a 250 L vessel, what is the pressure in the vessel?

17. 120 mL of NH_3 at 25 °C and 750 Torr was mixed with 165 mL of O_2 at 50 °C and 635 Torr and transferred to a 300-mL reaction vessel where they were allowed to react according to the equation

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

What was the total pressure (in Torr) in the reaction vessel at 150 °C after the reaction is over? Assume the reaction goes to completion.

18. A gas is collected by the displacement of water until the total pressure inside a 100-mL flask is 700 Torr at 25 °C. What volume the dry gas would occupy at STP? Given : Aqueous tension of water at 25 °C is 23.8 Torr.

19. A gas, at a total pressure of 800 Torr and a volume of 500 mL over water at 35 °C, is compressed to a volume of 250 mL, also over water at 35 °C. Calculate the final pressure of the wet gas in Torr. Given : Aqueous tension of water at 35 °C is 42.2 Torr.

20. If 250 mL of O_2 over water at 30 °C and a total pressure of 740 Torr is mixed with 300 mL of N_2 over water at 25 °C and a total pressure of 780 Torr, what will be the total pressure if the mixture is in a 500-mL vessel over water at 35 °C? Given : Aqueous tensions of water at 25 °C, 30 °C and 35 °C are 23.8, 31.8 and 42.2 Torr, respectively.

ANSWERS

1. 0.57 atm, 0.4 mol at 300 K and 0.3 mol at 400 K
2. 1838 m s^{-1}
3. 0.46 g cm^{-3}
4. 137 g mol^{-1}
5. 48.0 g mol^{-1}
6. 0.86
7. 82.05 cm^3 atm K^{-1} mol^{-1}
8. 47.0 mL
9. 8.314×10^{14} (dyn m^{-2}) (mm^3) K^{-1} mol^{-1}
10. 1.4 L^2 atm mol^{-2}
11. 0.42 CH_4
12. 75 mol %
13. 944 kPa
14. 58.73 and 41.27
15. (a) different, (b) same, (c) smaller, (d) greater, (e) smaller, (f) same.
16. 1.23 atm
17. 975 Torr
18. 81.5 mL
19. 1557.8 Torr
20. 8.71 Torr

SECTION II LIQUID STATE

VAPOUR PRESSURE

The vapour pressure of a liquid may be defined as the pressure of the vapour in equilibrium with the liquid. The vapour pressure of a liquid increases with the increase in temperature. The governing expression is

$$\log \frac{p_2}{p_1} = -\frac{\Delta_{\text{vap}} H_{\text{m}}}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta_{\text{vap}}H_{\text{m}}$ is the molar enthalpy of vaporization of the liquid.

The vapour pressure of a solvent invariably decreases when a nonvolatile solute is dissolved in it. This is due to the availability of lesser number of solvent molecules at its surface as compared to that available in pure solvent.

The boiling point of a liquid can be defined as the temperature at which its vapour pressure is equal to the external pressure. If the latter is equal to 1 atm, the corresponding temperature is known as the normal boiling point of the liquid.

SURFACE TENSION

The surface tension of a liquid is defined as the force acting along the surface of a liquid at right angle to any line of unit length. Its SI unit is N m^{-1} and is equal to 10^3 dyn cm^{-1}. The surface tension (symbol: γ) of a liquid decreases with increase in temperature. The governing expression is

$$\gamma (Mv)^{2/3} = k(t_c - t - 6)$$

where M is the molar mass, v is the specific volume and t_c is the critical temperature.

The surface active materials such as soap, salts of higher sulphonic acids and higher amines lower the surface tension of water. The cleansing action of soap or detergent solution is due to the lowering of surface tension between water and grease. The orientation of soap molecules at the surface is specific, —COO groups pointing towards the surface of water and hydrocarbon chains pointing outwardly. These hydrocarbon chains act as a solvent for the grease and thus the latter is detached from the cloth along with the dust.

The capillary action (rise or fall of a liquid level within the capillary tube) is due to the surface tension of the liquid. The expression governing this phenonmenon is given by

$$\gamma = \frac{1}{2} r\rho g l$$

where γ is surface tension, r is the radius of capillary tube, ρ is the density of liquid, g is acceleration due to gravity and l is the rise of liquid level in the capillary tube.

In a laboratory, the surface tension of a liquid can be determined by using a stalagmometer (Fig. 2.5). The liquid taken in the stalagmometer is allowed to fall dropwise. The average weight of the liquid drop is related to its surface tension by the expression

$$mg = (2\pi r)\gamma$$

where r is the radius of capillary tube of the stalagmometer. To avoid the measurement of r, the relative method is used where water (whose surface tension is known) is used as a reference liquid.

We have

For liquid : $m_l g = (2\pi r)\gamma_l$ and For water : $m_w g = (2\pi r)\gamma_w$

Hence $\gamma_l = (m_l/m_w)\gamma_w$. (2.1)

In drop-weight method, the mass of a fixed number of drops falling through the capillary tube is measured. In drop-number method, the number of drops obtained from a fixed volume of liquid is determined. We have

$$V = nv = n(m/\rho) \quad \Rightarrow \quad m = V\rho/n$$

Hence, Eq. (2.1) modifies to

$$\gamma_l = (\rho_l/\rho_w)\,(n_w/n_l)\,\gamma_w$$

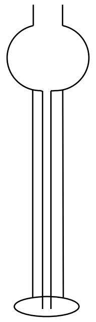


Fig. 2.5 Stalagmometer

VISCOSITY

The viscosity of a liquid is due to the forces of attraction between molecules flowing in different layers in a laminar flow of the liquid. The viscosity (or more precisely, the coefficient of viscosity) may be defined as the force per unit area required to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart. Its SI unit is N m^{-2} s. (= Pa s) and is equal to 10 dyn cm^{-2} s (= 10 poise). With increase in temperature, the viscosity of a liquid decreases due to decrease in the molecular attractions. This effect may be compared with the effect observed in gases where viscosity increases with increase in temperature. In case of gases, viscosity is due to the transfer of molecules (along with their momenta) from one layer to another.

The relation governing the variation of viscosity of a liquid with temperature is

$$\eta = A\,\exp(E/RT)$$

where A is a constant and E is the activation energy for viscous flow.

The viscosity of a liquid invariably increases with impurities. The associated liquids such as water, alcohols and glycerol have higher viscosities as compared to the nonassociated liquids (benzene, toluene, etc.).

In a laboratory, viscosity of a liquid can be determined by using a viscometer (Fig. 2.6). A fixed volume of liquid is taken in the bigger bulb of the viscometer. It is sucked into the smaller bulb and time taken to fall the liquid level from marked A to marked B is noted down. The experiment is repeated with a reference liquid (water). The expressions (known as Poiseuille equation) to be used are

$$\eta_l = \frac{\pi r^4 p_l t_l}{8lv} \quad \text{and} \quad \eta_w = \frac{\pi r^4 p_w t_w}{8lv}$$

Hence, $$\eta_l = \left(\frac{p_l\, t_l}{p_w\, t_w}\right)\eta_w$$

In the above expressions, p is the pressure due to which liquid flows in the capillary tube of viscometer. At any instant, it may be replaced by the density of the liquid. Hence

$$\eta_l = \left(\frac{\rho_l\, t_l}{\rho_w\, t_w}\right)\eta_w$$

Another method involves the falling of a steel ball in the viscous liquid. After some time, ball falls with a constant speed, such that

$$mg = 6\pi\,\eta\, rv \qquad \Rightarrow \qquad \eta = \frac{mg}{6\pi rv}$$

where r is radius of steel ball, v is the velocity the ball in the liquid and m is the mass of steel ball.

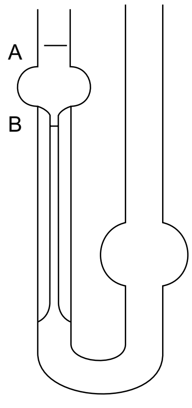


Fig. 2.6 Ostwald Viscometer

Straight Objective Type

1. Which of the following statements regarding a liquid is not correct?
(a) The vapour pressure of a liquid increases with increase in temperature
(b) The vapour pressure of a liquid decreases in the presence of a nonvolatile impurity
(c) The variation of vapour pressure with temperature is given by

$$\log p = \frac{\Delta_{\text{vap}} H_{\text{m}}}{2.303\, R}\,\frac{1}{T} + \text{constant}$$

(d) At the normal boiling point, the vapour pressure of a liquid is 1 atm.

2. Which of the following statements regarding a liquid is not correct?
(a) The surface tension of a liquid is a temperature dependent property
(b) The surface tension of a liquid is an intensive quantity.
(c) The SI unit of surface tension is N m^{-1}.
(d) For a liquid, surface tension and surface energy have different values.

3. Which of the following statements regarding a liquid is not correct?
(a) On dissolving sodium chloride in water, its surface tension decreases
(b) The variation of surface tension of a liquid is given by the expression $\gamma (Mv)^{2/3} = k(t_c - t - 6)$, where the various symbols have their usual meanings.
(c) Soap is a surface active substance
(d) 1 N m^{-1} = 10^3 dyn cm^{-1}

4. Which of the following statements regarding a liquid is not correct?
(a) The SI unit of viscosity is Pa s.
(b) 1 Pa s = 10 Poise.
(c) The viscosity of a liquid decreases with increase in temperature
(d) The viscosity of a gas decreases with increase in temperature

5. Which of the following statements is not correct?
(a) Viscosity of ethanol is smaller than that of glycol
(b) Viscosity of a liquid increases with impurities
(c) The variation of viscosity is given by $\eta = A \exp(-E/RT)$
(d) Capillary action is due to the surface tension of a liquid.

ANSWERS

1. (c) **2.** (d) **3.** (a) **4.** (d) **5.** (c)

Hints and Solutions

1. The correct expression is

$$\log p = \frac{\Delta_{\text{vap}}H_{\text{m}}}{2.303\,R}\frac{1}{T} + \text{constant}$$

2. The surface tension and surface energy has the same numerical value.
3. The surface tension of water increases when sodium chloride is dissolved in it.
4. The viscosity of a gas increases with increase in temperature.
5. The variation of viscosity of a liquid varies with temperature. The governing expression is

$$\eta = A\,\exp(E/RT)$$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

Liquid State

1. The normal boiling point of cyclohexane (enthalpy of vaporization: 30.08 kJ mol^{-1}) is 80.75 °C. What will be its vapour pressure at 25 °C?

Solution We have

$$T_1 = 80.75\ ^\circ\text{C} \equiv 353.9\ \text{K};\quad p_1 = 760\ \text{mmHg};\quad T_2 = 25\ ^\circ\text{C} \equiv 298.15\ \text{K};\quad p_2 = ?$$

Using the expression

$$\log\frac{p_2}{p_1} = -\frac{\Delta_{\text{vap}}H_{\text{m}}}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

we get

$$\log\left(\frac{p_2}{\text{mmHg}}\right) = \log(760) - \frac{30.08\times10^3\ \text{J mol}^{-1}}{(2.303)\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})}\left[\frac{1}{298.15\ \text{K}} - \frac{1}{353.9\ \text{K}}\right]$$

This gives $p_2 = 112.4$ mmHg

2. In the determination of the surface tension of a liquid A by the drop-number method, equal volumes of A and water gave 60 and 20 drops, respectively. Calculate the surface tension of A if ρ(A) = 0.86 g cm^{-3} and ρ(water) = 0.996 g cm^{-3}. Given: $\gamma(\text{H}_2\text{O}) = 72.75\times10^{-3}$ N m^{-1}.

Solution Using the expression

$$\gamma_1 = \left(\frac{\rho_1}{\rho_{\text{w}}}\frac{n_{\text{w}}}{n_1}\right)\gamma_{\text{w}}$$

we get

$$\gamma_1 = \left(\frac{0.86}{0.996}\frac{20}{60}\right)(72.75\times10^{-3}\ \text{N m}^{-1}) = 20.94\times10^{-3}\ \text{N m}^{-1}$$

3. The viscosity of diethyl ether in millipoise is 2.84 at 0 °C, 2.33 at 20 °C. Calculate the activation energy of diethyl ether for viscous flow and its viscosity at 60 °C.

Solution Using the expression $\eta = A\,\exp(E_{\text{a}}/RT)$, we get

$$\log\frac{\eta_2}{\eta_1} = \frac{E_{\text{a}}}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Hence

$$\log\left(\frac{2.33}{2.84}\right) = \frac{E_{\text{a}}}{(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})}\left[\frac{1}{293\ \text{K}} - \frac{1}{273\ \text{K}}\right]$$

This gives

$$E_{\text{a}} = -\frac{\log(2.33/2.84)(293\ \text{K})\,(273\ \text{K})\,(2.303)\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}]}{(20\ \text{K})} = 6583\ \text{J mol}^{-1}$$

For 60 °C, we will have

$$\log\left(\frac{\eta_1}{2.84}\right) = \frac{(6583\ \text{J mol}^{-1})}{(2.303)(8.314\ \text{J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{333\ \text{K}} - \frac{1}{273\ \text{K}}\right]$$

This gives $\eta_2 = 1.69$ millipoise

4. The viscosity of an oil is 0.05 N m^{-2} s and its density is 0.97 g cm^{-3} at 298 K. How long a given liquid of the oil will take to flow through a viscometer if the same volume of water takes 50 s? Given: $\eta(H_2O) = 8.9 \times 10^{-4}$ N m^{-2} s. Take $\rho(H_2O) = 1.0$ g cm^{-3}.

Solution From the expression

$$\eta_1 = \left(\frac{\rho_1 t_1}{\rho_w t_w}\right)\eta_w$$

we get

$$t_1 = \left(\frac{\eta_1}{\eta_w}\right)\left(\frac{\rho_w}{\rho_1}\right)t_w = \left(\frac{0.05}{8.9 \times 10^{-4}}\right)\left(\frac{1}{0.97}\right)(50\ \text{s}) = 2\,896\ \text{s}$$

5. A steel ball of density 7.90 g cm^{-3} and 4 mm diameter requires 55 s to fall through a distance of 1 m through a liquid of density 1.10 g cm^{-3}. Calculate the viscosity of the liquid in poise.

Solution Volume of steel ball, $V = \frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(0.2\ \text{cm})^3$

Mass of steel ball, $m = V\rho = (0.0335\ \text{cm}^3)(7.90\ \text{g cm}^{-3}) = 0.265$ g

The viscosity of liquid is

$$\eta = \frac{mg}{6\pi r v} = \frac{(0.265 \times 10^{-3}\ \text{kg})(9.8\ \text{m/s}^2)}{6(3.14)(2 \times 10^{-3}\ \text{m})(1\ \text{m}/55\ \text{s})} = 3.79\ \text{Pa s} \equiv 37.9\ \text{poise}$$

SECTION III SOLID STATE

Solids are characterized by their high density and low compressibility as compared to those of the gas phase. The values of these properties for solids indicate that the molecule (or ions) in them are relatively close together. Solids can be broadly classified into two categories, namely, crystalline and amporphous solids. The main characteristics of these are described in the following.

Crystalline Solids The outstanding characteristics of a crystal are its sharp melting point, its flat faces and sharp edges, which, in a well developed form, are usually arranged symmetrically. These properties are due to a high degree of internal order which extends throughout the crystal (a definite pattern constantly repeating in space). This is known as long-range order.

Amorphous Solids Amorphous solids do not have the long-range order but have a short-range order. In the latter, there exists some ordered arrangement around a particular atom or ion which lasts only upto short distances. This characteristics may not be found around a similar atom placed at a distance from the other atom. Examples of amorphous solids are glass, fused silica, rubber and polymers. Amorphous solids do not have the characteristics as possessed by crystalline solids. In many ways, they are more closely related to liquids than to the crystalline solids and are, therefore, regarded as supercooled liquids with high viscosity. A given material may be converted into the amorphous or glassy form by rapidly cooling the melt or freezing the vapour.

CLASSIFICATION OF CRYSTALS BASED ON BOND TYPE

The properties of most of the crystals are found to conform to one of the four general types of chemical bonds, in terms of which it is possible to classify them into four categories as described in the following.

Molecular Crystals (or van der Waals Crystals) Molecular crystals are those in which the crystalline state is composed of an aggregate of discrete molecules held together by van der Waals forces. Because of these weaker forces, molecular crystals are soft and possess comparatively low melting points. Examples are CO_2, CCl_4, Ar and most of the organic compounds.

Ionic Crystals Ionic crystals involve electrostatic forces amongst their structural units. Because of stronger forces, ionic crystals are strong and likely to be brittle. The melting points are high, which decrease with increasing size of the ions. In ionic crystals, some of the atoms may be held together by covalent bonds to form ions having definite positions and orientations in crystal lattice.

Covalent Crystals Covalent crystals involve forces of chemical nature (covalent bonds) extended in three dimensions. These forces are strong, and consequently the crystals are strong and hard, with high melting points. Examples are diamond, silicon, etc.

Metallic Crystals Electrons are held loosely in these type of crystals. They are good conductors of electricity. Metallic crystals are strong and can be bent.

SEVEN CRYSTAL SYSTEMS AND FOURTEEN BRAVAIS LATTICES

Space Lattice A space lattice represents a three-dimensional translational repetition of the centres of gravity of the unit of pattern in the crystals by means of points (known as lattice points).

Unit Cell A unit cell represents a parallelopiped obtained by connecting the lattice point such that each parallelopiped contains a complete unit of pattern of the crystal. By translation or stacking of the parallelopipeds the entire crystal structure can be generated.

Seven Crystal Systems To describe a unit cell, six parameters are required. These are the three basis vectors along the three crystallographic axes (represented by the symbols a, b and c) and the three angles between the crystallographic axes (represented by the symbols α, β and γ). Based on the presence of certain rotation axes in the unit cell, crystals can be classified into seven categories (known as seven crystal systems). These are described in Table 2.1.

Table 2.1 Seven Crystal Systems

Crystal system	*Minimum Symmetry*	*Parallelopiped dimensions*	*Examples*
Triclinic	1	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$
Monoclinic	2	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	S(monoclinic) $CaSO_4 \cdot 2H_2O$ $Na_2SO_4 \cdot 10H_2O$
Orthorhombic	222	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	S(rhombic), $BaSO_4$, KNO_3, K_2SO_4
Trigonal or Rhombohedral	3	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	$CaCO_3$
Cubic	3333	$a = b = c$ $\alpha = \beta = \gamma = 90°$	NaCl, diamond, Alums, CaF_2
Tetragonal	4	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	TiO_2, Sn(white) $ZrSiO_4$
Hexagonal	6	$a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	SiO_2, graphite, PbI_2, Mg, ZnO

Note: There is no crystal system with five-fold rotational axis, because the presence of such an axis does not satisfy the translational symmetry.

Fourteen Bravais Lattices In seven crystal systems, points are present at the corners of unit cell. Such a unit cell is known as primitive unit cell. Besides the points at the corners, there are lattices in which points are present at the centre of each face of unit cell (known as face-centered unit cell, symbol: F), or at the body centre of unit cell (known as body centred unit cell, symbol: I) or at the centre of two equivalent opposite faces (known as end-centred unit cell, symbol: C). Each of such unit cells (known as nonprimitive unit cells) also possesses the minimum rotational axes of the corresponding primitive unit cell. If such cells are counted, these are fourteen in all and are known as fourteen Bravais lattices (Table 2.2).

Table 2.2 Fourteen Bravais Lattices

Unit Cell	*Bravais Lattices*
Triclinic	P
Monoclinic	P and C
Orthorhombic	P, I, C and F
Trigonal	P
Cubic	P, I and F
Tetragonal	P and I
Hexagonal	P

PACKING IN CRYSTALLINE SOLIDS

The structure of crystalline solids is determined by the packing of their constituents. Most metals and nonmetals are found to have three types of packing. These are: (1) body-centred cubic (bcc) lattice packing, (2) hexagonal close-packed (hcp) lattice (ABAB ···, unit cell hexagon), and (3) cubical close-packed (ccp) lattice (ABCABC ···, unit cell face-centred cube). The hcp and ccp constitute the closest packings (Fig. 2.7).

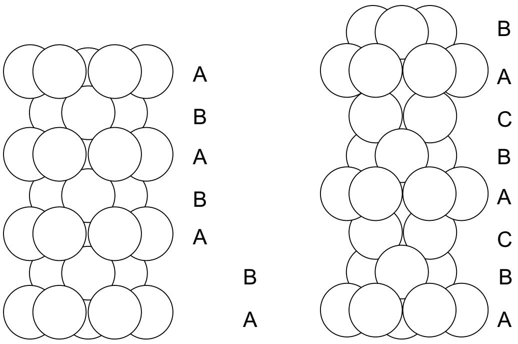


Fig. 2.7 Two Types of Packings

The total number of nearest neighbours of atom in bcc, hcp and ccp are 8, 12 and 12, respectively.

In many of the crystals, the void (or empty) spaces present in the closest-packed structures are also occupied by atoms of smaller sizes. There are two types of voides, namely, tetrahedral and octahedral. In three-dimensional closest-packed structures (hcp and ccp), there are two tetrahedral voids and one octahedral void present per closest packed atom. The two tetrahedral voids are present above and below each atom and the octahedral void is present midway between the two close-packed layers.

IONIC CRYSTALS

In ionic crystals, it is not possible for both cations and anions to have close-packed structures due to their different sizes. However, if one of the ions is bigger than the other, it is common for the bigger ions (usually anions) alone to approach a close-packed structure and smaller ions to fit into holes (or voids) in this structure. The limiting sizes of cations that can fit into these voids without disturbing the closest packing of anions are as follows.

$$\text{Octahedral void} \quad \frac{r_c}{r_a} = 0.414 \qquad\qquad \text{Tetrahedral void} \quad \frac{r_c}{r_a} = 0.225$$

A few common ionic lattices are described below.

1. *Rock-Salt Structure* In such a structure, anions form a face-centred cubic unit cell and cations occupy octahedral voids. There are four anions and four cations per unit cell of this structure, and hence, the formula of ionic compound is A_4B_4 or simply AB. Examples are NaCl, KCl, MgO, CaO and SrO.
2. *Anti-Fluorite Structure* In this, anions form a cubical-closest packing arrangement and cations occupy tetrahedral voids. There are four anions and eight cations per unit cell of this structure, and hence, the formula of the ionic compound is A_8B_4 or simply A_2B. Examples are Li_2O, Na_2O, K_2O and Rb_2O.
3. *Zinc-Blende Structure* In such a structure (also known as sphalerite structure), anions form cubical closest-packed structure and cations are present in the half of the tetrahedral holes. There are four anions and four

cations per unit cell of this structure, and hence, the formula of an ionic compound is A_4B_4 or simply AB. Examples are BeO and ZnS.

There is another polymorph of zinc sulphide in which S^{2-} ions form hexagonally close-packing and Zn^{2+} ions are present in half of the tetrahedral holes. This structure, which is known as *wurtzite structure*, also has (4,4)–coordination. Other examples of wurtzite structure are ZnO, AgI and one polymorph of SiC.

4. *Body-Centred Cubic Structure* In this structure, the cation is located at the body centre of a cube of anions, and the anion is located at the body centre of a cube of cations. There is one cation and one anion present per unit cell, and hence, the formula of an ionic compound is AB. In this structure, each ion has eight positively charged ions as its next nearest neighbours. Hence, the coordination number of each cation and anion is eight. Examples are CsCl, CsBr and CsI.
5. *Fluorite Structure* In this structure, cations form cubical-closest packing and anions occupy tetrahedral holes. Here

   Coordination number of cations = 8 Coordination number of anions = 4

   General formula : $M_{1/8}X_{1/4}$ or MX_2.

   Examples include UO_2, ThO_2 and CaF_2.
6. *Corundum Structure* In this structure, anions form hexagonal closest packing and cations are present in 2/3 of the octahedral holes. The general formula of the compound is $M_{2/3}X$ or M_2X_3. Examples include Fe_2O_3, Al_2O_3 and Cr_2O_3.
7. *Spinel Structure* In this structure, oxides are arranged in cubical-closest packing, one-eighth of the tetrahedral holes are occupied by divalent metal ion (A^{2+}) and one-half of the octahedral holes are occupied by trivalent metal ions (B^{3+}). In a unit cell, we have

   Number of divalent metal ions, $A^{2+} = \frac{1}{8}(8) = 1$ Number of trivalent metal ions, $B^{3+} = \frac{1}{2}(4) = 2$

   Number of oxide ions, $O^{2-} = 4$

   Hence, General formula of the compound: AB_2O_4. Examples are $ZnAl_2O_4$, $MgAl_2O_4$ and $ZnFe_2O_4$.

Stability of Ionic Structure Broadly, speaking, the stability of ionic structures depends upon the radius ratio of r_c and r_a. The structures predicted from the value of r_c/r_a are as follows.

Ratio	*Structure*	*Coordination number*
$\frac{r_c}{r_a} > 0.732$	Body-centred cube	8
$0.732 \geq \frac{r_c}{r_a} \geq 0.414$	face-centred cubic i.e. octahedral	6
$0.414 \geq \frac{r_c}{r_a} \geq 0.225$	tetrahedral	4

For example, chlorides of Li, K and Rb crystallize in the face-centred cubic lattice whereas the chloride of Cs crystallize in the body-centred cubic lattice.

DENSITY OF CUBIC CRYSTALS

This may be determined by using the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

where N is the number of molecules (or atoms) per unit cell, a is the edge length of the unit cell, M is the molar mass of the substance, and N_A is Avogadro's constant (= $6.022 \times 10^{23}\ \text{mol}^{-1}$).

For metallic and nonmetallic crystals, the number of atoms per cubic unit cell and the expression connecting radius of atom (r) and edge length (a) of a unit cell are as follows.

Primitive Cubic Unit Cell Atoms are present at the corners of the cube. Each of the eight atoms present at the eight corners is shared amongst eight unit cells. Hence,

$$\text{Number of atoms per unit cell} = 8\left(\frac{1}{8}\right) = 1$$

Atoms touch each other along edges. Hence, $r = a/2$

Body-Centred Cubic Unit Cell Besides atoms present at the corners of the cube, there is one atom in the centre of cube which belongs exclusively to this unit cell. Hence,

$$\text{Number of atoms per unit cell} = 8\left(\frac{1}{8}\right) + 1 = 2$$

Atoms touch each other along the cross diagonal of the cube. Hence

$$r = \left(\frac{\sqrt{3}}{4}\right) a$$

Face-Centred Cubic Unit Cell Besides atoms present at the corners of the cube, there are atoms at the centres of six faces, each of which is shared between two unit cells. Hence

$$\text{Number of atoms present per unit cell} = 8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$

Atoms touch each other along the face diagonal. Hence

$$r = \left(\frac{\sqrt{2}}{4}\right) a$$

For ionic crystals, the number of cations and anions (or molecules) per unit cell and the expressions connecting radii of cation and anion with the edge length are as follows.

Rock-Salt Structure There are four anions and four cations (i.e. four molecules) per unit cells. Cations and anions touch each along the edges. Hence,

$$N = 4$$

$$2r_c + 2r_a = a \quad \text{or} \quad r_c + r_a = \frac{a}{2}$$

Body-Centred Structure There is one anion and one cation (i.e. one molecule) per unit cell. Cation and anions touch each other along cross diagonal of the cube. Hence,

$$N = 1$$

$$2r_c + 2r_a = \sqrt{3}\, a \quad \text{or} \quad r_c + r_a = \left(\frac{\sqrt{3}}{2}\right) a.$$

PERCENTAGE OF VOID VOLUME

We calculate here the percentage of void volume in each of the three cubic Bravais lattices.

Primitive Cubic Lattice Here atoms touch each other along the edges, hence $r = a/2$. The number of atoms in a unit cell is one. Hence,

$$\text{Volume of unit cell} = a^3$$

$$\text{Volume occupied by atoms} = \frac{4}{3}\pi(a/2)^3$$

$$\text{Fraction of volume occupied} = \frac{(4/3)\pi(a/2)^3}{a^3} = \frac{\pi}{6} = 0.5236$$

Fraction of void volume = 1 – 0.5236 = 0.4764

Percentage of void volume = 47.64%

Body-Centred Cubic Lattice Here atoms touch each other along the body-diagonal of the cube, hence $4r = \sqrt{3}\, a$. The number of atoms in a unit cell is two. Hence,

$$\text{Volume of unit cell} = a^3$$

$$\text{Volume occupied by atoms} = 2\left[\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3\right]$$

$$\text{Fraction of volume occupied} = \frac{\sqrt{3}\,\pi}{8} = 0.6802$$

$$\text{Fraction of void volume} = 1 - 0.6802 = 0.3198$$

$$\text{Percentage of void volume} = 31.98\%$$

Face-Centred Cubic Lattice Here atoms touch each other along the face diagonal of the cube, hence $4r = \sqrt{2}\,a$. The number of atoms in a unit cell is two. Hence

$$N = 1$$

$$\text{Volume of unit cell} = a^3$$

$$\text{Volume occupied by atoms} = 4\left[\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3\right]$$

$$\text{Fraction of volume occupied} = \frac{\sqrt{2}\,\pi}{6} = 0.7405$$

$$\text{Fraction of void volume} = 1 - 0.7405 = 0.2595$$

$$\text{Percentage of void volume} = 25.95\%$$

POINT DEFECTS

The departure from the periodic arrangement around the vicinity of a lattice point is termed point defect. The following two types of point defects are commonly found in the crystalline ionic substances.

Schottky Defects The absence of a cation or anion from the position which it is expected to occupy in the periodic arrangement of ions is known as Schottky defect. The vacant positions give rise to vacancies or voids in the structure of the substance. The Schottky defects are more common in ionic compounds with high coordination numbers and where the positive and negative ions are of similar size, e.g. NaCl, CsCl, KCl and KBr. Since the solid with a Schottky defect contains lesser number of ions as compared to a perfect crystal, the density of the crystal exhibiting Schottky defect will be less as compared to that of the perfect crystal.

Frenkel Defect In this type of defect, the ion, instead of being in its expected location, is found in one of the interstices. Frenkel defects are more common in ionic crystals where size of the cation is such that it can be accommodated in the interstitial sites. That is, this type of defect is favoured by a large difference in size between the positive and negative ions and since the size of cation is smaller than that of the anion, the former can be accommodated in the interstitial position. Examples are ZnS, AgCl, AgBr and AgI. The density of crystals exhibiting Frenkel defects remains unchanged as the ions are present in the interstitial sites without changing the volume of the substance.

Straight Objective Type

Classification of Solids

1. Molecular solids are generally
(a) good conductors of electricity (b) quite hard
(c) quite brittle (d) volatile

2. Ionic solids are generally
(a) good conductor of electricity (b) soft
(c) volatile (d) quite brittle

3. CO_2 belongs to
(a) covalent crystal (b) molecular crystal (c) ionic crystal (d) metallic crystal

4. Which of the followings is an example of molecular crystal?
(a) CCl_4 (b) $CaCO_3$ (c) Silicon (d) Iron

5. Which of the following is an example of covalent crystal ?
(a) CCl_4 (b) $CaCO_3$ (c) Silicon (d) Iron

6. Which of the following crystal types has generally low melting point?
(a) Ionic crystals (b) Molecular crystals (c) covalent crystals (d) Metallic crystals

7. Which of the following crystal types is a good conductor of heat and electricity ?
(a) Ionic crystals (b) Molecular crystals (c) Covalent crystals (d) Metallic crystals

Crystal Systems

8. In the primitive unit cell, the points are present at the
(a) corners of the unit cell (b) centre of the unit cell
(c) centre of each face of the unit cell (d) one set of faces of the unit cell

9. In the body-centred unit cell, the points are present at the
(a) corners of unit cell only (b) corners and centre of unit cell
(c) corners and centre of each face of the unit cell (d) corners and at one set of faces of unit cell

10. In the face-centred unit cell, the points are present at the
(a) corners of unit cell only (b) corners and centre of the unit cell
(c) corners and face centres of the unit cell (d) face centres of the unit cell

11. Which of the following dimensions of a unit cell represents a cubic unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = 90° \neq \gamma$
(c) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma$

12. The number of crystal systems in which a crystal can be classified is equal to
(a) 5 (b) 7 (c) 8 (d) 10

13. The number of Bravais lattices in a cubic crystal system is equal to
(a) 1 (b) 2 (c) 3 (d) 4

14. The number of Bravais lattices in which a crystal can be classified is equal to
(a) 8 (b) 10 (c) 12 (d) 14

15. Which of the following dimensions of a unit cell represents a tetragonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$
(c) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$ (d) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$

16. $CuSO_4{\cdot}5H_2O$ belongs to
(a) triclinic system (b) cubic system (c) tetragonal system (d) hexagonal system

17. Which of the following dimensions of a unit cell represents a hexagonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$
(c) $a = b \neq c;\ \alpha = \beta = 90°,\ \gamma = 120°$ (d) $a \neq b \neq c;\ \alpha \neq b \neq \gamma \neq 90°$

18. Which of the following dimensions of a unit cell represents a trigonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$
(c) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$

19. Which of the following dimensions of a unit cell represents a orthorhomic unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$
(c) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$

20. The minimum rotational symmetry present in a triclinic unit cell is
(a) 1 (b) 2 (c) 3 (d) 4

21. The minimum rotational symmetry present in a cubic unit cell is
(a) 2 (b) 222 (c) four 3 (d) 4

22. The minimum rotational symmetry present in a monoclinic unit cell is
(a) 1 (b) 2 (c) 3 (d) 4

23. Which of the following rotational symmetry is never present in a unit cell?
(a) 2 (b) 3 (c) 4 (d) 5

24. The number of Bravais lattices having monoclinic unit cell is
(a) 2 (b) 3 (c) 4 (d) 6

25. The number of Bravais lattices having tetragonal unit cell is
(a) 2 (b) 3 (c) 4 (d) 6

26. The number of Bravais lattices having orthorhomic unit cell is
(a) 2 (b) 3 (c) 4 (d) 6

27. Which of the following has the body-centred cubic crystal lattice?
(a) NaCl (b) KCl (c) RbCl (d) CsCl

28. The number of crystallographic point groups is
(a) 7 (b) 14 (c) 32 (d) 230

29. The number of crystallographic space groups is
(a) 7 (b) 14 (c) 32 (d) 230

30. Which of the following Bravais lattices does not exit in the crystal lattice having cubic unit cell?
(a) Primitive (b) Body-centred (c) Face-centred (d) End-centred

31. The number of Bravais lattice in the crystal lattice having hexagonal cell is
(a) 1 (b) 2 (c) 3 (d) 4

32. Which of the following lattices exists only as primitive Bravais lattice?
(a) Monoclinic (b) Trigonal (c) Cubic (d) Tetragonal

33. Which of the following lattices does not have only the primitive Bravais lattice?
(a) Triclinic (b) Hexagonal (c) Monoclinic (d) Trigonal

34. Which of the following unit cells has all the three edge length and three crystallographic angles different values?
(a) Monoclinic (b) Orthorhombic (c) Cubic (d) Triclinic

35. The unit cell of graphite is
(a) Cubic (b) tetragonal (c) hexagonal (d) Orthorhombic

Packing in Crystalline Solids

36. The unit cell present in ABCABC ⋯ closest packing of atoms is
(a) hexagonal (b) tetragonal (c) face-centred cube (d) primitive cube

37. The unit cell present in ABAB ⋯ closest packing of atoms is
(a) hexagonal (b) tetragonal (c) face-centred cube (d) primitive cube

38. The number of nearest neighbours around each particle in a face-centred cubic lattice is
(a) 4 (b) 6 (c) 8 (d) 12

39. The closest packed layers in the face-centred cubic unit cell are perpendicular to
(a) the face of the cell (b) the face diagonal of the cell
(c) edges of the cell (d) the body diagonal of the cell

40. In the closest packing of atoms,
(a) the size of tetrahedral void is greater than that of octahedral void
(b) the size of tetrahedral void is smaller than that of octahedral void
(c) the size of tetrahedral void is equal to that of octahedral void
(d) the size of tetrahedral void may be greater or smaller or equal to that of octahedral void depending upon the size of atoms

41. In the closest packing of atoms, there are
(a) one tetrahedral void and two octahedral voids per atom
(b) two tetrahedral voids and one octahedral void per atom
(c) two of each tetrahedral and octahedral voids per atom
(d) one of each tetrahedral and octahedral void per atom

42. The unit cell present in the crystal lattice of diamond is
(a) cube (b) tetragonal (c) hexagonal (d) trigonal

43. In the closest packing of atoms A (radius: r_a), the radius of atom B that can be fitted into tetrahedral void is
(a) $0.155\ r_a$ (b) $0.225\ r_a$ (c) $0.414\ r_a$ (d) $0.732\ r_a$

44. In the closest packing of atoms A (radius: r_a), the radius of atom B that can be fitted into octahedral void is
(a) $0.155\ r_a$ (b) $0.225\ r_a$ (c) $0.414\ r_a$ (d) $0.732\ r_a$

45. If the same type of atoms are packed in cubical closest packing (CCP) and hexagonal closets packing (HCP), then
(a) density of HCP is smaller than that in CCP
(b) density of HCP is greater than that in CCP
(c) densities of HCP is the same as in CCP
(d) density of HCP may be smaller than or greater than or equal to the density of CCP depending upon the size of atom.

46. The closest packed layers in the cubical-closest packing are perpendicular to
(a) the face of its unit cell (b) the face-diagonal of its unit cell
(c) edges of its unit cell (d) the body diagonal of its unit cell

47. The interplanar distance between the closest packed layers in the face-centered cubic unit cell is
(a) equal to the edge length (b) equal to the half of the edge length
(c) equal to the one third of body diagonal (d) equal to the half of face diagonal.

Ionic Solids

48. Which of the following FCC structures contains cations in the alternate tetrahedral voids?
(a) Na_2O (b) ZnS (c) CaF_2 (d) CaO (2005)

49. Which of the following substances does not crystallize in the rock-salt structure?
(a) NaCl (b) KCl (c) MgO (d) CsCl

50. Which of the following statements is correct in the rock-salt structure of an ionic compound?
(a) Coordination number of cation is four whereas that of anion is six
(b) Coordination number of cation is six whereas that of anion is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

51. Which of the following statements is correct in the body-centred cubic structure of an ionic compound?
(a) Coordination number of each cation and anion is two
(b) Coordination number of each cation and anion is four
(c) Coordination number of each cation and anion is six
(d) Coordination number of each cation and anion is eight

52. The general formula of an ionic compound crystallizing in the rock-salt structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

53. The general formula of an ionic compound crystallizing in the body-centred cubic structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

54. Which of the following statements is correct in the zinc-blende type structure of an ionic compound?
(a) Coordination number of each cation and anion is two
(b) Coordination number of each cation and anion is four
(c) Coordination number of each cation and anion is six
(d) Coordination number of each cation and anion is eight

55. The general formula of an ionic compound crystallizing in zinc-blende structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

56. Which of the following statements is correct in the antifluorite structure of an ionic compound?
(a) Coordination number of anion is four and that of cation is eight
(b) Coordination number of anion is eight and that of cation is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

57. The general formula of an ionic compound crystallizing in antifluorite structure is
(a) AB (a) AB_2 (c) A_2B (d) AB_3

58. Which of the following statements is correct in the cubic-fluorite structure of an ionic compound?
(a) Coordination number of anion is four and that of cation is eight
(b) Coordination number of anion is eight and that of anion is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

59. The general formula of an ionic compound having cubic-fluorite structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

60. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(a) CA (b) CA_2 (c) C_2A_3 (d) C_3A_2

61. In the spinel structure, oxides ions are cubical-closest packed whereas 1/8th of tetrahedral voids are occupied by A^{2+} cations and 1/2 of octahedral voids are occupied by B^{3+} cations. The general formula of the compound having spinel structure is
(a) $A_2B_2O_4$ (b) AB_2O_4 (c) $A_2B_4O_2$ (d) $A_4B_2O_2$

62. In a cubic unit cell, seven of the eight corners are occupied by atoms A and centres of faces are occupied by atoms B. The general formula of the compound is
(a) A_7B_6 (b) A_7B_{12} (c) A_7B_{24} (d) $A_{24}B_7$

63. An ionic compound is expected to have octahedral structure if r_c/r_a lies in the range of
(a) 0.414 to 0.732 (b) 0.732 to 0.82 (c) 0.225 to 0.414 (d) 0.155 to 0.225

64. An ionic compound is expected to have tetrahedral structure if r_c/r_a
(a) lies in the range of 0.414 to 0.732 (b) lies in the range of 0.225 to 0.414
(c) lies in the range of 0.155 to 0.225 (d) is more than 0.732

65. An ionic compound is expected to have body-centred cubic unit cell if r_c/r_a
(a) is greater than 0.732 (b) lies in the range of 0.414 to 0.732
(c) lies in the range of 0.225 to 0.414 (d) lies in the range of 0.155 to 0.225

66. A compound formed by elements A and B crystallises in a cubic structure where A atoms are at the corners of a cube and B atoms are the face-centres of the cube. The formula of the compound is
(a) AB_4 (b) AB_3 (c) AB_2 (d) AB

67. The 8 : 8 type packing is present is
(a) NaCl (b) CaF_2 (c) CrCl (d) KCl

68. The coordination number of a metal crystalling in a hexagonal close packed structure is
(a) 12 (b) 4 (c) 8 (d) 6 (2000)

69. In a solid 'AB' having the NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4 (2001)

70. A substance $A_x B_y$ crystallizes in a face centered cubic (FCC) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance $A_x B_y$
(a) AB_3 (b) A_4B_3
(c) A_3B (d) Composition cannot be specified (2002)

71. If $r(\mathrm{Na^+})/r(\mathrm{Cl^-}) = 0.5$ and $r(\mathrm{Na^+})/r(\mathrm{K^+}) = 0.7$, then the ratio $a(\mathrm{KCl})/a(\mathrm{NaCl})$ of edge lengths of unit cell is about
(a) 1.14 (b) 1.24 (c) 1.34 (d) 1.44

Density of Crystalline Solids

72. The expression to compute the density of metals crystallizing in cubic crystal is
(a) $\rho = \dfrac{N}{a^3}\left(\dfrac{M}{N_A}\right)$ (b) $\rho = \dfrac{N}{a^3}\left(\dfrac{N_A}{M}\right)$ (c) $\rho = \dfrac{a^3}{N}\left(\dfrac{M}{N_A}\right)$ (d) $\rho = \dfrac{a^3}{N}\left(\dfrac{N_A}{M}\right)$

73. The number of atoms in a single primitive cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 8

74. The number of atoms in a single body-centred cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 8

75. The number of atoms in a single face-centred cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 6

76. In the primitive cubic unit cell of closest packed atoms, the radius of atom in terms of edge length (a) of unit cell is
(a) $a/2$ (b) $a/2\sqrt{2}$ (c) $\sqrt{3}\,a/4$ (d) $4a/\sqrt{3}$

77. In the body-centred cubic unit cell of closest packed atoms, the radius of atom in terms of edge length (a) of the unit cell is
(a) $a/2$ (b) $a/\sqrt{2}$ (c) $a/2\sqrt{2}$ (d) $\sqrt{3}\,a/4$

78. In the face-centred cubic unit cell of closest packed atoms, the radius of atoms in terms of edge length (a) of the unit cell is
(a) $a/2$ (b) $a/\sqrt{2}$ (c) $a/2\sqrt{2}$ (d) $\sqrt{3}\,a/4$

79. Which of the following expressions is correct in case of a sodium chloride unit cell (edge length, a)?
(a) $r_c + r_a = a$ (b) $r_c + r_a = a/2$ (c) $r_c + r_a = 2a$ (d) $r_c + r_a = \sqrt{2}\,a$

80. Which of the following expressions is correct in case of a CsCl unit cell (edge length, *a*)?
(a) $r_c + r_a = a$ (b) $r_c + r_a = a/\sqrt{2}$ (c) $r_c + r_a = \sqrt{3}\,a/2$ (d) $r_c + r_a = a/2$

81. In a closest Rock-salt structure (edge length, *a*), which of the following expressions is correct?
(a) $r_a = \sqrt{2}\,a$ (b) $r_a = a/\sqrt{2}$ (c) $r_a = a/\ 2\sqrt{2}$ (d) $r_a = a/4$

82. The unit cell length of sodium chloride crystal is 564 pm. Its density would be
(a) 1.082 g cm^{-3} (b) 2.165 g cm^{-3} (c) 3.247 g cm^{-3} (d) 4.330 g cm^{-3}

83. The cubic unit cell of aluminium (molar mass 27.0 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g cm^{-3}. The unit cell is
(a) primitive (b) face-centred (c) body-centred (d) end-centred

84. A substance has a density of 1.984 g cm^{-3} and it crystallizes in the face-centred cubic crystal with edge length equal to 630 pm. The molar mass of the substance is
(a) 37.35 g mol^{-1} (b) 56.02 g mol^{-1} (c) 74.70 g mol^{-1} (d) 65.36 g mol^{-1}

85. Ammonium chloride crystallizes in a body-centred cubic lattice with edge length of unit cell equal to 387 pm. If the size of Cl^- ion is 181 pm, the size of NH_4^+ ion would be
(a) 116 pm (b) 154 pm (c) 174 pm (d) 206 pm

86. The edge length of unit cell of sodium chloride is 564 pm. If the size of Cl^- ion is 181 pm, the size of Na^+ ion would be
(a) 101 pm (b) 167 pm (c) 202 pm (d) 383 pm

87. In sodium chloride crystal, the number of nearest neighbours of each Na^+ ion is
(a) 8 Cl^- ions (b) 8 Na^+ ions (c) 6 Cl^- ions (d) 12 Cl^- ions

88. In sodium chloride crystal, the number of next nearest neighbours of each Na^+ ion is
(a) 8 Cl ions (b) 12 Na^+ ions (c) 12 Cl^- ions (d) 24 Cl^- ions

89. If *a* is the edge length of unit cell of sodium chloride, the distance between the nearest Na^+ and Cl^- ion is
(a) a (b) $\sqrt{2}$ a (c) $a/2$ (d) $\sqrt{3}\,a$

90. If *a* is the edge length of unit cell of sodium chloride, the distance between two nearest Na^+ ions is
(a) a (b) $\sqrt{2}\,a$ (c) $\sqrt{3}\,a$ (d) $a/\sqrt{2}$

91. Lithium iodide occurs as cubical-closest packing. If the edge length of a unit cell is 624 pm, the ionic radii of Li^+ and I^- ions respectively would be
(a) 91.35 pm, 220.65 pm (b) 220.65 pm, 91.35 pm
(c) 182.7 pm, 110.32 pm (d) 110.32 pm, 182.7 pm

92. Chromium crystallizes with a body-centred cubic lattice with unit-cell edge length equal to 287 pm. The atomic radius of chromium atom is about
(a) 143.5 pm (b) 135.0 pm (c) 124.3 pm (d) 95.7 pm

93. A metal crystallises into two cubic phases, FCC and BCC with unit cell length equal to 3.5 Å and 3.0 Å, respectively. The ratio of densities of FCC and BCC is about
(a) 1.15 (b) 1.26 (c) 1.40 (d) 1.51

94. Silver has an atomic radius of 144 pm. The density of silver is 10.6 g cm^{-3}. The type of cubic crystal of silver is
(a) primitive (b) body-centred (c) face-centred (d) end-centred

95. Potassium has a body-centred cubic structure with the nearest neighbour distance 452 pm. Its density would be
(a) 1.01 g cm^{-3} (b) 0.91 g cm^{-3} (c) 0.81 g cm^{-3} (d) 0.71 g cm^{-3}

96. Ammonium chloride crystallizes in a body-centred cubic lattice with a unit distance of 387 pm. If the size of NH_4^+ is 154 pm, the size of Cl^- ion would be
(a) 90.5 pm (b) 119.6 pm (c) 39.5 pm (d) 181 pm

97. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X–ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is
(a) 5.96×10^{-2} (b) 5.96×10^{-1} (c) 5.96×10^{-3} (d) 5.96 (2003)

Void Volume in Cubic Unit Cells

98. The fraction of volume occupied by atoms in a primitive cubic unit cell is
(a) 0.48 (b) 0.52 (c) 0.55 (d) 0.68

99. The fraction of volume occupied by atoms in a body-centred cubic unit cell is
(a) 0.32 (b) 0.48 (c) 0.68 (d) 0.74

100. The fraction of volume occupied by atoms in a face-centred cubic unit cell is
(a) 0.32 (b) 0.48 (c) 0.68 (d) 0.74

Point Defects

101. Which of the following statements for crystals having Schottky defect is not correct?
(a) Schottky defect arises due to the absence of a cation or anion from the position which it is expected to occupy.
(b) Schottky defects are more common in ionic compounds with high coordination numbers.
(c) The density of the crystals having Schottky defect is larger than that of the perfect crystal.
(d) The crystal having Schottky defect is electrical neutral as a whole.

102. Which of the following statements for crystals having Frenkel defect is not correct?
(a) Frenkel defects are observed where the difference in sizes of cations and anions is large.
(b) The density of crystals having Frenkel defect is lesser than that of a pure perfect crystal.
(c) In an ionic crystal having Frenkel defect may also contain Schottky defect.
(d) Pure alkali halides do not have Frenkel defect.

103. The composition of a sample of wüstite is $Fe_{0.93}O_{1.00}$. The percentage of Fe(III) ions present in the sample is about
(a) 10% (b) 15% (c) 20% (d) 25%

104. A sample of wüstite Fe_xO contains one Fe(III) for every three Fe(II). The value of x is
(a) 9/8 (b) 8/9 (c) 3/4 (d) 4/3

105. Which of the following statements is not correct?
(a) The density of the crystal exhibiting Schottky defect is lesser than that of a perfect crystal
(b) The density of the crystal exhibiting Frenkel defect is lesser than that of a perfect crystal
(c) the Schottky defects are more common in ionic compounds with high coordination numbers and where the sizes of ions are small
(d) In alkali halides, Frenkel defects are not found

106. Which of the following statements is not correct?
(a) AgBr shows both Schottky and Frenkel defects
(b) Ferrous oxide can be prepared in its stoichiometric composition
(c) Cationic holes in an ionic crystals impart electrical conductivity to the crystal
(d) Zinc oxide gives a yellow coloured nonstoichiometric compound on heating.

107. Bragg equation for the scattering of X-rays by crystals is
(a) $n\lambda = d \sin \theta$ (b) $n\lambda = 2\, d \sin \theta$ (c) $\lambda = nd \sin \theta$ (d) $\lambda = (n/d) \sin \theta$

Multiple Correct Choice Type

1. Which of the following statements is/are correct?
(a) The coordination number of each type of ion in CsCl crystal is 8.
(b) A metal that crystallises in bcc structure has a coordination number of 12.
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(d) The length of the unit cell in NaCl is 552 pm. (r_{Na^+} = 95 pm, r_{Cl^-} = 181 pm)

2. In the crystal lattice of sodium chloride,
(a) there are six nearest neighbouring anions around a cation.
(b) there are twelve neighbouring cations around a cation.
(c) there are eight next nearest neighbouring anions around a cation.
(d) there are six next nearest neighbouring cation around a cation.

3. For a compound AB crystallises in a body-centred cubic lattice with a as the edge length of unit cell,
(a) the minimum distance between A and A is a
(b) the mean distance between A and B is $\sqrt{3}a/2$
(c) the density of crystal is given by $\rho = \dfrac{2}{a^3}\dfrac{M_{AB}}{N_A}$
(d) the minimum distance between B and B is $a/2$

4. For a compound AB crystallises in a rock salt structure with edge length *a* of the unit cell,

(a) the minimum distance between A and A is $a/\sqrt{2}$
(b) the minimum distance between B and B is $a/\sqrt{2}$
(c) The minimum distance between A and B is $a/2$
(d) the density of the crystal is given by $\rho = \frac{4}{a^3}\frac{M_{AB}}{N_A}$

5. Which of the following statements are correct?

(a) Amorphous solids have long-range order.
(b) Crystalline solids have flat faces and sharp edges.
(c) Amorphous solids may be classified as supercooled liquids with high viscosity.
(d) Amorphous solids have sharp melting points.

6. Which of the following statements are correct?

(a) Ionic crystals do not have long range order.
(b) Ions in ionic crystals can have coordination number of 12.
(c) Atoms in metallic crystals can have maximum coordination number of 12.
(d) The closest-packed layer in a cubical-closest packing is perpendicular to the body diagonal of its unit cell.

7. Which of the following statements are correct?

(a) The coordination number of an atom of a metal crystallizing in the body-centred cubic crystal is six.
(b) The coodination number of Na^+ ions in sodium chloride crystals is six.
(c) The nearest distance between Na^+ ions in sodium chloride crystal is equal to the edge length of its unit cell.
(d) The nearest distance between two like ions in an ionic crystal crystallizing in the body-centred cubic lattice is equal to the edge length of its unit cell.

8. Which of the following statements are correct?

(a) The void volume in a cubical-closest packing is 26%.
(b) The void volume in a metallic crystal crystallized as body-centered cubic crystal is 26%.
(c) Of the three unit cells, namely, primitive, body-centred and face-centred cube, the percentage of volume occupied by atoms is maximum in case of primitive unit cell.
(d) The cubical–closest packing is of the type ABAB... .

9. Which of the following statements are not correct?

(a) The closest-packing ABAB ... is known as hexagonal-closest packing.
(b) The closest-packing ABCABC ... is known as cubical-closest packing.
(c) The coordination number of A in the closest-packing ABAB ... is six.
(d) A metal crystallizes in body-centred cubic crystals. The coordination number of its atom is four.

10. Which of the following statements are not correct?

(a) The coordination number of a cation in the fluorite structure is eight.
(b) The coordination number of an anion in the fluorite structure is eight.
(c) The coordination number of a cation in the antifluorite structure is four.
(d) The coordination number of an anion in the antifluorite structure is four.

11. Which of the following statements are not correct?

(a) The coordination number of a cation in the zinc blende structure is four.
(b) The coordination number of an anion in the zinc blende structure is eight.
(c) An ionic compound has $r_c/r_a = 0.79$. The most probable structure of this compound will be face-centred cube.
(d) An ionic compound has $r_c/r_a = 0.65$. The most probable structure of this compound will be body-centred cube.

12. Which of the following statements are **not** correct?

(a) For an inonic compound crystallizing in the face-centred cubic structure, the value of r_c/r_a must lie in the range of 0.414 to 0.732.
(b) An ionic compound crystallizes as body-centred cubic lattice. The number of molecules per unit cell of this compound is two.

(c) An ionic compound crystallizes as rock-salt structure. The number of molecules per unit cell of this compound is eight.
(d) In antifluorite structure, cations occupy tetrahedral voids and anions form cubical-closest packing.

13. Which of the following statements are correct?
(a) In fluorite structure, tetrahedral voids are occupied by anions.
(b) In zinc-blende structure, half of tetrahedral voids are occupied by cations.
(c) In rock-salt structure, cations occupy tetrahedral voids.
(d) The general formula of an ionic compound crystallizing in antifluorite structure is A_2B.

14. Which of the following statements are not correct?
(a) The general formula of an ionic compound crystallizing in fluorite structure is AB.
(b) The general formula of an ionic compound crystallizing in zinc-blende structure is AB.
(c) The general formula of an ionic compound crystallizing in body-centred cubic structure is AB.
(d) The general formula of ani ionic compound crystallizing in corundum structure is AB.

15. Which of the following statements are correct?
(a) In corundum structure anions form hexagonal closest packing and cations occupy 2/3 of octahedral voids.
(b) In the sodium chloride structure, each Na^+ ion is surrounded by six Cl^- ions nearest neighbours and 12 Na^+ ions next nearest neighbours.
(c) The density of a crystal exhibiting Schottky defect is the same as that of its perfect crystal.
(d) A crystal exhibiting Frenkel defect involves the absence of a few cations and anions at their expected positions.

16. The correct statement(s) regarding defects in solids is (are)
(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
(b) Frenkel defect is a dislocation defect
(c) Trapping of an electron in the lattice leads to the formation of F-center
(d) Schottky defects have no effect on the physical properties of solids. (2009)

Linked Comprehension Type

1. Atoms of a substance in a solid can be closely packed resulting into either cubical-closest packing or hexagonal closest packing.
(i) Which of the following facts regarding their densities is correct?
(a) cubical closest packing > hexagonal closest packing
(b) cubical closest packing < hexagonal closest packing
(c) cubical closest packing = hexagonal closest packing
(d) cubical closest packiing > or < or = hexagonal closest packing depending upon the actual size of atoms.
(ii) The coordination number of atoms in closest packing is
(a) 4 (b) 6 (c) 8 (d) 12
(iii) The distance between the two-closest packed layers in terms of radius r of atom is
(a) $4r/\sqrt{6}$ (b) $\sqrt{6}\,r/4$ (c) $(2/3)r$ (d) $(1/2)r$

2. Atoms in a solid can be closely packed resulting into either cubical-closest packing or hexagonal closest packing. There exists two types of voids, namely, tetrahedral and octahedral.
(i) The number of tetrahedral and octahedral voids per atom respectively are
(a) 2 and 1 (b) 1 and 2 (c) 1 and 1 (d) 2 and 2
(ii) The sizes of voids follow the expression
(a) tetrahedral > octahedral (b) tetrahedral < octahedral
(c) tetrahedral = octahedral (d) tetrahedral > or < or = octahedral
(iii) In between the two closest packed layers, octahedral voids are situated
(a) near the top of the bottom layer (b) near the bottom of the top layer
(c) at the centre of two layers (d) randomly between the two layers

3. Atoms in solid can be closely packed resulting into either cubical-closest packing or hexagonal closest packing.
(i) Which of the following arrangements of occupancy of sites is correct in cubical-closest packing ?
(a) ABABAB... (b) ABCABCABC... (c) ABBAAB... (d) ABCACBABC...

(ii) The unit cell of cubical-closest packing is
(a) primitive cubic (b) body-centred cubic
(c) face-centred cubic (d) not known

(iii) The maximum size of atoms that can be fitted into octahedral voids in terms of radius r of atoms closely packed is
(a) $0.414\ r$ (b) $0.225\ r$ (c) $0.372\ r$ (d) $0.680\ r$

4. In a cubical packing of atoms, the arrangement of atoms may result into primitive (P), body-centred (I) and face-centred (F) cubical unit cell. Identify the correct choice in the following.

(i) The percentages of void volume follow the expression
(a) P : I : F :: 47.64 : 31.98 : 25.95 (b) P : I : F :: 47.64 : 25.95 : 31.98
(c) P : I : F :: 31.98 : 47.64 : 25.95 (d) P : I : F :: 31.98 : 25.95 : 47.64

(ii) The sizes of atoms in terms of the respective edge-length of the unit cell follow the expression
(a) P : I : F :: $a/2 : (\sqrt{2}/4)a : (\sqrt{3}/4)a$ (b) P : I : F :: $a/2 : (\sqrt{3}/4)a : (\sqrt{2}/4)a$
(c) P : I : F :: $(\sqrt{2}/4)a : a/2 : (\sqrt{3}/4)a$ (d) P : I : F :: $(\sqrt{2}/4)a : (\sqrt{3}/4)a : a/2$

(iii) The coordination numbers of atoms follow the expression
(a) P : I : F :: 12 : 6 : 8 (b) P : I : F :: 12 : 8 : 6
(c) P : I : F :: 6 : 8 : 12 (d) P : I : F :: 6 : 12 : 8

5. 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 sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely 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 spheres 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'.

(i) The number of atoms in this HCP unit cell is
(a) 4 (b) 6 (c) 12 (d) 17

(ii) The volume of this HCP unit cell is
(a) $24\sqrt{2}\,r^3$ (b) $16\sqrt{2}\,r^3$ (c) $12\sqrt{2}\,r^3$ (d) $(64/3\sqrt{3})r^3$

(iii) The empty space in this HCP unit cell is
(a) 74% (b) 47.6% (c) 32% (d) 26%

6. One of the common crystal systems has a cubic unit cell. Based on this, answer the following three queries.

(i) The crystallographic dimensions of this unit cell is
(a) $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$ (b) $a = b \neq c$; $\alpha = \beta = \gamma = 90°$
(c) $a = b = c$; $\alpha = \beta = \gamma = 90°$ (d) $a = b = c$; $\alpha = \beta = \gamma \neq 90°$

(ii) The example of the substance having cubic unit cell is
(a) graphite (b) diamond (c) SiO_2 (d) KNO_3

(iii) The Bravais lattice of this unit cell is/are
(a) P (b) P, F (c) P, F, C (d) P, I, F

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement –1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explanation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	Statement–2
1.	The densities of crystals of the same substance exhibiting Frenkel defects remain unchanged.	The ions present in the interstitial sites do not change the overall volume of the substance.
2.	In an ionic solid MX with Schottky defects, the number of positive and negative ions are same.	Equal number of cations and anions vacancies are present.

3.	The densities of crystals of the same substance exhibiting Schottky defects is less as compared to that of its perfect crystal.	The substance exhibiting Schottky defects involves vacant sites without the change in volume.
4.	ZnS has different densities in zinc blende and wurtzite structures.	Zn crystallises in cubical closest packing in zinc blende structure and in hexagonal packing in wurtzite structure.
5.	Tetragonal system does not have end-centred lattice.	There are two types of faces in tetragonal unit cell.
6.	Cubic system does not have end-centred Bravais lattice.	All the six sides of cubic unit cell are identical.
7.	The unit cell of KCl as determined from X-ray studies appears to have primitive cubic unit cell.	The X-rays diffraction experiment cannot distinguish between K^+ and Cl^- ion due to isoelectronic species.
8.	Fluorite and anti-fluorite structures have different void volume per unit cell.	Fluorite structure involves cubical-closest packing of cations while antifluorite involves anions.
9.	Diamond structure is based on a face-centred cubic lattice.	Only the lattice points are occupied by carbon atoms.

Matrix Match Type

1. Match the crystal systems/unit cells mentioned in Column I with their characteristic features mentioned in Column II.

Column I	**Column II**
(a) simple cubic and face-centred cubic	(p) have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
(b) cubic and rhombohedral	(q) are two crystal systems
(c) cubic and tetragonal	(r) have only two crystallographic angles of 90°
(d) hexagonal and monoclinic	(s) belong to same crystal system

2. Match the crystal system/unit cells mentioned in Column I with the crystallographic parameters given in Column II.

Column I	**Column II**
(a) Trigonal	(p) $a = b = c$
(b) Tetragonal	(q) $a = b \neq c$
(c) Hexagonal	(r) $a \neq b \neq c$
(d) Orthorhombic	(s) $\alpha = \beta = \gamma = 90°$
	(t) $\alpha = \beta = \gamma \neq 90°$
	(u) $\alpha = \beta = 90°,\ \gamma = 120°$

3. Match the Bravais lattices mentioned in Column I with the crystal systems mentioned in Column II.

Column I	**Column II**
(a) Primitive	(p) Triclinic
(b) End-Centred	(q) Monoclinic
(c) Face-Centred	(r) Orthorhombic
(d) Body-Centred	(s) Trigonal
	(t) Tetragonal
	(u) Hexagonal

4. Match the unit cell of ionic compounds mentioned in Column I with the coordination numbers of cations and anions given in the Column II

Column I	**Column II**
(a) Rock salt structure	(p) 4 : 8
(b) Fluorite structure	(q) 4 : 4
(c) Anti-fluorite structure	(r) 6 : 6
(d) Zinc-blende structure	(s) 8 : 4

ANSWERS

Straight Objective Type

1. (d)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (b)	**7.** (d)
8. (a)	**9.** (b)	**10.** (c)	**11.** (a)	**12.** (b)	**13.** (c)	**14.** (d)
15. (b)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (d)	**20.** (a)	**21.** (c)
22. (b)	**23.** (d)	**24.** (a)	**25.** (a)	**26.** (c)	**27.** (d)	**28.** (c)
29. (d)	**30.** (d)	**31.** (d)	**32.** (b)	**33.** (c)	**34.** (d)	**35.** (c)
36. (c)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (b)	**41.** (b)	**42.** (a)
43. (b)	**44.** (c)	**45.** (c)	**46.** (d)	**47.** (c)	**48.** (b)	**49.** (d)
50. (d)	**51.** (d)	**52.** (a)	**53.** (a)	**54.** (b)	**55.** (a)	**56.** (b)
57. (c)	**58.** (a)	**59.** (b)	**60.** (c)	**61.** (b)	**62.** (c)	**63.** (a)
64. (b)	**65.** (a)	**66.** (b)	**67.** (c)	**68.** (a)	**69.** (d)	**70.** (a)
71. (a)	**72.** (a)	**73.** (a)	**74.** (c)	**75.** (c)	**76.** (a)	**77.** (d)
78. (c)	**79.** (b)	**80.** (c)	**81.** (c)	**82.** (b)	**83.** (b)	**84.** (c)
85. (b)	**86.** (a)	**87.** (c)	**88.** (b)	**89.** (c)	**90.** (d)	**91.** (a)
92. (c)	**93.** (b)	**94.** (c)	**95.** (b)	**96.** (d)	**97.** (c)	**98.** (b)
99. (c)	**100.** (d)	**101.** (c)	**102.** (b)	**103.** (b)	**104.** (a)	**105.** (b)
106. (b)	**107.** (b)					

Multiple Correct Choice Type

1. (a), (c), (d)	**2.** (a), (b), (c), (d)	**3.** (a), (b)	**4.** (a), (b), (c), (d)
5. (b), (c)	**6.** (c), (d)	**7.** (b), (d)	**8.** (a), (d)
9. (c), (d)	**10.** (b), (d)	**11.** (b), (c), (d)	**12.** (b), (c)
13. (a), (b), (d)	**14.** (a), (d)	**15.** (a), (b)	**16.** (b), (c)

Linked Comprehension Type

1. (i) (c)	(ii) (d)	(iii) (a)
2. (i) (a)	(ii) (b)	(iii) (c)
3. (i) (b)	(ii) (c)	(iii) (a)
4. (i) (a)	(ii) (b)	(iii) (c)
5. (i) (b)	(ii) (a)	(iii) (d)
6. (i) (c)	(ii) (b)	(iii) (d)

Assertion and Reason Type

1. (a)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (b)	**6.** (a)	**7.** (a)
8. (d)	**9.** (c)					

Hints and Solutions

Straight Objective Type

Classification of Solids

1. Molecular solids are volatile.
2. Ionic solids are quite brittle.
3. Carbon dioxide is a molecular solid.
4. CCl_4 is an example of molecular crystal.
5. Silicon is an example of covalent crystal.
6. Molecular crystals generally have low melting point.
7. Metallic crystal are good conductor of heat and electricity.

Crystal System

8. In a primitive unit cell, the points are present at the corners of the unit cell.
9. In a body-centred unit cell, the points are present at the corners and at the centre of unit cell.
10. In a face-centred unit cell, the points are present at the corners and at the centre of faces of unit cell.
11. For a cubic unit cell $a = b = c$, $\alpha = \beta = \gamma = 90°$.
12. There are seven crystal systems.
13. A cubic crystal system has three Bravais lattices; Primitive, Body-centred, Face-centred.
14. There are fourteen Bravais lattices.
15. For tetragonal unit cell, $a = b \neq c$, $\alpha = \beta = \gamma = 90°$.
16. $CuSO_4 \cdot 5H_2O$ belongs to triclinic system.
17. For a hexagonal unit cell, $a = b \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$
18. For a trigonal unit cell, $a = b = c$; $\alpha = \beta = \gamma \neq 90°$
19. For a orthorhombic unit cell, $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
20. Triclinic unit cell has 1-fold rotational axis.
21. Cubic unit cell is characterised by four 3-fold rotational axes.
22. Monoclinic unit all has 2-fold rotational axis.
23. Five fold rotational axis is never present in a unit cell.
24. Monoclinic unit cell has two Bravais lattices, primitive and end-centred
25. Telragonal unit cell has two Bravais lattices: primitive and body-centred
26. Orthorhomic unit cell has four Bravais lattice : primitive, body-centred, end-centred and face-centred.
27. NaCl, KCl and RbCl crystallize as face-centred cubic lattice while CsCl crystallizes as body-centred cubic until cell
28. There are 32 point groups.
29. There are 230 space groups.
30. Cubic unit cell has only three Bravais lattices: primitive, body-centred and face-centred.
31. Hexagonal unit cell has only primitive unit cell.
32. Triogonal amongst the given unit cells has only primitive unit cell.
33. Monoclinic amongst the given unit cells has Bravais lattices other than primitive one.
34. Triclinic unit cell has all three sides and three angles different from each other.
35. Graphite has hexagonal unit cell.

Packing in Crystalline Solids

36. The packing ABCABC ... is known as face-centred cubical packing.
37. The packing ABAB ... is known as hexagonal packing.
38. The face-centred cubical closing packing involves twelve coordination number.
39. The closest packed layers in the face-centred cubic unit cell are perpendicular to the body diagonal of the cube.
40. The size of octahedral void is greater than that of tetrahedral void.
41. There are two tetrahedral voids and one octahedral void per atom in a cubical-closest packing.
42. The unit cell of diamond is a cube.
43. In the closest packing of atoms A, the size of atom B that can be fitted into tetrahedral void is $0.225r_c$.
44. For the atom B to fit into octahedral void created within the closest packing of atom A is $0.414r_a$.
45. Both ccp and HCP are closest packed, they have the same density.
46. The closest packed layers are along the perpendicular direction of body diagonal of a cube.
47. Along the body diagonal of a cube, there are three closest-packed layers.
48. Na_2O has an anti-fluorite structure in which anions form a cubical-closest packing and cations occupy tetrahedral voids.

ZnS has a zinc-blende structure in which anions form a cubical-closest packing and cations are present in half of the alternate tetrahedral voids.

CaF_2 has a fluorite structure in which cations form cubical-closest packing and anions occupy tetrahedral voids.

CaO has a rock-salt structure in which anions form a face-centred cubic unit cell and cations occupy octahedral voids.

Ionic Solids

49. CsCl has body-centred cubical packing.

50. The coordination number of each cation and anion is six in the rock-salt structure (which involves face-centred cubic unit cell).

51. The coordination number of each cation and anion is eight in the body-centred cubic structure of an ionic compound.

52. The rock-salt structure involves face-centred cubic unit cell. It has four cations and four anions per unit cell. The formula of ionic compound will be A_4B_4, i.e. AB.

53. In the body-centred cubic unit cell of an ionic compound, there will be one cation and one anions per unit cell. Hence, the formula is AB.

54. In zinc-blende structure, cations are present in tetrahedral holes. Hence, the coordination number of each cation and anion is four.

55. In zinc-blende structure, there are four cations and four anions per unit cell. Hence, the formula will be A_4B_4 or simply AB.

56. Cations occupy tetrahedral holes. The coordination number is four. There are eight tetrahedral holes around an anion; its coordination number is eight.

57. In anti-fluorite structure, anions form cubical-closest packing and cations occupy tetrahedral holes. There are four anions and eight cations per unit cell. Hence, its formula is A_8B_4, i.e. A_2B.

58. In cubic-fluorite structure, cations form face-centred cubical packing and anions occupy tetrahedral holes. There are eight anions and four cations per unit cell. The coordination number of anion is four while that of cation is eight.

59. See Q.58. The formula is AB_2.

60. There is one octahedral hole per atom in closest packing. Hence, the formula is $C_{2/3}A$, i.e. C_2A_3.

61. In cubical-closest packing, there will be four oxide anions, $8 \times 1/8 = 1$ A^{2+} cation and $4 \times 1/2 = 2$ B^{3+} cations. Hence, its structure will be AB_2O_4.

62. The general formula will be $A_{7/8}B_3$, i.e. A_7B_{24}.

63. For the octahedral structure, the ratio r_c/r_a lies in the range of 0.414 to 0.732.

64. For the tetrahedral structure, the ratio r_c/r_a lies in the range of 0.225 to 0.414.

65. For the body-centred cubic structure, the ratio r_c/r_a is greater that 0.732.

66. Three is 1/8th contrubition for the atoms occupying corners and 1/2 contribution from the atoms occupying the centres of faces. Since there are eight corners and six faces of a cube, the molecular formula will be AB_3.

67. Body-centred cubic unit cell has 8:8 coordination numbers. CsCl is such an example.

68. The coordination number of an atom of a metal crystallized in a hexagonal close-packed structure is twelve. There are six atoms in the same plane and three each above and below this plane.

69. The structure of AB is shown in Fig. 2.8

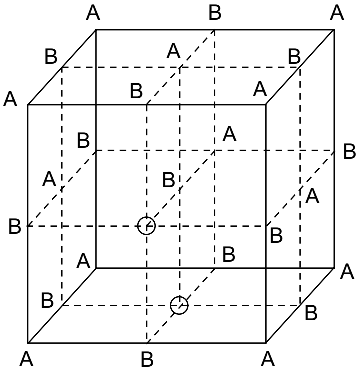


Fig. 2.8

$$\text{Number of A atoms per unit cell} = \underbrace{8(1/8)}_{\text{from corners}} + \underbrace{4(1/2)}_{\text{from face-centre}} = 3$$

$$\text{Number of B atoms per unit cell} = \underbrace{12(1/3)}_{\text{from edges}} + \underbrace{1}_{\text{from body-centre}} = 4$$

Hence, the stoichiometry of the solid is A_3B_4

70. Each atom at the corner is shared amongst eight unit cells. Hence, number of atoms A per unit cell is

$$n_A = \text{(Number of corners) (Contribution from each corner)} = 8(1/8) = 1$$

Each atom at the centre of each face is shared between two units cell. Hence, number of atoms B per unit cell is

$$n_B = \text{(Number of faces) (Contribution from each face)} = 6(1/2) = 3$$

The structure of the given substance is AB_3.

71. Given $r_{Na+}/r_{Cl-} = 0.5$ and $r_{Na+}/r_{K+} = 0.7$. Hence

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{Na^+}}{r_{Cl^-}}\frac{r_{K^+}}{r_{Na^+}} = \frac{0.5}{0.7} = \frac{5}{7}$$

Now $\dfrac{r_{Na^+}+r_{Cl^-}}{r_{Cl^-}} = \dfrac{3}{2}$ and $\dfrac{r_{K^+}+r_{Cl^-}}{r_{Cl^-}} = \dfrac{12}{7}$. Hence $\dfrac{a_{KCl}}{a_{NaCl}} = \dfrac{2(r_{K^+}+r_{Cl^-})}{2(r_{Na^+}+r_{Cl^-})} = \dfrac{12}{7}\cdot\dfrac{2}{3} = \dfrac{24}{21} = 1.14$

Density

72. The expression is $\quad \text{density} = \dfrac{\text{mass of atoms in a unit cell}}{\text{volume of a unit cell}} = \dfrac{N(M/N_A)}{a^3}$

73. The number of atoms in a single primitive cubic unit is 8 × 1/8 = 1.

74. The number of atoms in a body centred cubic unit is (8 × 1/8) + 1 = 2.

75. The number of atoms in a single face-centred cubic unit cell is (8 × 1/8) + (6 × 1/2) = 1 + 3 = 4.

76. In the primitive cubic unit cell, atoms touch each other along edges. Hence, $2\,r_A = a$.

77. In the body-centred cubic until cell, atoms touch each other along the body diagonal of the cube. Hence, $4\,r_A = \sqrt{3}\,a$, i.e. $r_A = \sqrt{3}\,a/4$.

78. In the face-centred cubic unit cell, atoms touch each other along the face diagonal of the cube. Hence, $4\,r_A = \sqrt{2}\,a$, i.e. $r_A = a/2\sqrt{2}$.

79. In sodium chloride unit cell, anion-cation-anion touch each other along the edges. Hence, $2\,r_c + 2\,r_a = a$, i.e. $r_c + r_a = a/2$.

80. CsCl crystallizes has body-centred cubic unit cell. Hence, $2\,r_c + 2\,r_a = \sqrt{3}\,a$, i.e. $r_c + r_a = \sqrt{3}\,a/2$.

81. In a closest Rock-salt structure, anions touch each other along the face diagonal of a cubic unit cell. Hence, $4r_a = \sqrt{2}\,a$, i.e. $r_a = a/2\sqrt{2}$.

82. In sodium chloride unit cell, there are four Na^+ and four Cl^- ions. Hence

$$\rho = \frac{N}{a^3}\frac{M}{N_A} = \frac{(4)\left\{(23+35.5)\text{ g mol}^{-1}\right\}}{(564\times10^{-10}\text{ cm})^3\,(6.022\times10^{23}\text{ mol}^{-1})} = 2.165\text{ g cm}^{-3}$$

83.
$$N = \frac{a^3\rho N_A}{M} = \frac{(405\times10^{-10}\text{ cm})^3\,(2.7\text{ g cm}^{-3})\,(6.022\times10^{23}\text{ mol}^{-1})}{(27.0\text{ g mol}^{-1})} = 4.0$$

84.
$$M = \frac{a^3\rho N_A}{N} = \frac{(630\times10^{-10}\text{ cm})^3\,(1.984\text{ g cm}^{-3})\,(6.023\times10^{23}\text{ mol}^{-1})}{4} = 74.70\text{ g mol}^{-1}$$

85. In body-centred cubic unit cell, ions touch each other along the body diagonal of the cube.

$$2\,r_+ + 2\,r_- = \sqrt{3}\,a \quad \text{i.e.} \quad 2\,(r_+ + 181\text{ pm}) = \sqrt{3}\,(387\text{ pm})$$

$$r_+ = (\sqrt{3}/2)\,(387\text{ pm}) - 181\text{ pm} = 154.15\text{ pm}$$

86. Sodium chloride has a face-centred cubic unit cell. Cation and anion touch each other along the edge of the cube.

$$2\,r_+ + 2\,r_- = a \quad \text{i.e.} \quad 2\,(r_+ + 181\text{ pm}) = 564\text{ pm}$$

$$r_+ = (564\text{ pm}/2) - 181\text{ pm} = 101\text{ pm}$$

87. There are six chlorides around each sodium ion.

88. The next nearest neighbours of Na^+ are 12 Na^+ ions.

89. For sodium chloride, $r_+ + r_- = a/2$.

90. The distance between two nearest Na^+ in sodium chloride unit cell is half of the face diagonal of the cube, i.e. $\sqrt{2}\,a/2 = a/\sqrt{2}$.

91. In cubical-closest packing, anions touch each other along the face-diagonal and cations-anions touch each other along edges. Hence

$$4r_- = \sqrt{2}\ (624\ \text{pm}) \quad \Rightarrow \quad r_- = 220.65\ \text{pm}$$

$$2(r_+ + r_-) = 624\ \text{pm} \quad \Rightarrow \quad r_+ = 91.35\ \text{pm}$$

Alternatively, we may proceed as follows.

Cations occupy octahedral voids for which we must have $r_+/r_- = 0.414$, which holds good for the choice a.

92. In a body-centred cubic unit cell, atoms touch each other along the body diagonal of the cube. Hence $\sqrt{3}\ a = 4r$ which gives $r = (\sqrt{3}/4)\ (287\ \text{pm}) = 124.47\ \text{pm}$

93. The expression of density is $\rho = (N/a^3)\ (M/N_A)$. For FCC, $N = 4$ and for BCC, $N = 2$. Hence

$$\frac{\rho(\text{FCC})}{\rho(\text{BCC})} = \left(\frac{N}{a^3}\right)_{\text{FCC}} \left(\frac{a^3}{N}\right)_{\text{BCC}} = \left(\frac{(4)}{3.5^3}\right)\left(\frac{3.0^3}{2}\right) = 1.26$$

94. From $\rho = (N/a^3)\ (M/N_A)$, we get

$$\frac{a^3}{N} = \frac{M}{\rho N_A} = \frac{107\ \text{g mol}^{-1}}{(10.6\ \text{g cm}^{-3})(6.023 \times 10^{23}\ \text{mol}^{-1})} = 1.68 \times 10^{-23}\ \text{cm}^3$$

For primitive, $N = 1$. Hence $a = 2.56 \times 10^{-8}$ cm. Also $2r = a$.

Hence $r = 1.28 \times 10^{-8}\ \text{cm} = 128\ \text{pm}$

For body centred, $N = 2$ Hence $a = 3.23 \times 10^{-8}$ cm. Also, $4r = \sqrt{3}\ a$.

Hence $r = 1.40 \times 10^{-8}\ \text{cm} = 140\ \text{pm}$

For face-centred, $N = 4$. Hence $a = 4.07 \times 10^{-8}$ cm. Also $4r = \sqrt{2}\,a$.

Hence, $r = 1.44 \times 10^{-8}\ \text{cm} = 144\ \text{pm}$

Only for face-centrd cubic unit cell, the calculated value tallies with the given one.

95. In body-centred cubic unit cell, atoms touch along the body-diagonal of the cube. Hence

$$4r = \sqrt{3}\ a \Rightarrow a = (4/\sqrt{3})\ r = (4/\sqrt{3})\ (452\ \text{pm}/2) = 521.9\ \text{pm}$$

Its density would be

$$\rho = \frac{N}{a^3}\frac{M}{N_A} = \frac{2}{(521.9 \times 10^{-10}\ \text{cm})^3}\ \frac{(39\ \text{g mol}^{-1})}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 0.91\ \text{g cm}^{-3}$$

96. $2\ (r_+ + r_-) = \sqrt{3}\ (154\ \text{pm})$. Since $r_+ = 154$ pm, this expression gives $r_- = 181$ pm.

97. We will have

$$f = \frac{(M/\rho_1) - (M/\rho_2)}{(M/\rho_2)} = \frac{(1/\rho_1) - (1/\rho_2)}{(1/\rho_2)} = \frac{\rho_2 - \rho_1}{\rho_1} = \frac{\rho_2}{\rho_1} - 1 = \frac{2\cdot178}{2\cdot165} - 1 = 1.006 - 1 = 0.006$$

98. In a primitive cubic unit cell, $2\ r_A = a$. There are four atoms per unit cell. Hence

$$\text{Fraction of volume occupied} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{a^3} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{(2r_A)^3} = \frac{\pi}{6} = 0.523$$

99. In a body-centred cubic unit cell, atoms touch each other along the body diagonal of the cube.

Hence, $4\ r_A = \sqrt{3}\ a$. There are two atoms per unit cell. Hence

$$\text{Fraction of volume occupied} = \frac{2\left(\frac{4}{3}\pi r_A^3\right)}{\left(4r_A/\sqrt{3}\right)^3} = \frac{\sqrt{3}\,\pi}{8} = 0.68$$

100. In a face-centred cubic unit cell, atoms touch each other along the face diagonal of the cube. Hence, $4\,r_A = \sqrt{2}\,a$. There are four atoms per unit cell. Hence

$$\text{Fraction of volume occupied} = \frac{4\left(\frac{4}{3}\pi r^3\right)}{\left(4 r_A/\sqrt{2}\right)^3} = \frac{\pi}{3\sqrt{2}} = 0.74.$$

Point Defects

101. The density of the crystals having Schottky defect is smaller than that of the perfect crystal because of the absence of cation(s) and anion(s) from their expected positions.

102. The density of crystals having Frenkel defect is identical to that of a pure crystal.

103. Let x and y be the Fe^{2+} and Fe^{3+} ions, respectively. We will have

$$x + y = 0.93$$

Also $2x + 3y = 2$ (condition of electroneutrality)

Solving for y, we get $y = 0.14$.

Hence Per cent of Fe^{3+} ions $= (0.14/0.93) \times 100 = 15$

104. Total positive charger per atom of iron will be $(1/4)\,3 + (3/4)\,2 = 2.25$

This will be equal to $2x$. Hence $x = 2.25/2 = 9/8$

105. Same as Q.101

106. Ferrous oxide forms a nonstoichiometric compound.

107. Bragg equation is $n\lambda = 2\,d\,\sin\,\theta$.

Multiple Correct Choice Type

1. The crystals of CsCl has body-centred cubic unit cell. Hence, each ion in this structure has coordination number of eight.

The crystals of NaCl has two interpenetrating face-centred cubic lattices, one composed entirely of Na^+ ions and the other of Cl^- ions. Each Na^+ ion is located halfway between two Cl^- ions and vice versa. A unit cell of NaCl crystals has Cl^- ions at the corners as well as at the face-centres and Na^+ ions are located in octahedral voids. On each edge of cubic unit cell, there are two Cl^- ions and one Na^+ ion. Hence.

$$a = 22\,(r_{Na}^{+} + r_{Cl}^{-}) = 2(95\text{ pm} + 181\text{ pm}) = 552\text{ pm}$$

2. In NaCl crystal, each cation and anion has six nearest neighbouring anions and cations, respectively. There are 12 next nearest neighbours of the same type of ions at a distance of $\sqrt{2}\,r$, where r is the distance between neighbouring cation and anion. Next to these, there are eight ions of the type at a distance of $\sqrt{3}\,r$.

3. In bcc cubic lattice, atoms at the corners (say, A) touch each other. Thus, their distance is equal to the edge length a. The unlike atoms touch each other along the body diagonal of the cube. Their arrangement will be ABA. Thus, the distance between A and B will be $\sqrt{3}\,a/2$.

4. The fcc structure of AB will be as shown in Q.2. Therefore, the $d_{A\text{–}A} = d_{B\text{–}B} = \sqrt{2}\,a/2$ and $d_{AB} = a/2$. There will be four molecules of AB in a unit cell. Hence, its density will be given as $\rho = (4/a^3)\,(M_{AB}/N_A)$.

5. (a) Only short-range order is present.

(b) Amorphous solids melt over a range of temperature. Only crystalline solids have sharp melting points.

6. (a) Ionic crystals have long range order.

(b) It is because cations and anions generally have different ionic radii and thus they cannot be packed like atoms in ccp and hcp structures.

7. (a) The coordination number is eight.

(b) There are six chlorides ions as the nearest neighbours of Na^+ ions and these are arranged octahedrally.

(c) In NaCl crystals, Na^+ ions may be assumed to occupy the lattice points in face-centred cubic unit cell with Cl^- ions in the octahedral voids or vice versa. The nearest distance between two Na^+ is (edge–length)/$\sqrt{2}$.

8. (b) It is 32%.
(c) This is in case of face-centred cubic unit cell.

16. In Frenkel defect, the ion, instead of being in its expected location, is found in one of the interstices. This defect is favoured by a large difference in size between the positive and negative ions.
Schottky defect involves the absence of cation or anion from the postion which it is expected to occupy in the periodic arrangement of ions. This affects the physical properties of solids.

Linked Comprehension Type

1. **(i)** Since both cubical and hexagonal are closely packed, their densities will be identical
(ii) The coordination of each atom in closest packed structure is twelve.
(iii) The unit cell of cubical closest packing is face centred cubic unit cell for which atoms touch each other along the face diagonal. Hence, $4r = \sqrt{2}\,a$ Also, the distance between closest packed layers is $\sqrt{3}\,a/3$ as three such layers lie along the body diagonal of the cube. Hence.

$$\text{distance} = \frac{\sqrt{3}}{3}a = \frac{\sqrt{3}}{3}\left(\frac{4}{\sqrt{2}}r\right) = \frac{4}{\sqrt{6}}r$$

2. **(i)** In a closest packing, there is a tetrahedral hole above and below each atom, hence, there are twice as many tetrahedral holes as there are closest packed atoms.
The number of octahedral holes is equal to the number of atoms present and these are located midway between the two closest packed layers.
(ii) The size of tetrahedral hole is smaller than octahedral hole.
(iii) see, part (i) of this question.

3. **(i)** Cubical closest packing is ABCABC….
(ii) The unit cell of cubical closest packing is face centred cube
(iii) The radius of atom that can be fitted into octahedral void is $0.414r$, where r is the radius of atom colsely packed.

4. **(i)** The void volumes in primitive, body-centred and face-centred are 47.64, 31.98 and 25.95, respectively.
(ii) In primitive cubic unit cell atoms touch each other along the edges. Hence, $2r = a$

In body-centred cubic unit cell, atoms touch each other along body diagonal.. Hence, $4r = \sqrt{3}\,a$.

In face-centred cubic unit cell, atoms touch each other along face diagonal. Hence, $4r = \sqrt{2}\,a$
(iii) The coordination number of atoms in primitive, body-centred and face diagonal are 6, 8 and 12, respectively.

5. **(i)** There are 6 atoms per unit cell of HCP. Three atoms are inside the cell, one atom comes from the corners of each of top and bottom of the cell (making a total of two atoms) and half of atom comes from each of the central atom at the top and bottom of unit cell (making a total of one atom).
(ii) The hexagonal base consists of six equilateral triangles, each with side $2r$ and altitude $2r \sin 60°$. Hence,

$$\text{Area of base} = 6\left[\tfrac{1}{2}(2r)(2r\sin 60°)\right] = 6\sqrt{3}\,r^3$$

The height of hexagonal is twice the distance between closest-packed layer. This can be determined with reference to the cubical-closest packing. There are three closest-packed layers in its body diagonal, and thus the distance between two closest-packed layers is $\sqrt{3}\,a/3 = a/\sqrt{3}$. The edge length is related to the radius atom by the relation $4r = \sqrt{2}a$ since atoms touch each other along the face diagonal of the cube. Hence, height of HCP unit cell is $2(a/\sqrt{3})$ where $a = 2\sqrt{2}\,r$. Hence

$$\text{Height of unit cell} = 2(2\sqrt{2}\,r/\sqrt{3}) = 4\sqrt{2}\,r/\sqrt{3}$$

$$\text{Volume of unit cell} = (\text{area of base})\ (\text{height}) = (6\sqrt{3}\,r^2)(4\sqrt{2}\,r/\sqrt{3}) = 24\sqrt{2}\,r^3$$

(iii) Since there are six atoms per unit cell, percentage of volume occupied by atoms is

$$\frac{6\left(\frac{4}{3}\pi r^3\right)}{24\sqrt{2}\,r^3}\times 100=\frac{\pi}{3\sqrt{2}}\times 100=\frac{3.14}{3\times 1.414}\times 100=74\%$$

Percentage of empty space = 100 – 74 = 26%

6. (i) The crystallographic dimensions are $a = b = c$ and $\alpha = \beta = \gamma = 90°$

(ii) Diamond has cubic unit cell.

(iii) There are three Bravais latties: Primitive (P), Body-centred (I) and Face-centred (F).

Assertion and Reason Type

4. ZnS will have the same density in both the structures as both have closest packing.

5. Though the tetragonal has two types of faces but the correct explanation is that the end-centred tetragonal lattice can be described by a primitive unit cell.

8. Both will have the same void volume because it does not matter whether cation or anion forms closest packing.

9. Carbon atoms also occuply half of the alternate tetrahedral voids as shown in the following figure.

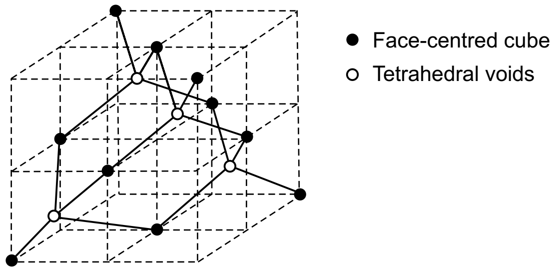


Fig. 2.9

Matrix Match Type

1. The crystallographic parameters of the given crystal systems are as follows.

Cubic system	$a = b = c$; $\alpha = \beta = \gamma = 90°$
Rhombohedral system	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$
Monoclinic	$a \neq b \neq c$; $\alpha = \beta = 90° \neq \gamma = 120°$

(a) Simple cubic and face-centred cubic (i) have the cell parameters $a = b = c$ and $\alpha = \beta = \gamma$ (choice p) and belong to same crystal system (choice s)

(b) Cubic and rhombohedral (i) have the cell parameters $a = b = c$ and $\alpha = \beta = \gamma$ (choice p), and (ii) are two crystal system (choice q).

(c) Cubic and tetragonal are two crystal systems (choice q).

(d) Hexagonal and monoclinic (i) are two crystal systems (choice q) and (ii) have only two crystallographic angles of 90° (choice r).

Thus, the matchings are as follows.

(a) – (p), (s) (b) – (p), (q) (c) – (q) (d) – (q), (r)

2. The matchings are as follows.

(a) – (p), (t) (b) – (q), (s) (c) – (q), (u) (d) – (r), (s)

3. The matchings are as follows.

(a) – (p), (q), (r), (s), (t), (u) (b) – (q), (r)
(c) – (r) (d) – (r), (t)

4. The matchings are as follows.

(a) – (r) (b) – (s) (c) – (p) (d) – (q)

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

Solid State

1. Calculate the radius of molybdenum atom if the element crystallizes as body-centred cubic crystals. Given: Density of Mo = 10.3 g cm^{-3} and molar mass of Mo = 95.94 g mol^{-1}.

Solution In a body-centred cubic unit cell, there are two atoms per unit cell. Hence, from the expression

$$r = \frac{N}{a^3}\left(\frac{M}{N_\mathrm{A}}\right)$$

we get $$a^3 = \frac{N}{\rho}\left(\frac{M}{N_\mathrm{A}}\right) = \left(\frac{2}{10.3\ \mathrm{g\ cm^{-3}}}\right)\left(\frac{95.94\ \mathrm{g\ mol^{-1}}}{6.023\times 10^{23}\ \mathrm{mol^{-1}}}\right) = 3.09 \times 10^{-23}\ \mathrm{cm^3}$$

or $$a = 3.13 \times 10^{-8}\ \mathrm{cm} = 313\ \mathrm{pm}$$

Now since in the body-centred cubic unit cell, atoms touch each other along the cross diagonal of the cube, we have

$$4\,r = \sqrt{3}\,a \quad \text{or} \quad r = (\sqrt{3})(313\ \mathrm{pm})/4 = 135.5\ \mathrm{pm}$$

2. The edge length of a cubic unit cell of metallic calcium is 556 pm. If the density of calcium is 1.54 g cm^{-3} and its molar mass is 40.08 g mol^{-1}, calculate the radius of calcium atom.

Solution From the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_\mathrm{A}}\right)$$

we get $$N = \frac{\rho\, a^3\, N_\mathrm{A}}{M} = \frac{(1.54\ \mathrm{g\ cm^{-3}})\,(556\times 10^{-12}\ \mathrm{m})^3\,(6.023\times 10^{23}\ \mathrm{mol^{-1}})}{(40.08\ \mathrm{g\ mol^{-1}})} = 3.98 \simeq 4$$

For $N = 4$, the unit cell is face-centred cube. Since atoms touch each other along the face diagonal in a face-centred cubic unit cell, we have

$$4\,r = \sqrt{2}\,a \qquad \text{or} \qquad r = \frac{a}{2\sqrt{2}} = \frac{556\ \mathrm{pm}}{2\sqrt{2}} = 196.6\ \mathrm{pm.}$$

3. Caesium chloride may be considered to form interpenetrating simple primitive cubic crystals. The edge length of unit cell is 412 pm. Determine : (a) the density of CsCl, and (b) the ionic radius of Cs$^+$ if the ionic radius of Cl$^-$ is 181 pm. Given: M(Cs) = 133 g mol^{-1}.

Solution The interpenetrating simple primitive cubic crystals means the unit cell is body-centred where Cl$^-$ ions occupy corners and Cs$^+$ ion occupy body centre of the cube. There is one Cs$^+$ ion and one Cl$^-$ ion (or one molecule of CsCl) per unit cell.

From the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_\mathrm{A}}\right)$$

we get $$\rho = \frac{1}{(412\times 10^{-12}\ \mathrm{m})^3}\left(\frac{168.5\ \mathrm{g\ mol^{-1}}}{6.023\times 10^{23}\ \mathrm{mol^{-1}}}\right) = 0.4 \times 10^7\ \mathrm{g\ m^{-3}} \equiv 4.0\ \mathrm{g\ cm^{-3}}$$

Now since Cs^+ ion touch the two chlorides along the cross diagonal of the cube, we will have

$$2\,r_c + 2\,r_a = \sqrt{3}\,a \quad \text{or} \quad r_c = \left(\frac{\sqrt{3}}{2}\right) a - r_a = \left(\frac{\sqrt{3}}{2}\right)(412\ \text{pm}) - (181\ \text{pm}) = 175.8\ \text{pm}.$$

4. The atomic radius of strontium is 215 pm and it crystallizes with a cubical closest-packed structure. Calculate the density of strontium. The molar mass of strontium is 87.6 g mol^{-1}.

Solution The cubical closest-packed structure has a face-centred cubic unit cell. In the latter atoms touch along the face diagonal of the cube. Hence

$$\sqrt{2}\ a = 4\ r = 4\ (215\ \text{pm}) = 860\ \text{pm} \quad \text{or} \quad a = \frac{860\ \text{pm}}{\sqrt{2}} = 608.2\ \text{pm}$$

Now using the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

we get

$$\rho = \frac{4}{(608.2\times10^{-12}\ \text{m})^3}\left(\frac{87.6\ \text{g mol}^{-1}}{6.023\times10^{23}\ \text{mol}^{-1}}\right) = 2.586\times10^6\ \text{g m}^{-3} \equiv 2.586\ \text{g cm}^{-3}$$

5. A solid A^+B^- has an NaCl type closest packed structure. If the radius of the anion is 250 pm, what is the radius of the cation?

Solution The structure of NaCl involves face-centred cubic arrangement of Cl^- ions and its octahedral holes are occupied by Na^+ ions. Now for a closest-packed structure $r_c/r_a = 0.414$. Hence

$$r_c = (0.414)\ r_a = (0.414)\ (250\ \text{pm}) = 103.5\ \text{pm}$$

6. If the radius of Cs^+ is 169 pm and that of Cl^- is 181 pm, predict the structure of CsCl. What is the coordination number of Cs^+ ion?

Solution We have

$$\frac{r_c}{r_a} = \frac{169}{181} = 0.94$$

Since this value is greater than 0.732, the structure of CsCl involves body-centred cubic unit cell, where Cs^+ is present at the body centre of cube and Cl^- ions are present at the corners. The coordination number of Cs^+ is eight.

7. KCl crystallizes in the same type of lattice as does NaCl. Given that

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.5 \qquad \text{and} \qquad \frac{r_{Na^+}}{r_{K^+}} = 0.7$$

Calculate (a) the ratio of side of the unit cell for KCl to that for NaCl, and (b) the ratio of density of NaCl to that of KCl.

Solution NaCl crystallizes in the face-centred cubic unit cell, such that

$$r_{Na^+} + r_{Cl^-} = a/2$$

where a is the edge length of unit cell. Now since $r_{Na^+}/r_{Cl^-} = 0.5$ and $r_{Na^+}/r_{K^+} = 0.7$, we will have

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5 \quad \text{and} \quad \frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{K^+}}{r_{Na^+}/0.5} = \frac{0.5}{r_{Na^+}/r_{K^+}} = \frac{0.5}{0.7}$$

or

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.2}{0.7}\times\frac{1}{1.5} \quad \text{or} \quad \frac{a_{KCl}/2}{a_{NaCl}/2} = \frac{1.2}{0.7\times1.5} \quad \text{or} \quad \frac{a_{KCl}}{a_{NaCl}} = \frac{1.2}{1.05} = 1.143$$

Now since $\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$, we will have

$$\frac{\rho_{NaCl}}{\rho_{KCl}} = \left(\frac{a_{KCl}}{a_{NaCl}}\right)^3\left(\frac{M_{NaCl}}{M_{KCl}}\right) = (1.143)^2\left(\frac{58.5}{74.5}\right) = 1.172.$$

8. LiI occurs as cubical-closest packing. If the edge length of a unit cell is 624 pm, determine the ionic radii of Li^+ and I^- ions.

Solution The cubical closest packing has a face-centred cubic unit cell. I^- ions occupy the corners and the face centres. These ions touch each other along the face diagonal of the cube. Hence

$$4\, r_{I^-} = \sqrt{2}\, a \quad \text{or} \quad r_{I^-} = \frac{a}{2\sqrt{2}} = \frac{624 \text{ pm}}{2(1.414)} = 220.65 \text{ pm}$$

Now along the edge, we will have $I^-\, Li^+\, I^-$ arrangement, where I^- are at the corners and Li^+ ion at the centre of the edge (octahedral void). Since in closest packing, they touch each other, we will have

$$2\, r_{I^-} + 2 r_{Li^+} = a$$

or $$r_{Li^+} = \frac{a}{2} - r_{I^-} = \frac{624 \text{ pm}}{2} - 220.65 \text{ pm} = 91.35 \text{ pm}$$

9. Calculate the percentage of void volume in the (a) primitive, (b) body-centred, and (c) face-centred cubic metallic crystals.

(a) In the primitive unit cell, atoms are present only at the corners of the cube. Each of the eight atoms is shared amongst eight unit cells. Hence, the number of atoms present in one unit cell is one. Moreover, atoms will touch each other along the edges of the cube. Hence, $2r = a$. Now

$$\text{Volume of the unit cell} = a^3 = 8r^3$$

$$\text{Volume occupied by the atoms} = 1\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Fraction of volume occupied by the atoms} = \frac{(4/3)\pi r^3}{8r^3} = \frac{\pi}{6} \simeq \frac{22}{42}$$

$$\text{Fraction of volume unoccupied by atoms} = \frac{20}{42}$$

$$\text{Percentage of void volume} = \frac{20}{42} \times 100 = 47.6\%.$$

(b) In the body-centred cubic unit cell, atoms are present at the corners and the body centre of the cube. There will be two atoms per unit cells and also atoms touch each other along the cross diagonal of the cube. Hence,

$$4r = \sqrt{3}\, a$$

Now, $$\text{Volume of unit cell} = a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3$$

$$\text{Volume occupied by atoms} = 2\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Fraction of volume occupied} = \frac{2(4/3)\pi r^3}{\left(4/\sqrt{3}\right)^3 r^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

$$\text{Fraction of volume unoccupied by atoms} = 0.32$$

$$\text{Percentage void volume} = 32\%$$

(c) In the face-centred cubic unit cell, atoms are present at the corners as well as at the centres of six faces. Since each atom at the corner is shared amongst eight unit cell and each atom at the centre of face is shared between two unit cells, the number of atoms per unit cell is 4 (= 8(1/8) + 6(1/2)). Moreover, atoms touch each other along the faces of the cube. Hence

$$4r = \sqrt{2}\, a$$

Now, $$\text{Volume of unit cell} = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = 16\sqrt{2}\, r^3$$

$$\text{Volume occupied by atoms} = 4\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Fraction of volume occupied by atoms} = \frac{4(4/3)\,\pi\, r^3}{16\sqrt{2}\, r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Fraction of volume unoccupied by atoms = 0.26

Percentage of void volume = 26%

10. The composition of a sample of wüstite is $Fe_{0.93}O_{1.00}$. What percentage of the ion is present in the form of Fe(III)? (1995)

Solution The compound $Fe_{0.93}O_{1.00}$ is a non-stoichiometric where electrical neutrality is achieved by converting appropriate Fe^{2+} ions into Fe^{3+} ions. There are 7 Fe^{2+} ions missing out of the expected 100 Fe^{2+} ions. The missing 2 × 7 positive charge is compensated by the presence of Fe^{3+} ions. Replacement of one Fe^{2+} ions by Fe^{3+} ion increases one positive charge. Thus, 14 positive charges is compensated by the presence of 14 Fe^{3+} ions out of a total of 93 iron ions.

Hence, $$\text{Per cent of } Fe^{3+} \text{ ions present} = \frac{14}{93} \times 100 = 15.05$$

11. A sample of wustite Fe_xO contains one Fe(III) for every three Fe(II). Calculate the value of x.

Solution Let there be 1 mol of iron atom. We will have

Amount of Fe(III) = (1/4) mol and Amount of Fe(II) = (3/4) mol

Total positive charges = (1 mol/4) (3) + (3 mol/4) (2) = (9/4) mol

Let x be the amount of oxygen atoms. We have

Total negative charges = $x(2)$

To satisfy electrical neutrality, we have

Total positive charges = Total negative charges

$$\frac{9}{4}\ \text{mol} = 2x \quad \text{or} \quad x = (9/8)\ \text{mol}$$

Hence, composition of the composition is $FeO_{9/8}$ or Fe_8O_9.

12. A metallic element crystallises into a lattice containing a sequence of layers of ABABAB . . . . Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (1996)

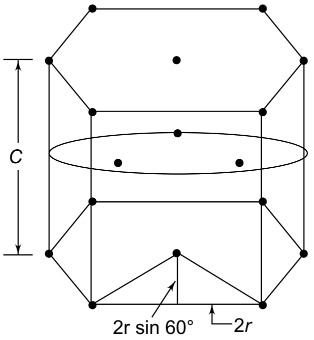


Fig. 2.10

Solution The hexagonal base consists of six equilateral triangles, each with side $2r$ and altitude $2r$ sin 60°. Hence,

$$\text{Area of base} = 6\left[\frac{1}{2}(2r)(2r\sin 60^\circ)\right] = 6\sqrt{3}\, r^2$$

The height of hexagonal is twice the distance between closest-packed layers. The latter can be determined by reference to a face-centred cubic lattice with unit cell length a. In such a lattice, the distance between closest-packed layers is one third the body diagonal, i.e. $\sqrt{3}\,a/3$. Hence

$$C = 2\left(\frac{\sqrt{3}\,a}{3}\right) = \frac{2a}{\sqrt{3}}$$

Now in the face-centred lattice, atoms touch one another along the face diagonal. Thus $4r = \sqrt{2}\,a$

With this, the height of the hexagonal becomes $C = \dfrac{2}{\sqrt{3}}\left(\dfrac{4r}{\sqrt{2}}\right) = \left(\dfrac{4\sqrt{2}}{\sqrt{3}}r\right)$

Volume of hexagontal unit is

$$V = \text{(base area) (height)} = \left(6\sqrt{3}\, r^2\right)\left(\frac{4\sqrt{2}}{\sqrt{3}}\, r\right) = 24\sqrt{2}\, r^3$$

In one hexagonal unit cell, there are 6 atoms as shown in the following.

(a) 3 atoms in the central layer which exclusively belong to the unit cell.

(b) 1 atom from the centre of the base. There are two atoms of this type and each is shared between two hexagonal unit cells.

(c) 2 atoms from the corners. There are twelve such atoms and each is shared amongst six hexagonal unit cells.

The volume occupied by atoms = $6\left(\frac{4}{3}\pi r^3\right)$

Fraction of volume occupied by atoms = $\dfrac{\text{Volume occupied by atoms}}{\text{Volume of hexagonal unit cell}} = \dfrac{6\left(\frac{4}{3}\pi r^3\right)}{24\sqrt{2}\, r^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74$

Fraction of empty space = 1 – 0.74 = 0.26

Percentage of empty space = 26%

13. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? (1997)

Solution Using the formula $\rho = \dfrac{N}{a^3}\dfrac{M}{N_A}$ we get

$$\rho = \frac{4}{(0.564 \times 10^{-7}\ \text{cm})^3}\left(\frac{58.5\ \text{g mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}}\right) = 2.166\ \text{g cm}^{-3}$$

14. Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3? (1997)

Solution In a body-centred cubic lattice, atoms touch each other along the body-diagonal of the cube. Hence

$$4r = \sqrt{3}\, a \quad \text{or} \quad r = \frac{\sqrt{3}\, a}{4} = \frac{(1.732)(287\ \text{pm})}{4} = 124.27\ \text{pm}$$

The expression of density is $\rho = \dfrac{N}{a^3}\left(\dfrac{M}{N_A}\right)$

Substituting the values, we get $\rho = \dfrac{2}{(287 \times 10^{-10}\ \text{cm})^3}\left(\dfrac{51.99\ \text{g mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}}\right) = 7.30\ \text{g cm}^{-3}$

15. A metal crystallises into two cubic phases, face centred cubic (FCC) and body centred cubic (BCC), whose unit cell length are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of FCC and BCC. (1999)

Solution The expression of density is

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

For face-centred cubic unit cell, $N = 4$. For body-centred cubic unit cell, $N = 2$

Hence, $\dfrac{\rho_{\text{FCC}}}{\rho_{\text{BCC}}} = \dfrac{N_{\text{FCC}}}{a_{\text{FCC}}^3}\dfrac{a_{\text{BCC}}^3}{N_{\text{BCC}}} = \dfrac{4}{(3.5\ \text{Å})^3}\dfrac{(3.0\ \text{Å})^3}{2} = 1.26$

16. Sodium metal crystallises in body-centred cubic lattice with the cell edge, $a = 4.29$ Å. What is the radius of sodium atom?

Solution In a body centred cubic lattice, atoms touch along the body diagonal of the cube. Thus,

$$4r = \sqrt{3}\, a$$

or $r = \dfrac{\sqrt{3}}{4}a = \left(\dfrac{\sqrt{3}}{4}\right)(4.29\ \text{Å}) = 1.86\ \text{Å}$

UNSOLVED PROBLEMS

1. The density of KF is 2.48 g cm^{-3}. The solid is made up of a cubic array of alternate K^+ and F^- ions at a spacing of 266.5 pm between centres. From these data, determine the value of Avogadro constant.
2. Iron may crystallize in the face-centred cubic system. If the radius of one atom of Fe is 126 pm, determine the density of the metal. Given: $M(\text{Fe}) = 55.85$ g mol^{-1}.
3. It is know that AgCl has the same structure as NaCl. The edge length of a unit cell of AgCl is found to be 555 pm and the density of AgCl is found to be 5.561 g cm^{-3}. Find the percentage of the sites that would appear empty. Assume that lattice vacancies are the only defects.
4. Use the data given below to find the type of cubic lattice to which the crystal belongs.

	Fe	V	Pd
a/pm	286	301	388
ρ/g cm^{-3}	7.86	5.96	12.16

5. Lithium forms body-centred cubic crystals with edge length of unit cell equal to 351 pm. Determine the atomic radius of lithium.
6. Caesium bromide crystallizes in the cubic system. Its unit cell has Cs^+ ion at the body centre and Br^- ion at each corner. Its density is 4.44 g cm^{-3}. Determine: (a) edge length of the unit cell and (b) fraction of volume occupied per unit cell.
7. Copper has a face-centred cubic lattice with a unit cell edge of 361 pm. What is the size of the largest atom which could fit into (a) octahedral voids, and (b) tetrahedral voids?
8. KF crystallizes in the NaCl type structure. If the radius of K^+ ion is 132 pm and that of F^- ion is 135 pm, what is the shortest K—F distance? What is the edge length of the unit cell? What is the closest K—K distance.
9. Silver has an atomic radius of 144 pm. If the density of silver is 10.6 g cm^{-3}, to which type of cubic crystal, silver belongs?

ANSWERS

1. 6.18×10^{23} mol^{-1}

2. 8.2 g cm^{-3}

3. 0.25%

4. Fe: body-centred cube
V: body-centred cube
Pd: face-centred cube

5. 151.9 pm

6. 430 pm, 0.77

7. 53 pm, 29 pm

8. 267 pm, 534 pm, 378 pm

9. face-centred

CHAPTER 3

ATOMIC STRUCTURE

CHARACTERISTICS OF ATOMS

The tiny constituent of an element is an atom. It is composed of a nucleus and electrons. The nucleus is present in the centre of an atom and contains positively charged protons and electrically neutral neutrons. Electrons are negatively charged species and these are present outside the nucleus. In a neutral atom, the number of protons is equal to the number of electrons. The main characteristics of fundamental particles proton, neutron and electron are described in Table 3.1.

Table 3.1 Main Characteristics of Fundamental Particles of an Atom

Particle	*Mass*	*Charge*
Proton	1.67265×10^{-27} kg	$+ 1.60216 \times 10^{-19}$ C
Neutron	1.6748×10^{-27} kg	Zero
Electron	9.10953×10^{-31} kg	-1.60216×10^{-19} C

Each element is characterized by the number of protons present in the nucleus of its atom. This number is known as *atomic number* of the element. The sum of protons and neutrons present in an atom is known as *mass number*. All atoms of an element have the same atomic number but may differ in mass number. Such species are known as *isotopes* of an element. For example, naturally occurring oxygen contains three isotopes $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$, (where the left hand inferior is the atomic number and superior is the mass number) with relative abundances as 99.759, 0.037 and 0.204 per cents respectively. The atomic mass of the atom is the weighted average of the masses of its isotopes.

The following terms are also used while dealing with different types of atoms.

Isobars Atoms having the same mass number but different atomic numbers are known as isobars. For example, $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$.

Isotones Atoms having the same number of neutrons but different number of protons are known as isotones. For example, $^{30}_{14}Si$, $^{31}_{15}P$ and $^{32}_{16}S$.

Isoelectronic The species having the same number of electrons are known as isoelectronic. Examples are Si, N_2, CO and CN^-.

RUTHERFORD'S SCATTERING EXPERIMENT

Rutherford based on his scattering experiment of α-particles by thin gold foil concluded that the atom is made up of positively charged tiny nucleus and a lot of extranuclear empty space containing electrons. The size of a nucleus is of the order of 10^{-15} m and that of an atom is 10^{-10} m.

SPECTRUM OF HYDROGEN ATOM

The hydrogen atom displays discrete spectrum. Experimentally, it was found by Balmer that the wavelength of emitted radiations in the visible and near-ultraviolet spectrum of hydrogen atom could be expressed as

$$\lambda = (364.56 \text{ nm}) \left(\frac{n_2^2}{n_2^2 - n_1^2} \right)$$

where $n_1 = 2$ and n_2 has any integral value greater than 2, i.e. 3, 4, 5, ...

It is now well established that hydrogen atom displays five spectral series (Table 3.2), the wave number of the absorption is given by the expression

$$\tilde{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R is Rydberg constant. It has a value of $1.097 \times 10^7 \text{ m}^{-1}$. The constants n_1 and n_2 have integral values (Table 3.2).

Table 3.2 Five Spectral Series of Hydrogen Atom

Spectral series	*Values of*		*Region of radiation*
	n_1	n_2	
Lyman	1	2, 3, 4, ...	Ultraviolet
Balmer	2	3, 4, 5	Visible
Paschen	3	4, 5, 6, ...	Near infrared
Brackett	4	5, 6, 7, ...	Infrared
Pfund	5	6, 7, ...	Far infrared

BOHR'S ATOMIC MODEL

In the Bohr model of the atomic structure, electrons revolve around the nucleus in certain allowed circular orbits without losing any energy. The stability of the circular motion of an electron requires that the centripetal force (due to the attraction between the nucleus and the electron) be equal to the centrifugal force, i.e.

$$\frac{(Z\,e)(e)}{(4\,\pi\,\varepsilon_0)\,r^2} = \frac{m\,v^2}{r} \tag{1}$$

In order to explain the spectral lines of the hydrogen atom, Bohr introduced the quantum restriction on the angular momentum of the electron. This restriction is

$$mvr = n \left(\frac{h}{2\pi} \right) \tag{2}$$

where n can have integral values (= 1, 2, 3, ...) and is known as quantum number. The energy of an electron in an orbit is given as

$$E = \text{KE} + \text{PE} = \frac{1}{2} mv^2 - \frac{Z\,e^2}{(4\,\pi\,\varepsilon_0)\,r} \tag{3}$$

From the three equations given above, the following expressions regarding the characteristics of electronic motion in the Bohr orbits can be derived.

$$r = n^2 \left[\frac{h^2}{4\pi^2\, m(Ze^2/4\pi\varepsilon_0)} \right]; \qquad E = -\frac{1}{n^2} \left[\frac{2\pi^2\, m(Ze^2/4\pi\varepsilon_0)^2}{h^2} \right]$$

$$v = \frac{2\pi(Ze^2/4\pi\varepsilon_0)}{n\,h}$$

The expression of spectral transitions is $\Delta E = Z^2 R_{\text{H}} hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

where R_{H}, known as Rydberg constant, is given as

$$R_{\text{H}} = \frac{2\pi^2\, m(e^2/4\pi\varepsilon_0)^2}{h^3 c} = 1.09678 \times 10^7 \text{ m}^{-1}$$

For one-electron species in the ground state ($n_1 = 1$), the ionization energy ($n_2 = \infty$) is given as

$$E_{\text{ioniz}} = Z^2 R_{\text{H}}\, hc$$

The Bohr theory could not explain the experimental facts for multielectron atoms.

QUANTUM NUMBERS

The discoveries of wave-particle duality ($p = h/\lambda$) by de Broglie and the uncertainty principle ($\Delta p \Delta x \geq h/4\pi$) by Heisenberg have completely changed the thinking about the behaviour of electrons in an atom. The behaviour of electrons in an atom is described by quantum theory. Each electron in an atom is characterized by a mathematical equation (known as wave function) whose square value at a given point gives the probability of finding the electron at that point. These wave functions are obtained by solving the appropriate Schrödinger equation. Each wave function constitutes an orbital in an atom and depends on three quantum numbers n, l and m as described in the following.

Principal Quantum Number (symbol: n) Each principal quantum number represents a major energy shell. It can have integral values 1, 2, 3, ... The energy shells are represented by the symbols K, L, M, ... depending upon the values of n equal to 1, 2, 3,..., respectively. For one-electron system, the expression of energy is the same as that obtained in Bohr's theory. For a multi-electron system, the energy of an orbital depends on the two quantum numbers n and l.

Azimuthal Quantum Number (Symbol: l) Each azimuthal quantum number represents a subshell within the major energy shell. The values of l are 0, 1, 2, ..., $(n - 1)$ and these are designated by the symbols s, p, d, f, g, ..., respectively. This quantum number also represents the quantized values of angular momentum of the electron in an orbital through the expression

$$L = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$$

This quantum number also describes the shape of an orbital which, according to the quantum theory, is the space around the nucleus where there exists 90 – 95% probability of finding the electron. The orbital with $l = 0$ is spherical, for $l = 1$, the shape is dumb-bell and for $l = 2$, the shape is double dumb-bell (Fig. 3.1).

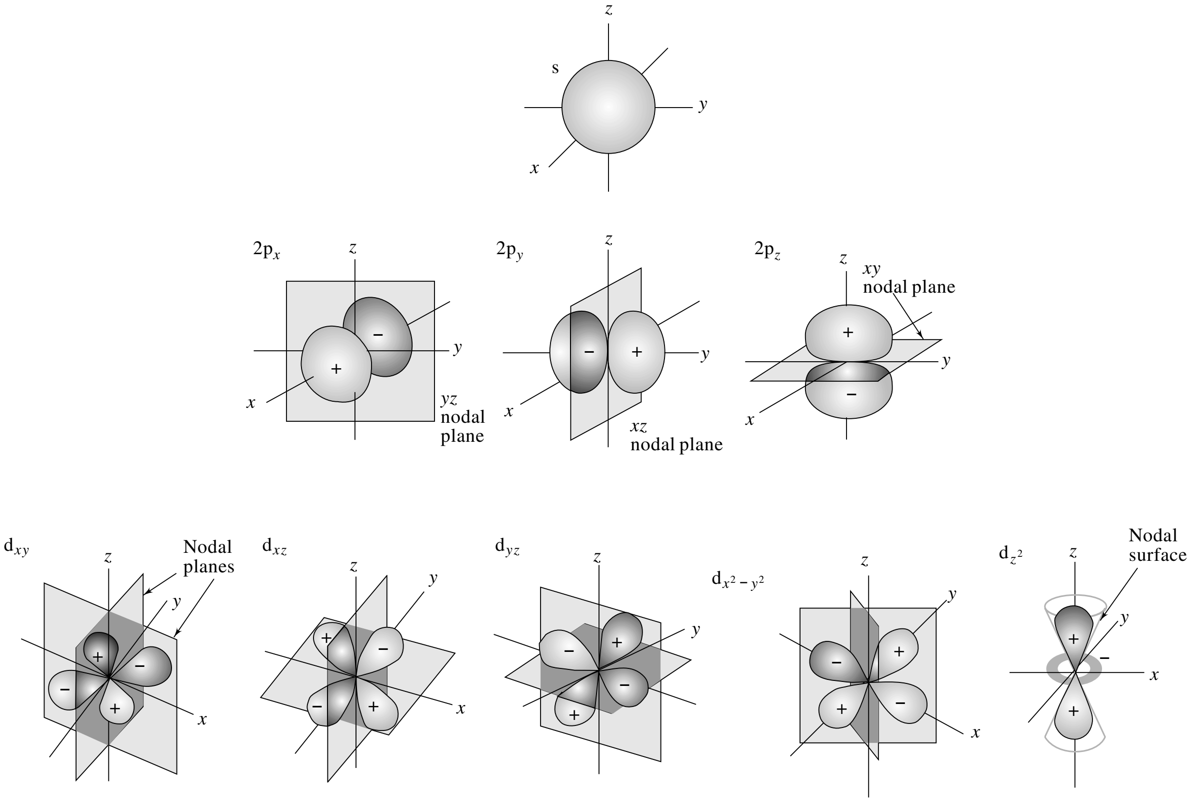


Fig. 3.1 s, p and d orbitals

Magnetic Quantum Number (Symbol: m) Each magnetic quantum number constitutes a separate orbital within a subshell. It also represents the quantized values of z-component of angular momentum of the electron in an orbital through the expression

$$L_z = m\left(\frac{h}{2\pi}\right)$$

The permitted values of m are 0, ±1, ±2, ..., ± l. For a given value of l, the total number of permitted values of m is equal to $2l + 1$.

If θ is the angle between z-axis and the angular momentum vector, it is obvious that

$$L_z = L\cos\theta$$

or

$$m\left(\frac{h}{2\pi}\right) = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)\cos\theta \quad \text{i.e.} \quad m = \sqrt{l(l+1)}\ \cos\theta$$

Since m is never equal to $\sqrt{l(l+1)}$, cos θ is never equal to one or the angle θ is never equal to zero. The quantum number m also fixes the direction of the orbital in space. For example, for p-orbitals, the value of l is equal to 1 and the permitted values of m are –1, 0, and +1. This means that there are three p orbitals and these are designated as p_0, p_{+1} and p_{-1}. The plots of p_0, p_x (= $p_{+1} + p_{-1}$) and p_y (= $p_{+1} - p_{-1}$) indicate that the shape of these orbitals are dumb-bell and these point along z-axis, x-axis and y-axis, respectively.

Spin Quantum Number (*Symbmol*: m_s) An electron can also spin around its own axis. Two types of spinning, namely, clockwise and anti-clockwise is possible. These spinning produces angular momentum equal to $\sqrt{s(s+1)}\,(h/2\pi)$, where $s = 1/2$. The direction of angular momentum is governed by the quantized values of z-component of angular momentum which is given as $m_s\,(h/2\pi)$, where m_s is either equal to +1/2 (clockwise spinning) or –1/2 (anti-clockwise spinning).

ELECTRONIC CONFIGURATIONS OF ELEMENTS

The filling of atomic orbitals by electrons are governed by the three major guidelines. These are aufbau principle, Pauli's exclusion principle and Hund's rule. These are described in the following.

Aufbau Principle Electrons are fillied in various orbitals in the increasing order of their energies. The order is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p.$$

Pauli's Exclusion Principle No two electrons in an atom can have all the four quantum numbers identical. According to this principle, each orbital can accommodate at the most two electrons with opposite spins.

Hund's Rule This rule operates when the filling of degenerate orbitals (orbitals having identical energies) are carried out. According to this rule, electrons enter one by one till all of them are singly occupied with parallel spins. This is followed by the double occupation of these orbitals.

Besides the above rules, the fact that the half-filled and fully-filled degenerate configurations are more stable than the others is also considered while writing the electronic configurations of some elements. For example, the electronic configurations of Cr and Cu are

$_{24}Cr$ $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1(3d)^5$
$_{29}Cu$ $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1(3d)^{10}$

instead of

$_{24}Cr$ $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^4$
$_{29}Cu$ $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^9$

SUPPLEMENTARY MATERIAL

The behaviour of electron in hydrogen-like species is described by the solutions of Schrödinger equation

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}\left(E - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right)\Psi = 0$$

where $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The solution of the Schrödinger equation provides more than one solution (known as wave functions) satisfying the expression

$$\Psi_{n,\,l,\,m} = R_{n,\,l}\;\Theta_{l,\,|m|}\;\Phi_m$$

where we have

(i) $R_{n,\,l}$ is a mathematical expression involving r (the distance of the electron from the nucleus). It depends on quantum numbers n and l (where n, known as principle quantum number, takes the values of 1, 2, 3, ... and l, known as azimuthal quantum number, takes the values of 0, 1, 2, ... $(n - 1)$). Different values of n and l give different r-dependent expressions.

(ii) $\Theta_{l,\,|m|}$ is a mathematical expression involving angle θ (an angle between r vector and z-axis). It depends on quantum numbers l and magnitude of m (where m, known as magnetic quantum number, takes the value of $0, \pm 1, \pm 2, \dots \pm l$). Different values of l and m give different θ-dependent expressions.

(iii) Φ_m is a mathematical expression involving angle ϕ (an angle between the projection of r vector on xy plane and x axis). It depends only on quantum number m.

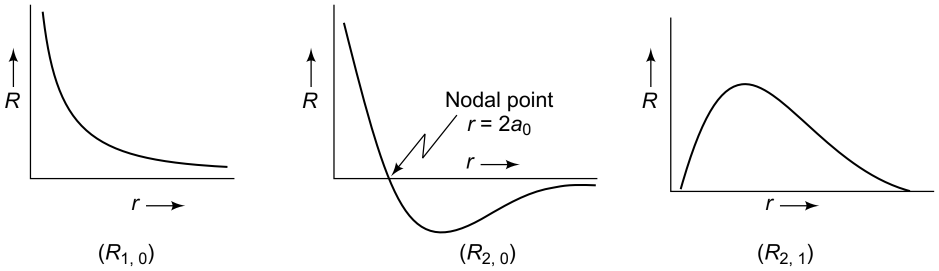
The probability of finding the electron at a point is directly proportional to the value of Ψ^2 evaluated at the given values of coordinates r, θ and φ of the point. It is equal to Ψ^2 if Ψ is normalized wave function satisfying the expression $\int \Psi^2\, \mathrm{d}\tau = 1$. If Ψ involves the complex quantity, then the probability is given by $\Psi^*\Psi$, where Ψ^* is the complex conjugate of Ψ.

The expressions of $\Psi_{n,l,m}$ upto $n = 2$ are as follows.

	$R_{n,l}$	$\Theta_{l,\lvert m\rvert}$	Φ_m
$\Psi_{1,0,0} =$	$\left[2\left(\frac{Z}{a_0}\right)^{3/2}\exp(-Z\,r/a_0)\right]$	$[(1/\sqrt{2})]$	$[(1/\sqrt{2\pi})]$
$\Psi_{2,0,0} =$	$\left[\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Z\,r}{a_0}\right)\exp(-Z\,r/2a_0)\right]$	[← same →]	[← same →]
$\Psi_{2,1,0} =$	$\left[\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Z\,r}{a_0}\right)\exp(-Z\,r/2a_0)\right]$	$[(\sqrt{3/2})\cos\theta]$	[← same →]
$\Psi_{2,1,+1} =$	[← same →]	$[(\sqrt{3/2})\sin\theta]$	$[(1/\sqrt{2\pi})\exp(i\varphi)]$
$\Psi_{2,1,-1} =$	[← same →]	[← same →]	$[(1/\sqrt{2\pi})\exp(-i\varphi)]$

where a_0 is the Bohr radius (= 52.9 pm) and Z is the nuclear charge.

The plots of $R_{1,\,0}$, $R_{2,\,0}$ and $R_{2,\,1}$ versus r are shown in Fig. 3.2.

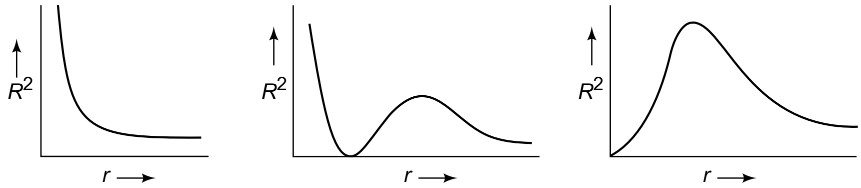


($R_{1,\,0}$) ($R_{2,\,0}$) ($R_{2,\,1}$)

Fig. 3.2

The point (or plane) at which the wave function has a zero value is known as the nodal point (or nodal plane). The number of radial nodes is equal to $n - (l + 1)$.

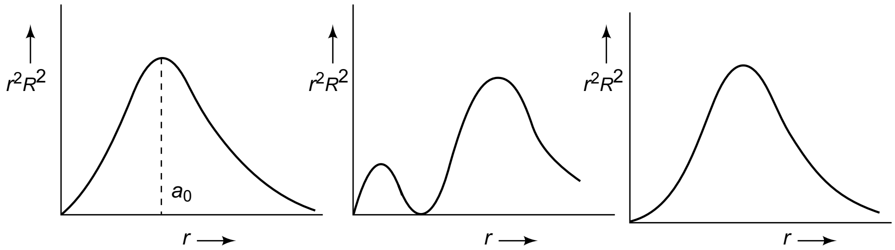
The plots of $R^2_{n,l}$ for the above three cases are shown in Fig. 3.3. These plots display the probability distribution with the variation of distance from the nucleus.



($R_{1,0}$) ($R_{2,0}$) ($R_{2,1}$)

Fig. 3.3

The total probability of finding the electron within a spherical shell of thickness dr situated at a distance r is given by the expression $4\pi r^2 R^2$. The plots of $4\pi r^2 R^2$ (or r^2R^2) versus r are as shown in Fig. 3.4.



($R_{1,0}$) ($R_{2,0}$) ($R_{2,1}$)

Fig. 3.4

The angular part of the wave function for an s orbital ($l = 0$) is a constant ($= 1/\sqrt{4\pi}$) with no θ and φ dependence for all values of the principal quantum number n. Thus, the functions Ψ_{100}, Ψ_{200}, ... (or simply 1s, 2s, ... orbitals) depend only on r and are spherical symmetrical.

For $l = 1$, the angular part depends on the value of m. For $m = 0$, it involves only cos θ which when plotted aginst angle θ gives two circles pointing along $+ z$ and $- z$ axes. It is for this reason, $\Psi_{2,1,0}$ is known as $2p_z$ orbital.

For $m = \pm 1$, Θ portion involves sin θ but Φ portion involves imaginary quantity i $(= \sqrt{-1})$ However, two real orbitals can be obtained by taking linear combinations of Φ_{+1} and Φ_{-1}. These combinations generate cos φ and sin φ as the φ-dependent functions. When combined with Θ portion, the angular dependences become sin θ cos φ and sin θ sin ϕ. If these functions are plotted against θ (for a fixed value or φ equal to 0° and 90°) or against φ (for a fixed value θ equal to 90°), one gets the pairs of circles along x- and y-axes, respectively. Because of this, these obritals are labeled as p_x and p_y orbitals, respectively. These angular plots also include nodal planes, whose numbers are equal to the value of l. These are known as angular nodes.

The shape of an orbital is the region around the nucleus where there is 90–95% probability of finding the electron. Such a shape can be shown by dot- population or equal-contour diagrams. The shapes of s, p and d orbitals have been shown in Fig. 3.1.

Straight Objective Type

Characteristic of Atoms

1. Rutherford's experiment on scattering of α-particles showed for the first time that the atom has
(a) electrons (b) protons (c) nucleus (d) neutrons (1981)

2. Rutherford's experiment, which established the nuclear model of the atom, used a beam of
(a) β-particales, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered (2002)

3. The triad of nuclei that is isotonic is
(a) ${}^{14}_{6}\mathrm{C}$, ${}^{15}_{7}\mathrm{N}$, ${}^{17}_{9}\mathrm{F}$ (b) ${}^{12}_{6}\mathrm{C}$, ${}^{14}_{7}\mathrm{N}$, ${}^{19}_{9}\mathrm{F}$ (c) ${}^{14}_{6}\mathrm{C}$, ${}^{14}_{7}\mathrm{N}$, ${}^{17}_{9}\mathrm{F}$ (d) ${}^{14}_{6}\mathrm{C}$, ${}^{14}_{7}\mathrm{N}$, ${}^{19}_{9}\mathrm{F}$ (1988)

4. The number of electrons carrying a total charge of 1 C is
(a) 6.023×10^{23} (b) 6.25×10^{18} (c) 6.24×10^{20} (d) 6.023×10^{22}

5. The mass of one mole of electrons is
(a) 0.548 g (b) 0.548 mg (c) 0.548 cg (d) 0.548 dg

6. Which one of the fllowing statements is correct?
(a) Mass of a proton is slightly larger than that of a neutron
(b) Mass of a proton is slightly lesser than that of a neutron
(c) Mass of a proton is exactly equal to that of a neutron
(d) Mass of a proton may be larger or smaller than that of a neutron depending upon the nucleus of isotopes of an atom.

Rutherford's Scattering Experiment

7. Rutherford’s scattering experiment is related to the size of the
(a) nucleus (b) atom (c) electron (d) neutron (1983)

8. Rutherford’s scattering experiment involves
(a) α-particles and thin gold foil (b) helium atom and thin gold foil.
(c) α-particles and thin copper foil. (d) helium atom and thin copper foil.

9. Rutherford’s alpha particle scattering experiment eventually led to the conclusion that
(a) mass and energy are related
(b) electrons occupy space around the nucleus
(c) neutrons are buried deep in the nucleus
(d) the point of impact with matter can be precisely determined (1986)

10. Which of the following does not characterise X-rays?
(a) The radiation can ionise gases. (b) It causes ZnS to fluoresce.
(c) Deflected by electric and magnetic fields. (d) Have wavelengths shorter than ultraviolet rays. (1992)

11. The radius of an atomic nucleus is of the order of
(a) 10^{-10} cm (b) 10^{-13} cm (c) 10^{-15} cm (d) 10^{-8} cm (1985)

Bohr Theory

12. Bohr model can explain
(a) the spectrum of hydrogen atom only
(b) spectrum of an atom or ion containing one electron only
(c) the spectrum of hydrogen molecule
(d) the solar system (1985)

13. Electromagnetic radiation with maximum wavelength is
(a) ultraviolet (b) radiowave (c) X-ray (d) infrared (1985)

14. The ratio of the energy of a photon of 200 nm wavelength radiation to that of 400 nm radiation is
(a) 1/4 (b) 4 (c) 1/2 (d) 2 (1986)

15. The wavelength of a spectral line for an electronic transition is inversely related to
(a) the number of electrons undergoing the transition
(b) the nuclear charge of the atom
(c) the difference in the energy of the energy levels involved in the transition
(d) the velocity of electron undergoing the transition (1988)

16. Which of the following statements is not true?
(a) Lyman spectral series of hydrogen atom lies in the ultraviolet region of electromagnetic radiation.
(b) Balmer spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.
(c) Pashen spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.
(d) Brackett spectral series of hydrogen atom lies in the infrared region of electromagnetic radiation.

17. Which of the following sets of quantum numbers are not correctly represented in case of the indicated spectral series of hydrogen atom?
(a) Lyman series $n_1 = 1$; $n_2 = 2, 3, 4, \ldots$ (b) Balmer series $n_1 = 2$; $n_2 = 3, 4, 5, \ldots$
(c) Paschen series $n_1 = 2$; $n_2 = 3, 4, 5, \ldots$ (d) Brackett series $n_1 = 4$; $n_2 = 5, 6, 7, \ldots$

18. The expression of Rydberg constant is

(a) $2\pi^2 m\, h^3 c/(e^2/4\pi\varepsilon_0)^2$ (b) $2\pi^2 m(e^2/4\pi\varepsilon_0)^2/h^3 c$

(c) $(e^2/4\pi\varepsilon_0)^2/2\pi^2 m h^3 c$ (d) $2\pi^2 m\, h^3 c/(e^2/4\pi\varepsilon_0)$

19. The expression of angular momentum of an electron in a Bohr orbit is

(a) $n(h/2\pi)$ (b) $\sqrt{l(l+1)}\ (h/2\pi)$ (c) $m(h/2\pi)$ (d) $h/4\pi$

20. The radius of first Bohr orbit in hydrogen atom is

(a) 52.9 cm (b) 52.9 μm (c) 52.9 nm (d) 52.9 pm

21. With increasing quantum number, the energy difference between adjacent orbits of hydrogen atom

(a) increases (b) decreases

(c) remains constant (d) first increases followed by a decrease

22. The velocity of an electron in the first Bohr orbit of a hydrogen atom is 2.19×10^6 m s^{-1}. Its velocity in the second orbit would be

(a) 1.10×10^6 m s^{-1} (b) 4.38×10^6 m s^{-1} (c) 5.5×10^5 m s^{-1} (d) 8.76×10^6 m s^{-1}

23. The ionization energy of the ground-state hydrogen atom is 2.18×10^{-18} J. The energy of an electron in its second orbit would be

(a) -1.09×10^{-18} J (b) -2.18×10^{-18} J (c) -4.36×10^{-18} J (d) -5.45×10^{-19} J

24. The expression of energy of an electron in a Bohr orbit of hydrogen-like species is

(a) $E = \dfrac{1}{n^2}\left[\dfrac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right]$ (b) $E = \dfrac{1}{n^2}\left[\dfrac{h^2}{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}\right]$

(c) $E = -\dfrac{1}{n^2}\left[\dfrac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right]$ (d) $E = -\dfrac{1}{n^2}\left[\dfrac{h^2}{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}\right]$

25. The value of Planck's constant is

(a) 6.626×10^{-34} J s (b) 6.023×10^{23} J s (c) 6.626×10^{-27} J s (d) 6.626×10^{-24} J s

26. The first use of quantum theory to explain the structure of atom was made by

(a) Heisenberg (b) Bohr (c) Planck (d) Einstein (1997)

27. Which of the following orbits has the same radius as that of the first Bohr's orbits of hydrogen atom?

(a) Second orbit of He$^+$ (b) Second orbit of Li^{2+} (c) Third orbit of Be^{3+} (d) Second orbit of Be^{3+}

(2004)

28. The expression of radius of a Bohr orbit in a hydrogen-like species is

(a) $r = n^2\left[\dfrac{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}{h^2}\right]$ (b) $r = \dfrac{1}{n^2}\left[\dfrac{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}{h^2}\right]$

(c) $r = n^2\left[\dfrac{h^2}{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}\right]$ (d) $r = \dfrac{1}{n^2}\left[\dfrac{h^2}{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}\right]$

29. The expression of velocity of an electron in a Bohr orbit of a hydrogen-like species is

(a) $v = \dfrac{2\pi(Ze^2/4\pi\varepsilon_0)}{nh}$ (b) $v = \dfrac{2\pi nh}{(Ze^2/4\pi\varepsilon_0)}$ (c) $v = \dfrac{nh}{2\pi(Ze^2/4\pi\varepsilon_0)}$ (d) $v = \dfrac{(Ze^2/4\pi\varepsilon_0)}{2\pi nh}$

30. The ratio of kinetic energy and potential energy of an electron in a Bohr orbit of a hydrogen-like species is

(a) 1/2 (b) –1/2 (c) 1 (d) –1

31. The ratio of kinetic energy and total energy of an electron in a Bohr orbit of a hydrogen-like species is

(a) 1/2 (b) –1/2 (c) 1 (d) –1

32. The ratio of potential energy and total energy of an electron in a Bohr orbit of a hydrogen-like species is

(a) 2 (b) –2 (c) 1 (d) –1

33. The value of Rydberg constant is

(a) 1.0978×10^7 cm^{-1} (b) 1.0978×10^7 m^{-1} (c) 1.0978×10^{-7} cm^{-1} (d) 1.0978×10^{-7} m^{-1}

34. The ionization energy of hydrogen atom in terms of Rydberg constant (R_H) is given by the expression

(a) $R_H hc$ (b) $R_H c$ (c) $2R_H hc$ (d) $R_H N_A hc$

35. The energy of an electron in the first Bohr orbit for hydrogen is –13.6 eV. Which one of the following is a possible excited state for electron in Bohr orbit of hydrogen atom?
(a) –3.4 eV (b) –6.8 eV (c) –1.7 eV (d) 13.6 eV

36. The spectral line obtained when an electron jumps from $n = 6$ to $n = 2$ levels in hydrogen atom belongs to the
(a) Balmer series (b) Lyman series (c) Paschen series (d) Pfund series

37. Which of the following species will produce the shortest wavelength for the transition $n = 2$ to $n = 1$?
(a) Hydrogen atom (b) Singly ionized helium (c) Deuterium atom (d) Doubly ionized lithium

38. The ionization potential of hydrogen atom is 13.6 eV. The energy required to remove an electron in the $n = 2$ state of the hydrogen atom is
(a) 3.4 eV (b) 6.8 eV (c) 13.6 eV (d) 27.2 eV

39. If the wavelength of the first line of the Balmer series of hydrogen atom is 656.1 nm, the wavelength of the second line of this series would be
(a) 218.7 nm (b) 328.0 nm (c) 486.0 nm (d) 640.0 nm

40. The energy of an electron in the first Bohr orbit of H atom is – 13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are)
(a) – 3.4 eV (b) – 4.2 eV (c) – 6.8 eV (d) + 6.8 eV (1998)

41. Which of the following statements about Bohr theory of hydrogen atom is not correct?
(a) Centripetal force acting on the electron is $Ze^2/(4\pi\ \varepsilon_0 r)$.
(b) Centrifugal force acting on the electron is mv^2/r
(c) Angular momentum of electron is $n(h/2\pi)$
(d) Bohr radius is about 52.9 pm

42. Which of the following statements regarding Bohr theory of hydrogen atom is not correct?
(a) Kinetic energy of an electron in an orbit is equal to half of magnitude of its potential energy
(b) Kinetic energy of an electron in an orbit is equal to the magnitude of its potential energy
(c) Total energy of an electron is equal to negative of its kinetic energy
(d) Potential energy of an electron in an orbit is equal to $-\ mv^2$.

43. Which of the following statements regarding Bohr theory of hydrogen atom is not correct?
(a) The ionization energy of atom is equal to the energy equivalent to Rydberg constant
(b) Speed of electron in the $n = 2$ orbit is larger than that in the $n = 1$ orbit
(c) Radius of orbit is directly proportional to square of quantum number n
(d) The distance between successive orbits increases with increase in the value of quantum number n.

44. The speed of electron in the first orbit ($n = 1$) of hydrogen atom is 2.19×10^6 m s^{-1}. Its speed in the second orbit ($n = 2$) of the helium ion will be
(a) 2.19×10^6 m s^{-1} (b) 1.10×10^6 m s^{-1} (c) 4.38×10^6 m s^{-1} (d) 3.29×10^6 m s^{-1}

45. The energy of electron in the first orbit ($n = 1$) of hydrogen atom is $-\ 2.18 \times 10^{-18}$ J. Its energy in the third orbit of lithium dipositive ion will be
(a) $-\ 1.09 \times 10^{-18}$ J (b) $-\ 2.18 \times 10^{-18}$ J (c) $-\ 3.27 \times 10^{-18}$ J (d) $-\ 4.36 \times 10^{-18}$ J

46. The radius of first orbit ($n = 1$) in hydrogen atom is 52.9 pm. The radius of third orbit of lithium dipositive ion will be
(a) 26.45 pm (b) 52.9 pm (c) 105.8 pm (d) 158.7 pm

47. Which of the following spectral series of hydrogen atom lies in the ultraviolet region of electromagnetic radiation?
(a) Lyman (b) Balmer (c) Paschen (d) Brackett

48. Which of the following spectral series of hydrogen atom lies in the visible region of electromagnetic radiation?
(a) Lyman (b) Balmer (c) Paschen (d) Brackett

49. Which of the following spectral series of hydrogen atom lies in the far infrared region of electromagnetic radiation?
(a) Lyman (b) Balmer (c) Paschen (d) Pfund

50. For the Lyman series of hydrogen atom, the values of n_1 and n_2 in the expression $\Delta E = Rhc[(1/n_1^2) - (1/n_2^2)]$ are given as
(a) $n_1 = 1, n_2 = 2, 3, 4, ...$ (b) $n_1 = 2, n_2 = 3, 4, 5, ...$
(c) $n_1 = 3, n_2 = 4, 5, 6, ...$ (d) $n_1 = 4, n_2 = 5, 6, ...$

51. For the Balmer series of hydrogen atom, the values of n_1 and n_2 in the expression $\Delta E = Rhc[(1/n_1^2) - (1/n_2^2)]$ are given as
(a) $n_1 = 1, n_2 = 2, 3, 4, ...$ (b) $n_1 = 2, n_2 = 3, 4, 5, ...$
(c) $n_1 = 3, n_2 = 4, 5, 6, ...$ (d) $n_1 = 4, n_2 = 5, 6, ...$

52. For the Paschen series of hydrogen atom, the values of n_1 and n_2 in the expression $\Delta E = Rhc[(1/n_1^2) - (1/n_2^2)]$ are given as
(a) $n_1 = 1, n_2 = 2, 3, 4, ...$ (b) $n_1 = 2, n_2 = 3, 4, 5, ...$
(c) $n_1 = 3, n_2 = 4, 5, 6, ...$ (d) $n_1 = 4, n_2 = 5, 6, ...$

53. For the Brackett series of hydrogen atom, the values of n_1 and n_2 in the expression $\Delta E = Rhc[(1/n_1^2) - (1/n_2^2)]$ are given as
(a) $n_1 = 1, n_2 = 2, 3, 4, ...$ (b) $n_1 = 2, n_2 = 3, 4, 5, ...$
(c) $n_1 = 3, n_2 = 4, 5, 6, ...$ (d) $n_1 = 4, n_2 = 5, 6, ...$

54. For the Pfund series of hydrogen atom, the values of n_1 and n_2 in the expression $\Delta E = Rhc[(1/n_1^2) - (1/n_2^2)]$ are given as
(a) $n_1 = 2, n_2 = 3, 4, 5, ...$ (b) $n_1 = 3, n_2 = 4, 5, 6, ...$
(c) $n_1 = 4, n_2 = 5, 6, ...$ (d) $n_1 = 5, n_2 = 6, 7, ...$

55. The transition $n_2 \rightarrow n_1$ in hydrogen atom has the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ ion. The values of n_2 and n_1, respectively, are
(a) 2, 1 (b) 3, 2 (c) 4, 3 (d) 3, 1

56. The value of Rydberg constant is 1.0974×10^7 m^{-1}. The ionization energy of Li^{2+} ions is about
(a) 9180 kJ mol^{-1} (b) 11825 kJ mol^{-1}
(c) 13180 kJ mol^{-1} (d) 15180 kJ mol^{-1}

57. The value of Rydberg constant is 1.096×10^7 m^{-1}. A spectral line of the Lyman series of hydrogen atom has a frequency of 2.466×10^{15} s^{-1}. This transition corresponds to
(a) $1 \rightarrow 2$ transition (b) $1 \rightarrow 3$ transition
(c) $2 \rightarrow 3$ transition (d) $2 \rightarrow 4$ transition

58. The ionization energy of He^+ is 19.6×10^{-18} J per atom. The energy of the second stationary state in Li^{2+} ion will be
(a) 4.9×10^{-18} J (b) 2.18×10^{-18} J
(c) 44.1×10^{-18} J (d) -11.025×10^{-18} J

59. In Bohr theory, which of the following expressions for the speed of an electron is correct?
(a) $v \propto Z / n$ (b) $v \propto n / Z$ (c) $v \propto Z^2 / n^2$ (d) $v \propto n^2 / Z^2$

60. Which of the following expressions for the radii of Bohr orbits is correct?
(a) $r \propto n / Z$ (b) $r \propto n^2 / Z^2$ (c) $r \propto n^2 / Z$ (d) $r \propto Z^2 / n^2$

61. Which of the following expressions for the energy of electron in Bohr orbits is correct?
(a) $E \propto Z / n^2$ (b) $E \propto -Z / n^2$ (c) $E = -n^2 / Z$ (d) $E \propto -Z^2 / n^2$

62. Which of the following electronic transitions in the spectrum of He^+ will have the same wavelength as that of the first line in the Lyman series of hydrogen atom?
(a) $4 \leftarrow 2$ (b) $2 \leftarrow 1$ (c) $3 \leftarrow 1$ (d) $4 \leftarrow 1$

63. The kinetic energy of an electron in He^+ is maximum when it is present in the orbit having
(a) $n = 1$ (b) $n = 2$ (c) $n = 3$ (d) $n = \infty$

64. The longest wavelength in Balmer series is
(a) 656.5 nm (b) 770 nm (c) 360 nm (d) 450 nm

65. An energy of 24.6 is required to remove one of the electrons from a neutral helium atom. The energy required to remove both the electrons from a neutral helium atom is
(a) 38.2 eV (b) 49.2 eV (c) 51.8 eV (d) 79.0 eV

66. As per Bohr model, the minimum energy required to remove an electron from the ground state of doubly ionized Li atom ($Z = 3$) is
(a) 1.51 eV (b) 13.6 eV (c) 40.8 eV (d) 122.4 eV

67. The electron in a hydrogen atom makes a transition from an excited state to the ground state. Which of the following statements is correct ?

(a) Its kinetic energy increases and its potential total energies decrease
(b) Its kinetic energy decreases, potential energy increases and its total energy remains constant
(c) Its kinetic and total energie decreases and its potential energy increases
(d) Its kinetic, potential and total energies decrease

68. The transition from the state $n = 4$ to $n = 3$ in a hydrogen like atom results in ultraviolet radiation. Infrared radiation will be obtained in the transition

(a) $2 \rightarrow 1$ (b) $3 \rightarrow 2$ (c) $4 \rightarrow 2$ (d) $5 \rightarrow 4$

69. If an atom $^{257}_{100}\text{Fm}$ follows the Bohr model and the radius of $^{257}_{100}\text{Fm}$ is m times the Bohr radius, then the value of m is

(a) 1/4 (b) 4 (c) 50 (d) 100

Quantum Numbers and Orbitals

70. The principal quantum number of an atom is related to the

(a) size of the orbital (b) spin angular momentum
(c) orbital angular momentum (d) orientation of the orbital in space (1983)

71. Which one of the following sets of quantum numbers represents an impossible arrangement?

	n	l	m_l	m_s		n	l	m_l	m_s
(a)	3	2	-2	1/2	(b)	4	0	0	1/2
(c)	3	2	-3	1/2	(d)	5	3	0	$-1/2$

(1986)

72. The angular momentum of an electron in an atomic orbital is governed by the

(a) principal quantum number (b) azimuthal quantum number
(c) magnetic quantum number (d) spin quantum number

73. The z-component of angular momentum of an electron in an atomic orbital is governed by the

(a) principal quantum number (b) azimuthal quantum number
(c) magnetic quantum number (d) spin quantum number

74. The number of orbitals in a subshell is equal to

(a) n^2 (b) $2l$ (c) $2l + 1$ (d) m

75. Which of the following orbitals is symmetric about the y-axis?

(a) p_x (b) p_y (c) $d_{x^2-y^2}$ (d) d_{xy}

76. The angular momentum of an electron in an orbital is given as

(a) $L = n(h/2\pi)$ (b) $L = l(h/2\pi)$ (c) $L = \sqrt{l(l+1)}\,(h/2\pi)$ (d) $L = m(h/2\pi)$

77. The angle made by angular momentum vector of an electron with z-axis is given as

(a) $\cos\theta = l/m$ (b) $\cos\theta = \sqrt{l/m}$ (c) $\cos\theta = \sqrt{l(l+1)}/m$ (d) $\cos\theta = m/\sqrt{l(l+1)}$

where l and m are azimuthal and magnetic quantum numbers.

78. Which of the following atoms would be expected to be most paramagnetic?

(a) $_3\text{Li}$ (b) $_4\text{Be}$ (c) $_5\text{B}$ (d) $_6\text{C}$

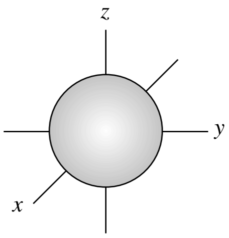
79. Which of the following statements is not correct?

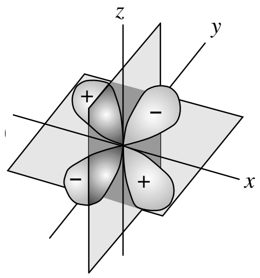
(a) The shape of an atomic orbital depends on the azimuthal quantum number.
(b) The orientation of an atomic orbital depends on the magnetic quantum number.
(c) The energy of an electron in an atomic orbital of multielectron atom depends on principal quantum number.
(d) The number of degenerate atomic orbitals of one type depends on the values of azimuthal and magnetic quantum numbers.

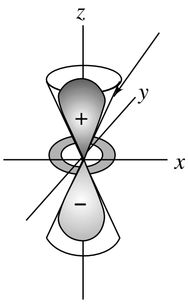
80. Which of the following sets of quantum numbers is not allowed?

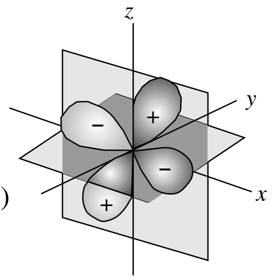
(a) $n = 3,\ l = 1,\ m = +2$ (b) $n = 3,\ l = 1,\ m = +1$
(c) $n = 3,\ l = 0,\ m = 0$ (d) $n = 3,\ l = 2,\ m = \pm 2$

81. Which of the following orbitals represents $3d_{z^2}$ orbital?

(a) 

(b) 

(c) 

(d) 

82. The orbital angular momentum of an electron in 2s orbital is:

(a) $+\frac{1}{2}\frac{h}{2\pi}$ (b) Zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\frac{h}{2\pi}$

83. For a d-electron, the orbital angular momentum is

(a) $\sqrt{6}\,(h/2\pi)$ (b) $\sqrt{2}\,(h/2\pi)$ (c) $(h/2\pi)$ (d) $2(h/2\pi)$ (1997)

84. In which of the following orbitals, the electrons has the maximum energy?

(a) 3p (b) 4f (c) 4p (d) 4s

85. The correct statement on the aufbau principle is that

(a) $(n-1)$d subshell is always lower in energy than ns orbital
(b) $(n-1)$f subshell always has energy more than np orbital
(c) 5d is lower in energy than 4f
(d) 6p is lower in energy than 5d

86. The quantum numbers +1/2 and –1/2 for the electron spin represent

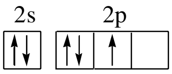
(a) rotation of the electron in clockwise and anticlockwise direction respectively
(b) rotation of the elctron in anticlockwise and clockwise direction respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

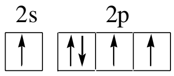
Electronic Configurations

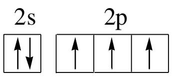
87. Any p-orbital can accommodate upto

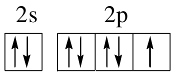
(a) four electrons (b) two electrons with parallel spins
(c) six electrons (d) two electrons with opposite spins

88. The orbital diagram in which the aufbau principle is violated is

(a) 

(b) 

(c) 

(d) 

(1988)

89. The outermost electronic configuration of the most electronegative element is

(a) $(ns)^2(np)^3$ (b) $(ns)^2(np)^4$ (c) $(ns)^2(np)^5$ (d) $(ns)^2(np)^6$ (1988)

90. The correct ground state electronic configuration of chromium atom is

(a) $[Ar](3d)^5(4s)^1$ (b) $[Ar](3d)^4(4s)^2$ (c) $[Ar](3d)^6(4s)^0$ (d) $[Ar](4d)^5(4s)^1$ (1989)

91. The correct set of quantum numbers for the unpaired electron of chlorine atom is

	n	l	m_l		n	l	m_l
(a)	2	1	0	(b)	2	1	1
(c)	3	1	1	(d)	3	0	0

(1989)

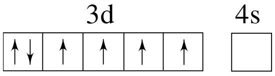
92. The maximum number of electrons that can be accommodated in a quantum shell is equal to

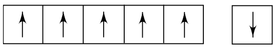
(a) n (b) n^2 (c) $2n^2$ (d) $n(n+1)$

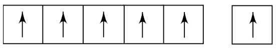
93. The correct set of four quantum numbers for the valence electron of rubidium ($Z = 37$) is

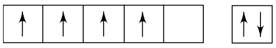
(a) $n = 5,\ l = 0,\ m = 0,\ m_s = +1/2$ (b) $n = 5,\ l = 1,\ m = 0,\ m_s = +1/2$
(c) $n = 5,\ l = 1,\ m = 1,\ m_s = +1/2$ (d) $n = 6,\ l = 0,\ m = 0,\ m_s = +1/2$ (1984)

94. Which of the following arrangements of electrons is most likely to be stable?

(a) 

(b) 

(c) 

(d) 

95. The number of unpaired electrons present in the ground state of Cr is
(a) 3 (b) 4 (c) 5 (d) 6

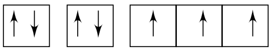
96. Hund's rule deals with the distribution of electrons in
(a) a quantum shell (b) an orbit (c) a orbital (d) degenerate orbitals

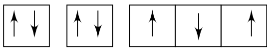
97. Which of the following statements is correct?
(a) $(n-1)$d subshell has lower energy than ns subshell
(b) $(n-1)$d subshell has higher energy than ns subshell
(c) $(n+1)$d subshell has lower energy that nf subshell
(d) nf subshell has lower energy than $(n+2)$s subshell

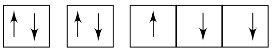
98. Which of the following statements is not correct?
(a) Special stability of half-filled and fully-filled atomic configurations amongst s- and p-block elements is reflected in ionization potential trends along a period.
(b) Special stability of half-filled and fully-filled atomic configurations amongst s- and p-block elements is reflected in electron affinity trends along a period.
(c) Aufbau order is not obeyed in cases where energy difference between ns and $(n-1)$d subshell is large.
(d) Special stability of half-filled subshell is attributed to higher exchange energy of stabilization.

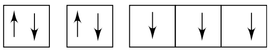
99. The electrons, identified by quantum numbers n and l (i) $n = 4$, $l = 1$, (ii) $n = 4$, $l = 0$, (iii) $n = 3$, $l = 2$ and (iv) $n = 3$, $l = 1$ can be placed in order of increasing energy, from the lowest to highest, as
(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii) (1999)

100. Ground state electronic configuration of nitrogen atom can be represented by

(a) 

(b) 

(c) 

(d) 

(1999)

101. The outer electronic configuration of cerium ($Z = 58$) is
(a) $(4d)^{10}\ (5s)^2\ (5p)^6\ (4f)^3\ (6s)^1$ (b) $(4d)^{10}\ (5s)^2\ (5p)^6\ (5d)^1\ (6s)^2$
(c) $(4d)^{10}\ (5s)^2\ (5p)^6\ (5d)^3\ (6s)^2$ (d) $(4d)^{10}\ (5s)^2\ (5p)^6\ (4f)^2\ (6s)^2$

102. If the nitrogen atom had electronic configuration $(1s)^7$, it would have energy lower than that of the normal ground state configuration $(1s)^2(2s)^2(2p)^3$, because the electrons would be closer to the nucleus. Yet, $(1s)^7$ is not observed because it violates
(a) Heisenberg uncertainty principle (b) Hund's rule
(c) Pauli exclusion principle (d) Bohr postulate of stationary orbits (2002)

Quantum Mechanical Approach

103. Which of the following relates to photon both as wave motion and as a stream of particles?
(a) Interferance (b) $E = mc^2$ (c) Diffraction (d) $E = h\nu$ (1992)

104. The energy of an electron in an atomic orbital of a multielectron atom depends on
(a) the principal quantum number only
(b) the principal and azimuthal quantum numbers only
(c) the principal, azimuthal and magnetic quantum numbers only
(d) the principal, azimuthal, magnetic and spin quantum numbers

105. The energy of an electon in an atomic orbital of hydrogen-like species depends on
(a) the principal quantum number only
(b) the principal and azimuthal quantum numbers only
(c) the principal, azimuthal and magnetic quantum numbers only
(d) the principal, azimuthal, magnetic and spin quantum numbers.

106. An orbital in an atom is represented by quantum number(s)
(a) n (b) n and l (c) n, l and m (d) n, l, m and m_s

107. An orbital with $l = 0$ is symmetrical about the
(a) x-axis only (b) y-axis only (c) z-axis only (d) nucleus

108. Which electronic level allows the hydrogen atom to absorb a photon but not emit a photon?
(a) 2s (b) 3s (c) 2p (d) 3d

109. Which of the following orbitals has zero probability of finding the electron in yz plane?
(a) p_x (b) p_y (c) p_z (d) d_{yz}

110. In an atomic orbital, the sign of lobes indicates the
(a) sign of the probability distribution (b) sign of charge
(c) sign of the wave function (d) presence or absence of electron

111. Which of the following atomic orbitals **does not** have the four lobes lying symmetrically between the axial directions?
(a) 3 d_{xy} (b) 3 d_{xz} (c) 3 d_{yz} (d) 3 $d_{x^2-y^2}$

112. 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) It is the region around the nucleus where there is 90 to 95% probability of finding all electrons in an atom
(d) An orbital is characterised by the three distinct quantum numbers n, l and m

113. Which of the following symbols correctly represents an orbital in an atom?
(a) $\Psi_{n,l,m} = R_n\ \Theta_l\ \Phi_m$ (b) $\Psi_{n,l,m} = R_{n,l}\ \Theta_l\ \Phi_m$
(c) $\Psi_{n,l,m} = R_{n,l}\ \Theta_{l,|m|}\ \Phi_m$ (d) $\Psi_{n,l,m} = R_n\ \Theta_{l,m}\ \Phi_m$

114. The probability of finding 1s electron is maximum
(a) at the nucleus
(b) at the Bohr radius
(c) at a larger distance than the Bohr radius
(d) in between the nucleus and the first Bohr radius

115. The number of nodal points in the plot of $R_{n,0}$ versus r is equal to the value of
(a) n (b) l (c) $n - l$ (d) $n - (l + 1)$

116. For 2s orbital of hydrogen atom, the nodal surface exists at a distance
(a) a_0 from the nucleus (b) $2a_0$ from the nucleus
(c) $2.5a_0$ from the nucleus (d) $4.0a_0$ from the nucleus

117. The number of radial nodes in the 3p probability density distribution is
(a) 0 (b) 1 (c) 2 (d) 3

118. In the plot of $r^2R^2_{1,0}$ versus r for hydrogen atom, maximum occurs at
(a) $r = 0$ (b) $r = a_0$ (c) $r = 2a_0$ (d) $r = \infty$

119. A d_{yz} orbital has
(a) no nodal plane (b) one nodal plane in the yz plane
(c) two nodal planes in the xy and xz planes (d) three nodal planes in the xy, xz and yz planes

120. A $d_{x^2-y^2}$ orbital has
(a) no nodal plane (b) one nodal plane in the xy plane
(c) two nodal planes in the xz and yz planes (d) two nodal planes at angles 45° to x and y-axes

121. A d_{xy} orbital is directed
(a) along the x-and y-axes (b) along the z-axes
(c) along the centre of x- and y-axes (d) along the centre of x- and z-axes

122. For $3d_{z^2}$ orbital, the value of l and m, respectively, are
(a) 2, 0 (b) 2, +1 (c) 2, –1 (d) 2, +2

123. The angular momentum of 4f electron is
(a) $4(h/2\pi)$ (b) $\sqrt{12}\ (h/2\pi)$ (c) $\sqrt{6}\,(h/2\pi)$ (d) $\sqrt{2}\ (h/2\pi)$

124. Which of the following statements on quantum numbers is **not** correct?
(a) Quantum numbers n, l, m and m_s are needed to describe completely an electron in an atom
(b) Quantum numbers n, l, m and s are obtained by solving the Schrödinger wave equation
(c) A subshell in an atom can be designated with two quantum numbers n and l
(d) The maximum value of l is equal to $n - 1$ and that of m is $\pm\ l$.

125. Which of the following statements is **not** correct?
(a) The wave function depicting the dependence on r involves two quantum numbers
(b) The wave function depicting the angular dependence involves two quantum numbers l and m
(c) The spin quantum number is not the outcome of the Schrödinger equation
(d) The lowest energy state of an atom corresponds to $n = 0$

126. In an orbital, the signal of lobes indicate the
(a) sign of the wave function (b) sign of the probability distribution
(c) presence or absence of electron (d) sign of charge

127. Which of the following statements on the atomic wave function Ψ is **not** correct?
(a) Ψ may be a real valued wave function
(b) Ψ may, in some cases, be a complex
(c) Ψ has a mathematical significance only
(d) Ψ is proportional to the probability of finding an electron

128. Which of the following statements on the square of atomic wave function is **not** correct?
(a) Ψ^2 may be positive, negative or imaginary
(b) Ψ^2 is proportional to electron density
(c) Ψ^2 is directly proportional to the probability of finding the electron
(d) Ψ^2 is equal to the probability of finding the electron if Ψ is a normalized wave function

129. Which of the following orbitals is symmetric about the y-axis?
(a) p_x (b) p_y (c) d_{xy} (d) d_{xy}

130. The plot of $r^2\Psi^2$ versus r for 2s orbital of hydrogen atom exhibits
(a) one maximum (b) two maxima (c) no maximum (d) three maxima

131. The angular momentum of an electron in p orbitals is equal to
(a) zero (b) $(h/2\pi)$ (c) $\sqrt{2}\,(h/2\pi)$ (d) $\sqrt{6}\,(h/2\pi)$

132. The angular momentum of an electron in d orbitals is equal to
(a) zero (b) $(h/2\pi)$ (c) $\sqrt{2}\,(h/2\pi)$ (d) $\sqrt{6}\,(h/2\pi)$

133. The p_z orbital corresponds to the magnetic quantum number m equal to
(a) 0 (b) + 1 (c) – 1 (d) + 2

134. The magnetic quantum number corresponding to d_{z^2} orbital is
(a) + 2 (b) + 1 (c) 0 (d) – 2

135. For which of the following species, the electronic distribution is spherically symmetrical?
(a) H (b) Na (c) Cl^- (d) B

136. The number of radial nodes in the 3p probability density distribution is
(a) 0 (b) 1 (c) 2 (d) 3

137. Which of the following sets of quantum numbers is not allowed?
(a) $n = 2$, $l = 1$, $m = +\ 2$ (b) $n = 2$, $l = 1$, $m = +\ 1$
(c) $n = 2$, $l = 0$, $m = 0$ (d) $n = 2$, $l = 1$, $m = -\ 1$

138. The number of allowed values of magnetic quantum numbers for a given value of azimuthal quantum number l is
(a) $l + 1$ (b) $l + 2$ (c) $2l + 1$ (d) $2l + 2$

139. For silver metal, threshold frequency for the emission of photoelectron is $1.13 \times 10^7\ s^{-1}$. The kinetic energy of electrons when silver is irradiated with a wavelength of 1.5 nm is
(a) 5.76×10^{-17} J (b) 5.76×10^{-16} J (c) 5.76×10^{-15} J (d) 5.76×10^{-14} J

140. The binding energy of electrons in a metal is 193 kJ mol^{-1}. The threshold frequency of the metal is
(a) 4.83×10^{10} Hz (b) 4.83×10^{12} Hz (c) 4.83×10^{14} Hz (d) 4.83×10^{16} Hz

141. The momentum of a particle having de Broglie wavelength of 0.1 nm is
(a) 6.626×10^{-21} kg m s^{-1} (b) 6.626×10^{-22} kg m s^{-1}
(c) 6.626×10^{-23} kg m s^{-1} (d) 6.626×10^{-24} kg m s^{-1}

142. An electron is accelerated through a potential difference of 500 V. Its de Broglie wavelength would be
(a) 55 pm (b) 5.5 pm (c) 0.55 pm (d) 55 nm

143. A proton is accelerated to one tenth the speed of light. Its speed can be measured with a precision of 1%. Its uncertainty in position is equal to or greater than
(a) 1.93 nm (b) 19.3 nm (c) 19.3 pm (d) 0.105 pm

144. The number of radial nodes in 3p and 4s orbitals, respectively, are
(a) 1,3 (b) 3,1 (c) 2,2 (d) 2,1

145. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order
(a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m

146. The work function of a substance is 4.0 eV. The longest wavelength of light that can cause photoelectron emission from this substance is approximately
(a) 540 nm (b) 400 nm (c) 310 nm (d) 220 nm

Multiple Correct Choice Type

1. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because
(a) alpha particles are much heavier than electrons (b) alpha particles are positively charged
(c) most part of the atom is empty space (d) alpha particles move with high speed

2. An isotone of $^{76}_{32}\text{Ge}$ is
(a) $^{77}_{32}\text{Ge}$ (b) $^{77}_{33}\text{As}$ (c) $^{77}_{34}\text{Se}$ (d) $^{78}_{34}\text{Se}$

3. Many elements have nonintegral atomic masses because
(a) they have isotopes
(b) their isotopes have non-integral masses
(c) their isotopes have different masses
(d) the constituents, neutrons, protons and electrons combine to give fractional masses

4. Which of the following statement(s) is (are) correct?
(a) The electronic configuration of Cr is [Ar] $(3d)^5(4s)^1$. (Atomic number of Cr = 24.)
(b) The magnetic quantum number may have negative values.
(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47.)
(d) The oxidation state of nitrogen in HN_3 is −3.

5. Which of the following sets of quantum numbers is/are allowed?
(a) $n = 1$, $l = 0$ and $m = 0$ (b) $n = 2$, $l = 1$ and $m = +1$
(c) $n = 1$, $l = 0$ and $m = +1$ (d) $n = 2$, $l = 2$ and $m = 0$

6. Which of the following expressions is/are correct for the Bohr orbits in a hydrogen atom?
(a) $r = n^2\left[\dfrac{h^2}{4\pi^2 m(e^2/4\pi\varepsilon_0)}\right]$ (b) $E = -\dfrac{1}{n^2}\left[\dfrac{2\pi^2 m(e^2/4\pi\varepsilon_0)^2}{h^2}\right]$
(c) $L = n(h/2\pi)$ (d) Kinetic energy of the electron = Potential energy of the electron

7. Which of the following statements regarding electron in an atom is/are correct?
(a) The complete description of electron in an atom is described by the three quantum numbers n, l and m.
(b) The energy of an electron is governed only by the principal quantum number.
(c) The magnitude of angular momentum is governed by the azimuthal quantum number.
(d) The spin of electron is characterised by the quantum number m_s.

8. Which of the following statements regarding Bohr theory is/are correct?
   (a) Kinetic energy of an electron is half of the magnitude of its potential energy.
   (b) Kinetic energy of an electron is negative of total energy of electron.
   (c) Energy of electron decreases with increase in the value of principal quantum number.
   (d) The ionization energy of hydrogen atom in the first excited state is the negative of one fourth of the energy of an electron in the ground state.

9. An electron which is accelerated through a potential diference of 100 V has the following characteristics.
   (a) Its wavelength is 1.2×10^{-10} m.
   (b) It moves with a speed of 5.9×10^{6} cm/s.
   (c) It has kinetic energy equal to 9.54×10^{6} J/mol.
   (d) Its momentum is 5.369×10^{-24} kg m/s.

10. Which of the following radius of orbits in a hydrogen atom is/are permissible?
   (a) 52.9 pm (b) 182 pm (c) 211 pm (d) 364 pm

11. Which of the following electronic energy in He^+ species is/are allowed?
   (a) – 13.6 eV (b) – 27.2 eV (c) – 54.4 eV (d) – 6.04 eV

12. The characteristics of X-ray produced in an X-ray tube subjected to 50 kV is/are
   (a) $\lambda = 2.5 \times 10^{-11}$ m (b) $n = 1.2 \times 10^{19}$ Hz (c) $E = 7.95 \times 10^{-12}$ (d) $= 4 \times 10^{10}$/m

13. Which of the following statements are **not** correct?
   (a) The outer electronic configuration of the ground state chromium atom is $(3d)^4\ (4s)^2$.
   (b) Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} cm to 10^{-5} cm.
   (c) The energy of the electron in the 3d-orbital is less than that in the 4s-orbital of a hydrogen atom.
   (d) The electron denstity in the *xy* plane in $3d_{x^2-y^2}$ orbital is zero.

14. Which of the following statements are **not** correct?
   (a) Dipositive zinc exhibits paramagnetism due to lost of two electrons from a 3d-orbital of neutral atom.
   (b) The magnetic moment of an atom is related to the number of unpaired electrons in its electronic configuration.
   (c) Bohr theory can be successfully modified to explain the electronic spectrum of multielectron atom.
   (d) The angular momentum of an electron in a atom is given as $n(h/2\pi)$.

15. Which of the following statements are correct?
   (a) The angular momentum of an electron due to its spinning is given as $\sqrt{s(s+1)}\,(h/2\pi)$ where s can take the value of 1/2.
   (b) The angular momentum of an electron due to its spinning is given as $m_s(h/2\pi)$ where m_s can take the value of +1/2.
   (c) According to Pauli's exclusion principle, no two electrons in an atom can have the same values of quantum numbers n, l and m.
   (d) The azimuthal quantum number cannot have negative values.

16. Which of the following statements are correct?
   (a) The potential energy of an electron in an orbit is twice in magnitude as compared to its kinetic energy.
   (b) The total energy of an electron in an orbit is half of its potential energy.
   (c) The speed of an electron in a orbit increases with increase in its quantum number n.
   (d) The energy of an electron in a orbit decreases with increase in its quantum number n.

17. Which of the following statements are **not** correct?
   (a) The ionization energy of a hydrogen-like species in its ground state is equal to the magnitude of energy of the orbit having $n = 1$.
   (b) The ionization energy of a hydrogen-like species in its ground state increases in proportion to the positive charge in its nucleus.
   (c) According to the uncertainty principle, $\Delta p \Delta x \leq h/4\pi$.
   (d) The energy of an electron in a orbital of a multielectron atom depends only on the principal quantum number n.

18. Which of the following statements are correct?
   (a) The energy of an electron in an orbital of a hydragen-like species depends only on the principal quantum number n.
   (b) The angular momentum of an elelctron in an orbital of a multielectron atom depends on the quantum numbers l and m.
   (c) The expression of angular momentum of an electron in an orbital is given as $\sqrt{l(l+1)}$ $(h/2\pi)$.
   (d) The z-component of angular momentum of an electron in an orbital is given as $m(h/2\pi)$.

19. Which of the following statements are correct?
   (a) The number of orbitals for a given value of l is equal to $2l + 1$.
   (b) The number of orbitals for a given value of n is equal to n^2.
   (c) An atom having unpaired electrons is diamagnetic in nature.
   (d) The half-filled and fully-filled electronic configurations are less stable than the other configuration having the same number of electrons.

20. Which of the following statements are correct?
   (a) All s orbitals are spherical symmetrical in shape.
   (b) The symbol s for the orbitals having $l = 0$ has its origin from the term spherical symmetrical.
   (c) The increasing order for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is $\text{n} < \alpha < \text{p} < \text{e}$.
   (d) Pfund spectral series for which $n_1 = 5$ and $n_2 = 6, 7, ...$ lies in the far infrared region of the electromagnetic.

21. Which of the following statements are correct?
   (a) Visible region of electromagnetic radiations have wavelength from 400 nm to 800 nm.
   (b) The energy of photon having wavelength 800 nm is larger than that having 400 nm.
   (c) Balmer spectral series lies in the visible portion of the electromagnetic radiation.
   (d) Lyman spectral series lies in the visible portion of the electromagnetic radiation.

22. Which of the following statements are correct?
   (a) Brackett spectral series for which $n_1 = 4$ and $n_2 = 5, 6, 7, ...$ lies in the infrared region of the electromagnetic radiation .
   (b) The orbital $3d_{z^2}$ is symmetrical about z-axis.
   (c) The orbital $3d_{xy}$ has no probability of finding electron along x- and y-axis.
   (d) The orbital $3d_{x^2-y^2}$ has no probability of finding electron along x- and y-axis.

23. Which of the following statements are correct?
   (a) The electron density in the xy plane in $3d_{xy}$ orbital is zero.
   (b) The electron densities in the xy and xz planes in $3d_{yz}$ orbital are zero.
   (c) The electron density in the xy plane in $3d_{z2}$ orbital is zero.
   (d) The d-orbitals are no more degenerate in the presence of a magnetic field.

24. Which of the following stantements are correct?
   (a) The spin quantum number was introduced to explain the splitting of spectral lines of hydrogen atom in the presence of a magnetic field.
   (b) Pauli exclusion principle is followed by fermions which have half-integral spins.
   (c) Pauli exclusion principle is followed by bosons which have integral spin.
   (d) A configuration with the maximum spin multiplicity has the minimum energy and thus is most stable.

25. Which of the following statements are correct?
   (a) The energy of an orbital in an atom remains the same with increase in the positive charge in its nucleus.
   (b) The energy of 3d orbital may be greater than or lesser than or equal to that of 4s orbital depending upon the atomic number of the atom.
   (c) All p orbitals have the same type of angular dependence irrespective of the value of principal quantum number n.
   (d) In a given electrical field, β-particles are deflected more than α- particles in spite of α- particles having larger charge.

26. Which of the the following statements are **not** correct?

(a) The mass of hydrogen atom is 1.667×10^{-27} kg.

(b) When there are two electrons in the same orbital, they have antiparallel spin.

(c) Isotopes of an element differ in the number of protons in their nuclei.

(d) The values of n_1 and n_2 in the Brackett spectral series of hydrogen atom are 3 and 4,5,6…, respectively.

27. Which of the following statements are correct?

(a) Elements of the same mass number but different atomic numbers are known as isobars.

(b) The uncertainty principle and the concept of wave nature of matter were proposed by Heisenberg and de Broglie, respectively.

(c) The energy of $n = 1$ orbit in hydrogen atom is the same as that of $n = 2$ orbit in helium ion.

(d) The radius of $n = 2$ orbit in hydrogen atom is the same as that of $n = 4$ orbit of Be^{3+}.

28. Which of the following statements are **not** correct ?

(a) The mass of a helium atom is 6.64×10^{-26} kg.

(b) The charge of an electron is -1.602×10^{-19}C.

(c) The charge of a positron is $+1.602 \times 10^{-19}$C.

(d) The atomic mass of an element is weighted average of the masses of its isobars.

29. Which of the following statements are correct?

(a) The values of n_1 and n_2 in the Lyman spectral series of hydrogen atom are 1 and 2,3,4,…, respectively.

(b) The values of n_1 and n_2 in the Balmer spectral series of hydrogen atom are 2 and 3,4,5,…, respectively.

(c) The values of n_1 and n_2 in the Paschen spectral series of hydrogen atom are 3 and 3,4,5,…, respectively.

(d) The values of n_1 and n_2 in the Pfund spectral series of hydrogen atom are 2 and 3,4,5,…, respectively.

30. Which of the following statements are **not** correct?

(a) The angular momentum of an electron in Bohr orbits is given as $l(l + 1)\ (h/2\pi)$.

(b) The uncertaintly principle states that $\Delta p \Delta x \geq h/4\pi$.

(c) The de Broglie expression is $p = h/m$.

(d) The filling of degenerate orbitals by electrons is governed by Hund's rule.

31. Which of the following statements are **not** correct?

(a) The maximum number of electrons in a orbital is governed by Pauli's exclusion principle.

(b) The sequence of filling atomic orbitals is governed by aufbau principle .

(c) The constant of proportionality which relates energy to frequency of electromagnetic radiation is Boltzmann constant and its value is 6.626×10^{-34} Js.

(d) The energies of a orbital in hydrogen-like species depend on the quantum numbers n and l.

32. Which of the following statements are **not** correct ?

(a) The energies of a orbital in a multi-electron atom depend on the quantum number(s) n and l.

(b) The degenerate orbitals have same values of quantum number(s) n and l.

(c) The angular momentum of an electron in a orbital is given as $n(h/4\pi)$.

(d) The z-component of angular of an electron in a orbital is given as $m_s(h/4\pi)$.

33. Which of the following statements are correct?

(a) The angular momentum of an electron due to its spin is given as $\sqrt{s(s+1)}\ (h/2\pi)$.

(b) The z-component of angular momentum of an electron due to its spin is given as $m_s(h/2\pi)$.

(c) The shape of an orbital is governed by the magnetic quantum number and is represented by the symbol m.

(d) The orientation of an orbital is governed by the azimuthal quantum number and is represented by the symbol l.

34. Which of the following statements are correct?

(a) d-orbitals are five fold degenerate and are spelled as d_{z^2} ,d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$.

(b) The p_z orbital has zero probability of occurrence along the x- and y-axis.

(c) According to Hund's rule, nitrogen atom has three unpaired electrons.

(d) Wave functions of electrons in atoms and molecules are called orbits.

35. Which of the following statements are **not** correct?

(a) The number of orbitals in a quantum shell is equal to n^2.

(b) The total allowed values of m for a given value of l are equal to $2l + 1$.

(c) The total allowed values of l for a given of n are equal to n^2.

(d) In the Rutherford experiment of radioactive element polonium was used as a source of β-particles.

36. Photoelectric effect supports quantum nature of light because
(a) there is a minimum frequency of light below which no photoelectron is emitted .
(b) the maximum kinetic energy of photoelectrons depends on the intensity of the light.
(c) even when the metal surface is faintly illuminated, the photoelectrons are emitted
(d) electric charge of the photoelecrons is quantized.

37. When photons of energy 4.25 eV strike the surface of a metal A, the ejected photoelectrons have maximum kinetic energy and de-Broglie wave length is λ_A . The maximum kinetic energy of photoelectrons liberated from another metal B by photons of energy 4.70 eV is $(KE)_B = (KE)_A - 1.50$ eV. If the de-Broglie wavelength of these photoelectrons is $\lambda_B = 2\lambda_A$, then.
(a) the work function of A is 2.25 eV
(b) the work function of B is 4.20 eV
(c) $(KE)_A$=2.00 eV
(d) $(KE)_B$=2.75 eV

38. The electron in a hydrogen atom makes a transition $n_1 \rightarrow n_2$ where n_1 and n_2 are the principal quantum numbers of the two states. Assume the Bohr model to be valid, if the time period of the electron in the initial state is eight times that in the final state then the possible values of n_1 and n_2 are
(a) $n_1 = 4, n_2 = 2$
(b) $n_1 = 8, n_2 = 2$
(c) $n_1 = 8, n_2 = 1$
(d) $n_1 = 6, n_2 = 3$

Linked Comprehension Type

1. Suppose Bohr therory is applicable to a negative particle of mass $2m_e$ and charge $2e$ revolving around a nucleus of charge Ze. Let r_1, v_1 and E_1 be the radius of the orbit, speed of the particle in the orbit and energy of the particle in the orbit, respectively. The values for the electron revolving in the corresponding orbit of hydrogen atom are r, v, and E, respectively.

(i) Which of the following expression regarding the ratio of radii is correct?
(a) $r_1/r = 2$ (b) $r_1/r = 1/2$ (c) $r_1/r = 4$ (d) $r_1/r = 1/4$

(ii) Which of the following expressions regarding the ratio of speeds is correct?
(a) $v_1/v = 2$ (b) $v_1/v = 1/2$ (c) $v_1/v = 4$ (d) $v_1/v = 1/4$

(iii) Which of the following expressions regarding the ratio of energies is correct?
(a) $E_1/E = 4$ (b) $E_1/E = 1/4$ (c) $E_1/E = 8$ (d) $E_1/E = 1/8$

2. In a mixture of H and He^+ gases, H atoms and He^+ ions are excited to their respective first excited states. Subsequently, H atoms transfer their total excitation energy to He^+ ion (by collision). Assuming that the Bohr model is applicable, answer the following three questions.

(i) The qunatum number n of the state finally populated in He^+ ions is
(a) 2 (b) 3 (c) 4 (d) 5

(ii) The wavelength of light emitted in the visible region by He^+ ions after collision with H atoms is
(a) 650 nm (b) 560 nm (c) 480 nm (d) 400 nm

(iii) The ratio of the kinetic energy of the $n = 2$ electron for the H atom to that of He^+ ion is
(a) 1/4 (b) 1/2 (c) 1 (d) 2

3. The Bohr model can account for the spectral transitions in hydrogen-like species. Based on this model, answer the following three questions.

(i) The radius of Bohr orbit is directly proportional to
(a) n/Z^2 (b) n^2/Z (c) n^2/Z^2 (d) n/Z

(ii) The speed of electron in the Bohr orbit is directly proportional to
(a) n/Z (b) n^2/Z (c) Z/n (d) Z/n^2

(iii) The magnitude of energy of an electron is the Bohr orbit is directly proportional to
(a) Z^2/n^2 (b) Z/n^2 (c) Z^2/n (d) Z/n^2

4. A gas of identical hydrogen-like species has some species in the lowest (ground) energy level and some species in a particular upper (excited) energy level and there are no species in any other energy level. The species of the gas make the transition to a higher energy level by absorbing monochromatic radiations of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photon energies. Some of the emitted photons have an energy of 2.7 eV, some have more energy and some less than 2.7 eV. Based on this observation, answer the following three questions.

(i) The initial excited level of the species involves the Bohr orbit of quantum number
(a) 2 (b) 3 (c) 4 (d) 5

(ii) The ionization energy of gaseous species is
(a) 13.5 eV (b) 12.8 eV (c) 14.4 eV (d) 10.8 eV

(iii) The maximum and minimum energies of the emitted photons respectively are
(a) 10.8 eV, 2.0 eV (b) 12.8 eV, 2.0 eV
(c) 10.8 eV, 0.7 eV (d) 13.5 eV, 0.7 eV

5. A hydrogen-like species is in a higher excited state of quantum number n. This excited state comes to the first-excited and second-excited states by releasing radiations of photon-energy equal to 27.2 eV and 10.2 eV, respectively. Based on this information, answer the following three questions. Given: $R_H hc = 13.6$ eV

(i) The nuclear charge number of the species is
(a) 3 (b) 5 (c) 6 (d) 7

(ii) The value of quantum number n is
(a) 4 (b) 5 (c) 6 (d) 7

(iii) The ionization energy of the species is
(a) 92.6 eV (b) 122.4 eV (c) 144.0 eV (d) 156.0 eV

6. An electron in a hydrogen-like species is in an excited state with a total electronic energy equal to –3.4 eV. Based on this, answer the following three questions.

(i) The kinetic energy of the electron is
(a) 1.7 eV (b) 3.4 eV (c) 5.1 eV (d) 6.8 eV

(ii) The de Broglie wavelength of the electron is about
(a) 333 pm (b) 444 pm (c) 555 pm (d) 666 pm

(iii) The possible species along with its excited state is
(a) H atom with $n = 2$ (b) He^+ ion with $n = 3$
(c) Li^{2+} ion with $n = 6$ (d) Be^{3+} ion with $n = 5$

7. A hydrogen-like species is in an excited state of quantum number $2n$. It can emit a maximum energyphoton of 20.4 eV. If it makes a transition to quantum state n, a photon of energy 40.8 eV is emitted. On this information, answer the following three questions.

(i) The value of n for the excited state is
(a) 2 (b) 3 (c) 4 (d) 5

(ii) The nuclear charge of the species is
(a) 2 (b) 3 (c) 4 (d) 5

(iii) The ground state energy of the species is
(a) –13.6 eV (b) –54.4 eV (c) –122.4 eV (d) –217.6 eV

8. The wave function $R_{2,0}$ for hydrogen atom is $R_{2,0} = K\,(2 - r/a_0)\exp(-r/2a_0)$
where K is constant. Based on this, answer the following three questions.

(i) The distance r at which $R_{2,0}$ exhibits nodel point is at
(a) a_0 (b) $2a_0$ (c) $3a_0$ (d) $4a_0$

(ii) The distance r at which $R^2_{2,0}$ exhibits maximum (besides at $r = 0$) is at
(a) $2a_0$ (b) $3a_0$ (c) $4a_0$ (d) $6a_0$

(iii) The distance from the nuclear at which r^2R^2 shows maximum is known as most probable distance. For $R_{2,0}$ function, the maxima lie at
(a) $r = (1 \pm \sqrt{5})a_0$ (b) $r = (2 \pm \sqrt{5})a_0$ (c) $r = (3 \pm \sqrt{5})a_0$ (d) $r = (4 \pm \sqrt{5})a_0$

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement–1 is correct and Statement–2 is correct and is the correct explanation of the statement–1.
(b) Statement–1 is correct and Statement–2 is correct but not the correct explantation of the statement–1.
(c) Statement–1 is correct and Statement–2 is incorrect.
(d) Statement–1 is incorrect and Statement–2 is correct.

	Statement–1	**Statement–2**
1.	In photoelectric effect, the number of electrons emitted is proportional to the frequency of incident radiation.	Larger the frequency of incident photon, larger the energy of photon.
2.	In photoelectric effect, the kinetic energy of emitted electrons depends on the frequency of the incident radiation.	The kinetic energy of emitted electrons is equal to the difference in energy of photon and the work function of the metal.
3.	Energy of 2p orbital is the same as that of 2s orbital in hydrogen-like species.	There is no electron-electron repulsion in hydrogen-like species.
4.	Electronic energy in 2p orbitals in an atom is no more degenerate in the presence of magnetic field.	Magnetic field has no effect on the electronic energy in an atom.
5.	$3d_{z^2}$ and $3d_{xz}$ orbitals in free Co^{3+} ion have the same energy but in $[Co(NH_3)_6]^{3+}$, the energy of $3d_{z^2}$ is larger than $3d_{xz}$ orbital.	The incoming ligands in octahedral crystal field cause more electron-electron repulsion in $3d_{z^2}$ as compared to $3d_{xz}$ orbital.
6.	Zn^{2+} is diamagnetic.	The electrons are lost from 4s orbitals to form Zn^{2+}.
7.	The electronic configuratin of $_{29}Cu$ is $(3d)^{10}$ $(4s)^1$ instead of $(3d)^9$ $(4s)^2$.	Fully-filled 3d subshell is more stable than $(3d)^9$ configuration.
8.	The orbital p_z may be identified with $m = 0$ but p_x and p_y orbitals are not identified with $m = +1$ and $m = -1$ (or vice versa), respectively.	p_+ and p_- orbitals are not the solution of Schrodinger equation.
9.	Subatomic particles such as neutron and proton also exhibit diffraction experiment.	Subatomic particles have significant wave nature as governed by de Broglie relation.
10.	3f orbital does not exist in an atom .	The value of l cannot be larger than value of n.
11.	d_{xy} orbital has xy plane as the nodal plane.	The wave function has a zero value at the nodal plane.
12.	Each d orbital has two nodal planes.	The number of angular nodal planes is equal to the value of principal quantum number n.
13.	$^{30}_{14}Si$ and $^{32}_{16}S$ are the examples of isotones.	Isotones have the same number of neutrons and different number of protons.
14.	The spin angular momentum vector can take two possible orientations in a magnetic field.	The orientation of spin angular momentum vector in a magnetic field is governed by the spin quantum number.
15.	p_x and p_y are the independent solution of Schröndinger equation of hydrogen atom.	p_x and p_y orbitals are obtained by the linear combinations of p_{+1} and p_{-1} orbitals.

Matrix Match Type

1. Match the scientists given in Column I with their discoveries given in Column II

Column I	**Column II**
(a) J. J. Thomson	(p) Cathode rays
(b) Henry Becquerel	(q) Mass spectrograph
(c) Moseley	(r) X-ray spectra
(d) Aston	(s) Laws of electrolysis
	(t) Nuclear model of atom
	(u) Radioactivity
	(v) Discovery of neutrons

2. In the following, V_n, K_n and E_n represent potential energy, kinetic energy and total energy of an electron in the nth Bohr orbit (radius: r) of hydrogen like species (nuclear charge: Z). Match entries in Column I with those given in Column II.

Column I	**Column II**
(a) $V_n/K_n = ?$	(p) -1
(b) $V_n/E_n = ?$	(q) -2
(c) $K_n/E_n = ?$	(r) 1
(d) $1/r \propto (Z)^x : x = ?$	(s) 2

3. Match the entries in Column I with the correctly related quantum number(s) in Column II.

Column I	**Column II**
(a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p) Principal quantum number
(b) A hydrogen-like one-electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(c) Shape, size and orientation of hydrogen like atomic orbitals	(r) Magnetic quantum number
(d) Probability density of electron at the nucleus in hydrogen-like atom	(s) Electron spin quantum number

4. Match the entries in Column I for the spectral series of hydrogen atom with those given in Column II. The symbols n_1 and n_2 are the quantum levels in the expression

$$\Delta E = R_{\mathrm{H}}hc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Column I	**Column II**
(a) Lyman series	(p) $n_1 = 2$ and $n_2 = 3, 4, 5, \ldots$
(b) Balmer series	(q) $n_1 = 4$ and $n_2 = 5, 6, 7, \ldots$
(c) Paschen series	(r) $n_1 = 5$ and $n_2 = 6, 7, \ldots$
(d) Pfund series	(s) $n_1 = 1$ and $n_2 = 2, 3, 4, \ldots$
	(t) $n_1 = 3$ and $n_2 = 4, 5, 6, \ldots$

5. Match the entries given in Column I with those given in Column II.

Column I	**Column II**
(a) Radius of Bohr orbit	(p) Directly proportional to Z/n
(b) Energy of Bohr orbit	(q) Directly proportional to n^2/Z
(c) Speed of electron in Bohr orbit	(r) Directly proportional to Z^2/n^2
(d) Time period of electron in Bohr orbit	(s) Directly proportional to n^3/Z^2

6. Match the quantum numbers given in Column I with the corresponding quantization of physical properties of the electron in hydrogen-like species mentioned in Colulmn II.

Column I	**Column II**
(a) n	(p) z-component of spin angular momentum
(b) l	(q) spin angular momentum
(c) m	(r) energy
(d) s	(s) z-component of orbital angular momentum
(e) m_s	(t) orbital angular momentum

7. Match the orbitals given in Column I with their characteristic properties mentioned in Column II.

Column I	**Column II**
(a) 2s orbital	(p) one radial node + one nodal plane
(b) 3s orbital	(q) one radial node + no nodal plane
(c) 3p orbitals	(r) two radial nodes + no nodal plane
(d) 4d orbitals	(s) one radial node + two nodal planes

8. Match the orbitals given in Column I with the characteristic angular momentum of the electron in the orbital mentioned in Column II.

Column I	**Column II**
(a) s orbital	(p) $\left(2\sqrt{3}\right)(h/2\pi)$
(b) p orbital	(q) $\left(\sqrt{6}\right)(h/2\pi)$
(c) d orbital	(r) zero
(d) f orbital	(s) $\left(\sqrt{2}\right)(h/2\pi)$

9. Identify the entries mentioned in Column I with the correct entries given in Column II.

Column I	**Column II**
(a) Identical energies	(p) $n = 2$ of H and $n = 4$ of Be^{3+}
(b) Identical orbit radius	(q) $1 \leftarrow 2$ of H and $2 \leftarrow 4$ of He^{+}
(c) Identical speed of electron	(r) $n = 2$ of H and $n = 1$ of He^{+}
(d) Identical spectral transition	(s) $n = 1$ of H and $n = 2$ of He^{+}
	(t) $2 \leftarrow 3$ of He^{+} and $3 \leftarrow 4$ of Li^{2+}

ANSWERS

Straight Objective Type

1. (c)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (b)	**7.** (a)
8. (a)	**9.** (b)	**10.** (c)	**11.** (b)	**12.** (b)	**13.** (b)	**14.** (d)
15. (c)	**16.** (c)	**17.** (c)	**18.** (b)	**19.** (a)	**20.** (d)	**21.** (b)
22. (a)	**23.** (d)	**24.** (c)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (c)
29. (a)	**30.** (b)	**31.** (d)	**32.** (a)	**33.** (b)	**34.** (a)	**35.** (a)
36. (a)	**37.** (d)	**38.** (a)	**39.** (c)	**40.** (a)	**41.** (a)	**42.** (b)
43. (b)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (a)	**48.** (b)	**49.** (d)
50. (a)	**51.** (b)	**52.** (d)	**53**. (d)	**54.** (d)	**55.** (a)	**56.** (b)
57. (a)	**58.** (d)	**59.** (a)	**60.** (c)	**61.** (d)	**62.** (a)	**63.** (a)
64. (a)	**65.** (d)	**66.** (d)	**67.** (a)	**68.** (d)	**69.** (a)	**70.** (a)
71. (c)	**72.** (b)	**73.** (c)	**74.** (c)	**75.** (b)	**76.** (c)	**77.** (d)
78. (d)	**79.** (c)	**80.** (a)	**81.** (c)	**82.** (b)	**83.** (a)	**84.** (b)
85. (b)	**86.** (d)	**87.** (d)	**88.** (b)	**89.** (c)	**90.** (a)	**91.** (c)
92. (c)	**93.** (a)	**94.** (c)	**95.** (d)	**96.** (d)	**97.** (b)	**98.** (c)
99. (a)	**100.** (a)	**101.** (d)	**102.** (c)	**103.** (d)	**104.** (b)	**105.** (a)
106. (c)	**107.** (d)	**108.** (a)	**109.** (a)	**110.** (c)	**111.** (d)	**112.** (d)
113. (c)	**114.** (a)	**115.** (d)	**116.** (b)	**117.** (b)	**118.** (b)	**119.** (c)
120. (d)	**121.** (c)	**122.** (a)	**123.** (b)	**124.** (b)	**125.** (d)	**126.** (a)
127. (d)	**128.** (a)	**129.** (b)	**130.** (b)	**131.** (c)	**132.** (d)	**133.** (a)
134. (c)	**135.** (c)	**136.** (b)	**137.** (a)	**138.** (c)	**139.** (a)	**140.** (c)
141. (d)	**142.** (a)	**143.** (d)	**144.** (a)	**145.** (c)	**146.** (c)	

Multiple Correct Choice Type

1. (a), (c)	**2.** (b), (d)	**3.** (a), (c)	**4.** (a), (b), (c)
5. (a), (b)	**6.** (a), (b), (c), (d)	**7.** (c), (d)	**8.** (a), (b), (d)
9. (a), (c), (d)	**10.** (a), (c)	**11.** (a), (c), (d)	**12.** (a), (b), (d)
13. (a), (b), (d)	**14.** (a), (c), (d)	**15.** (a), (d)	**16.** (a), (b)
17. (b), (c), (d)	**18.** (a), (c), (d)	**19.** (a), (b)	**20.** (a), (c), (d)
21. (a), (d)	**22.** (a), (b), (c)	**23.** (b), (d)	**24.** (a), (b), (d)
25. (b), (c), (d)	**26.** (c), (d)	**27.** (a), (b), (c), (d)	**28.** (a), (d)
29. (a), (b)	**30.** (a), (c)	**31.** (c), (d)	**32.** (c), (d)
33. (a), (b)	**34.** (a), (b), (c)	**35.** (c), (d)	**36.** (a), (c)
37. (a), (b), (c)	**38.** (a), (d)		

Linked and Comprehension Type

1. **(i)** (d) **(ii)** (a) **(iii)** (c)
2. **(i)** (c) **(ii)** (c) **(iii)** (a)
3. **(i)** (b) **(ii)** (c) **(iii)** (a)
4. **(i)** (a) **(ii)** (c) **(iii)** (d)
5. **(i)** (a) **(ii)** (c) **(iii)** (b)
6. **(i)** (b) **(ii)** (d) **(iii)** (a)
7. **(i)** (a) **(ii)** (c) **(iii)** (d)
8. **(i)** (b) **(ii)** (c) **(iii)** (c)

Assertion and Reason Type

1. (d) **2.** (a) **3.** (a) **4.** (c) **5.** (a) **6.** (b) **7.** (a)
8. (c) **9.** (a) **10.** (c) **11.** (d) **12.** (c) **13.** (a) **14.** (c)
15. (d)

Mtrix Match Type

1. (a) – (p); (b) – (u); (c) – (r); (d) – (q)
2. (a) – (q); (b) – (s); (c) – (p); (d) – (r)
3. (a) – (q); (b) – (s); (c) – (p), (q), (r); (d) – (p), (q), (r)
4. (a) – (s); (b) – (p); (c) – (t); (d) – (r)
5. (a) – (q); (b) – (r); (c) – (p); (d) – (s)
6. (a) – (r); (b) – (t); (c) – (s); (d) – (q); (e) – (p)
7. (a) – (q); (b) – (r); (c) – (p); (d) – (s)
8. (a) – (r); (b) – (s); (c) – (q); (d) – (p)
9. (a) – (s); (b) – (p); (c) – (s); (d) – (q)

Hints and Solutions

Straight Objective Type

1. α-particles originate from nucleus of an atom.

3. Isotones have the same number of neutrons. The choice a contains 8 neutrons in all the three species.

4. 6.022×10^{23} electrons carry 96500 C of charge. Hence, 1C of charge is carried by $(6.022 \times 10^{23}/96500)$ electrons. This comes out to be 6.25×10^{18}.

5. $m = N_A m_e = (6.022 \times 10^{23}\ \text{mol}^{-1})\ (9.1 \times 10^{-31}\ \text{kg}) = 5.48 \times 10^{-7}\ \text{kg} = 0.548\ \text{mg}$.

7. Rutherford's experiment involves the scattering of α-particles by nucleus of an atom.

9. Rutherford's experiment led to the conclusion that electrons occupy space around the nucleus.

10. X-rays are not deflected by electric and magnetic fields.

11. The radius of atomic nucleus is of the order of 10^{-13} cm.

12. Bohr model was successful in explaining the spectrum of one-electron species only.

13. Radiowaves have maximum wavelength as compared to ultraviolet, infrared and X-ray.

14. Since $E = hc/\lambda$, the ratio $E_{200\text{nm}}/E_{400\text{nm}}$ will be equal to 2.

15. The wavelength of spectral line is inversely related to the energy difference between two energy levels.

16. Paschen spectral series of hydrogen atom lies in the near infrared region.

17. For Paschen series, $n_1 = 3$ and $n_2 = 4, 5, 6, \ldots$

18. The correct expression is $R_H = 2\pi^2 m(e^2/4\pi\varepsilon_0)^2/h^3c$.

19. In Bohr theory, $L = n(h/2\pi)$.

20. For hydrogen atom, the radius of first orbit is 52.9 pm.

21. Since $E \propto -1/n^2$, we have $\Delta E = (\text{constant}) \left[-\dfrac{1}{n_2^2} + \dfrac{1}{n_1^2}\right]$

For adjacent orbits, we write ΔE = (constant) $\left[-\frac{1}{(n_1+1)^2}+\frac{1}{n_1^2}\right]$ = (constant) $\left[\frac{2n_1+1}{n_1^2\,(n_1+1)^2}\right]$

With increase in the value of n_1, ΔE decreases

22. Since $v \propto 1/n$, the velocity in the second orbital will be

$$v_2 = v_1/2 = (2.19 \times 10^6 \text{ m s}^{-1})/2 = 1.1 \times 10^6 \text{ m s}^{-1}$$

23. Since $E \propto -\,1/n^2$, the energy of an electron in the second orbit will be

$$E_2 = E_1/4 = (-2.18 \times 10^{-18} \text{ J})/4 = -5.45 \times 10^{-19} \text{ J}$$

24. The energy expression is $E = -\frac{1}{n^2}\left[\frac{2\pi^2 m\left(Ze^2/4\pi\varepsilon_0\right)^2}{h^2}\right]$

25. The value of Planck's constant is 6.626×10^{-34} J s.

26. Bohr theory was the first theory.

27. The expression of radius is $r = n^2\left[\frac{h^2}{4\pi^2 m(Ze/4\pi\varepsilon_0)}\right]$ that is $r \propto \frac{n^2}{Z}$

For Be^{3+}, $Z = 4$. Hence, when $n = 2$; $\quad r \propto \frac{2^2}{4} = 1$

For H, $Z = 1$. Hence, when $n = 1$; $\quad r \propto \frac{1^2}{1} = 1$

28. The radius of orbit is given by $r = n^2\left[\frac{h^2}{4\pi^2 m\left(Ze^2/4\pi\varepsilon_0\right)}\right]$

29. The expression of velocity is $v = \frac{2\pi\left(Ze^2/4\pi\varepsilon_0\right)}{nh}$

30. Since | PE | = 2KE, the ratio KE/PE = –1/2

31. Since | PE | = 2KE, the ratio $\frac{\text{KE}}{\text{E}} = \frac{\text{KE}}{\text{KE}+\text{PE}} = \frac{1}{1+\text{PE}/\text{KE}} = \frac{1}{1-2} = -1$

32. $\frac{\text{PE}}{\text{E}} = \frac{\text{PE}}{\text{KE}+\text{PE}} = \frac{1}{(\text{KE}/\text{PE})+1} = \frac{1}{(-1/2)+1} = 2$

33. The value of Rydberg constant is $1.0978 \times 10^7 \text{ m}^{-1}$.

34. Rydberg constant is usually expressed in the wavenumber unit. Hence, the ionization energy of hydrogen atom will be $R_H hc$.

35. Energy of the excited state is given by $E_n = E_1/n^2$. The choice a is equal to $E_1/2^2$.

36. The transition $n = 6 \rightarrow n = 2$ belongs to the Balmer series.

37. Larger the value of Z, larger the transition energy and hence shorter the wavelength.

38. Energy of the orbit with $n = 2$ is –13.6 eV/4 = –3.4 eV. Hence, energy required to remove electron from $n = 2$ will be 3.4 eV.

39. First line of Balmer series corresponds to $n = 3 \rightarrow n = 2$. Second line of this series will correspond to $n = 4 \rightarrow n = 2$.

We have

$$\Delta E_1 = R_H\left(\frac{1}{4}-\frac{1}{9}\right) \quad \text{and} \quad \Delta E_2 = R_H\left(\frac{1}{4}-\frac{1}{16}\right)$$

$$\frac{\Delta E_1}{\Delta E_2} = \frac{5/36}{3/16} = \frac{27}{20} \quad \text{i.e.} \quad \lambda_2 = \lambda_1\left(\frac{20}{27}\right) = (656.1 \text{ nm})\left(\frac{20}{27}\right) = 486.0 \text{ nm}$$

40. The energy of excited state of hydrogen is given by $E_n = E_1/n^2$. For $n = 2$, E_2 = –13.6 eV/4 = –3/4 eV.

41. The centripetal force is due to the attraction between the nucleus and the electron which inversely depends on the square of distance between them. The expression is $Ze^2/(4\pi\varepsilon_0)\, r^2$.

42. The energy expression is $E = \text{KE} + \text{PE} = \frac{1}{2}\, mv^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}$

The stability expression of the atom is | centripetal force | = centrifugal force. This gives

$$\frac{Ze^2}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r} \Rightarrow \frac{Ze^2}{(4\pi\varepsilon_0)r} = mv^2 \qquad \text{Hence} \qquad E = \frac{1}{2}\, mv^2 - mv^2 = -\,\frac{1}{2}\, mv^2$$

The kinetic energy is half of the magnitude of potential energy. Hence, the choice b is not correct.

43. The speed of the electron is given by $v = \frac{2\pi\left(Ze^2/4\pi\varepsilon_0\right)}{nh}$

It is inversely proportional to the quantum number n. Hence, the choice b is incorrect.

44. From the expression of speed, we find that $v \propto Z/n$. For the second orbit in helium ion, the value of Z/n is the same as that of first orbit in hydrogen atom. Hence, their speeds will be identical.

45. The dependence of energy on Z and n is $E \propto -Z^2/n^2$. The value of Z^2/n^2 of the third orbit in Li^{2+} is the same as the first orbit of H atom. Hence, the energy will also the same, i.e. -2.18×10^{-18} J.

46. The dependence of radius on Z and n is $r \propto n^2/Z$. The value of n^2/Z for the third orbit of Li^{2+} will be three times that of the first orbit of hydrogen atom. Hence, $r = 3 \times 52.9$ pm $= 158.7$ pm.

55. We have

$$\Delta E = Z^2 R_H hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 4R_H hc \left(\frac{1}{4} - \frac{1}{16}\right) = \frac{3}{4}\, R_H hc$$

For hydrogen atom, the factor 3/4 will be obtained when the values of n_1 and n_2 are 1 and 2, respectively.

56. The ionization energy is given by

$$\begin{aligned}\Delta E' &= Z^2 R_H hc = (3^2)\,(1.0974 \times 10^7\ \text{m}^{-1})\,(6.626 \times 10^{-34}\ \text{J s})\,(3 \times 10^8\ \text{m s}^{-1})\\ &= 1.96 \times 10^{-17}\ \text{J}\end{aligned}$$

For one mole of Li^{2+} ions,

$$\begin{aligned}\Delta E &= N_A \Delta E' = (6.022 \times 10^{23}\ \text{mol}^{-1})\,(1.96 \times 10^{-17}\ \text{J}) = 1.1825 \times 10^7\ \text{J mol}^{-1}\\ &= 11825\ \text{kJ mol}^{-1}\end{aligned}$$

57. We have

$$\frac{\Delta E}{h} = Z^2 R_H c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$2.466 \times 10^{15}\ \text{s}^{-1} = (1^2)\,(1.096 \times 10^7\ \text{m}^{-1})\,(3 \times 10^8\ \text{m s}^{-1}) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

This gives $\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 0.75$. Obviously, $n_1 = 1$ and $n_2 = 2$.

58. For He^+, $\Delta E_{\text{ioniz}} = (2^2)\, R_H hc = 19.6 \times 10^{-18}$ J atom^{-1}. Energy of the second stationary state in Li^{2+} is

$$E = -\frac{Z^2}{n^2}\, R_H hc = -\{(3^2)/(2^2)\}\,(19.6 \times 10^{-18}\ \text{J atom}^{-1}/4) = -\,1.1025 \times 10^{-18}\ \text{J atom}^{-1}$$

62. First line in the Lyman series of hydrogen atom corresponds to $\Delta E = R_H hc \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4}\, R_H hc$. For He^+, the spectral line occurs at $\Delta E = Z^2 R_H hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (2^2)\, R_H hc \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3}{4}\, R_H hc$

63. Velocity of electron decreases with increase in the value of n in Bohr theory. The electron will have maximum kinetic energy in the $n = 1$ orbit.

64. For Balmer series, the longest wave length corresponds to the transition $3 \leftarrow 2$.

$$\Delta E = R_{\mathrm{H}}hc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = R_{\mathrm{H}}hc\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = \frac{5}{36}R_{\mathrm{H}}hc$$

$$\lambda = \frac{hc}{\Delta E}=\frac{36}{5\,R_{\mathrm{H}}}=\frac{36}{5\times1.09678\times10^{7}\ \mathrm{m}^{-7}} = 6.565\times10^{-7}\ \mathrm{m} = 656.5\ \mathrm{nm}$$

65. After the removal of one electron, the species formed is He^+. The energy required to remove the electron from He^+ is four times the energy required to remove the electron from the hydrogen atom. Thus

$$E_{\mathrm{He}^+} = Z^2E_{\mathrm{H}} = (2)^2\,E_{\mathrm{H}} = 4(13.6\ \mathrm{eV}) = 54.4\ \mathrm{eV}$$

Hence, the energy required to remove both the electrons from helium atom is (24.6 eV + 54.4 eV) which is 79.0 eV.

66. As per Bohr model, the ionization energy of an atom (or ion) in the ground state is directly proportional to the square of the atomic number. Hence, $(\mathrm{IE})_{\mathrm{Li}^{2+}} = Z^2\,(\mathrm{IE})_{\mathrm{H}} = (3^2)\,(13.6\ \mathrm{eV}) = 122.4\ \mathrm{eV}$

67. The various expressions are

$$\mathrm{PE} = -\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right);\quad \mathrm{KE} = \frac{1}{2}\,\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right);\quad E = \mathrm{KE} + \mathrm{PE} = -\frac{1}{2}\,\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right)$$

When an electron undergoes transition from an excited state to the ground state, the value of r decreases. From the above expressions, it follows that the electronic kinetic energy increases while its potential and total energies decrease.

68. For a hydrogen-like species, we have $\Delta E = Z^2R_{\mathrm{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

Hence $\Delta E_{4\leftarrow3} = Z^2R_{\mathrm{H}}\left(\frac{1}{9}-\frac{1}{16}\right) = \left(\frac{7}{144}\right)Z^2R_{\mathrm{H}} = 0.049\ Z^2R_{\mathrm{H}}$

$$\Delta E_{1\leftarrow2} = Z^2R_{\mathrm{H}}\left(\frac{1}{1}-\frac{1}{4}\right) = \left(\frac{3}{4}\right)Z^2R_{\mathrm{H}} = 0.75\ Z^2R_{\mathrm{H}}$$

$$\Delta E_{2\leftarrow3} = Z^2R_{\mathrm{H}}\left(\frac{1}{4}-\frac{1}{9}\right) = \left(\frac{5}{36}\right)Z^2R_{\mathrm{H}} = 0.139\ Z^2R_{\mathrm{H}}$$

$$\Delta E_{4\leftarrow5} = Z^2R_{\mathrm{H}}\left(\frac{1}{16}-\frac{1}{25}\right) = \left(\frac{9}{400}\right)Z^2R_{\mathrm{H}} = 0.023\ Z^2R_{\mathrm{H}}$$

Since $\Delta E_{4\leftarrow5} < \Delta E_{4\leftarrow3}$, the transition $4 \leftarrow 5$ may result into the emission of infrared radiation.

69. In Bohr model $r = \frac{n^2}{Z}$ (53 pm) where $n = 5$ for $Z = 100$

Hence r = (25/100) (53 pm) = (53 pm)/4

Thus $m = 1/4$

70. The principal quantum number can be correlated with size of an orbital.

71. The choice c is not correct as the value of m_l cannot be greater than l.

72. The angular momentum of electron in an atom is described by azimuthal quantum number through the expression $L = \sqrt{l(l+1)}\,(h/2\pi)$

73. The z-component of angular momentum of electron in an atom is described by magnetic quantum number through the expression $L_z = m(h/2\pi)$.

74. The number of orbitals in a subshell is equal to $2l + 1$.

75. The orbital p_y is symmetrical about the y-axis.

76. The expression is $L = \sqrt{l(l+1)}\,(h/2\pi)$

77. The angle is given by $\cos\theta = \dfrac{L_z}{L} = \dfrac{m}{\sqrt{l(l+1)}}$

78. Larger the number of unpaired electrons, larger the paramagnetic behaviour. Among the given species, $_6$C has maximum number of unpaired electrons.

79. The energy of an electron in an atomic orbital of a multielectron atom depends on two quantum numbers; principal and azimuthal.

80. The value of m greater than l is not allowed.

81. The choice c represents $3d_{z^2}$ orbital.

82. The orbital angular momentum is given by $L = \sqrt{l(l+1)}\,(h/2\pi)$. For s orbital, $l = 0$. Hence $L = 0$.

83. For d-electron, $l = 2$. hence $L = \sqrt{l(l+1)}\,(h/2\pi) = \sqrt{6}\,(h/2\pi)$.

84. Larger the value of $n + l$, larger the energy.

85. Same as Q.84.

87. A single p orbital can accommodate two electrons.

88. The choice b violates aufbau principle as 2s orbital contains one electron. It should be filled completely before filling 2p orbitals.

89. One electron short of stable configuration is the most electronegative element. Thus, configuration is $(ns)^2(np)^5$.

90. The electronic configuration of Cr is $[\mathrm{Ar}](3d)^5(4s)^1$.

91. The electronic configuration of $_{17}$Cl is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$. The quantum numbers of 3p orbital are $n = 3$, $l = 1$ and m may be equal to 1.

92. The number of electrons that can be accommodated in a quantum shell is equal to $2n^2$.

93. The electronic configuration of $_{37}$Rb is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^6(5s)^1$
The quantum numbers of $5s^1$ are $n = 5$, $l = 0$, $m = 0$ and $m_s = +1/2$.

94. Hund's rule requires that the configuration given by the choice c will be most stable.

95. The configuration of Cr is $(3d)^5(4s)^1$. The number of unpaired electrons is six.

96. Hund's rule is applicable for allocating electrons to degenerate orbitals.

97. $(n - 1)$d subshell has higher energy than ns subshell.

98. Aufbau order is obeyed in cases where energy difference between ns and $(n - 1)$d subshell is large.

99. Larger the value of $n + l$, larger the energy of electron. For the same value of $n + l$, the larger value of n has larger energy. So, the correct order is given by the choice a.

100. The ground state electronic configuration of nitrogen atom is $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$

101. The complete electronic configuration of cerium (atomic number 58) is

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^6(5s)^2(4d)^{10}(5p)^6(6s)^2(4f)^2$$

103. The expression $E = h\nu$ relates photon as wave motion and particle nature.

104. In a multielectron atom, the energy of electron depends on two quantum numbers. These are principal and azimuthal quantum numbers.

105. For a hydrogen-like species, the energy of electron depends only on the principal quantum number.

106. An orbital in an atom is represented by the three quantum numbers n, l and m.

107. An orbital with $l = 0$ is spherical around nucleus.

108. Electronic transition requires $\Delta l \neq 0$. There 2s → 1s is not allowed, but 2s → 3p is allowed.

109. p_x orbital has yz nodal plane.

110. The sign on an atomic orbital indicates the sign of wave function.

111. $3d_{x^2-y^2}$ has lobes along the x- and y-axes.

112. An orbital is characterised by the three distinct quantum numbers n, l and m.

113. The function R depends on n and l, Θ depends on l and $|m|$, and Φ depends on m.

115. The number of nodal points is $n - (l + 1)$.

116. In the 2s orbital, the nodal point is due to the term $(2 - r/a_0)$ in the R dependent term.

117. The number of radial nodes in 3p orbital is equal to $n - (l + 1) = 3 - (1 + 1) = 1$

118. The maximum in the plot of $r^2R^2_{1,0}$ versus r occurs at $r = a_0$

119. In d_{yz} orbital, two nodal planes (xy and xz) exist.

120. $d_{x^2-y^2}$ orbital, the lobes lie along the positive and negative directions of x and y axes. Thus, two nodal planes at angles 45° to x- and y-axes exist.

121. A d_{xy} orbital is directed at +45° and −45° to the x- and y-axes.

122. For $3d_{z^2}$, the values of l and m are 2 and 0, respectively.

123. The angular momentum is given by the expression $\sqrt{l(l+1)}\,(h/2\pi)$ and for f-orbital $l = 3$.

124. The quantum number s is not the outcome of solution of Schrödinger equation.

125. The quantum number $n = 0$ is not allowed.

126. The wave function can have positive as well as negative value.

127. The probability of finding electron is given by the square of wave function and not by the wave function.

128. Ψ^2 always has positive value provided Ψ is a real valued wave function.

131. For p orbitals, $l = 1$. Hence, $L = \sqrt{l(l+1)}\,(h/2\pi) = \sqrt{2}\,(h/2\pi)$

132. For d orbitals, $l = 2$. Hence, $L = \sqrt{l(l+1)}\,(h/2\pi) = \sqrt{6}\,(h/2\pi)$

133. For p_z orbital, $m = 0$

134. For d_{z^2} orbital, $m = 0$

135. Cl^- has fully occupied p orbitals and hence the angular dependence of $p_x^2 + p_y^2 + p_z^2$ is independent of angles θ and φ.

137. The value of m cannot be greater than the value of l.

138. The allowed values of m are $+l$, $+(l-1)$, ...,0, ... $-(l-1)$, $-l$ — a total of $2l + 1$ values.

139. We have

$$E = \frac{hc}{\lambda} - h\nu_0 = h\left(\frac{c}{\lambda} - \nu_0\right) = (6.626 \times 10^{-34}\ \text{J s})\left[\frac{3\times10^8\ \text{m s}^{-1}}{1.5\times10^{-9}\ \text{m}} - 1.13\times10^7\ \text{s}^{-1}\right]$$

$$= (6.266 \times 10^{-34}\ \text{J s})\ (0.87 \times 1017\ \text{s}^{-1}) = 5.76 \times 10^{-17}\ \text{J}$$

140. We have $N_A h\nu$ = Binding energy per mole

$$\nu = \frac{(193\times10^3\ \text{J mol}^{-1})}{\left(6.022\times10^{23}\ \text{mol}^{-1}\right)\left(6.626\times10^{-34}\ \text{J s}\right)} = 4.84 \times 10^{14}\ \text{s}^{-1}$$

141. We have $p = \dfrac{h}{\lambda} = \dfrac{(6.626\times10^{-34}\ \text{J s})}{(0.1\times10^{-9}\ \text{m})} = 6.626 \times 10^{-24}\ \text{kg m s}^{-1}$

142. $E = eV$ and $E = \dfrac{1}{2}mv^2 = \dfrac{p^2}{2m} = \dfrac{(h/\lambda)^2}{2m} \Rightarrow \lambda = \left(\dfrac{h^2}{2\,meV}\right)^{1/2}$

$$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\left\{2\left(9.1\times10^{-31}\ \text{kg}\right)\left(1.6\times10^{-19}\ \text{C}\right)\left(500\ \text{V}\right)\right\}^{1/2}} = 5.49 \times 10^{-11}\ \text{m} = 54.9\ \text{pm}$$

143. Uncertainty in speed is 1% of one-tenth of the speed of light. Hence $\Delta v = 3 \times 10^5\ \text{m s}^{-1}$

$$\Delta p = m_p\,\Delta v = (1.67 \times 10^{-27}\ \text{kg})\ (3 \times 10^5\ \text{m s}^{-1}) = 5.01 \times 10^{-22}\ \text{kg m s}^{-1}$$

$$\Delta x = \frac{h/4\pi}{\Delta p} = \frac{\left(6.626\times10^{-34}\text{J s}\right)/(4\times3.14)}{\left(5.01\times10^{-22}\ \text{kg m s}^{-1}\right)} = 0.105 \times 10^{-12}\ \text{m}$$

144. Number or radial nodes in an orbital is equatl to $n - l - 1$, where n and l are the principal and azimuthal quantum numbers, respectively. For 3p and 4s orbitals, we have

3p $n = 3$, $l = 1$ radial nodes = 3 − 1 − 1 = 1

4s $n = 4$, $l = 1$ radial nodes = 4 − 0 − 1 = 3

145. The de-Broglie wavelength is $\lambda = \dfrac{h}{mv} = \dfrac{(6.626\times10^{-34}\,\text{J s})}{(0.200\,\text{kg})\{5\,\text{m}/(60\times60\,\text{s})}$ = 2.4×10^{-30} m

146. $\lambda_{\text{max}} = \dfrac{hc}{W} = \dfrac{(6.626\times10^{-34}\,\text{J s})(3\times10^{8}\,\text{m s}^{-1})}{4(1.6\times10^{-19}\,\text{J})}$ = 3.10×10^{-7} m = 310 nm

Multiple Correct Choice Type

1. The penetration of α-particles in Rutherford's experiment is due to empty space in atom. Also α-particles are much heavier than electrons, thus, these are not reflected much while passing through empty spaces.

2. Isotones involve the same number neutrons, which in the present case, is 44.

3. Non-integral atomic mass is due to isotopes which have different masses.

4. The choices a, b and c are correct. The choice D is incorrect as the oxidation state of N in HN_3 is −1/3 and not −3.

13. (a) The configuration is $(3d)^5(4s)^1$.

(b) The wavelength of gamma rays is of the order of 10^{-11} m.

(c) In hydrogen atom, the energy of an electron depends only on the principal quantum number of the orbital which it occupies.

(d) In *xz*-plane, there is no electron density if an electron occupies $3d_{x^2-y^2}$ orbital.

14. (a) The electronic configuration of Zn^{2+} (atomic number 30) is $(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(3d)^{10}$. There is no unpaired electrons, hence, it is diamagnetic.

(b) The expression of magnetic moment is $\mu_{\text{m}} = \sqrt{n(n+2)}\,\mu_{\text{B}}$ where *n* is the number of unpaired electrons.

(d) The correct expression is $L = \sqrt{l(l+1)}\,(h/2\pi)$

15. (b) The expression $m_s(h/2\pi)$ is that of *z*-component of angular momentum.

(c) The correct statement is as under:
No two electrons in an atom can have the same values of all the four quantum numbers *n*, *l*, *m* and m_s.

(d) The azimuthal quantum number has the value 0, 1, 2, ..., (*n* – 1).

16. (a) The expressions are $\text{KE} = \dfrac{1}{2}mv^2 = \dfrac{1}{2}\dfrac{Ze^2}{(4\pi\varepsilon_0)\,r}$ and $\text{PE} = -\dfrac{Ze^2}{(4\pi\varepsilon_0)\,r}$.

(b) The expressions are $\text{PE} = -\dfrac{Ze^2}{(4\pi\varepsilon_0)\,r}$; $E = \text{KE} + \text{PE} = \dfrac{1}{2}\dfrac{Ze^2}{(4\pi\varepsilon_0)\,r} - \dfrac{Ze^2}{(4\pi\varepsilon_0)\,r} = -\dfrac{1}{2}\dfrac{Ze^2}{(4\pi\varepsilon_0)\,r}$

(c) The expression of velocity is $v = \dfrac{1}{n}$(constant).

(d) The expression of energy is $E = -\dfrac{1}{n^2}$(constant). It increases with increase in the value of quantum number *n*.

17. (a) For ionization, $n_2 = \infty$. Hence $\Delta E = R\,(1/n_1^2)$

(b) The ionization energy increases in proportion to the square of positive charge in the nucleus as is evident from the expression

$$R = \frac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^3 c} \qquad \text{and} \qquad \Delta\tilde{E}_{\text{ioniz}} = R$$

(c) The correct expression is $\Delta p \Delta x \geq h/4\pi$.

(d) For a multi-electron atom, the energy of an orbital depends on both principal and azimuthal quantum numbers. The larger the value of *n* + *l*, larger the energy. For the same value of *n* + *l*, larger the value of *n*, larger the energy.

18. (b) The angular momentum depends only on the azimuthal quantum number.

19. (a) The number of orbitals for a given value of l is equal to the permitted value of m which can take values, 0, ±1, ±2, ... $\pm l$, a total of $2l+1$ values.
(c) A diamagnetic atom has no unpaired electrons.
(d) The half-filled and fully-filled electronic configurations are more stable. It is due to the larger exchange energy.

20. (b) The symbol s stands for sharp—a term used in the characterization of spectral lines. The symbols p, d and f stand for principal, diffuse and fundamental, respectively.

21. (b) The expression is $E = hc/\lambda$. Hence, energy and wavelength are inversely related.
(d) Lyman spectral series lies in the ultraviolet region.

22. (b) See Fig. 1.1; (c) See Fig. 1.1; (d) See Fig. 1.1.

23. (a) See Fig. 1.1; (b) See Fig. 1.1.; (c) See Fig. 1.1.
(d) It is due to the fact that the electron interacts in different manner with the external magnetic field.

24. (a) This splitting is known as Zeeman effect.
(c) Bosons does not follow Pauli exclusion principle.
(d) This is in accordance with Hund's rule of maximum multiplicity.

25. (a) It decreases with increase in the value of atomic number as is evident from the expression

$$E = -\frac{1}{n^2}\left[\frac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right].$$

(c) The deflection in a given electric field depends on the value of e/m. For β-particles, e/m is larger than α-particles because electrons are much lighter than He^{2+} species.

37. The ejected photoelectrons satisfy the expression

Energy of photon = Work function + KE of electron

Hence, $4.25\ \text{eV} = (\text{KE})_A + W_A$ and $4.70\ \text{eV} = (\text{KE})_B + W_B$

The expression of de Broglie wavelength is $\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mE}}$ (since $E = \dfrac{1}{2}mv^2 = \dfrac{p^2}{2m}$)

Hence $$\frac{\lambda_A}{\lambda_B} = \left[\frac{(\text{KE})_B}{(\text{KE})_A}\right]^{1/2} = \frac{1}{2}\text{(given)} \Rightarrow (\text{KE})_A = 4(\text{KE})_B$$

Since $(\text{KE})_B = (\text{KE})_A - 1.50\ \text{eV}$, we get $(\text{KE})_B = 4(\text{KE})_B - 1.50\ \text{eV}$ or $(\text{KE})_B = 0.50\ \text{eV}$

Thus $(\text{KE})_A = 2.00\ \text{eV}$

With these, $W_A = 4.25\ \text{eV} - (\text{KE})_A = 2.25\ \text{eV}$ and $W_B = 4.70\ \text{eV} - (\text{KE})_B = 4.20\ \text{eV}$

38. The time period of the electron in a Bohr orbit is given by $T = 2\pi r/v$, where v is the speed of the electron in the orbit. Since $mvr = n(h/2\pi)$, we get

$$T = \frac{2\pi r}{nh/(2\pi m r)} = \left(\frac{4\pi^2 m}{nh}\right)r^2$$

The expression of Bohr radius of hydrogen atom is $r = n^2\left(\dfrac{h^2\varepsilon_0}{\pi m e^2}\right)$

Hence $$T = \left(\frac{4\pi m}{nh}\right)\left(\frac{n^4 h^4 \varepsilon_0^2}{\pi^2 m^2 e^4}\right) = n^3\left(\frac{4\pi^3\varepsilon_0^2}{me^4}\right)$$

For two orbits $$\frac{T_1}{T_2} = \frac{n_1^3}{n_2^3}$$

Since $T_1/T_2 = 8$, we will have $n_1/n_2 = 2$.

Linked Comprehension Type

1. The relevant expressions to be used are

$$r = n^2\left[\frac{h^2}{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}\right]; \quad v = \frac{2\pi(Ze^2/4\pi\varepsilon_0)}{nh}; \quad E = -\frac{1}{n^2}\left[\frac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right]$$

(i) $\dfrac{r_1}{r} = \dfrac{mZ}{m_1 Z} = \dfrac{m_e e}{(2m_e)(2e)} = \dfrac{1}{4}$ **(ii)** $\dfrac{v_1}{v} = \dfrac{Z_1}{Z} = \dfrac{2e}{e} = 2$

(iii) $\dfrac{E_1}{E} = \dfrac{m_1 Z_1^2}{mZ^2} = \dfrac{(2m_e)(2e)^2}{(m_e)e^2} = 8$

2. **(i)** The energy difference between two orbits of hydrogen - like species is $\Delta E = Z^2 R_H\, hc\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

For hydrogen atom, $\Delta E_{1\to 2}$ is $\Delta E_{1\to 2} = R_H\, hc\left(\dfrac{1}{1} - \dfrac{1}{4}\right) = \dfrac{3}{4} R_H\, hc$

When this is transferred to the first excited state of He$^+$, we get

$$\frac{3}{4} R_H\, hc = (2^2)\, R_H hc\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

This gives $n_2 = 4$

(ii) The electron in $n_2 = 4$ in He$^+$ ion can undergo transition to $n_1 = 1$ or 2 or 3. The energy difference in each of these transition is an follows.

$$|\,\Delta E_{4\to 1}\,| = 4R_H\, hc\left(\frac{1}{1^2} - \frac{1}{4^2}\right) = 4R_H\, hc\left(\frac{15}{16}\right)$$

$$\lambda = \frac{hc}{\Delta E} = \frac{16}{60 R_H} = \frac{16}{60\times 1.09678\times 10^7\ \text{m}^{-1}} = 0.243\times 10^{-7}\ \text{m} = 24.3\ \text{nm}$$

$$|\,\Delta E_{4\to 2}\,| = 4R_H\, hc\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 4R_H\, hc\left(\frac{3}{16}\right)$$

$$\lambda = \frac{hc}{\Delta E} = \frac{16}{12\times 1.09678\times 10^7\ \text{m}^{-1}} = 1.216\times 10^{-7}\ \text{m} = 121.6\ \text{nm}$$

$$\Delta E_{4\to 3} = 4R_H hc\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = 4R_H hc\left(\frac{7}{144}\right)$$

$$\lambda = \frac{hc}{\Delta E} = \frac{144}{28\times 1.09678\times 10^7\ \text{m}^{-1}} = 4.689\times 10^{-7}\ \text{m} = 468.9\ \text{nm}$$

(iii) The expression of kinetic energy of electron in Bohr orbit of hydrogen-like species is

$$\text{KE} = \frac{1}{2} m_e v^2 = \frac{Z^2(2\pi e/4\pi\varepsilon_0)^2}{n^2 h^2}, \text{ that is KE} \propto \frac{Z^2}{n^2}$$

Hence, for the state $n = 2$, we have $\dfrac{(\text{KE})_H}{(\text{KE})_{He^+}} = \dfrac{1^2}{2^2} = \dfrac{1}{4}$

4. **(i)** Since only six different photons are emitted, the highest occupied level must be having $n = 4$. The value of n may be determined from the combination formula ${}^{n}C_2$ $(= n!/\ \{2!(n-2)!\})$ which gives number of ways of picking two levels from a total of n levels. From this level, the six possible photons emitted must correspond to the following transitions.

$\Delta E_{3\leftarrow 4}$; $\Delta E_{2\leftarrow 4}$; $\Delta E_{1\leftarrow 4}$; $\Delta E_{2\leftarrow 3}$; $\Delta E_{1\leftarrow 3}$; $\Delta E_{1\leftarrow 2}$

The absorption of 2.7 eV will not correspond to the transition $\Delta E_{1\to 4}$ as the photon of higher energy is also emitted.

This absorption will also not correspond to the transition $\Delta E_{3\to 4}$ as the photon of less energy is also emitted.

The only possibility left is the transition $\Delta E_{2\to 4}$.

Thus, initially the excited level of the species must have $n = 2$.

The above conclusion may be derived quantitatively by using the expression

$$\Delta\tilde{E} = Z^2R_{\mathrm{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

which gives

$$\Delta\tilde{E}_{2\neg 1} = \frac{3}{4}\,Z^2R_{\mathrm{H}} = \frac{108}{144}\,Z^2R_{\mathrm{H}}\ ;\quad \Delta\tilde{E}_{3\leftarrow 2} = \frac{5}{36}\,Z^2R_{\mathrm{H}} = \frac{20}{144}\,Z^2R_{\mathrm{H}}$$

$$\Delta\tilde{E}_{3\leftarrow 1} = \frac{8}{9}\,Z^2R_{\mathrm{H}} = \frac{128}{144}\,Z^2R_{\mathrm{H}}\ ;\quad \Delta\tilde{E}_{4\leftarrow 2} = \frac{3}{16}\,Z^2R_{\mathrm{H}} = \frac{27}{144}\,Z^2R_{\mathrm{H}}$$

$$\Delta\tilde{E}_{4\leftarrow 1} = \frac{15}{16}\,Z^2R_{\mathrm{H}} = \frac{135}{144}\,Z^2R_{\mathrm{H}}\ ;\quad \Delta\tilde{E}_{4\leftarrow 3} = \frac{7}{144}\,Z^2R_{\mathrm{H}}$$

Only the absorption $\Delta E_{4\leftarrow 2}$ will cause emission of photons of lower and higher energies.

(ii) Ionization energy corresponds to the transition $1\to\infty$, which will have energy $\Delta E_{\infty\leftarrow 1} = Z^2R_{\mathrm{H}}$

Since $\Delta E_{4\leftarrow 2} = 2.7$ eV (given). Hence, $\dfrac{27}{144}\,Z^2R_{\mathrm{H}} = 2.7$ eV

which gives $Z^2R_{\mathrm{H}} = \dfrac{2.7\times 144}{27}$ eV $= 14.4$ eV

(iii) The maximum and minimum energies are

$$\Delta E_{4\leftarrow 1} = \frac{135}{144}\,Z^2R_{\mathrm{H}} = \frac{135}{144}(14.4\text{ eV}) = 13.5\text{ eV}$$

$$\Delta E_{2\leftarrow 1} = \frac{7}{144}\,Z^2R_{\mathrm{H}} = \frac{7}{144}(14.4\text{ eV}) = 0.7\text{ eV}$$

5. The expression of electronic transition energy for hydrogen-like species is

$$\Delta E = Z^2R_{\mathrm{H}}\,hc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = Z^2(13.6\text{ eV})\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

(i) and (ii)

For the given informations, we have

$$\Delta E_{n\to 2} = Z^2(13.6\text{ eV})\left(\frac{1}{4}-\frac{1}{n^2}\right) = 27.2\text{ eV};\quad \Delta E_{n\to 3} = Z^2(13.6\text{ eV})\left(\frac{1}{9}-\frac{1}{n^2}\right) = 10.2\text{ eV}$$

Solving for Z and n, we get $Z = 3$ and $n = 6$

(iii) The ionization energy is $\Delta E_{\infty\leftarrow 1} = Z^2R_{\mathrm{H}}\,hc = (9)\,(13.6\text{ eV}) = 122.4$ eV

6. **(i)** The energy of an electron in hydrogen-like species is given by $E = \mathrm{KE} + \mathrm{PE}$

Also, $\mathrm{KE} = -\dfrac{1}{2}\mathrm{PE}$. Hence $E = \mathrm{KE} + (-2\mathrm{KE}) = -\,\mathrm{KE}$ or $\mathrm{KE} = -\,E = 3.4$ eV

(ii) We know that

$$\mathrm{KE} = \frac{1}{2}mv^2 \quad \text{and} \quad \lambda = \frac{h}{p} = \frac{h}{mv}; \quad \text{(de-Broglie relation)}$$

$$\lambda = \frac{h}{m[2(\mathrm{KE})/m]^{1/2}} = \frac{h}{[2m(\mathrm{KE})]^{1/2}} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})}{\left[2(9.1\times10^{-31}\ \mathrm{kg})(3.4\times1.6\times10^{-19}\ \mathrm{J})\right]^{1/2}}$$

$$= 6.66 \times 10^{-10}\ \mathrm{m} = 666\ \mathrm{pm}$$

(iii) $E_n = -Z^2(13.6\ \mathrm{eV})/n^2$. Obviously, $Z = 3$ and $n = 6$.

7. (i) and (ii)

The expression for the electronic transition in hydrogen-like species is

$$\Delta E = (Z^2)R_\mathrm{H}\ hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{where } R_\mathrm{H}\ hc = 13.6\ \mathrm{eV}.$$

For the transition from $2n$ level to n level, we have

$$\Delta E = Z^2(13.6\ \mathrm{eV}) \left(\frac{1}{n_1^2} - \frac{1}{4n_2^2}\right) = \frac{3}{4}\frac{Z^2}{n^2}(13.6\ \mathrm{eV})$$

It is given that $\Delta E = 40.8$ eV. Hence,

$$\frac{3}{4}\left(\frac{Z}{n}\right)^2 (13.6\ \mathrm{eV}) = 40.8\ \mathrm{eV} \quad \Rightarrow \quad \frac{Z}{n} = 2$$

For the maximum-energy photon emitted from $2n$ level, we will have de-excitation to $n = 1$ level. For this transition, we will have

$$\Delta E_\mathrm{max} = Z^2 R_\mathrm{H}\ hc \left[\frac{1}{1^2} - \frac{1}{(2n)^2}\right] = Z^2(13.6\ \mathrm{eV}) \left(1 - \frac{1}{4n^2}\right)$$

$$= (13.6\ \mathrm{eV}) \left[Z^2 - \frac{1}{4}\left(\frac{Z}{n}\right)^2\right] = (13.6\ \mathrm{eV}) \left[Z^2 - \frac{1}{4}(2)^2\right]$$

$$= (13.6\ \mathrm{eV})\ \ (Z^2 - 1)$$

It is given that $\Delta E_\mathrm{max} = 204$ eV. Hence $204\ \mathrm{eV} = (13.6\ \mathrm{eV})\ (Z^2 - 1)$

This gives $Z = [(204/13.6) + 1]^{1/2} = 4$. Since $(Z/n) = 2$, we have $n = Z/2 = 2$

(iii) The ground state energy is $E = -Z^2(R_\mathrm{H}\ hc) = -(4)^2\ (13.6\ \mathrm{eV}) = -217.6\ \mathrm{eV}$

8. (i) The function $R_{2,0}$ will be zero where $2 - r/a_0 = 0$. This gives $r = 2a_0$.

(ii) We have

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[\left(2 - \frac{r}{a_0}\right)^2 \mathrm{e}^{-r/a_0}\right] = 0 \qquad \text{i.e.} \qquad \frac{\mathrm{d}}{\mathrm{d}r}\left[4 + \left(\frac{r}{a_0}\right)^2 - 4\left(\frac{r}{a_0}\right)\right]\mathrm{e}^{-r/a_0} = 0$$

$$\text{or} \quad \left\{\left[2\left(\frac{r}{a_0^2}\right) - \frac{4}{a_0}\right] - \frac{1}{a_0}\left[4 + \left(\frac{r}{a_0}\right)^2 - 4\left(\frac{r}{a_0}\right)\right]\right\}\mathrm{e}^{-r/a_0} = 0$$

This gives $\left(\frac{r}{a_0}\right)^2 = 6\left(\frac{r}{a_0}\right) + 8 = 0$

which have roots $\frac{r}{a_0} = \frac{6 \pm \sqrt{36-32}}{2} = \frac{6 \pm 2}{2} = 4,\ 2$

At $r/a_0 = 2$, the function R^2 exhibits the minimum and at $r/a_0 = 4$, there exists a maximum.

(iii) The maximum in $r^2\, R^2$ can be obtained by setting $\mathrm{d}(r^2\, R^2)/\mathrm{d}r = 0$. Thus

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\left(2-\frac{r}{a_0^2}\right)^2 \mathrm{e}^{-r/a_0}\right] = 0 \qquad \text{i.e.} \qquad \frac{\mathrm{d}}{\mathrm{d}r}\left[4r^2+\frac{r^4}{a_0^2}-\frac{4r^3}{a_0}\mathrm{e}^{-r/a_0}\right] = 0$$

This gives $\left\{\left(8r+\frac{4r^3}{a_0^2}-\frac{12r^2}{a_0}\right)-\frac{1}{a_0}\left(4r^2+\frac{r^4}{a_0^2}-\frac{4r^3}{a_0}\right)\right\}e^{-r/a_0} = 0$

or $$8r + \frac{8r^3}{a_0^2} - \frac{6r^2}{a_0} - \frac{r^4}{a_0^3} = 0 \qquad \text{or} \qquad \left(\frac{r}{a_0}\right)^3 - 8\left(\frac{r}{a_0}\right)^2 + 16\left(\frac{r}{a_0}\right) - 8 = 0$$

or $$\left[\left(\frac{r}{a_0}\right)^2 - 6\left(\frac{r}{a_0}\right) + 4\right]\left(\frac{r}{a_0}-2\right) = 0$$

The roots are $(r/a_0) = 2$ and $(r/a_0) = 3 \pm \sqrt{5}$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is -5.42×10^{-19} J and -2.41×10^{-19} J, respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. (1981)

Solution We have

$$|\Delta E_{2 \leftarrow 3}| = -2.41 \times 10^{-19}\ \text{J} - (-5.42 \times 10^{-19}\ \text{J}) = 3.01 \times 10^{-19}\ \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(3.01 \times 10^{-19}\ \text{J})} = 6.604 \times 10^{-7}\ \text{m}.$$

2. Calculate the wavelength of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionization potential of the ground state of hydrogen atom is 2.17×10^{-18} J per atom. (1982)

Solution From the given data, it follows that

$$E_1 = -2.17 \times 10^{-18}\ \text{J}$$

$$E_2 = \frac{E_1}{n^2} = -\frac{2.17 \times 10^{-18}}{4}\ \text{J} = -5.425 \times 10^{-19}\ \text{J}$$

Hence,

$$|\Delta E_{1 \leftarrow 2}| = -5.425 \times 10^{-19}\ \text{J} - (-2.17 \times 10^{-18}\ \text{J}) = 1.6275 \times 10^{-18}\ \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \text{J})(3 \times 10^{8}\ \text{m s}^{-1})}{(1.6275 \times 10^{-18}\ \text{J})} = 1.2214 \times 10^{-7}\ \text{m}.$$

3. The energy of an electron in hydrogen atom is given by $E_n = (-21.7 \times 10^{-19}\ \text{J})/n^2$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of radiation that can be used to cause this transition? (1984)

Solution The energy of $n = 2$ orbit is

$$E = -\frac{21.7 \times 10^{-19}\ \text{J}}{4} = -5.425 \times 10^{-19}\ \text{J}$$

To remove electron completely, we will require

$$E = 5.425 \times 10^{-19}\ \text{J}$$

Hence,

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(5.425 \times 10^{-19}\ \text{J})} = 3.664 \times 10^{-7}\ \text{m}.$$

4. According to Bohr's theory, the electronic energy of hydrogen atom in the nth Bohr's orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19}\ \text{J}}{n^2}$$

Calculate the longest wavelength of radiation that will be needed to remove an electron from the third orbit of the He^+ ion. (1990)

Solution In a one electron system, the expression of electronic energy is

$$E = -Z^2 E_H$$

where Z is the nuclear charge. Hence, for He^+ ion, we have

$$E = -\frac{4 \times 21.76 \times 10^{-19}\ \text{J}}{n^2}$$

To remove the electron from third orbit of He$^+$, the energy needed would be

$$E = \frac{4 \times 21.76 \times 10^{-19}\ \text{J}}{9}$$

Hence, $$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})}{(4 \times 21.76 \times 10^{-19}\ \text{J}/9)} = 2.055 \times 10^{-7}\ \text{m} = 205.5\ \text{nm}.$$

5. Estimate the difference in energy between the 1st and 2nd Bohr orbit for a hydrogen atom. At what minimum atomic number, would a transition from $n = 2$ to $n = 1$ energy level result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen atom-like species does this atomic number correspond to? (1993)

Solution For a hydrogen atom, the expression of energy difference between two electronic levels is

$$\Delta E = Rhc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Hence, $$\Delta E_{2 \leftarrow 1} = (1.09677 \times 10^{7}\ \text{m}^{-1})(6.626 \times 10^{-34}\ \text{J s}) \times (3 \times 10^{8}\ \text{m s}^{-1})\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 1.635 \times 10^{-8}\ \text{J}$$

For hydrogen-like species, the expression is

$$\Delta E = Z^2 Rhc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{or} \quad \frac{1}{\lambda} = Z^2 R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Thus $$\frac{1}{3 \times 10^{-8}\ \text{m}} = Z^2\ (1.09677 \times 10^{7}\ \text{m}^{-1})\left(\frac{3}{4}\right)$$

or $$Z^2 = \frac{1}{(3 \times 10^{-8}\ \text{m})(1.09677 \times 10^{7}\ \text{m}^{-1})(3/4)} \simeq 4.0$$

or $$Z = 2$$

The species is He$^+$.

6. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, $n = 4$, to $n = 2$ of He$^+$ spectrum? (1993)

Solution For He$^+$ ion, we have

$$\frac{1}{\lambda} = Z^2 R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (2)^2\ R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3}{4}R \quad (1)$$

Now for hydrogen atom $$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad (2)$$

Equating Eqs (1) and (2), we get $$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Obviously, $n_1 = 1$ and $n_2 = 2$. Hence, the transition $n = 2$ to $n = 1$ in hydrogen atom will have the same wavelength as the transition, $n = 4$ to $n = 2$ in He$^+$ species.

7. Calculate the speed of an electron in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus. Given: $4\pi\varepsilon_0 = 1.112 \times 10^{-10}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$.

Solution The expression of speed is

$$v = \frac{2\pi (Z e^2/4\pi \varepsilon_0)}{nh}$$

For hydrogen atom $Z = 1$. Hence,

$$v = \frac{2(3.14)(1.6 \times 10^{-19}\text{C})^2 / (1.112 \times 10^{-10}\text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})}{(3)(6.626 \times 10^{-34}\text{J s})} = 7.27 \times 10^{5}\ \text{m s}^{-1}$$

The number of revolutions made by the electron would be $\nu = \dfrac{v}{2\pi r}$

where $$r = n^2 \left[\frac{h^2}{4\pi^2 m\,(Ze^2/4\pi\varepsilon_0)}\right] = 9\left[\frac{\dfrac{(6.626\times10^{-34}\,\text{J s})^2}{(4)(3.14)^2(9.1\times10^{-31}\,\text{kg})}}{(1.6\times10^{-19}\,\text{C})^2/(1.112\times10^{-10}\,\text{C}^2\,\text{N}^{-1}\,\text{m}^{-2})}\right] = 4.782\times10^{-10}\ \text{m}$$

Hence, $$\nu = \frac{(7.27\times10^5\ \text{m s}^{-1})}{2(3.14)\,(4.782\times10^{-10}\ \text{m})} = 2.42\times10^4\ \text{s}^{-1}$$

8. Calculate the ionization energy of (a) one Li^{2+} ion, and (b) one mole of Li^{2+} ions. Given: Rydberg constant, $R = 1.0974\times10^7\ \text{m}^{-1}$.

Solution The expression of ionization energy is $\Delta E = RZ^2hc$

For Li^{2+} ion, $Z = 3$. Hence $\Delta E = (1.0974\times10^7\ \text{m}^{-1})\,(9)\,(6.626\times10^{-34}\ \text{J s})\,(3\times10^8\ \text{m s}^{-1}) = 1.964\times10^{-17}\ \text{J}$

For one mole of ions, we have $\Delta E = N_\text{A}\,\Delta E = (6.023\times10^{23}\ \text{mol}^{-1})\,(1.964\times10^{-17}\ \text{J})$
$= 1.118\times10^7\ \text{J mol}^{-1} = 11180\ \text{kJ mol}^{-1}$.

9. A spectral line of the Lyman series of hydrogen atom has a frequency of $2.466\times10^{15}\ \text{s}^{-1}$. What is the transition responsible for this spectral line? Given: Rydberg constant for hydrogen is $1.096\times10^7\ \text{m}^{-1}$.

Solution In Lyman series, the spectral lines are due to the electron transfer from the level $n > 1$ to the level $n = 1$. Hence, we have

$$\nu = Rc\left(1-\frac{1}{n^2}\right) = (1.096\times10^7\ \text{m}^{-1})\quad(3\times10^8\ \text{m s}^{-1})\left(1-\frac{1}{n^2}\right)$$
$$= (3.288\times10^{15}\ \text{s}^{-1})\left(1-\frac{1}{n^2}\right)$$

Equating this to the given value, we get

$$(3.288\times10^{15}\ \text{s}^{-1})\left(1-\frac{1}{n^2}\right) = 2.466\times10^{15}\ \text{s}^{-1}$$

Hence, $$\frac{1}{n^2} = 1 - \frac{2.466\times10^{15}\ \text{s}^{-1}}{3.288\times10^{15}\ \text{s}^{-1}} = 1 - 0.75 = 0.25 \quad \text{or} \quad n = \sqrt{\frac{1}{0.25}} = 2$$

Hence, the transition 1 → 2 is responsible for the spectral line $2.466\times10^{15}\ \text{s}^{-1}$.

10. Calculate the ionization energy of Li^{2+} ions in the ground state. What wavelength of the radiation will be required to cause this ionization? Given: $4\pi\varepsilon_0 = 1.112\times10^{-10}\ \text{C}^2\,\text{N}^{-1}\,\text{m}^{-2}$.

Solution The expression of electronic energy in a one-electron system is $E = -\dfrac{1}{n^2}\left[\dfrac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right]$

The energy difference between two quantum levels is $\Delta E = \dfrac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\left(\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right)$

For ionization energy from the ground-state level, we have $n_1 = 1$ and $n_2 = \infty$

Hence, the expression of ionization energy is $\Delta E_\text{ioniz} = \dfrac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}$

For Li^{2+} ions, $Z = 3$. Hence,

$$\Delta E_\text{ioniz} = \frac{(2)(3.14)^2\,(9.1\times10^{-31}\ \text{kg})[(9)(1.6\times10^{-19}\ \text{C})^4]}{(6.626\times10^{-34}\ \text{J s})^2\,(1.112\times10^{-10}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})^2} = 1.95\times10^{-17}\ \text{J}$$

Now $$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ \text{J s})(3\times10^8\ \text{m s}^{-1})}{(1.95\times10^{-17}\ \text{J})} = 1.019\times10^{-8}\ \text{m}.$$

11. Calculate the first spectral line in the Balmer series for hydrogen atom. Compute the frequency, wave number and wavelength of the spectral line.

Solution The expression of energy difference between two orbits of a hydrogen atom is

$$\Delta E = \frac{2\pi^2 me^4}{h^2(4\pi\varepsilon_0)^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = \frac{(2)(3.14)^2(9.1\times10^{-31}\ \text{kg})(1.6\times10^{-19}\ \text{C})^4}{(6.626\times10^{-34}\ \text{J s})^2(1.112\times10^{-10}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= (2.18\times10^{-18}\ \text{J})\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

For the first spectral line in the Balmer series, $n_1 = 2$ and $n_2 = 3$. Hence,

$$\Delta E = (2.18\times10^{-18}\ \text{J})\left(\frac{1}{4}-\frac{1}{9}\right) = (2.18\times10^{-18}\ \text{J})\left(\frac{5}{36}\right) = 3.03\times10^{-19}\ \text{J}$$

$$\nu = \frac{\Delta E}{h} = \frac{3.03\times10^{-19}\ \text{J}}{6.626\times10^{-34}\ \text{J s}} = 4.57\times10^{14}\ \text{s}^{-1};\quad \tilde{\nu} = \frac{\nu}{c} = \frac{4.57\times10^{14}\ \text{s}^{-1}}{3\times10^{8}\ \text{m s}^{-1}} = 1.52\times10^{6}\ \text{m}^{-1}$$

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{1.52\times10^{6}\ \text{m}^{-1}} = 6.56\times10^{-7}\ \text{m} = 656\ \text{nm}.$$

12. The ionization energy of He^+ is 19.6×10^{-18} J per atom. Calculate the energy of the second stationary state in Li^{2+} ion.

Solution The energy of the first orbit in one electron species is related to that in hydrogen atom by an expression

$$E = Z^2 E_\text{H}$$

For He^+ ion, $Z = 2$. Hence, $E_\text{H} = \dfrac{E}{Z^2} = -\dfrac{19.6\times10^{-18}}{4}$ J

Now for Li^{2+} ion, where $Z = 3$, we will have $E = (9)\,E_\text{H} = 9\left(-\dfrac{19.6\times10^{-18}}{4}\ \text{J}\right) = -44.1\times10^{-18}$ J

Now for the second orbit, the energy is $E' = \dfrac{E}{n^2} = \dfrac{-44.1\times10^{-18}\ \text{J}}{2^2} = -11.025\times10^{-18}$ J

13. A particle of charge equal to that of an electron and mass 208 times the mass of the electron moves in a circular orbit around a nucleus of charge $+3e$. Assuming that the Bohr model of the atom is applicable to this system, (a) derive an expression for the radius of the nth Both orbit, (b) find the value of n for which the radius of the orbit is approximately the same as that of the first Bohr orbit for the hydrogen atom, and (c) find the wavelength of the radiation emitted when the revolving particle jumps from the third orbit to the first.

Solution The basic expressions in Bohr model of the atoms are:

1. *Stability of the circular motion of the electron*, i.e.

Attractive force = Centrifugal force

$$\frac{(Ze)e}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r} \tag{1}$$

2. *Quntization of angular momentum* $\quad m\mathbf{v}r = n\left(\dfrac{h}{2\pi}\right)$ (2)

Eliminating v in the above two expressions, we get

$$\frac{(Ze)e}{(4\pi\varepsilon_0)r^2} = \frac{m}{r}\left[\frac{n}{mr}\left(\frac{h}{2\pi}\right)\right]^2$$

which on simplifying and rearranging gives

$$r = n^2\left[\frac{h^2}{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}\right] = n^2\left[\frac{h^2}{4\pi^2(208\ m_\text{e})(3e^2/4\pi\varepsilon_0)}\right]$$

(a) Now for the given problem $m = (208)m_e$ and $Z = 3$

Now, $$r = n^2\left[\frac{h^2}{4\pi^2(208\,m_e)(3e^2/4\pi\varepsilon_0)}\right] \tag{3}$$

Substituting the values of h, m_e and e, we get

$$r = n^2\left[\frac{(6.626\times10^{-34}\ \text{J s})^2\,(1.112\times10^{-10}\ \text{N}^{-1}\ \text{C}^2\ \text{m}^{-2})}{4(3.14)^2\,(208\times9.1\times10^{-31}\ \text{kg})(3)(1.6\times10^{-19}\ \text{C})^2}\right] = n^2\ (8.51\times10^{-14}\ \text{m})$$

(b) Equating Eq. (3) with the first Bohr orbit for hydrogen atom, we get

$$n^2\left[\frac{h^2}{4\pi^2(208\,m_e)(3e^2/4\pi\varepsilon_0)}\right] = \frac{h^2}{4\pi^2 m_e\,(e^2/4\pi\varepsilon_0)}$$

or $n^2 = 208\times3$ or $n = \sqrt{208\times3} \simeq 25$

(c) The energy of electron in the Bohr model of atom is

$$E = \text{KE} + \text{PE} = \frac{1}{2}mv^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}$$

Using Eq. (1), we get

$$E = \frac{1}{2}\left[\frac{Ze^2}{(4\pi\varepsilon_0)r}\right] - \frac{Ze^2}{(4\pi\varepsilon_0)r} = -\frac{1}{2}\frac{Ze^2}{(4\pi\varepsilon_0)r}$$

Substituting the expression of r (Eq. 3), we get

$$E = -\frac{1}{n^2}\left[\frac{2\pi^2(208\,m_e)(3e^2/4\pi\varepsilon_0)^2}{h^2}\right]$$

$$= -\frac{1}{n^2}\left[\frac{2(3.14)^2\,(208\times9.1\times10^{-31}\ \text{kg})\,(9)(1.6\times10^{-19}\ \text{C})^4}{(6.626\times10^{-34}\ \text{J s})^2\,(1.112\times10^{-10}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})^2}\right] = -\frac{1}{n^2}(4.055\times10^{-15}\ \text{J})$$

Hence, for the transition $1 \leftarrow 3$, we get

$$\Delta E = (4.055\times10^{-15}\ \text{J})\left(1-\frac{1}{3^2}\right) = 3.604\times10^{-15}\ \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ \text{J s})(3\times10^8\ \text{m s}^{-1})}{(3.604\times10^{-15}\ \text{J})} = 5.52\times10^{-11}\ \text{m} = 55.2\ \text{pm}.$$

14. What is the speed and de Broglie wavelength of an electron that has been accelerated by a potential difference of 300 V?

Solution The kinetic energy of the electron under a potential difference of 300 V is given by the expression

$$\frac{1}{2}mv^2 = eV$$

Hence $$v = \left(\frac{2eV}{m}\right)^{1/2} = \left(\frac{2(1.602\times10^{-19}\ \text{C})\,(300\ \text{V})}{9.1\times10^{-31}\ \text{kg}}\right)^{1/2} = 1.028\times10^7\ \text{m s}^{-1}$$

Now using de Broglie relation, we get

$$\lambda = \frac{h}{mv} = \frac{(6.626\times10^{-34}\ \text{J s})}{(9.1\times10^{-31}\ \text{kg})\,(1.208\times10^7\ \text{m s}^{-1})} = 7.08\times10^{-11}\ \text{m}.$$

15. If the radius of the first Bohr orbit in a hydrogen atom can be determined with an uncertainty of 1% of its actual value, what will be the uncertainty in the velocity of electron? Compare the value with the velocity of electron in the first orbit. Given: $m_e = 9.1\times10^{-31}$ kg and $\varepsilon_0 = 8.854\times10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$.

Solution The expression of radius of Bohr orbit in a hydrogen atom is

$$r = n^2\left(\frac{h^2}{4\pi^2 m(e^2/4\pi\varepsilon_0)}\right) = n^2\left(\frac{h^2\varepsilon_0}{\pi m e^2}\right)$$

Substituting the values of variables, we get

$$r = 1^2\left[\frac{(6.626\times10^{-34}\ \text{J s})^2\ (8.854\times10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})}{(3.14)\ (9.1\times10^{-31}\ \text{kg})\ (1.6\times10^{-19}\ \text{C})^2}\right] = 5.3\times10^{-11}\ \text{m}$$

Now, the uncertainty in the location of Bohr orbit = 1% of 5.3×10^{-11} m, i.e. 5.3×10^{-13} m.

Now since $\Delta p \Delta x \geq \dfrac{h}{4\pi}$, we get $(m\Delta v)\ \Delta x \geq \dfrac{h}{4\pi}$

or
$$\Delta v \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{m\Delta x}\right) = \frac{(6.626\times10^{-34}\ \text{J s})}{(4)\ (3.14)(9.1\times10^{-31}\ \text{kg})(5.3\times10^{-13}\ \text{m})} = 1.094\times10^{8}\ \text{m s}^{-1}$$

Now, the velocity of an electron in a Bohr orbit of hydrogen atom is given as

$$v = \frac{2\pi\,(e^2/4\pi\varepsilon_0)}{nh} = \frac{1}{2}\frac{e^2}{nh\varepsilon_0} = \frac{(1.602\times10^{-19}\ \text{C})^2}{(2)\ (1)\ (6.626\times10^{-34}\ \text{J s})\ (8.854\times10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})}$$
$$= 2.19\times10^{6}\ \text{m s}^{-1}.$$

16. Calculate the kinetic energy of a photoelectron emitted by a sodium surface when light of wavelength 400 nm is incident on it. The work function of sodium is 2.28 eV. Calculate also the value of the longest wavelength which can result in the emission of a photoelectron from a sodium surface.

Solution We have

Work function of sodium = 2.28 eV

i.e. Minimum energy required to eject electron from sodium = $2.28 \times 1.602 \times 10^{-19}$ J

Wavelength of radiation having above energy is

$$\lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34}\ \text{J s})(3\times10^{8}\ \text{m s}^{-1})}{(2.28\times1.602\times10^{-19}\ \text{J})} = 5.44\times10^{-7}\ \text{m} = 544\ \text{nm}$$

Energy carried by photon of wavelength 400 nm $= \dfrac{hc}{\lambda} = \dfrac{(6.626\times10^{-34}\ \text{J s})(3\times10^{8}\ \text{m s}^{-1})}{(400\times10^{-9}\ \text{m})} = 4.97\times10^{19}$ J

Kinetic energy of photoelectron emitted = $(4.97 - 2.28 \times 1.602) \times 10^{-19}$ J = 1.317×10^{-19} J.

17. 1.0 g of Mg atoms (atomic mass = 24.0 amu) in the vapour phase absorb 50.0 kJ of energy. Find the composition of the final mixture, if the first and second ionization energies of Mg are 740 and 1450 kJ mol^{-1}, respectively.

Solution We have,

Amount of Mg atoms $= \dfrac{1.0\ \text{g}}{24.0\ \text{g mol}^{-1}} = 4.167\times10^{-2}$ mol

Energy used in ionizing Mg to Mg$^+$ = $(4.167 \times 10^{-2}$ mol) (740 kJ mol^{-1}) = 30.84 kJ

Energy used in ionizing Mg$^+$ to Mg^{2+} = (50.0 – 30.84) kJ = 19.16 kJ

Amount of Mg$^+$ converted into Mg^{2+} $= \dfrac{19.16\ \text{kJ}}{1450\ \text{kJ mol}^{-1}} = 1.321\times10^{-2}$ mol

Amount of Mg$^+$ remaining as such = $(4.167 \times 10^{-2} - 1.321 \times 10^{-2})$ mol = 2.846×10^{-2} mol

Composition of the final mixture is as follows.

Percentage of Mg$^+$ $= \dfrac{2.846\times10^{-2}}{4.167\times10^{-2}} \times 100 = 68.3$

Percentage of Mg^{2+} = 100 – 68.3 = 31.7.

18. A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of the sample absorbs 284 kJ while the addition of an electron to each atom of the mixture releases 68.8 kJ. Determine the percentage composition of the mixture, given that the ionization energies of F and Cl are 27.91×10^{-22} kJ and 20.77×10^{-22} kJ, respectively, and that the electron affinities are 5.53×10^{-22} kJ and 5.78×10^{-22} kJ, respectively.

Solution Let the amounts of F and Cl atoms in the mixture be x and y, respectively

$$(x \times 6.023 \times 10^{23}\ \text{mol}^{-1})\ (27.91 \times 10^{-22}\ \text{kJ}) + (y \times 6.023 \times 10^{23}\ \text{mol}^{-1})\ (20.77 \times 10^{-22}\ \text{kJ}) = 284\ \text{kJ}$$

$$(x \times 6.023 \times 10^{23}\ \text{mol}^{-1})\ (5.53 \times 10^{-22}\ \text{kJ}) + (y \times 6.023 \times 10^{23}\ \text{mol}^{-1})\ (5.78 \times 10^{-22}\ \text{kJ}) = 68.8\ \text{kJ}$$

or $$x(1681) + y(1251) = 284\ \text{mol}$$

$$x(333.1) + y(348.1) = 68.8\ \text{mol}$$

Solving for x and y, we get

$$x = 0.076\ \text{mol} \quad \text{and} \quad y = 0.125\ \text{mol}$$

Hence, $$\text{Percentage of F} = \frac{0.076}{0.076 + 0.125} \times 100 = 37.81$$

$$\text{Percentage of Cl} = 100 - 37.81 = 62.19.$$

19. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996)

Solution The shortest wavelength transition in the Balmes series corresponds to the transition $n = 2 \rightarrow n = \infty$. Hence,

$$\Delta \tilde{E} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (109\ 677\ \text{cm}^{-1}) \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) = 27\ 419.25\ \text{cm}^{-1}$$

20. Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. (1996)

Solution Work obtained in the neutralisation process is

$$w = -\int_{\infty}^{a_0} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r^2}\, \mathrm{d}r = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0}$$

This work will be obtained from the average total energy of electron.

Hence, $$\overline{\text{TE}} = -w = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0}$$

It is given that $$\overline{\text{KE}} = \frac{1}{2}\left|\overline{\text{PE}}\right|$$

Hence, $$\overline{\text{TE}} = \overline{\text{KE}} + \overline{\text{PE}} \quad \text{i.e.} \quad -\frac{e^2}{(4\pi\varepsilon_0)a_0} = -\frac{1}{2}\overline{\text{PE}} + \overline{\text{PE}}$$

or $$\overline{\text{PE}} = -2\overline{\text{TE}} = -2\left(\frac{e^2}{4\pi\varepsilon_0} \frac{1}{a} \right)$$

21. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. (1998)

Solution For 1.54 Å wavelength, the momentum of electron would be given by the expression

$$p = \frac{h}{\lambda} \Rightarrow v = \frac{h}{m\lambda}$$

The potential to which a beam of electrons be accelerated is given by the expression $eV = \frac{1}{2}mv^2$

Thus $$V = \frac{1}{2me}\left(\frac{h}{\lambda}\right)^2 = \frac{1}{(2)(9.1 \times 10^{-31}\ \text{kg})(1.6 \times 10^{-19}\ \text{C})} \left(\frac{6.626 \times 10^{-34}\ \text{J s}}{1.54 \times 10^{-10}\ \text{m}} \right)^2 = 63.573\ \text{m s}^{-1}$$

22. Calculate the energy required to excite on litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol^{-1}. (2000)

Solution Amount of hydrogen gas is $n_1 = \dfrac{pV}{RT} = \dfrac{(1\ \text{atm})(1\ \text{L})}{(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})(298\ \text{K})} = 0.040\ 92\ \text{mol}$

Energy consumed in dissociating hydrogen molecules

$$E_1 = (0.040\ 92\ \text{mol})\ (436\ \text{kJ mol}^{-1}) = 17.84\ \text{kJ}$$

Since each hydrogen molecule gives two hydrogen atoms, the amount of hydrogen atoms will be

$$n_2 = 2n_1 = 2 \times 0.040\ 92\ \text{mol} = 0.081\ 84\ \text{mol}$$

Energy required to excite one mole of hydrogen atoms from the ground electronic state to the first excited state is

$$\Delta E = N_A R_H\ hc\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4} N_A R_H\ hc$$

$$= \left(\frac{3}{4}\right)(6.023 \times 10^{23}\ \text{mol}^{-1})\ (109\ 679\ \text{cm}^{-1})\ (6.626 \times 10^{-34}\ \text{J}) \times (3 \times 10^{8}\ \text{cm s}^{-1})$$

$$= 9\ 848.5\ \text{J mol}^{-1}$$

For exciting 0.081 84 mol of hydrogen atoms, we will have $E_2 = (0.081\ 84\ \text{mol})\ (9.848\ 5\ \text{kJ mol}^{-1}) = 0.806\ \text{kJ}$

Hence, the total energy required will be $E = E_1 + E_2 = (17.84 + 0.81)\ \text{kJ} = 18.65\ \text{kJ}$

UNSOLVED NUMERICALS

1. Two hydrogen atoms collide head on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. Which transition leads to this wavelength? How fast the hydrogen atoms were travelling before the collision? Given: $R_H = 1.097 \times 10^7\ \text{m}^{-1}$ and $m_H = 1.67 \times 10^{-27}$ kg.
2. A hydrogen atom undergoes a transition from the $n = 105$ level to the $n = 104$ level. Calculate the wavelength of the emitted photon?
3. Calculate the difference in potential energy of electron between the first and second Bohr orbits of (a) hydrogen atom and (b) Li^{2+} ion.
4. The wave numbers of the first line in the Balmer series of hydrogen is 15200 cm^{-1}. What is the wave number of the first line in the Balmer series of Be^{3+}?
5. The ionization energy of hydrogen atom is 1314 kJ mol^{-1}. What will be the ionization energy of He^{+} ion?
6. The wavelength of a certain line in the Balmer series is observed to be 434.1 nm. To what value of n_2 does this line correspond?
7. Find the relation between the Bohr radii for H and He^{+}. Are there any combinations of value of n for which the radii are equal?
8. Calculate the speed of an electron in the ground state of hydrogen atom. What fraction of the speed of light is this value? How long does it take for the electron to complete one revolution around the nucleus? How many times does the electron travel around the nucleus in one second?
9. The hypothetical element positronium consists of an electron moving in space around a nucleus consisting of a positron (a subatomic particle similar to the electron except possessing a positive charge).Using the Bohr theory calculate the radius of the first orbit of the electron.
10. The ionization energy of hydrogen atom is 13.6 eV. Calculate the wavelength of the series limit of the Balmer series of hydrogen atom?
11. Calculate the radius of third Bohr orbit of the hydrogen atom.
12. Find the radius of second Bohr orbit of the singly ionized helium atom and calculate the velocity of an electron in this orbit.
13. What is the longest wavelength radiation capable of ionizing a hydrogen atom in the ground state?
14. An excited hydrogen atom could, in principle, have a radius of 1.0 mm. What would be the value of n for a Bohr orbit of this size? What would its energy be?
15. The ionization energy of a one-electron species is found to be 11180 kJ mol^{-1}. Find the number of protons in its nucleus.
16. What is the speed and the de Broglie wavelength of an electron that has been accelerated by a potential difference of 500 V?

17. (a) Find the velocity of an electron emitted by a metal whose threshold frequency is 2.25×10^{14} s^{-1} when exposed to visible light of wavelength 5.0×10^{-7} m. (b) What is the de Broglie wavelength of the emitted electrons?

18. An electron is accelerated to one tenth the speed of light. Suppose its speed can be measured with a precision of +1%, what must be its uncertainty in position?

19. When a certain metal was irradiated with a radiation of frequency 3.2×10^{16} s^{-1}, the photoelectrons emitted had twice the kinetic energy as did the photoelectrons emitted when the same metal was irradiated with a radiation of frequency 2.0×10^{16} s^{-1}. Calculate the threshold frequency for the metal.

20. (a) What is the speed of an electron whose de Broglie wavelength is 0.1 mm?
(b) By what potential difference must have an electron been accelerated from an initial speed of zero?
(c) If all the energy of such an electron be transferred to a single photon, what is the wavelength of this photon?

ANSWERS

1. $n_2 = 2 \leftarrow n_1 = 1$; 4.43×10^4 m s^{-1}
2. 5.22 cm
3. (a) 3.27×10^{-18} J (b) 2.94×10^{-17} J
4. 2.43×10^5 cm^{-1}
5. (a) 5256 kJ mol^{-1}
6. $n_2 = 5$
7. $r_n(\mathrm{H})/r_n(\mathrm{He}^+) = 2(n_\mathrm{H}/n_{\mathrm{He}^+})^2$; No
8. 2.186×10^6 m s^{-1}, 7.29×10^{-3}, 1.522×10^{-16} s, 57×10^{15} s^{-1}
9. 106 pm [*Hint*: use $\mu = m_\mathrm{e} m_\mathrm{p}/(m_\mathrm{e} + m_\mathrm{p}) = m_\mathrm{e}/2$ instead of m_e.]
10. 365 nm
11. 478 pm
12. 106 pm, 2.19×10^6 m s^{-1}
13. 91.2 nm
14. $\simeq$ 4300, -7×10^{-7} eV
15. 3
16. 1.326×10^7 m s^{-1}, 5.5×10^{-11} m^2
17. 7.38×10^5 m s^{-1}, 9.9×10^{-10} m
18. $\geq 1.93 \times 10^{-10}$ m
19. 0.8×10^{16} s^{-1}
20. 7.274×10^6 m s^{-1}, 150.6 V, 8.248 nm

CHAPTER 4

PERIODICITY OF PROPERTIES OF ELEMENTS

The scientific approach to study the vast information available about the behaviour of over 100 elements involves the systematic classification of the available information into different well-defined categories, so that the elements behaving in a similar manner can be studied collectively. Such an attempt was made from time to time to achieve the goal of classification. A few of them are as follows.

Dobereiner's Triads (1829) A classification in which three chemically similar elements (known as triad) were grouped together in increasing order of their atomic masses. The atomic mass of the middle element was found to be the average of the atomic masses of the other two elements. Examples include Li-Na-K; Ca-Sr-Ba; P-As-Sb; S-Se-Te and Cl-Br-I.

Newland Law of Octaves (1864) A classification in which elements were arranged in the increasing atomic masses and it is found that every eighth element has the properties similar to that of the first element.

Mendeleev Law A little more extensive study was made independently by J. Lother Meyer (1869) and Dmitri I. Mendleev (1869). Lother Meyer plotted atomic volumes versus atomic masses of elements and obtained a plot in which elements occupying similar positions were having similar properties.

Mendeleev presented an extensive table in which 63 elements known at that time were classified into various groups. This table, known as Mendeleev Table, was constructed on the basis of atomic masses of elements. Based on this, Mendeleev established the periodic law that *the properties of elements are periodic function of their atomic masses*.

Modern Periodic Table After the discovery of radioactivity, isotopes and x-rays, Moseley proposed a new periodic law replacing Mendeleev's one. The periodic law on which the modern periodic table is based states that *the properties of elements are periodic function of their atomic numbers*.

The chemical properties of an element are largely governed by the electrons in the outermost quantum shell of its atom. So, it was realized that elements having similar properties must be having similar electronic configurations and vice versa. Now, the similar electronic configuration is repeated after regular interval of atomic number. This forms the main basis of modern classification of elements. Table 4.1 (see page 4.2) displays the modern version of the periodic table (known as Long Form of Periodic Table).

While describing the table, two terms are commonly used. These are :

1. *Periods* Each horizontal row of the table constitutes a period. Each period starts with the filling up of a new quantum shell and is continued till the p orbitals of the same shell is completely filled up in accordance with aufbau principle. The number of elements in a period is equal to the number of intervening elements in the process of filling up of electronic configuration from $n\mathrm{s}^1$ to $n\mathrm{p}^6$, where n is the principal quantum number. Based on the energy sequence

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d$$

one can determine the number of elements in each period. This is shown in Table 4.2.

Table 4.1 Long Form of Periodic Table

Periods	1	2	3	4	5	6	7	VIII			11	12	13	14	15	16	17	Noble gases 18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	8	9	10	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.00674	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
3	11 Na 22.98977	12 Mg 24.3050											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.95591	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.93320	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98.9072	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.90447	54 Xe 131.29
6	55 Cs 132.90543	56 Ba 137.327	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.96654	80 Hg 200.59	81 Ti 204.3833	82 Pb 207.2	83 Bi 208.98037	84 Po 208.9824	85 At 209.9871	86 Rn 222.0176
7	87 Fr 223.0197	88 Ra 226.0254	89 ⊕Ac 227.0278	104 Unq 261.11	105 Unp 262.114	106 Unh 263.118	107 Uns 262.12											

*	58 Ce 140.115	59 Pr 140.90765	60 Nd 144.24	61 Pm 144.9127	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
⊕	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu 244.0642	95 Am 243.0614	96 Cm 247.0703	97 Bk 247.0703	98 Cf 242.0587	99 Es 252.083	100 Fm 257.0951	101 Md 258.10	102 No 259.1009	103 Lr 260.105

Table 4.2 Number of elements in the different periods of modern periodic table

*Period Number**	*Orbitals being filled*	*Number of elements*
1	1s	2
2	2s, 2p	8
3	3s, 3p	8
4	4s, 3d, 4p	18
5	5s, 4d, 5p	18
6	6s, 4f, 5d, 6p	32
7	7s, 5f, 6d	incomplete

*Period number is the value of the principal quantum number or the quantum shell which starts filling.

2. *Groups* Each vertical column of the periodic table constitutes a group. According to IUPAC (International Union of Pure and Applied Chemistry) recommendations, the groups are numbered from 1 to 18 (Table 2.1). Group number of an element locates the position of element in the period. Members belonging to any one group have similar outer electronic configurations.

CLASSIFICATION OF ELEMENTS

The elements can be classified into five types depending on their electronic configurations.

1. *Noble Gases* Noble gases constitute Group 18 of the periodic table. Except the first element of the group, helium (which has $1s^2$ configuration) all other elements, namely, neon, argon, krypton, xenon and radon have $(ns)^2(np)^6$ electronic configuration in the outermost shell. Because of the stable arrangement of electrons in these elements, they exhibit a very low chemical reactivity.

2. s-*Block Elements* Elements belonging to Group 1 (alkali metals; Li, Na, K, ..., Fr) with outermost electronic configuration ns^1 and those belonging to Group 2 (alkaline earth metals : Be, Mg, Ca, ..., Ra) with outermost electronic configuration ns^2 are known as s-block elements.

3. p-*Block Elements* Elements of Group 13 to 17 are known as p-block elements. The outermost electronic configurations of these groups are as follows.

Group	13	14	15	16	17
Configuration	$(ns)^2(np)^1$	$(ns)^2(np)^2$	$(ns)^2(np)^3$	$(ns)^2(np)^4$	$(ns)^2(np)^5$

The elements of s and p blocks taken together are known as the *representative elements*. Noble gases which appear at the end of each period are also included in the representative elements.

4. d-*Block Elements* Elements belonging to Groups 3 to 12 (in the middle of the periodic table) with an outer electronic configuration $(n-1)d^{1-10}\ ns^{1-2}$ constitute the d-block of the periodic table and are called *transition elements*. In these elements, *n* is 4, 5, or 6 with corresponding filling of 3d, 4d, or 5d orbitals.

5. f-*Block Elements* At the bottom of the periodic table, there are two rows–one of lanthanides or lanthanide series ($Z = 58$ to 71) and the other of actinides or actinide series ($Z = 90$ to 107) containing incomplete 4f and 5f orbitals, respectively. The elements are characterized by the outer electronic configuration $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$. In these elements, f orbitals are in the process of filling. These elements are also known as *inner transition elements*.

MAIN CHARACTERISTICS OF REPRESENTATIVE ELEMENTS

As we move from left to right across a period, there is transition from metals to metalloids to nonmetals. Thus, elements of Groups 1 and 2 are metals, and those at the extreme right (baring noble gases) are nonmetals. Elements B, Si, Ge, As, Sb, Po and At are metalloids. Down a particular group, there is an increase in the metallic character or decrease in the nonmetallic character.

MAIN CHARACTERISTICS OF TRANSITION ELEMENTS

All transition elements are metallic. These are characterized by variable oxidation states, formation of coloured ions and complexes. Many of them behave as catalysts.

PERIODICITY IN PROPERTIES

As we move along the elements in the increasing atomic number, we find periodicity in the properties of these elements. Basically, this is due to the repetition of similar outer electronic configurations of atoms. Within a group, elements have similar outer atomic electronic configuration, and thus behave chemically similar. A few periodicity in properties are described in the following.

Atomic radius Atomic radius can be expressed in one of the three following ways.

Van der Waals radius It is half the shortest internuclear distance between two adjacent non-bonded atoms.

Metallic radius It is half the shortest internuclear distance between two atoms in the metallic crystal.

Covalent bond radius It is half the internuclear distance between two identical atoms joined by a single covalent bond.

Covalent-bond radius is always smaller than van der Waals radius, because the covalent bond formation involves the overlapping of orbitals of the outermost shell of adjacent atoms. Metallic radius is about 15 per cent larger than the covalent radius. The covalent radius is known for most elements and the term atomic radius is generally taken for covalent radius.

Atomic radius increases down a group. This is because the outermost shell successively have higher principal quantum number.

Atomic radius decreases across a period. This is due to the increase in the effective nuclear charge with increase in the atomic number across a period.

Ionic radius It is the radius of a cation or an anion. If an atom forms an anion, its radius increases, since the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electronic cloud. On the other hand, a cation is smaller than the neutral atom, since removing one or more electrons reduces electron-electron repulsion and there will be a shrinkage of the electronic cloud.

Ionization energy Ionization energy is defined as the minimum energy required to remove an electron from a gaseous atom in its ground state. This is, infact, the first ionization energy. The second ionization energy is the energy required to remove an electron from the singly charged cation in the gaseous state and so on.

In general, the ionization energy of atom decreases within a group from top to bottom. This is due to the fact that the electron to be removed belongs to the higher successive quantum shell.

Within a period, there is a tendency to increase the ionization energy as one moves from left to right. This is basically due to the increase in the effective nuclear charge. This increase is met with two exceptions where a decrease in ionization energy is observed. The first exception occurs when one moves from Group 2 to 3 and the second exception occurs from Group 15 to 16. These exceptions can be explained on the basis of electronic configurations.

Elements of Group 3 contain one extra electron in p orbital as compared to those of Group 2. The p electron is well-shielded by the inner electrons and ns^2 electrons. Consequently, less energy is required to remove a single p electron than to remove a paired s electrons from the same principal energy level.

Elements of Groups 16 contain one extra electron in p orbital as compared to the stable half-filled p orbitals of Group 15. Consequently, lesser energy is required to remove this extra electron as compared to the removal of electron from the half-filled p orbital.

In general, second ionization energy is always greater than the first one.

Electron affinity Electron affinity is defined as the energy released when an electron is added to an isolated gaseous atom.

In general, the electron affinity increases as we move from left to right across a period. Within a group, there is little change in the electron affinity values. The halogens (Group 17) have the maximum values of electron affinity. This can be explained on the basis that after accepting electron, one gets the stable electronic configuration of the noble gas.

Amongst halogens, chlorine has the maximum value of electron affinity. This is because fluorine, which otherwise is expected to have maximum value, involves more electron-electron repulsion due to the more compact electronic configuration causing the value less than chlorine.

Electronegativity The electronegativity of an element is a measures of the relative tendency of an atom to attract electrons towards itself when it is chemically bonded with another atom.

Linus Pauling devised a method for calculating relative electronegativities of most elements. According to him

$$\chi_A - \chi_B = (0.1088\ \mathrm{kJ}^{-1/2}\mathrm{mol}^{1/2})\sqrt{\Delta} \qquad \text{where} \qquad \Delta = \varepsilon_{A-B} - \sqrt{\varepsilon_{A-A}\ \varepsilon_{B-B}}$$

where ε's refer to the numerical values of to bond enthalpies expressed in kJ mol^{-1}. The numerical value of $\sqrt{\Delta}$ is a measure of ionic character of the bond A-B. By assigning $\chi_F = 4.0$, χ values of other atoms can be computed.

Mullikan's scale uses the expression

$$\chi = \frac{\mathrm{IE} + \mathrm{EA}}{2}$$

to compute electronegativities. However, Pauling scale is most widely used.

The electronegativity increases across a period and decreases down the group.

Atoms of elements with a difference of 2.0 or more in electronegativity values form ionic bond.

Oxidation states Oxidation state (or oxidation number) refers to the number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred following a set of some rules. Oxidation states can be positive, negative or zero and thus differ from valency which is always positive.

Metallic elements mostly have positive oxidation states, whereas nonmetallic elements may have either positive or negative oxidation states. The highest oxidation state of a representative element is its group number (or group number – 10) in the periodic table. For example, the highest oxidation number of halogen is +7 which is observed for Cl and I. The transition metals usually have several oxidation numbers.

METALLIC AND NONMETALLIC CHARACTER

As we travel in a period, the metallic character of element decreases while its nonmetallic character increases. On descending a group, the metallic character increases. Thus, the elements of Groups 1 and 2 are essentially metals. Group 13 starts with a metalloid and ends with a metal. Group 14 and 15 start with a nonmetal, followed by metalloid and ends with a metal. Group 16 starts with a nonmetal and ends with a metal. Elements of Group 17 are nonmetals and ends with an element with a feeble metallic character.

All metals are electropositive elements and have a tendency to lose electrons. On the other side, nonmetals are electronegative elements and have a tendency to gain electrons. Metals form basic oxides while nonmetals form acidic oxides.

LANTHANIDE CONTRACTION

The metallic radii of the lanthanides and their tripositive ionic radii decrease on passing across the lanthanides due to the increase in effective nuclear charge as the 4f shell is successively filled. This is because the 4f electrons shield each other from nuclear charge poorly. As more 4f electrons are added the effective nuclear charge felt by each of them increases. As a consequence, the whole 4f electron shell contracts on passing across the lanthanides. The steady decrease in metallic and ionic radii on crossing the lanthanides is known as the lanthanide contraction.

The effect of lanthanide contraction is of sufficient magnitude to cause the elements which follow in the third transition series (5d series) to have sizes very similar to those of the second row of transition elements (4d series). The normal increase in size from Sc to Y to La disappears after the lanthanides. Thus, the pairs of elements such as Zr-Hf, Nb-Ta, Mo-W have nearly identical sizes. They have similar chemical properties and their separation is very difficult.

The effect of lanthanide contraction is also important in the chemistry of lanthanides themselves. A general decrease in ionic radii on crossing the series results in a corresponding increase in the polarizing power of the ions and in the stability of the complex ions. Increasing polarizing power makes the hydroxides less and less basic on crossing the lanthanides. For example, $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is less basic.

BRIEF SYNOPSIS OF REPRESENTATIVE ELEMENTS

A brief synopsis of representative elements groupwise is in order.

Group 1 Elements—Alkali Metals

Group 1 contains lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr).

All alkali metals contain one electron in their outermost orbitals. Due to contribution of one electron per atom towards the metallic bonding, all the elements are soft and low melting. Because of low ionization energies, the metals are strong reducing agents. The alkali metals dissolve in liquid ammonia and form a deep blue solution when dilute. The blue colour is due to the solvated electrons. The conducting ability of their ions in aqueous solution follows the order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

The alkali metals are very reactive and tarnish in air to form oxide. They burn in air, Li forms Li_2O, Na forms Na_2O_2 and higher alkali metals form superoxide (MO_2). The oxides of alkali metals are basic in nature. The peroxides are diamagnetic and are oxidizing agents. The superoxides are paramagnetic and are stronger oxidising agents than peroxides.

The melting points of alkali metal halides decrease in the order MF > MCl > MBr > MI. Lithium halides have melting points less than those of sodium halides due to the more covalent character possessed by lithium salts.

The solubilities of carbonates and bicarbonates increase on descending the group.

Group 2 Elements—Alkaline Earth Metals

Group 2 contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

All alkaline earth metals contain two electrons in their outermost orbitals. These are soft. But compared to alkali metals, they are harder and have higher cohesive energy. Their melting points are higher than those of Group 1 elements and vary irregularly because of different structures. The atomic and ionic radii are smaller than those of the elements of Group 1. The alkaline earth metals dissolve in liquid ammonia giving bright blue colour due to the solvated electrons.

Alkaline earth metals are typically divalent and form colourless ionic compounds. When burnt in air, Be, Mg and Ca form monoxide while Sr, Ba and Ra form peroxides. When burnt in oxygen, they all form oxides which are basic in nature. The base strength of hydroxides increases on descending the group. Their solubility also increases on descending the group.

The solubilities of carbonates and sulphates decrease on descending the group. In deciding the solubilities of hydroxides, lattice energy predominates over hydration energy whereas in carbonates and sulphates, hydration energy predominates over lattice energy.

Group 13 Elements—Boron Family

Group 13 contains boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have outer electronic configuration $(ns)^2 (np)^1$, where n varies form 2 to 6. Boron is nonmetal while others are metals. The atomic litter of Ga, In and Tl are smaller than the expected values due to d-block contraction. The atomic radius of Tl is a little larger than in due to lanthanide contraction. On descending the group, +1 oxidation state becomes more stable than +3 state due to the inert pair effect.

The very high melting point of boron is due to its icosahedral structure. In boron family, gallium has the lowest melting point. The ionization energies do not follow the expected trend of decreasing values on descending the group.

All elements burn in oxygen at high temperatures forming M_2O_3. The reaction of aluminium with oxygen (known as thermite reaction) is strongly exothermic. Aluminium is amphoteric. It dissolves in dilute mineral acids and in aqueous sodium hydroxide.

The acidic character of hydroxides decreases on descending the group.

Boric acid is a very weak monobasic acid. It does not liberate hydrogen ion but accepts a hydroxyl ion. In the presence of *cis*-diol (glycerol, mannitol or sugars), boric acid behaves as a strong acid and can be titrated with NaOH in the presence of phenolphthalein indicator.

BF_3 is hydrolysed as follows.

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$
$$12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

Hydrolysis of BCl_3 or BI_3 produces boric acid.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Due to back bonding, the electron density on boron is increased. The tendency to form pπ-pπ bond is maximum in BF_3 and falls rapidly on passing to BCl_3 to BBr_3. The increasing order of acid strength follows the order $BF_3 < BCl_3 < BBr_3$.

Group 14 Elements—Carbon Family

Group 14 contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is $(ns)^2 (np)^2$, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is a nonmetal but also has some metallic characteristics, and Sn and Pb are metals. The melting points decrease on descending the group, with the exception of Pb whose melting point is slightly higher than that of Sn. Carbon has extremely high melting point. This is due to the stronger C—C bonds in the network of carbon atoms.

The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling d and f sub-shells.

Carbon forms single, double and triple bonds with carbon itself and with other elements. The tendency to form multiple bond by other elements is rare. However, silicon can form double bond due to back bonding in which the lone pair in p orbitals of an atom is extended to an empty orbital of Si. One of the examples of back bonding is trisilylamine, $N(SiH_3)_3$.

The chemical reactivity of elements decreases down the group. The inert pair effect becomes increasingly effective on descending the group.

The stability of +4 oxidation state decreases while that of the +2 oxidation state increases on descending the group.

C, Si and Ge are unaffected by dilute acids. Sn and Pb react with dilute nitric acid.

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannate, $[Sn(OH)_6]^{2-}$, and plumbate, $[Pb(OH)_6]^{2-}$, respectively.

All the elements of Group 14 form tetrahalides with the exception of PbI_4, which is not known. The stability of halides decreases down the group. CCl_4 is stable while other halides are hydrolysed. The hydrolysis of $SiCl_4$ produces SiO_2 while SiF_4 produces SiO_2 as well as $[SiF_6]^{2-}$.

The acidic nature of the dioxides of carbon family decreases down the group; CO_2 and SiO_2 are acidic, GeO_2 is weakly acidic and SnO_2 and PbO_2 are amphoteric.

Silicones are organosilicon polymers with general formula $(R_2SiO)_n$, where R may be methyl, ethyl or phenyl group.

Group 15 Elements-Nitrogen Family

Group 15 contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Their outer electronic configuration is $(ns)^2 (np)^3$, where n varies from 2 to 6. The metallic character of these elements increases on descending the group; N and P are nonmetals, As and Sb are metalloids and Bi is a metal. The melting and boiling points follow the order

melting point	N < P < As > Sb > Bi
boiling point	N < P < As < Sb > Bi

Phosphorus has two common allotropic forms; white and red. White phosphorus is more reactive than red form due to highly strained structure (P—P—P angle is 60°).

Black phosphorus is a highly polymerized form and is most stable.

Nitrogen form triple bond in dinitrogen because bond enthalpy $\varepsilon(N \equiv N)$ is greater than three times bond enthalpy $\varepsilon(N—N)$. In phosphorus, the reverse is true, hence, it involves single bonds.

The melting points of hydrides follow the order $NH_3 > PH_3 < AsH_3 < SbH_3$.

All the five elements of Group 15 form trihalides. Of these nitrogen halides are least stable. All the trihalides with the exception of NF_3 hydrolyse in aqueous solution.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \rightarrow SbO^+ + 2H^+ + 3Cl^-$$
$$BiCl_3 + H_2O \rightarrow BiO^+ + 2H^+ + 3Cl^-$$

Nitrogen forms many oxides; N_2O, NO, N_2O_3, NO_2 and N_2O_5. The most common oxides of phosphorus are P_4O_6 and P_4O_{10}. Phosphorus trioxide is an acidic oxide and is anhydride of orthophosphorous acid (H_3PO_3). Phosphorus pentoxide is anhydride of phosphoric acid (H_3PO_4).

Nitrogen forms two acids; nitrous acid (HNO_2) and nitric acid (HNO_3). Phosphorus forms two series of oxoacids. These are phosphorus and phosphoric series. In phosphorous series, the acids include pyrophosphorous acid ($H_4P_2O_5$), orthophosphorous acid (H_3PO_3), metaphosphorous acid (HPO_2) and hypophosphorous acid (H_3PO_2). The acids $H_4P_2O_5$ and H_3PO_3 are reducing agents as they involve P—H bond.

In phosphoric series, the acids include orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and polymetaphosphoric acid, $(HPO_3)_n$.

Group 16 Elements—Oxygen Family

Group 16 contains oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their electronic configuration is $(ns)^2\,(np)^4$, where n varies from 2 to 6.

The metallic character of these elements increases on descending the group; O and S are nonmetallic, Se and Te are weaker nonmetallic and Po is metallic.

Electron affinity of sulphur is larger than that of oxygen, this is due to the more repulsion experienced by the incoming electron from the smaller, more compact electronic cloud of oxygen atom.

Oxygen is diatomic with two unpaired electrons. Sulphur exists in two allotropic forms—rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature while monoclinic sulphur is stable above 369 K. Selenium exists in six allotropic forms. Tellurium has only one crystalline form and polynium has two allotropic forms (cubic and rhombohedral).

Ozone is another allotropic form of oxygen. It is very reactive. It is formed in the upper layer of atmosphere (about 20 km from the earth) by the action of ultraviolet radiation on oxygen. Ozone is a strong oxidizing agent. In organic chemistry, ozone is used to locate the carbon-carbon double and triple bonds. The ozone molecule is angular with bond angle about 117° and bond length 127.8 pm.

The melting and boiling points of hydrogen compounds of elements of Group 16 follow the order $H_2O > H_2S < H_2Se < H_2Te$. The exceptional high values of H_2O is due to hydrogen bondings.

H_2O_2 is a strong oxidizing agent. With stronger oxidizing agents such as $KMnO_4$, KIO_3, O_2, hydrogen peroxide acts as a reducing agent.

Group 17 Elements—Halogen Family

Group 17 contains fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Their outer electronic configuration is $(ns)^2\,(np)^5$, where n varies from 2 to 6. The trends in this group are as follows.

Covalent and ionic radii—*increase down the group.*

Electronegativity and ionization energy—*decrease down the group.*

Electron affinity—*increases from* F to Cl *followed by a decrease.*

Melting and boiling points—*increase down the group.*

Bond enthalpy ε(X—X)—*increases from* F *to* Cl *followed by a decrease.*

Oxidizing ability—decreases down the group.

Halogens are very reactive and do not occur in free state. Fluorine is most electronegative atom, there exists hydrogen bondings in gaseous HF.

HF is a weak acid and HCl, HBr and HI behave as strong acids. In the glacial acetic acid medium, the acid strength follows the order HI > HBr > HCl > HF.

Halogens with the exception of F form a number of oxoacids—hypohalous acids (HOX), halous acids (HXO_2), halic acid (HXO_3) and perhalic acid (HXO_4). The acid strength follows the order $HXO_4 > HXO_3 > HXO_2 > HXO$. Fluorine forms only hypofluorous acid (HOF).

Halogens also form interhalgoen compounds AX, AX_3, AX_5 and AX_7. The compounds AX and AX_3 are formed where the electronegativity is not very large. The compounds AX_5 and AX_7 are formed by large Br and I atoms surrounded by small atom F. The molecule AX_3 is T-shaped with two lone pair of electrons at the equilateral positions. The orientations of five pair of electrons around the atom A is trigonal bipyramidal.

The six pairs of electrons around atom A in AX_5 acquire octahedral orientation. The seven pairs of electrons around atom A in AX_7 acquire pentagonal bipyramidal orientation.

Halogens are nonmetallic and have high electron affinity. The nonmetallic character decreases down the group and iodine shows some metallic character. With metals, they form ionic compounds by accepting one electron and with nonmetals covalent compounds are formed by sharing an electron.

All halogens exhibit –1 oxidation state. Except fluorine, rest of the halogens also exhibit 1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative and thus there exists hydrogen bonding in HF with the result that it has exceptionally high melting and boiling points as compared to those of HCl, HBr and HI.

Because of high reactivity, halogens do not exist in the free state.

Group 18 Elements—Noble Gases

The group 18 contains helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Their outer electronic configurations is $(ns)^2\ (np)^6$ with the exception of the electronic configuration of He which is $(1s)^2$. All elements exist as monatomic gas.

Xenon forms a number of fluorides—XeF_2, XeF_4 and XeF_6. The other compounds are XeO_3, $XeOF_4$, XeO_2F_2, XeO_4 and $[XeO_6]^{4-}$

Straight Objective Type

Classification of Elements

1. The fifth period of modern periodic table includes
(a) 8 elements (b) 18 elements (c) 32 elements (d) unknown elements

2. In the sixth period, the orbitals being filled are
(a) 5s, 5p, 5d (b) 6s, 6p, 6d, 6f (c) 6s, 5f, 6d, 6p (d) 6s, 4f, 5d, 6p

3. In Lother Meyer plot of atomic volume versus atomic mass, the peaks are occupied by
(a) alkali metals (b) alkaline earth metals (c) halogens (d) noble gases

4. The number of periods in the long form of periodic table is
(a) 5 (b) 6 (c) 7 (d) 8

5. The elements with atomic numbers 21 to 30 belong to
(a) halogens (b) noble gas
(c) first transition elements (d) lanthanides

6. The atomic number of element next to $_{53}I$ in the same group is
(a) 61 (b) 71 (c) 85 (d) 93

7. The number of elements in the fourth period of the periodic table is
(a) 8 (b) 18 (c) 32 (d) 64

8. An element X belongs to Group 14 and 2nd period of the periodic table. Its atomic number will be
(a) 6 (b) 14 (c) 32 (d) 50

9. The atomic numbers of elements of the second inner transition elements lie in the range of
(a) 88 to 101 (b) 89 to 102 (c) 90 to 103 (d) 91 to 104

10. The total number of elements in Groups 8 to 10 of the periodic table is
(a) 3 (b) 5 (c) 7 (d) 9

11. The atomic numbers of elements of the lanthanide series lie in the range of
(a) 58 to 71 (b) 57 to 70 (c) 59 to 72 (d) 56 to 69

12. An element X belongs to Group 16 and 5th period. Its atomic number is
(a) 34 (b) 50 (c) 52 (d) 85

13. The atomic number of In is 49. It belongs to
(a) 4th period (b) 5th period (c) 6th period (d) 3rd period

14. the elements $_{30}Zn$, $_{48}Cd$ and $_{80}Hg$ belong to
(a) 10th group (b) 11th group (c) 12th group (d) 13th group

15. The element with atomic number 105 is known as
(a) Unq (b) Unp (c) Unh (d) Uns

Atomic/Ionic Radius

16. Atomic radii of fluorine and neon in Angstrom units are respectively given by
(a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) none of these values (1987)

17. Which one of the following is the smallest in size?
(a) N^{3-} (b) O^{2-} (c) F^- (d) Na^+ (1989)

18. Which one of the following has the minimum atomic size?
(a) Li (b) Be (c) Na (d) Mg

19. Atomic sizes of the following elements decreases in the order
(a) B > Be > Li (b) Be > Li > B (c) Li > B > Be (d) Li > Be > B

20. Identify the correct order of increasing ionic sizes
(a) $Al^{3+} < O^{2-} < F^- < Cl^-$ (b) $F^- < O^{2-} < Cl^- < Al^{3+}$
(c) $Al^{3+} < F^- < O^{2-} < Cl^-$ (d) $Al^{3+} < F^- < Cl^- < O^{2-}$

21. The ionic sizes decreases in the order
(a) $K^+ > S^{2-} > Sc^{3+} > V^{5+} > Mn^{7+}$ (b) $S^{2-} > K^+ > Sc^{3+} > V^{5+} > Mn^{7+}$
(c) $Mn^{7+} > V^{5+} > Sc^{3+} > K^+ > S^{2-}$ (d) $Mn^{7+} > V^{5+} > Sc^{3+} > S^{2-} > K^+$

22. The size of Zr is very similar to
(a) La (b) Hf (c) Ta (d) W

23. The size of Nb is very similar to
(a) La (b) Hf (c) Ta (d) W

24. Which of the following elements has the largest size?
(a) Co (b) Ni (c) Cu (d) Zn

25. The size of Mo is very similar to W due to
(a) the difference of atomic number by one
(b) the contraction in size in the first transition series elements
(c) lanthanide contraction
(d) actinide contraction

26. Ionic sizes decreases in the order
(a) $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+}$ (b) $N^{3-} > O^{2-} > F^- > Mg^{2+} > Na^+$
(c) $N^{3-} > F^- > O^{2-} > Na^+ > Mg^{2+}$ (d) $O^{2-} > N^{3-} > F^- > Na^+ > Mg^{2+}$

27. Ionic sizes increase in the order
(a) $Ca^{2+} < Cl^- < S^{2-} < Ar$ (b) $Ar < Ca^{2+} < Cl^- < S^{2-}$
(c) $Cl^- < Ca^{2+} < Ar < S^{2-}$ (d) $S^{2-} < Cl^- < Ca^{2+} < Ar$

28. In the isoelectronic species the ionic radii of N^{3-}, O^{2-} and F^- are respectively given by
(a) 136 pm, 140 pm, 171 pm (b) 136 pm, 171 pm, 140 pm
(c) 171 pm, 140 pm, 136 pm (d) 171 pm, 136 pm, 140 pm

29. The sizes of the following ions is in the order
(a) $Mg^{2+} < Na^+ < Al^{3+} < F^-$ (b) $F^- < Al^{3+} < Na^+ < Mg^{2+}$
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (d) $Na^+ < Al^{3+} < F^- < Mg^{2+}$

30. The correct order of radii is
(a) N < Be < B (b) $F^- < O^{2-} < N^{3-}$ (c) Na < Li < K (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$ (2000)

31. Ionic radii of
(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < {}^{37}Cl^-$ (c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$ (1999)

32. The ionic radii of Li^+, Be^{2+} and B^{3+} follow the order
(a) ${}_3Li^+ < {}_4Be^{2+} < {}_5B^{3+}$ (b) $B^{3+} < Be^{2+} < Li^+$ (c) $Li^+ < B^{3+} < Be^{2+}$ (d) $B^{3+} < Li^+ < Be^{2+}$

33. For which of the elements of different groups, the change in nonpolar covalent radii is maximum?
(a) Groups 1 and 2 (b) Groups 13 and 14 (c) Groups 14 and 15 (d) Groups 16 and 17

34. For which of the elements of different groups, the change in nonpolar covalent radii is maximum?
(a) Groups 1 and 2 (b) Groups 14 and 15 (c) Groups 16 and 17 (d) Groups 17 and 18

35. Which of the following orders regarding metallic atomic radii is correct?
(a) ${}_{28}Ni < {}_{29}Cu < {}_{30}Zn$ (b) Ni < Zn < Cu (c) Cu < Ni < Zn (d) Cu < Zn < Ni

36. Which of the following orders regarding metallic atomic radii is correct?
(a) ${}_{45}Rh < {}_{46}Pd < {}_{47}Ag$ (b) Rh < Ag < Pd (c) Pd < Rh < Ag (d) Pd < Ag < Rh

37. Which of the following elements is expected to have the least density?
(a) Co (b) Ni (c) Cu (d) Zn

38. The ionic radii of Na^+, Mg^{2+} and Al^{3+} follow the order
(a) $Na^+ > Mg^{2+} > Al^{3+}$ (b) $Na^+ < Mg^{2+} < Al^{3+}$ (c) $Na^+ > Al^{3+} > Mg^{2+}$ (d) $Al^{3+} < Na^+ < Mg^{2+}$

39. The ionic radii of Cl^-, S^{2-} and P^{3-} follow the order
(a) $Cl^- > S^{2-} > P^{3-}$ (b) $Cl^- < S^{2-} < P^{3-}$ (c) $Cl^- > P^{3-} > S^{2-}$ (d) $Cl^- < P^{3-} < S^{2-}$

Ionization Energy

40. The first ionization potentials in electron volts of nitrogen and oxygen atoms are respectively given by
(a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6 (1987)

41. The first ionization potential of Na, Mg, Al and Si are in the order
(a) Na < Mg > Al < Si (b) Na > Mg > Al > Si
(c) Na < Mg < Al > Si (d) Na > Mg > Al < Si (1988)

42. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is
(a) [Ne] $(3s)^2(3p)^1$ (b) [Ne] $(3s)^2(3p)^3$ (c) [Ne] $(3s)^2(3p)^2$ (d) [Ar] $(3d)^{10}(4s)^2(4p)^3$ (1990)

43. The correct order of ionization energy is
(a) C > N > O (b) C > N < O (c) C < N > O (d) C < N < O

44. The correct order of ionization energy is
(a) Si > P > S (b) Si > P < S (c) Si < P > S (d) Si < P < S

45. 1 eV of energy is equivalent to
(a) 1.602×10^{-18} J (b) 1.602×10^{-19} J (c) 1.602×10^{-20} J (d) 1.602×10^{-21} J

46. Which of the following configurations is expected to have maximum difference in second and third ionization energies ?
(a) $(1s)^2(2s)^2(2p)^2$ (b) $(1s)^2(2s)^2(2p)^6(3s)^1$ (c) $(1s)^2(2s)^2(2p)^6(3s)^2$ (d) $(1s)^2(2s)^2(2p)^1$

47. In the periodic table, the ionization energy of elements
(a) decreases (i) from left to right across a period and (ii) on descending a group
(b) decreases from left to right across a period and increases on descending a group
(c) increases, (i) from left to right across period and (ii) on descending a group
(d) increases from left to right across a period and decreases on descending a group.

48. In the plot of ionization energy versus atomic number, the peaks are occupied by
(a) alkali metals (b) alkaline-earth metals (c) noble gases (d) halogens.

49. In the plot of ionization energy versus atomic number, the minimum positions are occupied by
(a) alkali metals (b) alkaline-earth metals (c) noble gas (d) halogens

50. Which of the following orders regarding the ionization energy is correct?
(a) Be > B > C (b) Be < B < C (c) Be > B < C (d) Be < C < B

51. Which of the following orders regarding the ionization energy is correct?
(a) N > O > F (b) F > O > N (c) N > O < F (d) O > F > N

52. The correct order of the second ionization energy of C, N, O and F is
(a) C > N > O > F (b) O > N > F > C (c) O > F > N > C (d) F > O > N > C (1981)

53. The first ionization energy of K, Ca and Ba follows the order
(a) K > Ca > Ba (b) Ca > Ba > K (c) Ba > K > Ca (d) K > Ba > Ca

54. A large difference between the second and third ionization energies will be observed for the element having electronic configuration of
(a) $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^1$ (b) $(1s)^2$ $(2s)^2$ $(2p)^6(3s)^2$
(c) $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^1$ (d) $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^2$

55. The incorrect statement among the following is
(a) first ionization energy of Al is lesser than that of Mg
(b) second ionization energy of Mg is greater that that of Na
(c) first ionization energy of Na is lesser than that of Mg
(d) third ionization energy of Mg is greater than that of Al (1997)

56. If the ionization potential of Na is 5.48 eV. Potassium is expected to have a value of
(a) 5.48 eV (b) 4.34 eV (c) 5.68 eV (d) 8.4 eV

57. The set representing the correct order of first ionization potential is
(a) K > Na > Li (b) Be > Mg > Ca (c) B > C > N (d) Ge > Si > C (2001)

58. The second ionization energies amongst Li, Be, B and C is lowest for
(a) Li (b) Be (c) B (d) C

59. The third ionization energy amongst Li, Be, B and C is lowest for
(a) Li (b) Be (c) B (d) C

60. Amongst Ni, Cu and Zn, the highest first ionization energy and the highest second ionization energy are shown, respectively, by the metals
(a) Ni, Cu (b) Ni, Zn (c) Zn, Cu (d) Cu, Cu

Electron Affinity

61. The correct order of electron affinity is
(a) F > Cl > Br (b) F > Cl < Br (c) F < Cl > Br (d) F < Cl < Br

62. Which of the following elements has zero electron affinity?
(a) Fluorine (b) Nitrogen (c) Neon (d) Oxygen

63. Which of the following elements has the highest value of electron affinity?
(a) O (b) S (c) Se (d) Te

64. Which of the following will have the lowest value of electron affinity?
(a) Be (b) Cl (c) N (d) B

65. Electron affinities of C, Si and Ge follow the order
(a) C > Si > Ge (b) C < Si > Ge (c) C > Ge > Si (d) Ge > Si < C

66. Electron affinities of Be, B and Al follow the order
(a) Al > B > Be (b) Al > Be > B (c) Al < B < Be (d) Al < Be < B

67. Electron affinities of Li, Na and K follow the order
(a) Li < Na < K (b) Li < K < Na (c) K < Na < Li (d) K < Li < Na

Electropositivity and Electronegativity of Elements

68. The electronegativity of the following elements increases in the order
(a) C, N, Si, P (b) N, Si, C, P (c) Si, P, C, N (d) P, Si, N, C (1987)

69. The correct order of Pauling electronegativity is
(a) F > Cl > Br (b) F > Cl < Br (c) F < Cl > Br (d) F < Cl < Br

70. The Pauling electronegativity value of fluorine is
(a) 3.0 (b) 3.5 (c) 4.0 (d) 4.5

71. Which of the following elements is expected to have maximum value of Pauling electronegativity?
(a) Al (b) S (c) Si (d) P

72. With the increase in atomic number in a period
(a) chemical reactivity increases (b) electropositive character increases
(c) electronegative character increases (d) electron affinity decreases

73. In the periodic table, electonegativity of elements
(a) decreases, (i) from left to right across a period and (ii) on descending a group
(b) decreases from left to right across a period and increases on descending a group.

(c) increases from left to right across a period and decreases on descending a group.
(d) increases, (i) from left to right across a period and (ii) on descending a group.

74. Which of the following elements never has an oxidation state +1?
(a) F (b) Cl (c) Br (d) I

75. Which of the following elements is most electropositive?
(a) Na (b) Mg (c) Al (d) Si

76. Which of the following statements regarding electropositive nature of elements in a period is correct?
(a) Increases (b) Decreases
(c) Remains constant (d) First increases followed by a decrease

77. The Pauling electronegativity for H is
(a) 1.6 (b) 2.1 (c) 2.6 (d) 3.2

78. The correct order of Pauling electronegativity values for Li, Na and K is
(a) Li > Na > K (b) Li > K > Na (c) Na > Li > K (d) Li > K > Na

79. According to Pauling, the electronegativity difference between two atoms A and B is directly proportional to
(a) $2\,\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})$ (b) $\varepsilon^2_{AB} - \varepsilon_{AA}\,\varepsilon_{BB}$
(c) $\varepsilon_{AB} - \sqrt{\varepsilon_{AA}\,\varepsilon_{BB}}$ (d) $\left[\varepsilon_{AB} - \sqrt{\varepsilon_{AA}\,\varepsilon_{BB}}\right]^{1/2}$
where ε represents bond enthalpy.

80. According to Mulliken, the electronegativity of an atom is given by
(a) Ionization energy + Electron affinity (b) Ionization energy – Electron affinity
(c) $\frac{1}{2}$[Ionization energy + Electron affinity] (d) $\frac{1}{2}$[Ionization energy – Electron affinity]
where ionization energy and electron affinity are expressed in electron-volt.

81. A bond is said to be 50% ionic if the electronegativity difference between two atoms is about
(a) 1.0 (b) 1.7 (c) 2.5 (d) 3.0

82. If $\varepsilon_{C—C}$ = 348 kJ mol^{-1}, $\varepsilon_{C—H}$ = 412 kJ mol^{-1} and $\varepsilon_{H—H}$ = 436 kJ mol^{-1}, the Pauling electronegativity of C is about (Given: electronegativity of H = 2.1)
(a) 1.64 (b) 1.82 (c) 2.58 (d) 2.91

Metallic-Nonmetallic

83. In the periodic table, the metallic character of elements
(a) increases, (i) from left to right across a period and (ii) on descending a group
(b) decreases (i) from left to right across a period and (ii) on descending a group
(c) increases from left to right across a period and decreases on descending a group
(d) decreases from left to right across a period and increases on descending a group

84. Which of the elements is metalloids?
(a) C (b) As (c) Pb (d) Mg

85. Which of the following elements has the basic oxide?
(a) Mg (b) Cl (c) N (d) S

86. Which of the following elements will form alkaline oxide?
(a) K (b) P (c) S (d) Cl

87. Which of the following oxides will be more acidic in nature?
(a) Na_2O (b) MgO (c) SiO_2 (d) Cl_2O_7

88. Which of the following oxides will be more basic in nature?
(a) Na_2O (b) MgO (c) SiO_2 (d) Cl_2O_7

S-Block Elements

89. The number of alkali metals known so far is
(a) 4 (b) 5 (c) 6 (d) 7

90. Which of the following statements regarding alkali metals is **not** correct?
(a) Alkali metals are soft and have comparatively low melting points as compared to other metals
(b) Francium is a radioactive element

(c) Alkali metals are strongly reducing agents
(d) Sodium is used in the photoelectric cells

91. Which of the following statements regarding alkali metals is **not** correct?
(a) Alkali metals tarnish in air
(b) They are kept under kerosene
(c) All alkali metals form oxides on burning in air
(d) The reaction of alkali metals with water increases in violence on descending the group.

92. Lithium exhibits diagonal relationship with
(a) magnesium (b) calcium (c) aluminium (d) strontium

93. Lithium and magnesium in many respect behave in identical manner. Which of the following facts **does not** describe the correct behaviour of Li and Mg in comparison to the other alkali metals?
(a) Carbonates and hydroxides of Li and Mg decompose on heating to give oxides whereas those of other alkali metals remain unchanged on heating
(b) Nitrates of Li and Mg decompose to give oxides on heating whereas those of other alkali metals decompose to give nitrites
(c) LiCl and $MgCl_2$ are soluble in alcohol whereas chlorides of other alkali metals are insoluble
(c) Li and Mg give peroxides on heating with oxygen whereas the other alkali metals give oxides

94. Sodium is not ordinarily observed in the +2 ionization state because of its
(a) high first ionization potential (b) high second ionization potential
(c) high ionic radius (d) high electronegativity

95. When rubidium is reacted with oxygen, the compound formed is
(a) RbO (b) Rb_2O (c) Rb_2O_2 (d) RbO_2

96. The metallic luster exhibited by sodium is explained by the presence of
(a) Na^+ ions (b) conduction electrons
(c) free protons (d) a body-centred cubic lattice

97. Ionic radii of alkali metal ions in water are in the order
(a) $Li^+ > Na^+ > K^+ > Rb^+$ (b) $Li^+ < Na^+ < K^+ < Rb^+$
(c) $Li^+ > Na^+ > K^+ < Rb^+$ (d) $Li^+ > Na^+ < K^+ < Rb^+$

98. Which of the following ions has the highest reduction potential?
(a) Li^+ (b) Na^+ (c) K^+ (d) Rb^+

99. Which of the following metals has the maximum metallic bond strength?
(a) Li (b) Na (c) K (d) Rb

100. Which of the following metals has the maximum enthalpy of sublimation?
(a) Li (b) Na (c) K (d) Rb

101. Which of the following metals has the minimum enthalpy of sublimation?
(a) Li (b) Na (c) K (d) Rb

102. Which one of the following is a better reducing agent in aqueous solution?
(a) Li (b) Na (c) Rb (d) Cs

103. Which of the following statements is **not** correct?
(a) The elements of Group 1 of the periodic table are soft metals with comparatively low melting points
(b) Francium is an radioactive element
(c) Atomic number of francium is 86
(d) Potassium and caesium are used in the photoelectric cells

104. Which of the following statements is **not** correct?
(a) The elements of Group 1 can be distinguished on the basis of flame photometry.
(b) The metals of Group 1 are strong reducing agents
(c) The abundance of potassium in the earth's crust is more than that of sodium
(d) The ionization energies, melting and boiling points of Group 1 decrease on moving down the group.

105. The melting point of alkali metals
(a) increases on descending the Group 1
(b) decreases on descending the Group 1
(c) initially decreases followed by an increase at the end of Group 1
(d) initially increases followed by a decrease at the end of Group 1

106. Which of the following orders regarding the melting points of alkali metal halides is correct?
(a) MF > MCl > MBr (b) MF > MBr > MCl (c) MCl > MF > MBr (d) MCl > MBr > MF

107. Which of the following orders regarding the melting points of alkali metals chlorides is correct
(a) LiCl > NaCl > KCl (b) LiCl > KCl > NaCl (c) LiCl > NaCl > KCl (d) LiCl > NaCl < KCl

108. The boiling points of alkali metals follow the order
(a) Li < Na < K < Rb (b) Li > Na > K > Rb (c) Li < K < Na < Rb (d) Li < Rb < K < Na

109. The number of alkaline earth metals is
(a) 4 (b) 5 (c) 6 (d) 7

110. Which of the following statements is not correct?
(a) Alkaline earth metals are harder and denser than alkali metals
(b) The melting and boiling points of alkaline earth metals are higher than those of alkali metals
(c) Alkaline earth metals are more reactive than alkali metals
(d) The reactivities of alkaline earth metals increase down the group

111. Which of the following alkaline earth metal salts does not impart any colour to the Bunsen flame?
(a) Magnesium nitrate (b) Calcium chloride (c) Barium chloride (d) Strontium chloride

112. Which of the following statements is **not** correct?
(a) The standard reduction potentials of alkaline earth metal ions become more negative on descending the group
(b) Beryllium differs considerably from the rest of the alkaline earth metals
(c) Anhydrous salts of beryllium are covalent whereas those of Ca, Ba and Sr are ionic
(d) Be and Mg burn in air to form oxide while Ca, Ba and Sr form peroxides

113. Beryllium shows a diagonal relationship with
(a) magnesium (b) aluminium (c) boron (d) sodium

114. Which of the following statements is **not** correct?
(a) Beryllium does not react with water
(b) Magnesium reacts with boiling water and not with cold water
(c) Calcium reacts even with cold water
(d) The solubility of alkaline earth metal hydroxide decreases on descending the group

115. Which of the following statements is **not** correct?
(a) The basic strength of hydroxides of alkaline earth metal increases down the group
(b) The solubility of sulphates and carbonates of alkaline earth metal increases down the group
(c) The sulphates of alkaline earth metal are stable to heat
(d) The carbonates of alkaline earth metal decompose on heating

116. Which of the following diatomic molecules is **not** observed?
(a) Be_2 (b) B_2 (c) C_2 (d) N_2

117. Which of the following statements is not correct?
(a) The alkaline earth metals are harder and denser than alkali metals
(b) The melting and boiling points of alkaline earth metals are higher than the corresponding nearby alkali metals
(c) Alkaline earth metals are too reactive to occur freely in nature
(d) Magnesium and calcium can be obtained by chemical reduction of their compounds.

118. The order of melting points of Ba, Mg and Ca follow the order
(a) Ba > Mg > Ca (b) Ba > Ca > Mg (c) Ca > Mg > Ba (d) Ca > Ba > Mg

119. Property of the alkaline earth metals that increases with their atomic number is
(a) ionization energy (b) solubility of their hydroxides
(c) solubility of their sulphates (d) electronegativity (1997)

p-Block Elements

120. Which of the following elements does not belong to Group 13 of the periodic table?
(a) Boron (b) Aluminium (c) Gallium (d) Tin

121. The number of elements in Group 13 is
(a) 4 (b) 5 (c) 6 (d) 7

122. The atomic number of indium which belongs to 5th period is
(a) 47 (b) 48 (c) 49 (d) 50

123. Which of the following oxides is an acidic oxide?
(a) B_2O_3 (b) Al_2O_3 (c) Ga_2O_3 (d) In_2O_3

124. Which of the following oxides is an amphoteric oxide?
(a) B_2O_3 (b) Al_2O_3 (c) In_2O_3 (d) Tl_2O_3

125. Which of the following oxides is a basic oxide?
(a) B_2O_3 (b) Al_2O_3 (c) Ga_2O_3 (d) In_2O_3

126. Which of the following elements has highest first ionization potential?
(a) B (b) Al (c) Ga (d) In

127. Which of the following ions is hydrolysed to the maximum extent?
(a) Al^{3+} (b) Ga^{3+} (c) Tl^{+} (d) Tl^{3+}

128. Which of the following elements has the largest melting point?
(a) B (b) Al (c) Ga (d) In

129. Which of the following elements has the minimum melting point?
(a) B (b) Al (c) Ga (d) In

130. Which of the following statements regarding boron is not correct?
(a) Boron compounds act as Lewis acids
(b) Boron is a good conductor of electricity
(c) Colemanite is one of the chief minerals of boron
(d) Boron exists in two isotopic forms ^{10}B and ^{11}B

131. The diagonal relationship of boron is with
(a) carbon (b) silicon (c) magnesium (d) phosphorus

132. Which of the following facts regarding boron and silicon is **not** true?
(a) Boron and silicon are semiconductors
(b) Boron and silicon form halides which are not hydrolysed
(c) Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively
(d) Both boron and silicon react with alkalis to form borates and silicates containing BO_4 and SiO_4 tetrahedral units, respectively.

133. Which of the following statements regarding aluminium is **not** correct?
(a) Aluminium is a light metal with considerable strength
(b) Aluminium is a good conductor of heat and electricity
(c) The corrosion of the aluminium metal is prevented by the formation of a coat of aluminium oxide on its layer
(d) Aluminium dissolves in hydrochloric acid but not in concentrated sodium hydroxide

134. The melting points of the elements of Group 13
(a) increases on descending the group
(b) decreases on descending the group
(c) firstly decreases up to Ga followed by an increase
(d) firstly increases up to Ga followed by a decrease

135. Which of the following elements does not belong to Group 14?
(a) Carbon (b) Silicon (c) Germanium (d) Arsenic

136. The atomic number of the element tin which belongs to 5th period is
(a) 49 (b) 50 (c) 81 (d) 82

137. Which of the following elements may be regarded as nonmetal?
(a) Carbon (b) Silicon (c) Germanium (d) Tin

138. Which of the following elements may be regarded as semi-metals?
(a) Carbon (b) Germanium (c) Tin (d) Lead

139. Which of the following elements behaves like a metal?
(a) Carbon (b) Silicon (c) Germanium (d) Tin

140. Which of the following orders regarding the melting points is correct?
(a) $C > Si > Ge > Sn$ (b) $C < Si < Ge > Sn$ (c) $C > Si < Ge < Sn$ (d) $C < Si > Ge > Sn$

141. Which of the following orders regarding the boiling point is correct?
(a) Si > Ge > Sn (b) Si < Ge < Sn (c) Si > Ge < Sn (d) Si < Ge > Sn

142. Which of the following oxides is an acidic oxide?
(a) CO_2 (b) Ge_3O_2 (c) SnO_2 (d) PbO_2

143. Which of the following oxides is an amphoteric oxide?
(a) CO_2 (b) SiO_2 (c) GeO_2 (d) PbO_2

144. Which of the following oxides is a basic oxide?
(a) CO_2 (b) SiO_2 (c) GeO_2 (d) PbO_2

145. Which of the following elements does not belong to Group 15?
(a) Nitrogen (b) Phosphorus (c) Arsenic (d) Tin

146. Atomic number of bismuth which belongs to 6th period is
(a) 51 (b) 52 (c) 83 (d) 84

147. The number of elements in Group 15 is
(a) 3 (b) 4 (c) 5 (d) 6

148. Which of the following orders regarding the melting points of hydrides of Group 15 is correct?
(a) $NH_3 > PH_3 > AsH_3$ (b) $NH_3 < PH_3 < AsH_3$
(c) $NH_3 > PH_3 < AsH_3$ (d) $NH_3 < PH_3 > AsH_3$

149. Coordination number of nitrogen in its compounds never exceeds
(a) 3 (b) 4 (c) 5 (d) 6

150. Which of the following elements does not belong to Group 16?
(a) Oxygen (b) Sulphur (c) Selenium (d) Bismuth

151. Atomic number of tellurium which belongs to 5th period is
(a) 50 (b) 51 (c) 52 (d) 84

152. The number of elements in Group 16 is
(a) 3 (b) 4 (c) 5 (d) 6

153. Which of the following orders of melting points of hydrides of Group 16 elements is true?
(a) $H_2S > H_2Se > H_2Te$ (b) $H_2S < H_2Se < H_2Te$
(c) $H_2S > H_2Se < H_2Te$ (d) $H_2S < H_2Se > H_2Te$

154. Which of the following hydrides of Group 16 has the lowest boiling point?
(a) H_2O (b) H_2S (c) H_2Se (d) H_2Te

155. Which of the following statements is **not** correct?
(a) The stability of hydrides of elements of Group 16 increases down the group
(b) Oxygen cannot display oxidation states of +2, +4 and +6
(c) Oxygen exists as diatomic gaseous molecules while other elements of the Group 16 catenate to form chains or rings
(d) Rhombic sulphur is stable at room temperature

156. The elemental sulphur is written as
(a) S (b) S_2 (c) S_4 (d) S_8

157. Which of the following statements is true?
(a) Both rhombic and monoclinic sulphur are soluble in water
(b) Both rhombic and monoclinic sulphur are soluble in carbon disulphide
(c) Both rhombic and monoclinic sulphur are insoluble in carbon disulphide
(d) Rhombic sulphur can be converted into monoclinic sulphur but the reverse is not possible.

158. The number of halogens known so far is
(a) 4 (b) 5 (c) 6 (d) 7

159. The atomic number of astatine which belongs to six period is
(a) 53 (b) 54 (c) 85 (d) 86

160. Which of the following is radioactive halogen?
(a) Cl (b) Br (c) I (d) At

161. Which of the following orders of electron affinities of halogens is correct?
(a) F < Cl < Br (b) F > Cl > Br (c) F > Cl < Br (d) F < Cl > Br

162. Which of the following orders of bond dissociation enthalpy of halogens is correct?
(a) F—F > Cl—Cl > Br—Br (b) F—F < Cl—Cl < Br—Br
(c) F—F > Cl—Cl < Br—Br (d) F—F < Cl—Cl > Br—Br

163. Which of the following halogens does not exhibit positive oxidation state?
(a) F (b) Cl (c) Br (d) I

164. Which of the following orders of melting point of hydrides of halogens is correct?
(a) HF > HCl > HBr (b) HF < HCl < HBr
(c) HF > HCl < HBr (d) HF < HCl > HBr

165. Which of the following statements regarding halogens is **not** true?
(a) Ionization energy decreases with increase in atomic number
(b) Electronegativity decreases with increase in atomic number
(c) Electron affinity decreases with increase in atomic number
(d) Enthalpy of fusion increases with increase in atomic number

166. Which of the following halogens does not show positive oxidation states?
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine

167. Which of the following orders regarding the boiling point of halogens is true?
(a) HF > HCl > HBr > HI (b) HF < HCl < HBr < HI
(c) HF > HCl < HBr < HI (d) HF > HCl > HBr < HI

168. Which of the following halogens is the strongest oxidizing agent?
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine

169. The number of elements in Group 18 is
(a) 4 (b) 5 (c) 6 (d) 7

170. Which of the following inert gases has the largest abundance (by volume) in air?
(a) Helium (b) Neon (c) Argon (d) Krypton

Multiple Correct Choice Type

1. The statement that are true for the long form of the periodic table are
(a) It reflects the sequence of filling the electrons in the order of sub energy levels s, p, d and f.
(b) It helps predict the stable valency states of the elements.
(c) It reflects trends in physical and chemical properties of the elements.
(d) It helps predict the relative ionicity of the bond between any two elements. (1988)

2. The statement that is correct for the periodic classification of elements is
(a) The properties of elements are the periodic function of their atomic numbers.
(b) Non-metallic elements are lesser in number than metallic elements.
(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements the d subshells are filled with electrons monotonically with increase in atomic number. (1992)

3. Which of the following statements are **not** correct?
(a) Modern periodic law is based on the atomic masses of elements.
(b) 5f-elements are known as lanthanides.
(c) F^- ion has smaller size than F atom.
(d) Amongst the isoelectronic species Na^+, Mg^{2+} and Al^{3+}, the ion having smallest radius is Al^{3+} ion.

4. Which of the following statements are **not** correct?
(a) The ionization energy of nitrogen atom is smaller than oxygen.
(b) Electronegativity is the property of an isolated atom.
(c) Electronegativity and electron affinity represent the same property of an atom.
(d) The electron affinity of fluorine is greater than that of chlorine.

5. Which of the following statements are **not** correct?
(a) The electronegativity of fluorine is 4.0.
(b) The third period of periodic table contains 18 elements because third quantum shell includes 3s, 3p and 3d orbitals.
(c) The electronic configuration of Group 15 is $(ns)^2 (np)^5$.
(d) Periodic table includes more metalloids than nonmetals.

6. Which of the following statements are correct?
(a) Inert gases were known at the time of Mendeleev classification of elements.
(b) Electronegativity of an element depends upon its atomic size.

- (c) The elements having electronic configuration $(ns)^2 (np)^5$ are known as halogens.
- (d) The electron affinity values of alkaline earth metals are greater than those of alkali metals.

7. Which of the following statements are correct?
- (a) Half of the transition elements are metals and others are nonmetals.
- (b) Amongst the metals, alkali metals have lowest ionization energies.
- (c) In Group 13, the first member is metalloid and the rest are metals.
- (d) Inert-pair effect is more effective in the elements of higher atomic numbers.

8. Which of the following statements are correct?
- (a) Metalloids do not form ionic compounds.
- (b) All halogens are nonmetals.
- (c) The electronic configuration of actinides is given as $(4f)^{1-14} (5d)^{0-1} (6s)^2$.
- (d) Modern periodic table was developed by Mendeleev.

9. Which of the following statements are **not** correct?
- (a) It is possible to determine absolute values of electronegativity of an element.
- (b) The second ionization energy of sodium is greater than that of magnesium.
- (c) The first and second ionization energies of nitrogen are greater than those of oxygen.
- (d) The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. (1993)

10. Which of the following statements are correct?
- (a) Lanthanides are known as inner-transition elements and belong to 4f block.
- (b) Na^+, Ne and Mg^{2+} contain the same number of electrons. Such species are known as isoelectronic species.
- (c) Electron affinity of noble gases is zero..
- (d) Most widely used electronegativity scale is due to Linus Pauling.

11. Which of the following statements are **not** correct?
- (a) Due to inner-pair effect, +2 oxidation state of lead is more stable than +4 oxidation state.
- (b) Amongst Group 15, metalloids are silicon and germanium.
- (c) Amongst Group 14, metalloids are assenic and antimony.
- (d) Amongst Group 13, metalloids is boron..

12. Which of the following statements are correct?
- (a) Amongst Group 16, metalloids are tellurium and polonuim.
- (b) The vast majority of the alkali metal and alkaline earth metals form ionic compounds with halogens.
- (c) Copper belongs to 4d transition elements.
- (d) Silver belongs to 5d transition elements.

13. Which of the following statements are **not** correct?
- (a) There are 14 elements in each of inner-transition elements.
- (b) There are seven elements known in noble gases.
- (c) The atomic number of elements Unq is 104.
- (d) Except helium and neon, other noble gases are totally inert chemically.

14. Which of the following statements are **not** correct?
- (a) Covalent-bond radius of an atom is larger than van der Waals radius.
- (b) The second ionization energy is always larger than the first ionization energy.
- (c) The second electron affinity is always larger than the first electron affinity.
- (d) Moving down the Group 13, unipositive ion becomes more stable than the tripositive ion.

15. Which of the following facts are correct?
- (a) First ionization of calcium is more than that of potassium.
- (b) Second ionization of magnesium is more than that of aluminium.
- (c) Third ionization of beryllium is larger than that of carbon.
- (d) Second ionization of nitrogen is more than that of oxygen.

16. Which of the following statements for the elements $_{21}Sc$ to $_{28}Ni$ is **not** true?
- (a) These elements belong to the second transition series with an incompletely filled d sub-shell
- (b) These elements are metals with high melting points
- (c) The ionization energy decreases in the order $_{21}Sc$ to $_{28}Ni$
- (d) These elements are paramagnetic in nature

17. Which of the following orders regarding the basicity of hydroxides of alkali and alkaline earth hydroxides is correct?

(a) $Be(OH)_2 > Mg(OH)_2 > Ca(OH)_2$ (b) $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2$
(c) LiOH > NaOH > KOH (d) LiOH < NaOH < KOH

Linked Comprehension Type

1. Dobereiner, in 1829, pointed out that when elements are arranged in the order of increasing relative atomic masses, in a triad, the relative atomic mass of the middle element was approximately equal to the mean of the relative atomic masses of the first and third elements. Based on this information, answer the following three questions.

(i) The element in between the elements calcium and barium in the Dobereiner triad series is
(a) beryllium (b) magnesium (c) strontium (d) iodine

(ii) The element in between the elements sulphur and tellurium in the Dobereiner triad series is
(a) calcium (b) selenium (c) barium (d) oxygen

(iii) If two members of a Dobereiner triad are phosphorus and antimony, the third member of this triad is
(a) arsenic (b) sulphur (c) iodine (d) nitrogen

2. The trend in ionization energy may be predicted from the electronic configurations of elements. The removal of electron requires comparatively lesser energy if the species obtained after the removal of electron has fully-filled orbital configuration. The removal of electron from the fully-filled orbital or half-filled orbitals of one type requires comparatively higher energy as these represent stable configurations. Based on these information, answer the following three questions.

(i) The correct order of elements having first ionization energies of 900, 518, 2370 and 800 kJ mol^{-1}, respectively, is
(a) Be, B, He, Li (b) Bi, Li, He, B (c) B, Be, Li, He (d) He, B, Be, Li

(ii) The correct order of elements having second ionization energies of 1757, 5247, 2423 and 7293 kJ mol^{-1}, respectively, is
(a) Be, Li, He, B (b) Be, Li, B, He (c) Be, He, B, Li (d) B, He, Li, Be

(iii) The correct order of elements having third ionization energies of 14841, 4615, 3657 and 11807 kJ mol^{-1}, respectively, are
(a) Be, C, B, Li (b) Be, C, Li, B (c) Be, Li, C, B (d) Li, Be, B, C

3. Given are the elements Na, Mg, Al, Si and P. For these elements answer the following three questions.

(i) The element having minimum first ionization energy is
(a) Na (b) Mg (c) Al (d) Si

(ii) The element having maximum second ionization energy is
(a) Na (b) Mg (c) Al (d) Si

(iii) The element having maximum third ionization energy is
(a) P (b) Si (c) Al (d) Mg

4. For the elements having atomic numbers 6, 14, 32, 50 and 82, answer the following three questions.

(i) The group number of elements is
(a) 13 (b) 14 (c) 15 (d) 16

(ii) The elements classified as metals have atomic number(s)
(a) 6, 14 (b) 14, 32 (c) 32, 50 (d) 50, 82

(iii) The elements classified as metalloids have atomic number(s)
(a) 6, 14 (b) 14, 32 (c) 32, 50 (d) 50, 82

5. For the elements having atomic numbers 6, 14, 32, 50 and 82, answer the following three questions.

(i) The atomic number(s) of element(s) having acidic oxide is/are
(a) 6 (b) 14 (c) 32, 50 (d) 50, 82

(ii) The atomic number(s) of elements(s) having basic oxide is/are
(a) 6, 14 (b) 14, 32 (c) 32, 50 (d) 50, 82

(iii) The atomic number(s) of element(s) having amphoteric oxide is/are
(a) 6, 14 (b) 14, 32 (c) 32, 50 (d) 50, 82

6. For the classification of elements in the periodic table, answer the following three questions.

(i) The most electropositive element is placed at

(a) first position of Group 1 (b) last position of Group 1

(c) first position of Group 17 (d) last position of Group 17

(ii) The most electronegative element is placed at

(a) first position of Group 1 (b) last position of Group 1

(c) first position of Group 17 (d) last position of Group 17

(iii) The total number of elements having metalloid characteristics is about

(a) 3 or 4 (b) 4 or 5 (c) 5 or 6 (c) 7 or 8

7. In a multi-electron atom, the energy of an electron in a orbital is determined by using the effective nuclear charge. (Z^*) defined as

$$Z^* = Z - S$$

where Z is the nuclear charge and S is the shielding or screening constant. The latter is determined by the number and nature of other electrons in the atom. Slater have recommended the following rules to determine the shielding constant.

1. The electrons in an atom is classified into the following groups.
(1s) (2s, 2p) (3s, 3p) (3d) (4s 4p) (4d) (4f) …

2. Electrons in the right of the group (*n*s, *n*p) contribute nothing to the shielding constant.

3. Electrons other than the electron understudy in the group (*n*s, *n*p) shield to an extent of 0.35 each.

4. All electrons in *n*–1 shell shield to an extent of 0.85 each if the electron under consideration is not in *n*d or *n*f orbital. If the electron is in *n*d or *n*f orbital, all electrons in *n*–1 shell shield to an extent of 1.00

5. All electrons in *n*–2 or lower shield to an extent of 1.0.

Based on this information, answer the following three questions.

(i) The screening constant for an p-electron in $_7$N is

(a) 3.45 (b) 3.10 (c) 2.75 (d) 2.4

(ii) The screening constant for 4s electron in $_{30}$Zn is

(a) 25.65 (b) 26.4 (c) 29 (d) 24.15

(iii) The screening constant for 3d electron in $_{30}$Zn is

(a) 21.85 (b) 21.5 (c) 21.15 (d) 20.8

8. The Pauling electronegativity values is based on the expression $\chi_A - \chi_B = (0.1018 \text{ kJ}^{-1/2} \text{ mol}^{1/2})\sqrt{\Delta}$

where $\Delta = \varepsilon_{A-B} = \sqrt{\varepsilon_{A-A}\,\varepsilon_{B-B}}$

The symbol Δ represents ionic resonance energy of the molecule A – B. Given are the bond energies, ε, of the following molecules.

$\varepsilon_{H-H} = 420 \text{ kJ mol}^{-1}$, $\varepsilon_{H-F} = 570 \text{ kJ mol}^{-1}$, $\varepsilon_{H-Cl} = 440 \text{ kJ mol}^{-1}$, $\varepsilon_{F-F} = 160 \text{ kJ mol}^{-1}$, and $\varepsilon_{Cl-Cl} = 250 \text{ kJ mol}^{-1}$

Also given is the value of electronegativity of F which is $\chi_F = 4.0$. Based on these information, answer the following three questions.

(i) The electronegativity of H is about

(a) 1.6 (b) 2.2 (c) 2.4 (d) 2.8

(ii) The electronegativity of Cl is

(a) 2.9 (b) 2.5 (c) 3.5 (d) 2.2

(iii) The bond energy of Cl—F is about

(a) 240 kJ mol^{-1} (b) 260 kJ mol^{-1}

(c) 247.3 kJ mol^{-1} (d) 275 kJ mol^{-1}

Assertion Reason Type

In the following questions, two statements are given. For each question, select the correct choice from the following.

(a) Statement-1 is True. Statement-2 is True. Statement-2 is correct explanation for Statement-1.

(b) Statement-1 is True. Statement-2 is True. Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement-1 is True. Statement-2 is False.

(d) Statement-1 is False. Statement-2 is True.

	Statement–1	**Statement–2**
1.	F atom has a less negative electron affinity than Cl atom.	Additional electrons are repelled more effectively by 3p electrons in Cl atom than by 2p electrons in F atom. (1998)
2.	The first ionization energy of Be is greater than that of B.	2p orbital is lower in energy than 2s. (2000)
3.	The fifth period includes 18 elements.	The orbitals filled up in the fifth period are 5s, 4d and 5p orbitals. There are 9 orbitals hence 18 electrons are added.
4.	First ionization energy of Mg is larger than that of Na but reverse is true for the second ionization energy.	Mg has larger atomic number than Na.
5.	Noble gases do not enter into chemical combination with other elements.	The ionization energy of $Xe \rightarrow Xe^+ + e^-$ is nearly the same as that of $O_2 \rightarrow O_2^+ + e^-$
6.	The ionization energy of N is larger than those of C and O.	The half-filled 2p orbitals in N is more stable than $(2p)^2$ and $(2p)^4$ configurations of C and O, respectively.
7.	The electronegativity of Be in its common oxidation state is zero.	The electronic configuration of Be is $(1s)^2\ (2s)^2$.
8.	The electronegativity of Zn^{2+} ion is lesser than that of Cu^{2+} in their compounds.	The electronic configuration of Zn^{2+} is $(3d)^{10}$ while that of Cu^{2+} is $(3d)^9$.
9.	The value of $\Delta = \varepsilon_{A-B} - \sqrt{\varepsilon_{A-A}\,\varepsilon_{B-B}}$ is almost always positive.	The bond between A and B is stronger than the single bond energies between A and A, and B and B.
10.	The ionic radii of isoelectronic species decrease moving from left to right across any period in the periodic table.	This decrease of ionic radii of isoelectronic species is primarily due to increased number of charges on the nucleus.
11.	The sizes of the second and third row transition elements are almost identical.	f-orbital electrons do not shield the nuclear charge very effectively.
12.	Sulphur like chlorine has more negative electron affinity than oxygen.	Additional electron is associated with repulsion by the electrons in oxygen atom.
13.	The sizes of O^+, O and O^- are identical.	The removal of electron decreases the size while the addition of electron increases the size. This is primarily due to decrease and increase in electronic repulsion, respectively.
14.	The alkaline earth metals are harder than the alkali metals.	Alkaline earth metals have $(ns)^2$ configuration while alkali metals have $(ns)^1$ configuration.
15.	The solubilities of hydroxide of alkaline earth metals increase on descending the group while those of carbonates and sulphates decrease.	For hydroxides, lattice energy predominates over hydration energy while reverse is true for carbonates and sulphates.
16.	The solubility of sulphates of alkaline earth metals in water decrease on descending the group.	Decrease in hydration energy of M^{2+} ion of alkaline earth metals is responsible for the decrease in solubility of sulphates.
17.	On descending Group 13, + 1 oxidation state becomes less stable than + 3 state.	The inert pair effect become predominant on descending Group 13.
18.	Acidic character of hydroxides of elements of Group 13 decreases on descending the group.	Metallic character of elements of Group 13 decreases on descending the group.

19.	Bond enthalpy of Cl—Cl is larger than that of F—F.	Fluorine is more electronegative than chlorine.
20.	Halogens form interhalogen compounds AX_n, where *n* varies from 1 to 7.	Interhalogens are more reactive than halogens.
21.	Electronegativity of an atom varies slightly with the hybridization involved in the atom.	More the s contribution in the hybridization, lesser the electronegativity.

Matrix Match Type

1. Column I lists the main type of elements in the periodic table. Column II mentions atomic numbers of some of the elements. Match correctly each entry in column I with those given in Column II.

Column I	**Column II**
(a) s-block element	(p) 63
(b) p-block element	(q) 57
(c) d-block element	(r) 38
(d) f-block element	(s) 50
	(t) 48
	(u) 51

2. Column I includes atomic numbers of some of the elements and column II lists the locations of these elements in the periodic table. Identify the correct choice from Column II for each entry of Column I.

Column I	**Column II**
(a) 41	(p) 6th period Group 8
(b) 76	(q) 6th period Group 15
(c) 83	(r) 5th period and Group 15
(d) 89	(s) 7th period and Group 3

3. Column I lists some of the facts about ionization energies of two elements A and B and Column II lists the elements A and B. Match each entry of Column I with those listed in Column II.

Column I	**Column II**	
	Element A	**Element B**
(a) First ionization energy of A is greater than that of B.	(p) Be	B
(b) First ionization energy of A is lesser than that of B.	(q) N	O
(c) Second ionization energy of A is greater than that of B.	(r) Na	Mg
(d) Second ionization energy of A is lesser than that of B.	(s) Al	Si
	(t) P	S
	(u) B	C

4. Column I lists some of the facts about ionization energies of two elements A and B and Column II lists the elements A and B. Match each entry of Column I with those listed in Column II.

Column I	**Column II**	
	Element A	**Element B**
(a) First ionization energy of A is is greater than that of B.	(p) Be	B
(b) First ionization energy of A is is lesser than that of B.	(q) B	C
(c) Third ionization energy of A is greater than that of B.	(r) C	N
(d) Third ionization energy of A is lesser than that of B.	(s) N	O

5. Column I lists the sets of three elements A, B and C. The order of their melting points are given in Column II. Match correctly each entry of Column I with those given in Column II.

Column I			**Column II**
Element A	**Element B**	**Element C**	
(a) Li	Be	B	(p) $C < B < A$
(b) K	Ca	Ga	(q) $B < C < A$
(c) Ge	As	Se	(r) $A < B < C$
(d) Si	P	S	(s) $C < A < B$
			(t) $B < A < C$

ANSWERS

Straight Objective Type

1. (b)	**2.** (d)	**3.** (a)	**4.** (c)	**5.** (b)	**6.** (c)	**7.** (b)
8. (a)	**9.** (c)	**10.** (d)	**11.** (a)	**12.** (c)	**13.** (b)	**14.** (c)
15. (b)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (d)	**20.** (c)	**21.** (b)
22. (b)	**23.** (c)	**24.** (d)	**25.** (c)	**26.** (a)	**27.** (a)	**28.** (c)
29. (c)	**30.** (b)	**31.** (d)	**32.** (b)	**33.** (a)	**34.** (d)	**35.** (a)
36. (a)	**37.** (d)	**38.** (a)	**39.** (b)	**40.** (a)	**41.** (a)	**42.** (b)
43. (c)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (d)	**48.** (c)	**49.** (a)
50. (c)	**51.** (c)	**52.** (c)	**53.** (a)	**54.** (b)	**55.** (b)	**56.** (b)
57. (b)	**58.** (b)	**59.** (c)	**60.** (c)	**61.** (c)	**62.** (c)	**63.** (b)
64. (a)	**65.** (b)	**66.** (a)	**67.** (c)	**68.** (c)	**69.** (a)	**70.** (c)
71. (b)	**72.** (c)	**73.** (c)	**74.** (a)	**75.** (a)	**76.** (b)	**77.** (b)
78. (a)	**79.** (d)	**80.** (c)	**81.** (b)	**82.** (c)	**83.** (d)	**84.** (b)
85. (a)	**86.** (a)	**87.** (d)	**88.** (a)	**89.** (c)	**90.** (d)	**91.** (c)
92. (a)	**93.** (d)	**94.** (b)	**95.** (d)	**96.** (b)	**97.** (a)	**98.** (a)
99. (a)	**100.** (a)	**101.** (d)	**102.** (c)	**103.** (c)	**104.** (c)	**105.** (b)
106. (a)	**107.** (c)	**108.** (b)	**109.** (c)	**110.** (c)	**111.** (a)	**112.** (d)
113. (b)	**114.** (d)	**115.** (b)	**116.** (a)	**117.** (d)	**118.** (b)	**119.** (b)
120. (d)	**121.** (b)	**122.** (c)	**123.** (a)	**124.** (b)	**125.** (d)	**126.** (a)
127. (a)	**128.** (a)	**129.** (c)	**130.** (b)	**131.** (b)	**132.** (b)	**133.** (d)
134. (c)	**135.** (d)	**136.** (b)	**137.** (a)	**138.** (b)	**139.** (d)	**140.** (c)
141. (a)	**142.** (a)	**143.** (c)	**144.** (d)	**145.** (d)	**146.** (c)	**147.** (c)
148. (c)	**149.** (b)	**150.** (d)	**151.** (c)	**152.** (c)	**153.** (b)	**154.** (b)
155. (a)	**156.** (d)	**157.** (b)	**158.** (b)	**159.** (c)	**160.** (d)	**161.** (d)
162. (d)	**163.** (a)	**164.** (c)	**165.** (c)	**166.** (a)	**167.** (c)	**168.** (a)
169. (c)	**170.** (c)					

Multiple Correct Choice Type

1. (a), (b), (c), (d)	**2.** (a), (b), (d)	**3.** (a), (b), (c)	**4.** (a), (b), (c), (d)
5. (b), (c), (d)	**6.** (b), (c)	**7.** (b), (c), (d)	**8.** (a), (b)
9. (a), (c), (d)	**10.** (a), (b), (c), (d)	**11.** (b), (c)	**12.** (a), (b)
13. (b), (d)	**14.** (a), (c)	**15.** (a), (c)	**16.** (a), (c)
17. (b), (d)			

Linked Comprehension Type

1. **(i)** (c)	**(ii)** (b)	**(iii)** (a)
2. **(i)** (b)	**(ii)** (c)	**(iii)** (a)
3. **(i)** (a)	**(ii)** (a)	**(iii)** (d)
4. **(i)** (b)	**(ii)** (d)	**(iii)** (b)
5. **(i)** (a)	**(ii)** (d)	**(iii)** (b)
6. **(i)** (b)	**(ii)** (c)	**(iii)** (d)
7. **(i)** (b)	**(ii)** (a)	**(iii)** (c)
8. **(i)** (b)	**(ii)** (a)	**(iii)** (c)

Assertion and Reason Type

1. (c) **2.** (c) **3.** (a) **4.** (b) **5.** (d) **6.** (a) **7.** (d)
8. (b) **9.** (a) **10.** (a) **11.** (b) **12.** (b) **13.** (d) **14.** (b)
15. (b) **16.** (a) **17.** (d) **18.** (c) **19.** (c) **20.** (d) **21.** (c)

Matrix Match Type

1. (a)-(r) (b)-(u), (s) (c)-(q), (t) (d)-(p)
2. (a)-(r) (b)-(p) (c)-(q) (d)-(s)
3. (a)-(p), (q), (t) (b)-(r), (s), (u) (c)-(r), (s), (u) (d)-(p), (q), (t)
4. (a)-(p), (s) (b)-(q), (r) (c)-(p), (r) (d)-(q), (s)
5. (a)-(r) (b)-(s) (c)-(p) (d)-(q)

Hints and Solutions

Straight Objective Type

Classification of Elements

1. The fifth period includes 18 elements due to filling of 5s, 4d and 5p orbitals.

2. In the sixth period, the orbitals being filled are 6s, 4f, 3d and 6p.

4. Long form of the periodic table contains seven periods as the last element contains 7th valence shell.

5. 21 = 2 + 8 + 8 + 3. Thus, the element of atomic number 21 belongs to 4th period and 3rd group. Its electronic configuration will be $(4s)^2\ (3d)^1$. Hence, the elements from 21 to 30 belongs to the first transition elements.

6. The element $_{53}$I belongs to the 5th period and group 17. Its atomic number can be computed by adding the numbers 2, 8, 8, 18 and 17. The next element will have atomic number 85 (= 53 + 32).

7. Fourth period involves the filling of 4s, 3d and 4p orbitals. Thus, the number of elements in this period will be 2 + 10 + 6 = 18.

8. The atomic number will be 2 + (14 – 10) = 6

9. The second inner transition elements involves the filling of 5f orbitals. Prior to this 7s and $6d^1$ orbitals are filled. The seventh period starts with atomic number 87 (= 2 + 8 + 8 + 18 + 18 + 32 + 1). 5f orbitals start filling with atomic number 90.

10. Groups 8 to 10 include three elements each from 3d, 4d and 5d elements—a total of nine elements.

11. In lanthanides, 4f orbitals are filled. Prior to this, $6s^2$ and $5d^1$ are filled. The sixth period starts from atomic number 55 (= 2 + 8 + 8 + 18 + 18 + 1). Hence, lanthanide starts from atomic number 58 and go up to atomic number 71.

12. The atomic number will be 2 + 8 + 8 + 18 + 16 = 52.

13. Atomic number 49 = 2 + 8 + 8 + 18 + 13. Hence, it belongs to 5th period and 13th group.

14. Atomic number 30 = 2 + 8 + 8 + 12. Thus, it belongs to 12th group.

15. The symbol u, n and p in Unp stand for unit, null and penta which is 1, 0 and 5.

16. Atomic radius of neon will be larger than fluorine.

17. Amongst the given species, Na^+ will have the smallest size.

18. In the periodic table, size decreases in a period and it increases in a group. In the given elements, Be belongs to lower period and higher group and thus will have least size.

19. Size decreases in a period.

20. The electronic configurations of the given ions are

Al^{3+} : $(1s)^2\ (2s)^2\ (2p)^6$ F^- : $(1s)^2\ (2s)^2\ (2p)^6$
O^{2-} : $(1s)^2\ (2s)^2\ (2p)^6$ Cl^- : $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6$

The size of Cl^- will be the largest as its outer shell belongs to the quantum number $n = 3$. Of the remaining species Al^{3+} will have the minimum ionic size because of three positive charge and O^{2-} will have maximum ionic size because of two negative charge.

21. The given species are isoelectronic. The size of these species decreases with increase in the positive charge.

22. The size of Zr is similar to Hf due to the lanthanide contraction.

23. The size of Nb is similar to Ta due to the lanthanide contraction.

24. The last element Zn in a transition elements Co, Ni, Cu and Zn has the largest size.

25. Mo belongs to 5th period and 6th group. W belongs to 6th period and 6th group. Their sizes are more or less identical due to intervening lanthanides.

26. For isoelectronic species, the size of an ion increases with increase in the negative charge.

27. Same as Q.26.

28. Same as Q.26.

29. Same as Q.26.

30. The ions F^-, O^{2-} and N^{3-} are isoelectronic and belongs to the same period. The size of such ions decreases with increase in atomic number or increases with increase in the negative charge.

31. The electronic configuration of $_{15}P$ is $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^3$

With the removal of 3 electrons to give P^{3+}, 3p electrons are removed. There are 2 electrons in 3s orbital. With the removal of 5 electrons to give P^{5+}, all the five electrons in the outer shell are removed. Electrons are present only in the inner shells. Hence, the size follows the order $P^{3+} > P^{5+}$.

32. The ions Li^+, Be^{2+} and B^{3+} are isoelectronic and their sizes decrease with increase in atomic number.

33. The change is maximum in going from Group 1 to Group 2 as the electron is added in the same orbital.

34. Inert gases has the largest atomic radii and also the change from Group 17 to Group 18 is maximum.

35. With increase in atomic number, size is generally decreased but due to the larger electronic repulsion the reverse of this is observed in Ni, Cu and Zn.

36. See Q.35.

37. The atomic radii is largest for Zn and its atomic volume will also be largest. In going from Co to Ni to Cu to Zn, the increase in atomic size is unusually high for Zn. Hence, in spite of increase in atomic mass, its density is the minimum.

40. The electronic configurations are

$$_7N\ (1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1 \quad \text{and} \quad _8O\ (1s)^2(2s)^2(2p_x)^2(2p_y)^1(2p_z)^1$$

Nitrogen is expected to have higher ionization energy because it has stable half-filled electronic configuration.

41. The electronic configurations are $_{11}Na\ (3s)^1$; $_{12}Mg\ (3s)^2$; $_{13}Al\ (3s)^2(3p)^1$; $_{14}Si\ (3s)^2(3p)^2$;
The ionization energy of Mg will be larger than that of Na due to fully-filled configuration $(3s)^2$.
The ionization of Al will be smaller than that of Mg due to one electron extra than the stable configuration.
The ionization of Al will be smaller than that of Si due to increase in effective nuclear charge of Si. Hence, the trend will follow the order Na < Mg > Al < Si.

42. The configuration $[Ne](3s)^2(3p)^3$ will have highest ionization energy due to the stable half-filled electronic configuration. $[Ar](3d)^{10}(4s)^2(4p)^3$ is expected to have lesser value due to the larger distance of valence electrons from the nucleus.

43. Nitrogen has maximum ionization energy because of its half-filled electronic configuration. The correct order is C < N > O.

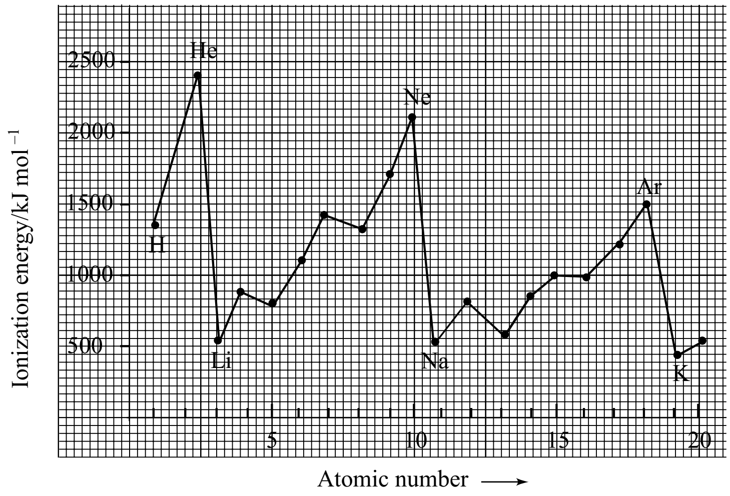
44. Phosphorus has maximum ionization energy because of its half-filled electronic configuration. The correct order is Si < P > S.

45. $1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$

46. The configuration $(1s)^2(2s)^2(2p)^6(3s)^2$ will have maximum difference in second and third ionization energies. Second ionization implies removal of 3s electron and third ionization implies removal of electron from stable configuration of noble gas.

47. The statement d is correct.

48. The variation of ionization energy versus atomic number is as shown in the following figure.



Peaks are occupied by noble gases as the electron is to be removed from the stable fully occupied sub-shell.

49. The minimum positions are occupied by alkali metals as they contain one extra electron than the stable noble gas configuration. Their removable is easier as the resultant ions are having stable configurations.

50. The electronic configurations are

Be (1s)2 $(2s)^2$; B $(1s)^2$ $(2s)^2$ $(2p)^1$; C $(1s)^2$ $(2s^2)$ $(2p)^2$

Obviously, the ionization energy of Be will be greater than B as here fully-filled 2s orbital (which has lesser energy than 2p orbital) will require more energy for the removal of electron. Boron has lower ionization energy than carbon as the removal of a single electron will lead to more stable configuration, i.e. $(2p)^1$ electron is loosely held as compared to $(2p)^2$ electrons. Moreover, the effective nuclear charge seen by cation valence electron will be more than that of boron.

51. The electronic configurations are

N $(1s)^2$ $(2s)^2$ $(2p)^3$; O $(1s)^2$ $(2s)^2$ $(2p)^4$; F $(1s)^2$ $(2p)^2$ $(2p)^5$

Nitrogen has half-filled electronic configuration and hence more stable than that of oxygen. Hence, the ionization energy of nitrogen will be more than that of oxygen.

52. Boron has the highest melting point due to icosahedral (20-faced) structure with boron atoms at all 12 corners.

53. The second ionization energy implies the removal of electron from O^+, F^+, N^+ and C^+ species. Their configurations are

O^+ : $(1s)^2$ $(2s)^2$ $(2p)^3$; F^+ : $(1s)^2$ $(2s)^2$ $(2p)^4$
N^+ : $(1s)^2$ $(2s)^2$ $(2p)^2$; C^+ : $(1s)^2$ $(2p)^2$ $(2p)^1$

The species O^+ will have maximum value due to the stable half-filled electronic configuration. The species C^+ will have minimum value as the removal of electron leads to the stable inert-gas configuration.

54. For the configuration $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$, the second and third ionizations imply

$$(1s)^2\ (2s)^2\ (2p)^6\ (3s)^1 \rightarrow (1s)^2\ (2s)^2\ (2p)^6$$
$$(1s)^2\ (2s)^2\ (2p)^6 \rightarrow (1s)^2\ (2s)^2\ (2p)^5$$

For the second ionization, the removal of 3s electron will require comparatively lesser energy as its removal gives stable electronic configuration.

For the third ionization, the removal of 2p electron will require comparatively higher energy as the electron is to be removed from the stable fully-filled quantum shell.

55. The removal of electron from Mg will require higher energy due to higher nuclear charge.

56. The ionization energy decreases down a group due to the removal of electron from the higher quantum shell which is farther away from the nucleus.

57. Same as Q.56.

58. The second ionization energy will be minimum for Be as the removal of electron gives stable fully-filled quantum shell.

Electron Affinity

61. Chlorine has the maximum electron affinity. Fluorine has lesser value due to its compact electronic configuration. The correct order is F < Cl > Br.
62. Neon has stable configuration. Its electron affinity is zero.
63. Sulphur has the highest value of electron affinity.
64. Be has fully-filled orbital configuration $(1s)^2$ $(2s)^2$.

Electronegativity

68. Electronegativity increases along a period and decreases down the group. Nitrogen is expected to have maximum electronegativity.
69. The electronegativity of an element decreases down the group. The correct order is F < Cl < Br.
70. The electronegativity of F is 4.0.
71. Sulphur will have maximum electronegativity.
72. With the increase in atomic number in a period, the electronegative character of elements increases.
73. The statement c is correct.
74. Fluorine being most electronegative atom never has oxidation state + 1.
75. Sodium is the most electropositive element.
76. Electropositivity decreases along the period.
78. Electronegativity generally decreases on descending a group.

82. $\Delta/\text{kJ mol}^{-1} = (\varepsilon_{AB} - \sqrt{\varepsilon_{AA}\,\varepsilon_{BB}})/\text{kJ mol}^{-1} = 412 - \sqrt{348 \times 436} = 412 - \sqrt{151728} = 412 - 389.5 = 22.5$

Hence $\chi_C - \chi_H = 0.1018\sqrt{22.5} = 0.1018 \times 4.74 \simeq 0.48$. $\chi_C = \chi_H + 0.4 = 2.1 + 0.48 = 2.58$

Metallic-Nonmetallic

83. The statement D is correct.
84. Arsenic is a metalloid.
85. Mg being metal has the basic oxide.
86. Oxide of metal is alkaline in nature.
87. The larger the nonmetallic character of the element, more the acidic nature of the oxide.
88. The larger the metallic character of the element, more the basic nature of the oxide.
89. Basicity increases down the group as element become more and more metallic.
90. Potassium and caesium are used in the photoelectric cells.
91. Lithium forms lithium oxide, sodium forms sodium peroxide and higher alkali metals form superoxides.
93. Li and Mg form monoxide while other alkali metals form peroxides or superoxides.
94. The second ionization energy of Na is very high as the electron is to be removed from Na^+ which has stable fully-filled configuration $(1s^2\ 2s^2\ 2p^6)$.
97. Because of extensive hydration, the sizes are $Li^+ > Na^+ > K^+ > Rb^+$. The extent of hydration depends on the positive charge density which varies in the order shown above.
98. Li^+ has the highest reduction potential.
99. The enthalpy of atomization decreases on descending the Group 1.
100. The enthalpy of sublimation decreases on descending the Group 1.
102. The reduction potential of Li^+ has the maximum negative value.
103. Atomic number of francium is 87.
104. The abundance of sodium is more than that of potassium.
105. The melting point decreases on descending the Group 1.
106. Melting point of halides of the same metal decreases with increase in the atomic number of halogen.
107. For the same halogen, lithium halide has a lower melting point due to higher covalent character because of high polarization power of the larger charge density of Li^+.
108. Boiling point decreases with increase in atomic number.
110. Alkaline earth metals are less reactive than alkali metals.

111. Calcium, barium and strontium salts impart brick red, green and crimson red colour, respectively.
112. Be, Mg and Ca form monoxides while Sr, Ba and Ra form peroxides.
114. The solubility of hydroxides increases down the group.
115. The solubilities of sulphates and carbonates decrease down the group.
116. Be_2 is not observed as the number of electrons in the bonding orbitals is equal to the number of electrons in the antibonding orbitals (i.e. bond order of Be_2 is zero).
117. Magnesium and calcium are obtained by electrolytic reduction.
122. The atomic number of indium is 2 + 8 + 8 + 18 + 13 = 49.
130. Boron has a very low electrical conductivity.
132. The halides of B and Al are hydrolysed.

$$\mathrm{BCl_3 + 3H_2O \rightarrow \underset{\text{Boric acid}}{B(OH)_3} + 3HCl;} \qquad \mathrm{SiCl_4 + 4H_2O \rightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl}$$

133. Aluminium dissolves both in HCl and conc. NaOH

$$\mathrm{2Al + 6HCl \rightarrow Al_2Cl_3 + 3H_2} \; ; \qquad \mathrm{2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2O}$$

134. B has high melting point due to its unusual crystal structure of isosahedral (20 faced) with boron atoms at all 12 corners.
140. Because of catenation of carbon, its melting point is greater than silicon.
141. Boiling point decreases from Si to Pb.
142. Acidic nature of the oxides decreases down the group.
145. Tin belongs to Group 14.
146. Atomic number of bismuth will be 2 + 8 + 8 + 18 + 18 + 14 + 15 = 83
148. Because of hydrogen bonding, the melting point of NH_3 is greater than PH_3.
150. Bismuth belongs to Group 15.
151. Atomic number of tellurium is 2 + 8 + 8 + 18 + 16 = 52.
154. Because of hydrogen bondings, the boiling point of H_2O is greater than H_2S. H_2Se and H_2Te have higher boiling points than H_2S because of heavier atoms Se and Te.
155. The stability of hydrides of elements of Group 16 decreases down the group.
159. The atomic number of astatine is 2 + 8 + 8 + 18 + 18 + (14 + 17) = 85
161. Because of small size (electrons held in small volume), the electron affinity of F is smaller than Cl, which, in turn, has higher electron affinity than Br.
162. Cl—Cl bond is the strongest.
163. F is the most electronegative atom.
164. Because of hydrogen bonding, HF has higher melting point than HCl, which, in turn, has smaller melting point than HBr.
165. Electron affinity of Cl is larger than F.
166. Fluorine being most electronegative always exhibits the oxidation state of –1.
167. Because of small size and highly electronegative nature of F, there occurs extensive hydrogen bonding in HF. It is because of this, melting and boiling points of HF are greater than those of HCl.

Multiple Correct Choice Type

2. The first ionization energy tends to increase along the period.
3. (a) It is based on the atomic number of elements.
(b) 5f-elements are known as actinides.
(c) Anions have bigger size as compared to the atom from which it is formed.
4. (a) The ionization energy of nitrogen is higher than oxygen because the former has half-filled electronic configuration. Oxygen has one extra electron which can be readily removed to get more stable electronic configuration.
(b) It is a relative property and refers to the tendency of an atom to attract bonded electron pair towards itself.
(c) Electron affinity refers to an atom in the gaseous phase while electronegativity refers to the bonded atom in a molecule.
(d) Chlorine has larger electron affinity than fluorine.
5. (b) The third period contains eight elements as only 3s and 3p orbitals are filled. The 3d orbital is filled after 4s orbital.

(c) It is $(ns)^2\,(np)^3$.

(d) There are only seven metalloids.

6. (a) Only 63 elements excluding inert gases were known at the time of Mendeleev.

(d) Alkaline earth metals show little affinity towards the addition of electron.

7. (a) All elements of transition series are metals.

(c) Boron is a metalloid.

(d) Inert-pair effect refers to the two relatively stable and unreactive outer s electrons. It is more important for elements of higher atomic number. For example, Tl ($6s^2 6p^1$) shows more stable unipositive ion than the tripositive ion.

8. (c) The electronic configuration is represented as $(5f)^{1-14}\,(6d)^{0-1}\,(7s)^2$.

9. (a) Electronegativity values as developed by Pauling are relative values with respect to fluorine which is assigned a value of 4.0.

(b) The electronic configurations of ${}_{11}Na^+$ and ${}_{12}Mg^+$ are $(1s)^2(2s)^2(2p)^6$ and $(1s)^2(2s)^2(2p)^6(3s)^1$, respectively. The second ionization means converting Na^+ to Na^{2+} and Mg^+ to Mg^{2+}. In Na^+, the removal of one electron from the stable noble gas configuration would be difficult as compared to Mg^+ which contains one extra electron.

(c) The electronic configurations of ${}_7N$ and ${}_8O$ are $(1s)^2(2s)^2(2p)^3$ and $(1s)^2(2s)^2(2p)^4$, respectively. Those of N^+ and O^+ are $(1s)^2(2s)^2(2p)^2$ and $(1s)^2(2s)^2(2p)^3$ respectively. The first ionization energy of nitrogen would be greater than oxygen, as half-filled configuration is more stable. The second ionization energy of oxygen would be greater than nitrogen as O^+ has more stable (half-filled) electronic configuration.

(d) The correct order is Cl > F > Br. The larger electronic repulsion in F atom due to its small size is responsible for lesser electron affinity in F atom than in Cl atom.

15. The electronic configurations are as follows.

(a) ${}_{20}Ca$ $(4s)^2$ and ${}_{19}K$ $(4s)^1$. In calcium, electron is to be removed (i) from fully-filled s orbital, and (ii) against larger nuclear charge.

12. (b) ${}_{12}Mg$ $(3s)^2$ and ${}_{13}Al$ $(3s)^2\,(3p)^1$. Second ionization means the removal of the electron from $(3s)^1$ in Mg and $(3s)^2$ from Al. The latter will require larger energy due to (i) fully-filled s orbital and (ii) larger nuclear charge. Thus, aluminium will require larger energy.

(c) Be $(2s)^2$ and C $(2s)^2\,(2p^2)$. Third ionization for Be required more energy as the electron is to be removed from fully-filled inner orbital is

(d) N $(2s)^2\,(2p)^3$ and O $(2s)^2\,(2p)^4$. Second ionization requires more energy for oxygen due to the larger nuclear charge.

CHAPTER 5

BONDING AND MOLECULAR STRUCTURE

The formation of a chemical bond between two atoms implies that the system consisting of these two atoms at stable internuclear distance is energetically more stable than the two isolated atoms. A general study on the reactivity of different elements revealed that noble gases have little tendency to combine with other elements. This leads to the fact that the noble gases have stable outer configuration $(ns)^2(np)^6$ (octet configuration). All other atoms combine to achieve the stable octet configuration either by mutual sharing of electrons (covalent bond) or by complete transfer of electron(s) from one atom to other (ionic bond).

COVALENT BOND

Mutual sharing of electrons leads to the formation of covalent bond. A single bond is formed when a single pair of electrons is shared between two atoms, a double bond results when two pairs of electrons are shared and so on. After sharing, each atom has stable octet configuration. This type of bond is formed between two electronegative atoms. Examples include Cl_2, O_2, N_2, CO_2 and so on. Organic compounds also involve covalent bonds between atoms. The sharing of electrons may be shown by *Lewis structures*.

The octet rule holds, with several exceptions in the first two eight-membered periods of the periodic table. A few exceptions are $BeCl_2$, AlF_3, PF_5 and SF_6.

Polar Covalent Bond Because of the difference between the electronegativities of two atoms, the electron pair lies nearer to atom of higher electronegativity. Consequently, this atom acquires a partial negative charge and the other atom (with lesser electronegativity) acquires an equal positive charge. Such a distortion of charges gives rise to a polar covalent bond. The above polarization of bonded electrons is expressed quantitatively with a physical quantity, known as *dipole moment*, which is defined as

$$\boldsymbol{p} = \text{(partial charge on either atom) (distance between the two partial charges)} = (\delta q)r$$

The dipole moment is a vector quantity. Chemists often represent it by an arrow pointing towards the electron pull, i.e. from a lesser electronegative atom to a more electronegative atom. In SI units, the dipole moment has a unit of C m. In CGS units, the dipole moment is expressed in the unit of esu cm. The unit of 10^{-18} esu cm is known as the Debye unit (symbol: D) and its SI equivalent is

$$1\ \text{D} = 3.3356 \times 10^{-30}\ \text{C m}$$

The dipole moment of a molecule can be determined experimentally. This, in turn, can be used to determine the per cent ionic character of the molecule. For example, Hydrogen chloride has a dipole moment of 1.03 D. Had the molecule been 100% ionic, its dipole moment would have been

$$\begin{aligned}\boldsymbol{p}_{\text{ionic}} &= \text{(electronic charge) (bond distance of HCl)} = (4.8 \times 10^{-10}\ \text{esu})\ (127.5 \times 10^{-10}\ \text{cm})\\ &= 6.12 \times 10^{-18}\ \text{esu cm} \equiv 6.12\ \text{D}\end{aligned}$$

But the actual value of dipole moment is 1.03 D. So, its ionic character is

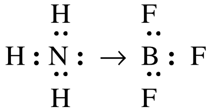
$$\text{Per cent ionic character} = \frac{\boldsymbol{p}_{\text{observed}}}{\boldsymbol{p}_{\text{ionic}}} \times 100 = \frac{1.03\ \text{D}}{6.12\ \text{D}} \times 100 \simeq 17$$

According to Pauling, the per cent ionic character of H–X bond may be computed from the expression $18(\chi_X - \chi_H)^{1.4}$, where χ_X and χ_H are the electronegativity values of atom X and hydrogen, respectively.

In a polyatomic molecule, the individual bonds may be polar, but the overall molecule may be polar or nonpolar. The dipole moment of the molecule is obtained by vector addition of bond moments. If the vector addition is zero, the molecule is nonpolar. A few examples of nonpolar molecules are CO_2, BCl_3, CCl_4, and SF_6. In these molecules, the individual bonds are symmertically arranged so as to give a net zero dipole moment.

COORDINATE BOND

If the pair of electrons shared between two atoms is exclusively contributed by one of the atoms, a coordinate bond is said to be formed. One of the examples is



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{F} & \\ & \cdot\cdot & & \cdot\cdot & \\ \mathrm{H}: & \mathrm{N} & :\rightarrow & \mathrm{B} & :\mathrm{F} \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{F} & \end{array}$$

Another example is NH_4^+ ion. Once the bond is formed, it is not possible to distinguish between the covalent and coordinate bond.

IONIC BOND

The second way of acquiring stable electronic configuration is through the complete transfer of valence electron(s) from one atom to the valence shell of another atom. The resultant positively and negatively charged species (known as cation and anion, respectively) is held together by electrostatic forces of attraction. This type of bond is formed between electropositive and electronegative atoms. Examples include NaCl, $MgCl_2$ and AlF_3.

QUANTUM MECHANICAL EXPLANATION OF COVALENT BOND

When two atoms are brought together upto the stable internuclear distance, there occurs an overlapping of an orbital of one of the atoms with the orbital of the second atom. If before overlapping, each of the involved orbitals contains one unpaired electron, then both the electrons couple with each other and thus belong to both the orbitals of both the two atoms. This is quantum mechanical explanation of the formation of covalent bond between the two atoms. The orbitals involved may be of s-s type, s-p type or p-p type. In the latter two types of overlap may occur. These are (a) end-to-end overlap leading to the formation of a σ bond and (b) side-ways overlap leading to the formation of a π bond.

Thus, the two essential conditions for the formation of a covalent bond are as follows.

1. The two involved atomic orbitals must have positive overlap with each other.
2. Each of the two involved atomic orbitals must possess one unpaired electron with an opposite spin, so that the two electrons involved in the bonding have opposite spins.

The essential criteria for the formation of a coordinate covalent bond will be as follows.

1. One of the atoms must possess an orbital containing a lone pair of electrons.
2. The second atom must possess an empty atomic orbital.
3. The two atomic orbitals mentioned in the above two conditions should have a positive overlap at the stable internuclear distance.

HYBRIDIZATION

As per quantum mechanical explanation of covalent bond formation, an atom can form as many covalent bonds as the number of its orbitals, each possessing one electon. This does not explain the bivalency of Be ($1s^22s^2$), trivalency of boron ($1s^22s^22p^1$) and tetravalency of carbon ($1s^22s^22p_x^12p_y^1$). To explain this as well as the geometry of the molecules formed by these atoms, the process of hybridization has been developed. In this process, two or more orbitals of the same atom combine to give the same number of equivalent orbitals, known as *hybrid orbitals*. The latter are completely identical in size, shape, orientation and energy. During the hybridization, no gain or loss of energy takes place. Each of the hybrid orbitals contains one electron and can overlap with the pure or hybrid orbital of the other atom to form a covalent bond.

Table 5.1 includes some of the characteristics of hybrid orbitals.

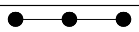
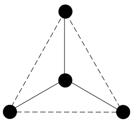
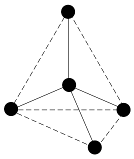
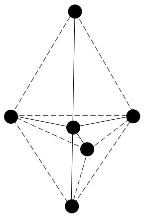
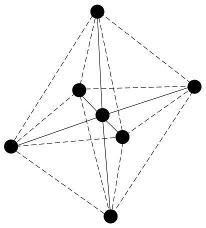
VALENCE SHELL ELECTRON-PAIR-REPULSION MODEL

A simple theory to account for the molecular shape of covalent molecules was developed by Gillespie and Nyholm. This theory is known as VSEPR(abbreviation of valence shell electron-pair repulsion). It predicts the shape of a molecule by considering the most stable configuration of the bond angles in the molecule. The guiding rules of this theory are as follows.

Table 5.1 Characteristics of Hybrid Orbitals

Types of Atomic Orbitals	*Number and Type of Hybrid Orbitals*	*Directional Characteristics*	*Examples*
s + p	2, sp	Linear, bond angle 180°	BeH_2, CO_2, HCN, C_2H_2
s + 2p	3, sp^2	Triangular planar, bond angle 120°	BCl_3, SO_2, C_2H_4
s + 3p	4, sp^3	Tetrahedral, bond angle 109° 28'	CH_4, NH_3, H_2O, NH_4^+, ClO_3^-, SO_4^{2-}
$d_{x^2-y^2}$ + s + 2p	4, dsp^2	Square planar, bond angle 90°	$Cu(NH_3)_4^{2+}$
s + 3p + d_{z^2}	5, sp^3d	Trigonal bipyramidal	PF_5, PCl_5
s + 3p + $d_{x^2-y^2}$ + d_{z^2}	6, sp^3d^2	Octahedral	SF_6, AlF_6^{3-}

Table 5.2 Shapes of Some Molecules on the Basis of VSEPR Model

	Number of Valence				*Basic*	
Molecule	*Electrons around the Central Atom*	*Electron Pair*	*Bonding Pairs*	*Lone Pairs*	*Shape**	
(i) $BeCl_2$	4	2	2	0	Linear	
(ii) BCl_3	6	3	3	0	Triangular Planar	
(iii) CH_4 NH_3 H_2O	8 8 8	4 4 4	4 3 2	0 1 2	Tetrahedron	
(iv) PF_5 SF_4 ClF_3	10 10 10	5 5 5	5 4 3	0 1 2	Trigonal Bipyramid	
(v) SF_6 IF_5	12 12	6 6	6 5	0 1	Octahedron	

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* The actual shapes of the molecules containing lone pairs is a little distorted from the basic shape. This is due to the fact that lone pair-bonded pair repulsion is larger than bonded pair-bonded pair repulsion.

1. Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs, are regarded as occupying localized orbitals around the atom. These orbitals arrange themselves in space so as to minimize the mutual electronic repulsions.

2. The different types of electronic repulsion follow the order given below.

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

The shapes of the molecules as predicted by VSEPR model are shown in Table 5.2.

HYDROGEN BOND

A bond between a hydrogen atom and a highly electronegative atom of small size (e.g. F, N, O) is a polar bond in which hydrogen atom acquires a small positive charge while the electronegative atom acquires small negative charge. This hydrogen atom can get attached to the electronegative atom of other molecule carrying a lone pair of electrons due to the electrostatic attractions. This type of interaction is known as hydrogen bond. Since the lone pair has directional characteristics, the hydrogen bond is also directional in nature. This is shown in Fig. 5.1 where hydrogen bonds in solid water are displayed.

A hydrogen bond may be intramolecular or intermolecular. In the former, the hydrogen atom is attached to the electronegative atom belonging to the same molecule whereas in the latter, it is attached to the electronegative atom of some other molecules. Examples are *o*-nitrophenol and *p*-nitrophenol (Fig. 5.2).

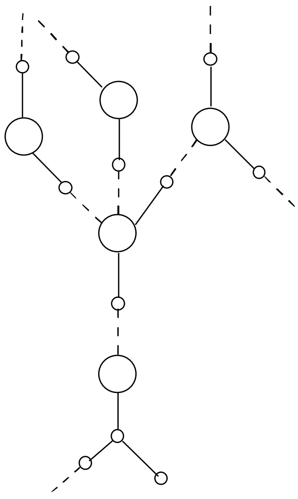


Fig. 5.1 Hydrogen Bonding in Ice

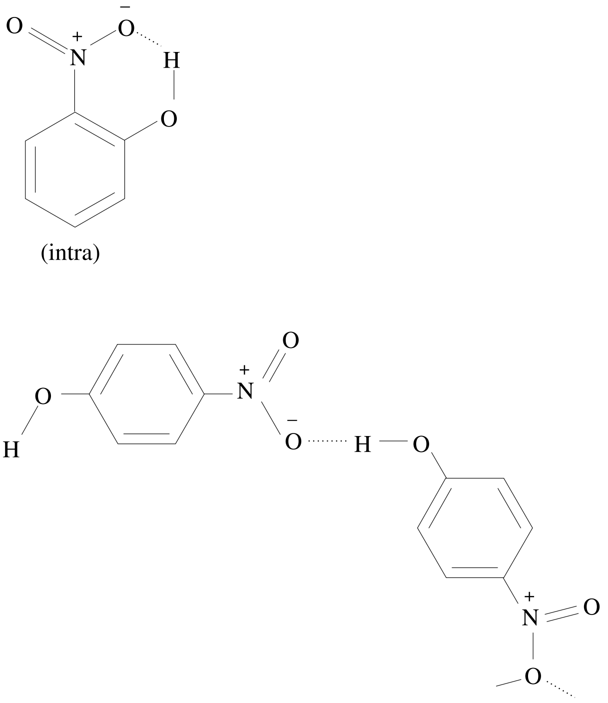
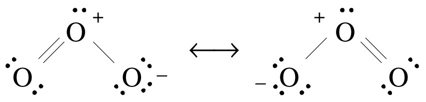


Fig. 5.2 Intra-and Inter-Molecular Hydrogen Bondings

The hydrogen bonding affects the properties of a substance to a large extent. For example, the boiling point of water is much more than hydrogen sulphide.

RESONANCE

The term resonance means the use of two or more Lewis structures to represent a particular molecule. A single structure cannot account satisfactorily the experimental characteristics of the molecule. One has to consider all the resonating structures together to explain the characteristics. For example, ozone may be represented by the following two resonating structures.



The actual structure of ozone is the resonance hybrid of the two resonating structures. This is established from the fact that both the oxygen-oxygen bond lengths in ozone are identical.

MOLECULAR ORBITAL METHOD

Like atomic orbitals in an atom, there exist molecular orbitals in a molecule. These molecular orbitals belong to whole of the molecule. Electrons in these molecular orbitals are distributed by following aufbau principle, Pauli exclusion principle and Hund's rule.

One of the methods to construct molecular orbitals is the linear combination of atomic orbitals (the abbreviation is LCAO). For example, the ground-state molecular orbital of hydrogen molecule is written as

$$\psi_{\mathrm{MO}} = C_1\, \psi_{1\mathrm{s}(\mathrm{H_a})} + C_2\, \psi_{1\mathrm{s}(\mathrm{H_b})}$$

It can be shown that the combination of two atomic orbitals gives two molecular orbitals; one involves positive combination, whereas the other involves negative combination. Of these, one involving positive overlap gives a molecular orbital which is more stable than the stabler of the two atomic orbitals and the second one involving negative overlap gives a molecular orbital which is lesser stable than the less stable atomic orbital. The former is known as *bonding* molecular orbital and the latter as *antibonding* molecular orbital.

For homonuclear diatomic molecules involving atoms of the second period, one can construct molecular orbitals from the following combinations.

Combination involving 2s(A) and 2s(B)

Combination involving $2p_z$(A) and $2p_z$(B)

Combination involving $2p_x$(A) and $2p_x$(B)

Combination involving $2p_y$(A) and $2p_y$(B)

The end-to-end overlap leads to σ molecular orbital and side-ways overlap leads to π molecular orbital. Thus, the above combinations lead to $\sigma 2s$, σ^*2s, $\sigma 2p_z$, σ^*2p_z, $\pi 2p_x$, π^*2p_x, $\pi 2p_y$ and π^*2p_y molecular orbitals, where the orbital with an asterisk represents antibonding molecular orbital. Because of small energy difference between 2s and 2p orbitals, both of them participate jointly in the chemical combination, i.e. a σ2p orbital has some contribution from 2s atomic orbital and σ2s orbital has some contribution from 2p atomic orbital. The relative order of increasing energies of molecular orbital is as follows.

$$E(\sigma 2s) < E(\sigma^*2s) < E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p_z) < E(\pi^*2p_x) = E(\pi^*2p_y) < E^*(\sigma^*2p_z)$$

The above order is valid from Li_2 to N_2 and for O_2 and F_2, the following sequence is observed.

$$E(\sigma 2s) < E(\sigma^*2s) < E(\sigma 2p_z) < E(\pi 2p_x) = E(\pi 2p_y) < E(\pi^*2p_x) = E(\pi^*2p_y) < E(\sigma^*2p_z)$$

The electronic configuration of a molecule can be written following aufbau principle, Pauli's exclusion principle and Hund's rule. For example, the electronic configuration of O_2 which contains 12 valence electrons is

$$(\sigma 2s)^2\, (\sigma^*2s)^2\, (\pi 2p_x)^2\, (\pi 2p_y)^2\, (\sigma 2p_x)^2\, (\pi^*2p_x)^1\, (\pi^*2p_y)^1$$

The characteristics of a molecule can be predicted by using the following facts.

1. The strength of a bond depends on the net excess electrons in bonding orbitals over those of antibonding orbitals. Larger the bond strength, larger the dissociation energy of the molecule.
2. The number of bonds in a molecule is one-half of the net excess of the bonding electrons. The physical quantity to define this is the bond order:

$$\text{Bond order} = \frac{\text{Number (bonding – antibonding) electrons}}{2}$$

3. The addition of an electron in the bonding orbital makes the molecule more stable, whereas that in the antibonding orbital makes it less stable.
4. The removal of an electron from the bonding molecular orbital makes the molecule less stable and from antibonding orbital makes it more stable.
5. Paramagnetism in a substance is due to the presence of unpaired electron(s) in its molecule.
6. The bond length of a molecule is inversely related to its bond order.

Straight Objective Type

General Characteristics

1. The compound with no dipole moment is
(a) methyl chloride (b) carbon tetrachloride (c) methylene chloride (d) chloroform (1982)

2. Carbon tetrachloride has no net dipole moment because of
(a) its planar structure (b) its regular tetrahedral structure
(c) similar sizes of carbon and chlorine atoms (d) similar electron affinities of carbon and chlorine (1983)

3. Which one among the following does not have the hydrogen bond?
(a) Phenol (b) Liquid NH_3 (c) Water (d) Liquid HCl (1983)

4. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only
(a) electrovalent and covalent (b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent (d) covalent and coordinate covalent (1983)

5. The molecule having one unpaired electron is
(a) NO (b) CO (c) CN^- (d) O_2 (1985)

6. The bond between two identical nonmetal atoms has a pair of electrons
(a) unequally shared between the two (b) transferred fully from one atom to another
(c) with identical spins (d) equally shared between them. (1986)

7. The hydrogen bond is strongest in
(a) O—H ··· S (b) S—H ··· O (c) F—H ··· F (d) F—H ··· O (1986)

8. The bonds present in N_2O_5 are
(a) only ionic (b) covalent and coordinate
(c) only covalent (d) covalent and ionic (1986)

9. The ion that is isoelectronic with CO is
(a) CN^- (b) O_2^+ (c) O_2^- (d) N_2^+

10. The molecule which has zero dipole moment is
(a) CH_2Cl_2 (b) BF_3 (c) NF_3 (d) ClO_2 (1989)

11. The maximum number of hydrogen bonds a water molecule can form is
(a) 2 (b) 4 (c) 3 (d) 1 (1992)

12. The octet rule is not obeyed by the molecule
(a) CO_2 (b) H_2O (c) O_2 (d) CO (1979)

13. The order of strength of hydrogen bonds is
(a) ClH···Cl > NH···N > OH···O > FH···F (b) ClH···Cl < NH···N < OH···O < FH···F
(c) ClH···Cl < NH···N > OH···O > FH···F (d) ClH···Cl < NH···N < OH···O > FH···F

14. *o*-nitrophenol is more volatile than *p*-nitrophenol. It is due to
(a) intramolecular hydrogen bonding in *o*-nitrophenol and intermolecular hydrogen bonding in *p*-nitrophenol
(b) intermolecular hydrogen bonding in *o*-nitrophenol and intramolecular hydrogen bonding in *p*-nitrophenol
(c) more stronger intramolecular hydrogen bonding in *o*-nitrophenol as compared to *p*-nitrophenol.
(d) more stronger intermolecular hydrogen bonding in *o*-nitrophenol as compared to *p*-nitrophenol.

15. Per cent ionic character is maximum in
(a) H—F (b) H—Cl (c) H—Br (d) H—I

16. Which of the following statements is correct for carbon monoxide?
(a) A double bond between carbon and oxygen
(b) 1σ, 1π and 1 coordinate bond between carbon and oxygen
(c) One lone pair of electrons only on oxygen atom
(d) 1σ and 2π bonds between carbon and oxygen.

17. Most favourable conditions for the formation of ionic bonds are
(a) large cation and small anion (b) large cation and large anion
(c) small cation and small anion (d) small cation and large anion

18. Which of the following combinations would lead to a covalent bond?
(a) electronegative element + electropositive element
(b) electronegative element + electronegative element
(c) electropositive element + elecropositive element
(d) inert gas + electropositive element.

19. The bonds present in N_2O_4 are
(a) only ionic (b) covalent and coordinate
(c) only covalent (d) covalent and ionic

20. Most favourable conditions to form a covalent bond is
(a) large cation and small anion (b) large cation and large anion
(c) small cation and small anion (d) small cation and large anion

21. The molecule having nonzero dipole moment is
(a) CH_4 (b) BF_3 (c) NF_3 (d) CO_2

22. Which of the following statements regarding valence-bond method is **not** true?
(a) The molecule is considered to be the collection of atoms and then interactions between different atoms is considered.
(b) For a molecule to be stable, the electrostatic attractions must predominate over the repulsions
(c) The potential energy of a diatomic molecule is less than the sum of potential energies of free atoms
(d) The net force of attraction acting on the atoms in a molecule is not zero.

23. Which of the following resonating structures is **not** correct for CO_2?
(a) $:\ddot{O}=C=\ddot{O}:$ (b) $^{-}:\overset{..}{\underset{..}{O}}-C\equiv O:^{+}$ (c) $^{+}:\ddot{O}-C\equiv\ddot{O}:^{-}$ (d) $:^{+}O\equiv C-\overset{..}{\underset{..}{O}}:^{-}$

24. Which of the following contains both polar and non-polar bonds?
(a) NH_4Cl (b) HCN (c) H_2O_2 (d) CH_4 (1997)

25. The dipole moment of hydrogen chloride is 1.03 D. Its per cent ionic character is about 17%. Its bond distance in pm is about
(a) 150 (b) 127 (c) 190 (d) 210

26. *o*-Nitrophenol is more volatile than *p*-nitrophenol. It is due to
(a) intermolecular hydrogen bond in *o*-nitrophenol (b) intramolecular hydrogen bond in *o*-nitrophenol
(c) ionization of *p*-nitrophenol (d) more resonating structures of *p*-nitrophenol

27. The hydration energy of Mg^{2+} is larger than that of
(a) Al^{3+} (b) Na^+ (c) Be^{2+} (d) Ca^{2+} (1984)

28. The cyanide ion, CN^- and N_2 are isoelectronic. But in contrast to CN^-, N_2 is chemically inert, because of
(a) low bond energy (b) absence of bond polarity
(c) unsymmetrical electron distribution (d) presence of more number of electrons in bonding orbitals. (1992)

29. Which of the following statements is correct for $CsBr_3$?
(a) It is a covalent compound. (b) It contains Cs^{3+} and Br^- ions.
(c) It contains Cs^+ and Br_3^- ions. (d) It contains Cs^+, Br^- and lattice Br_2 molecule. (1996)

30. KF combines with HF to form KHF_2. The compound contains the species:
(a) K^+, F^- and H^+ (b) K^+, F^- and HF (c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^- (1996)

31. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^- (c) KO_2 only (d) BaO_2 only (1997)

32. The correct order of increasing C—O bond length of CO, CO_3^{2-}, CO_2 is
(a) $CO_3^{2-} < CO_2 < CO$ (b) $CO_2 < CO_3^{2-} < CO$
(c) $CO < CO_3^{2-} < CO_2$ (d) $CO < CO_2 < CO_3^{2-}$ (1999)

33. The geometry of H_2S and its dipole moment are
(a) angular and nonzero (b) angular and zero
(c) linear and nonzero (d) linear and zero (1999)

34. Which of the following facts is correct?
(a) $N(CH_3)_3$ is nonplanar and $N(SiH_3)_3$ is planar (b) $N(CH_3)_3$ is planar and $N(SiH_3)_3$ is nonplanar
(c) Both $N(CH_3)_3$ and $N(SiH_3)_3$ are planar (d) Both $N(CH_3)_3$ and $N(SiH_3)_3$ are nonplanar

VSEPR and Hybridization

35. The hybridization in sulphur dioxide is
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2 (1986)

36. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is
(a) PH_3 (b) NH_3 (c) CH_3^+ (d) SbH_3 (1988)

37. Among the following, the molecule that is linear is
(a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2 (1988)

38. The molecule which has a pyramidal shape is
(a) PCl_3 (b) SO_3 (c) CO_3^{2-} (d) NO_3^- (1989)

39. The linear structure is assumed by
(a) $SnCl_2$ (b) NCO^- (c) NO_2^+ (d) SO_2 (1991)

40. The type of hybrid orbitals used by chlorine atom in ClO_2^- is
(a) sp^3 (b) sp^2 (c) sp (d) dsp^2 (1992)

41. The state of hybridization of oxygen in OF_2 is
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

42. Hybridization involves
(a) mixing of atomic orbitals centred on the same atom
(b) mixing of atomic orbitals centred on the different atoms
(c) addition of an electron to an atom
(d) addition of an electron pair to an atom.

43. Which of the following molecules has a tetrahedral shape?
(a) $HgCl_2$ (b) CO_2 (c) NH_4^+ (d) $Ni(CN)_4^{2-}$

44. The compound in which $\underline{C}$ uses its sp^3 hybrid orbitals in bonding is
(a) $H\underline{C}OOH$ (b) $(H_2N)_2\underline{C}O$ (c) $(CH_3)_3\underline{C}OH$ (d) $CH_3\underline{C}HO$

45. According to the VSEPR theory, the geometry of the molecule OF_2 would be
(a) linear (b) square planar (c) tetrahedral (d) octahedral

46. The bonding of S in SCl_4 molecule involves
(a) sp orbitals (b) sp^2 orbitals (c) dsp^3 orbitals (d) dsp^2 orbitals

47. The structure of XeF_2 is
(a) square planar (b) tetrahedral (c) octahedral (d) trigonal bipyramidal

48. According to the VSEPR theroy, the arrangement of lone pairs of an atom containing a total of four such pairs is
(a) linear (b) tetrahedron (c) square planar (d) octahedron

49. According to the VSEPR theory, the arrangement of lone pairs of an atom containing a total of three such pairs is
(a) linear (b) trigonal planar (c) tetrahedron (d) octahedron

50. According to the VSEPR theory, the arrangement of lone pairs of an atom containing a total of five such pairs is
(a) triangular planar (b) trigonal bibyramid (c) tetrahedron (d) octahedron

51. According to the VSEPR theory, the molecule IF_5 has a shape of
(a) trigonal pibyramid (b) tetrahedron (c) octahedron (d) pentagonal bipyramid

52. Which of the following compounds has sp^2 hybridisation?
(a) CO_2 (b) SO_2 (c) N_2O (d) CO (1997)

53. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is
(a) H_2CO_3 (b) SiF_4 (c) BF_3 (d) $HClO_2$ (1997)

54. Molecular shapes of SF_4, CF_4 and XeF_4 are
(a) the same, with 2, 0 and 1 lone pair of electrons, respectively.
(b) the same, with 1, 1 and 1 lone pair of electrons, respectively
(c) different, with 0, 1 and 2 lone pair of electrons, respectively
(d) different with 1, 0 and 2 lone pair of electrons, respectively (2000)

55. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
(a) sp, sp^3 and sp^2 respectively (b) sp, sp^2 and sp^3 respectively (2000)
(c) sp^2, sp and sp^3 respectively (d) sp^2, sp^3 and sp respectively

56. The bonding of S with Cl in SCl_2 molecule involves
(a) sp orbitals (b) sp^2 orbitals (c) sp^3 orbitals (d) sp^3d orbitals

57. The geometry arrangement of CN groups around Ni in $[Ni(CN)_4]^{2-}$ is
(a) tetrahedron (b) square planar (c) trigonal bipyramid (d) octahedran

58. Which of the following species does not involve tetrahedral structure?
(a) SO_4^{2-} (b) SF_4 (c) SeO_4^{2-} (d) SO_2Cl_2

59. Which of the following species involves sp^2 hybridization?
(a) CO_2 (b) N_2O (c) SO_2 (d) H_2S

60. The species ClO_2^- involves
(a) sp hybridization (b) sp^2 hybridization (c) sp^3 hybridization (d) dsp^2 hybridization

61. Which of the following species involves sp^3 hybridization?
(a) PCl_3 (b) SO_3 (c) NO_4^- (d) BF_3

62. The species ClO_3^- involves
(a) sp hybridization (b) sp^2 hybridization (c) sp^3 hybridization (d) dsp^3 hybridization

63. Which of the following statements is correct?
(a) BF_3 involves sp^3 hybridization and NF_3 involves sp^2 hybridization
(b) BF_3 involves sp^2 hybridization and NF_3 involves sp^3 hybridization
(c) Both BF_3 and NF_3 involve sp^3 hybridization
(d) Both BF_3 an^d NF_3 involve sp^2 hybridization

64. The hybridization in OF_2 is
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

65. Which of the following species involves the smallest bond angle?
(a) NH_3 (b) H_2O (c) BeF_2 (d) CH_4

66. Which of the following species involves the largest bond angle?
(a) H_2Se (b) H_2S (c) H_2O (d) SO_2

67. The bond angle in PH_3 is expected to be
(a) 90° (b) 105° (c) 109° (d) 120°

68. On hybridization of one s and one p orbitals, we get
(a) two mutually perpendicular orbitals (b) two orbitals at 180°
(c) four orbitals directed tetrahedrally (d) three orbitals in a plane. (1984)

69. Among the following species, identify the isostructural pairs. NF_3, NO_3^-, BF_3, H_3O^+, HN_3
(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$ (b) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(d) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$ (d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$ (1996)

70. The geometry and the type of hybrid orbitals present about the central atom in BF_3 is
(a) linear, sp (b) trigonal planar, sp^2 (c) tetrahedral, sp^3 (d) pyramidal, sp^3 (1998)

71. The correct order of hybridisation of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is
(a) dsp^2, dsp^3, sp^2 and sp^3 (b) sp^3, dsp^2, dsp^3, sp^2
(c) dsp^2, sp^2, sp^3, dsp^3 (d) dsp^2, sp^3, sp^2, dsp^3 (2001)

72. Specify the coordination geometry around and hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3 (b) N : pyramidal, sp^3 ; B : pyramidal, sp^3
(c) N : pyramidal, sp^3 ; B : planar, sp^2 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3 (2002)

73. Total number of lone pair of electrons in XeF_4 is
(a) 0 (b) 1 (c) 2 (d) 3 (2004)

74. Which of the following contains maximum number of lone pairs of electrons on the central atom?
(a) ClO_3^- (b) XeF_4 (c) I_3^- (d) SF_4 (2005)

75. The percentage of p-character in the orbitals forming P—P bonds in P_4 is
(a) 25 (b) 33 (c) 50 (d) 75 (2007)

76. The hybridization involved in the molecules PCl_5 and BrF_5, respectively, are
(a) dsp^3, dsp^3 (b) dsp^3, d^2sp^3 (c) d^2sp^3, dsp^3 (d) d^2sp^3, d^2sp^3

77. The hybridization involved in the molecules OSF_4 and $XeOF_4$, respectively, are
(a) sp^3d and sp^3d^2 (b) sp^3d^2, sp^3d (c) sp^3d and sp^3d (d) sp^3d^2, sp^3d^2

78. Which of the following facts is correct?
(a) NF_3 is nonpolar and BF_3 is polar (b) NF_3 is polar and BF_3 is nonpolar
(c) Both NF_3 and BF_3 are polar (d) Both NF_3 and BF_3 are nonpolar

79. The bond angles in NO_2^+, NO_2 and NO_2^- follow the order
(a) $NO_2^+ > NO_2 > NO_2^-$ (b) $NO_2^+ > NO_2^- > NO_2$
(c) $NO_2 > NO_2^+ > NO_2^-$ (d) $NO_2 > NO_2^- > NO^+$

80. Which of the following pairs is isostructural?
(a) I_3^-, XeF_2 (b) I_3^-, ClO_3^- (c) I_3^-, PO_4^{3-} (d) XeF_2, ClO_3^-

81. Hybridization of nitrogen atomic orbitals in nitrate anion is
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

Molecular Orbital Method

82. Which of the following is paramagnetic?
(a) O_2^- (b) CN^- (c) CO (d) NO^+ (1989)

83. Which one of the following statements is correct?
(a) Molecular hydrogen is paramagnetic (b) Molecular nitrogen is paramagnetic
(c) Molecular oxygen is paramagnetic (d) Molecular oxygen is diamagnetic

84. Which of the following species is **not** paramagnetic?
(a) B_2 (b) N_2^+ (c) O_2 (d) N_2

85. Which of the following species is **not** diamagnetic?
(a) N_2 (b) F_2 (c) Li_2 (d) O_2

86. Which of the following molecules is paramagnetic?
(a) C_2 (b) N_2 (c) O_2 (d) F_2

87. In which of the following species, the bond length is expected to be the largest?
(a) O_2^{2-} (b) O_2^- (c) O_2 (d) O_2^+

88. The bond order of O_2 molecule is
(a) 1.5 (b) 2 (c) 2.5 (d) 3

89. The bond order of N_2 molecule is
(a) 1.5 (b) 2 (c) 2.5 (d) 3

90. The number of molecular orbitals obtained by mixing two atomic orbitals from each of the two atoms is
(a) 2 (b) 3 (c) 4 (d) 6

91. Which of the following statements is not correct from the viewpoint of molecular orbital?
(a) Be_2 is not a stable molecule
(b) He_2 is not stable but He^+ is expected to exist
(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules
(d) The order of energies of molecular orbitals in F_2 molecule is
$E(\sigma 2s) < E(\sigma^* 2s) < E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p_z) < E(\pi^* 2p_x) = E(\pi^* 2p_y) < E(\sigma^* 2p_z)$

92. Which of the following orders regarding the bond order is correct?
(a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$ (c) $O_2^- > O_2 < O_2^+$ (d) $O_2^- < O_2 > O_2^+$

93. Which of the following orders regarding the bond length is correct?
(a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$ (c) $O_2^- > O_2 < O_2^+$ (d) $O_2^- < O_2 > O_2^+$

94. The number of bonds in nitrogen molecule is
(a) one σ and one π (b) one σ and two π (c) two σ and one π (d) three σ

95. The bond order of the superoxide (O_2^-) is
(a) 1 (b) 1.5 (c) 2 (d) 2.5

96. Which of the following molecules has unpaired electrons in antibonding molecular orbitals?
(a) O_2 (b) N_2 (c) C_2 (d) B_2

97. The molecular electronic configuration of B_2 is
(a) KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$ (b) KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2$
(c) KK $(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2$ (d) KK $(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^1(\pi 2p)^1$

98. Which of the following order to energies of molecular orbitals of N_2 is correct?
(a) $E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p) < E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(b) $E(\pi 2p_x) = E(\pi 2p_y) > E(\sigma 2p) > E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(c) $E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p) > E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(d) $E(\pi 2p_x) = E(\pi 2p_y) > E(\sigma 2p) < E(\pi^* 2p_x) = E(\pi^* 2p_y)$

99. Which of the following order of energies of molecular orbitals of O_2 is correct?
(a) $E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p) < E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(b) $E(\pi 2p_x) = E(\pi 2p_y) > E(\sigma 2p) > E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(c) $E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p) > E(\pi^* 2p_x) = E(\pi^* 2p_y)$
(d) $E(\pi 2p_x) = E(\pi 2p_y) > E(\sigma 2p) < E(\pi^* 2p_x) = E(\pi^* 2p_y)$

100. Which of the following facts regarding change in bond length is correct?
(a) increases in going from N_2 to N_2^+, decreases in going from O_2 to O_2^+
(b) decreases in going from N_2 to N_2^+ increases in going from O_2 to O_2^+
(c) increases in going from N_2 to N_2^+ and O_2 to O_2^+
(d) decreases in going from N_2 to N_2^+ and O_2 to O_2^+

101. Which of the following orders is correct for the bond dissociation energy of O_2, O_2^-, O_2^- and O_2^{2-}?
(a) $O_2^+ > O_2 > O_2^- > O_2^{2-}$ (b) $O_2^+ > O_2 < O_2^- < O_2^{2-}$
(c) $O_2^+ < O_2 < O_2^- < O_2^{2-}$ (d) $O_2^+ > O_2 > O_2^- > O_2^{2-}$

102. Which of the following species has the shortest bond length?
(a) N_2^+ (b) N_2 (c) N_2^- (d) N_2^{2-}

103. The number and type of bonds between two carbon atoms in CaC_2 are:
(a) one sigma (σ) and one pi (π) bonds (b) one sigma (σ) and two pi (π) bonds
(c) one sigma (σ) and one and a half pi (π) bonds (d) one sigma (σ) bond. (1996)

104. The common features among the species CN^-, CO and NO^+ are
(a) bond order three and isoelectronic (b) bond order three and weak field ligands
(c) bond order two and π-acceptors (d) isoelectronic and weak field ligands (2001)

105. Which of the following molecular species has unpaired electron(s)?
(a) N_2 (b) F_2 (c) O_2^- (d) O_2^{2-} (2002)

106. 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 σ-bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ-bond (2002)

107. Which of the following statements regarding O_2^- is correct?
(a) paramagnetic, bond order greater than that of O_2
(b) paramagnetic, bond order lesser than that of O_2
(c) paramagnetic, bond order is equal to that of O_2
(d) diamagnetic, bond order greater than that of O_2 (2004)

108. Among the following, the paramagnetic compound is
(a) Na_2O_2 (b) O_3 (c) N_2O (d) KO_2 (2007)

109. The species having bond order different from that in CO is
(a) NO^- (b) NO^+ (c) CN^- (d) N_2 (2007)

110. The increasing bond length of O—O bond in O_2, $O_2[AsF_6]$, and KO_2 is
(a) $O_2[AsF_6] < KO_2 < O_2$ (b) $O_2[AsF_6] < O_2 < KO_2$
(c) $KO_2 < O_2[AsF_6] < O_2$ (d) $KO_2 < O_2 < O_2[AsF_6]$

111. Which of the following pairs have identical bond order?
(a) CN^- and O_2^- (b) CN^- and NO^+ (c) CN^- and O_2^+ (d) NO^+ and O_2^+

Multiple Correct Choice Type

1. Carbon dioxide is isostructural with
(a) $HgCl_2$ (b) $SnCl_2$ (c) C_2H_2 (d) NO_2 (1986)

2. Which of the following have identical bond order?
(a) CN^- (b) O_2^- (c) NO^+ (d) CN^+ (1992)

3. Pick out the isoelectronic structures from the following:
I. CH_3^+ II. H_3O^+ III. NH_3 IV. CH_3^-
(a) I and II (b) III and IV (c) I and III (d) II, III and IV (1993)

4. Which of the following statements are correct?
(a) Linear overlap of two atomic p-orbitals leads to a sigma bond.
(b) The bond angle H—N—H in NH_3 is greater than the bond angle H—As—H in AsH_3.
(c) Anhydrous HCl is a band conductor of electricity but aqueous HCl is a good conductor.
(d) *o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not.

5. Which of the following statements are **not** correct?
(a) All molecules with polar bonds have dipole moment.
(b) $SnCl_2$ is a nonlinear molecule.
(c) Intramolecular hydrogen bond is present between two different molecules.
(d) Intermolecular hydrogen bond is present within the molecule.

6. Which of the following statements are **not** correct?
(a) Hybrid orbitals are obtained by mixing orbitals in CO molecule.
(b) Octet rule is not followed in CO molecule.
(c) The hydrogen bond is simply an electrostatic bond with no directional characteristics.
(d) SO_2 molecule has zero dipole moment.

7. Which of the following statements are **not** correct?
(a) Hydrogen bonds are not present amongst gaseous hydrogen fluoride.
(b) Both SO_4^{2-} and SO_3^{2-} have tetrahedral geometry.
(c) In ozone both the bond lengths between oxygen atoms are not identical because it contains one double bond and one coordinate-covalent bond.
(d) In CO_3^{2-}, all the three carbon-oxygen bond length are identical.

8. Which of the following statements are **not** correct?
(a) Beryllium, like nitrogen, forms diatomic molecule Be_2.
(b) He_2 molecule does not exist but He_2^+ does exist.
(c) The dipole moment of CH_3F is greater than that of CH_3Cl.
(d) HBr is a stronger acid than HI because of hydrogen bonding.

9. Which of the following statements are **not** correct?
(a) The angle between two covalent bonds in CH_4, H_2O and CO_2 is maximum in CH_4.
(b) Pair of molecules (SiH_4, SiF_4; CH_3COCH_3 and $CHCl_3$, HCOOH and CH_3COOH) which forms strongest intermolecular hydrogen bonding is CH_3COCH_3 and $CHCl_3$.
(c) There are two π bonds in nitrogen molecule.
(d) sp^3 hybrid orbitals of nitrogen are involved in the formation of ammonium ions.

10. Which of the following statements are **not** correct?
(a) Sodium dissolved in liquid ammonia conducts electricity because of the presence of solvated electrons.
(b) The value of Debye unit of dipole moment in CGS units is 10^{-8} esu cm.
(c) The value of Debye unit of dipole moment in SI units is 3.34×10^{-30} C m
(d) The bond angle in BH_4^- is about 90°.

11. Which of the following statements are correct?
(a) The dipole moment of HCl is 1.03 D and its internuclear distance is 127.5 pm. Its per cent ionic character is about seventeen.
(b) The s character in sp orbitals is larger than in the sp^2 orbitals.
(c) The p character in sp orbitals is larger than in the sp^2 orbitals.
(d) The lone pair-bonding pair repulsion is larger than the bonding pair-bonding pair repulsion.

12. Which of the following statements are **not** correct?
(a) PF_5 contains five bonding pairs and zero lone pairs of electrons on phosphorus.
(b) The shape of ClF_3 is trigonal planar because it contain three bonding pairs and two lone pairs of electrons on chlorine.
(c) The shape of IF_5 is octahedron because it contains five bonding pairs and one lone pair of electrons on iodine.
(d) The bond angle HNH in NH_3 is smaller than that of HOH in H_2O.

13. Which of the following statements are **not** correct?
(a) Hydrogen bond has directional characteristics.
(b) *o*-Nitrophenol involves intermolecular hydrogen bonding while *p*-nitrophenol involves intramolecular hydrogen bonding.
(c) The dipole moment of NH_3 is greater than that of NF_3.
(d) The two lone pair(s) on Cl in ClF_3 occupy opposite directions.

14. Which of the following statements are correct?
(a) The shape of SF_4 is unsymmetrical tetrahedron.
(b) The shape of BrF_5 is square pyramidal.
(c) The lone pair on Br in BrF_5 occupies axial direction.
(d) The shape of XeF_4 is tetrahedral.

15. Which of the following statements are not correct?
(a) The shape of PCl_3 is trigonal pyramidal.
(b) The geometrical arrangement of electron pairs around Cl in ClO_2^- is square planar.
(c) The geometrical arrangement of electron pair around I in IF_4^- is octahedral.
(d) The geometrical arrangement of electron pairs around I in ICl_3 is trigonal planar.
(e) The geometrical arrangement of electron pairs on P in $POCl_3$ is tetrahedral.

16. Resonance structure of a molecule should have
(a) identical arrangement of atoms (b) nearly the same energy content
(c) the same number of paired electrons (d) identical bonding.

17. Which of the following have linear shape?
(a) N_2O (b) SO_2 (c) I_3^+ (d) I_3^-

18. Which of the following pairs are isostructural?
(a) $[NF_3, NO_3^-]$ (b) $[NF_3, H_3O^+]$ (c) $[NO_3^-, BF_3]$ (d) $[NF_3, HN_3]$

19. Which of the following pairs are isostructural?
(a) $[CO_3^{2-}, SO_3^{2-}]$ (b) $[XeF_2, IF_2^-]$ (c) $[NH_2^-, BeF_2]$ (d) $[SO_4^{2-}, BF_4^-]$

20. Which of the following repulsive interaction involving lone pair (lp) and bonding pair (bp) are correct?
(a) lp – lp > lp – bp (b) lp – lp < lp – bp (c) lp – lp > bp – bp (d) lp – bp > bp – bp

Linked Comprehension Type

The bonding in a molecule can be described by using molecular orbital theory. In this theory, electrons in a molecule are distributed amongst its molecular orbitals which are built as a linear combination of atomic orbitals of the constituent atoms of the molecule. Electrons are distributed by using aufbau principle, Hund's rule and Pauling exclusion principle. Based on this information, answer the following two sets of questions, each carrying three queries.

1. **(i)** In oxygen molecule, $\sigma 2p$ molecular orbital has lower energy than $\pi 2p$ orbitals. This is due to
(a) mixing of s and p orbitals of the two oxygen atoms
(b) nonmixing of s and p orbitals of the two oxygen atoms
(c) the inclusion of d orbitals in the molecular orbitals.
(d) electronic repulsion between the electrons of the two atoms.

(ii) Oxygen molecule is paramagnetic due to
(a) the presence of one unpaired electron in $\pi 2p_x$ orbital
(b) the presence of two unpaired electrons in the $\pi 2p_x$ and $\pi 2p_y$ orbitals
(c) the presence of one unpaired electron in the $\pi^* 2p_x$ or $\pi^* 2p_y$ orbital.
(d) the presence of one unpaired electron in each of the $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals.

(iii) The addition of one electron in O_2 gives O_2^- while the removal of one electron gives O_2^+. Which of the following facts is correct for O_2^+ and O_2^- species relative to O_2 molecule?

(a) Bond order increases in O_2^+ and decreases in O_2^-
(b) Bond order decreases in O_2^+ and increases in O_2^-
(c) Bond order decrease in both O_2^+ and O_2^-
(d) Bond order increase in both O_2^+ and O_2^-.

2. **(i)** In nitrogen molecule, σ2p molecular orbital has higher energy than π2p orbitals. This is due to

(a) mixing of s and p_z orbitals of the two nitrogen atoms
(b) nonmixing of s and p_z orbitals of the two nitrogen atoms
(c) the inclusion of 1s orbitals along with 2s and $2p_z$ orbitals
(d) electronic repulsion between the electrons of the two atoms.

(ii) Nitrogen molecule is

(a) paramagnetic with one unpaired electron
(b) paramagnetic with two unpaired electrons
(c) diamagnetic with four pairs of valence electrons in bonding orbitals and one in the antibonding orbital.
(d) diamagnetic with three pairs of valence electrons in bonding orbitals and two in the antibonding orbitals.

(iii) The addition of one electron in N_2 gives N_2^- while the removal of one electron gives N_2^+. Which of the following facts is correct for N_2^+ and N_2^- species relative to N_2 molecule?

(a) Bond order increases in N_2^+ and decreases in N_2^-
(b) Bond order decreases in N_2^+ and increases in N_2^-
(c) Bond order decrease in both N_2^+ and N_2^-
(d) Bond order increase in both N_2^+ and N_2^-

3. The per cent ionic character of a polar bond may be computed from the expression

$$\text{Per cent ionic character} = \frac{p_{\text{observed}}}{p_{\text{ionic}}} \times 100$$

where ***p*** stands for dipole moment. Based on the values of per cent ionic character computed by the above expression, Pauling obtained the expression

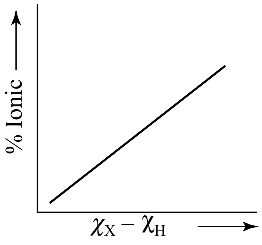
$$\text{Per cent ionic character} = 18\,(\chi_X - \chi_H)^{1.4}$$

where χ_X and χ_H are the electronegativity values of a halogen atom and H, respectively.
Based on this information, answer the following three questions

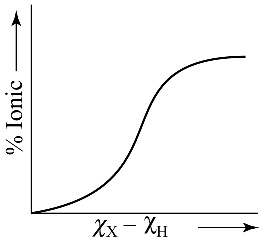
(i) Per cent ionic characters for HF, HBr and HI follow the order.

(a) HF < HBr < HI
(b) HF > HBr > HI
(c) HF > HI > HBr
(d) HI > HBr > HF

(ii) The variation of per cent ionic character and electronegativity difference for H—X (where X is halogen) is as shown in Figure.



(a)



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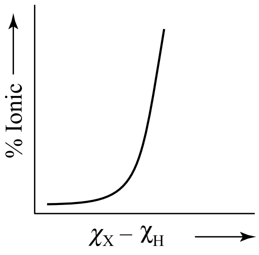

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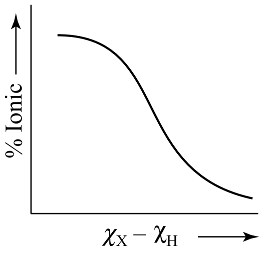


(d)

(iii) The value of $\chi_X - \chi_H$ for 50% ionic character in H—X bond as calculated from the expression described above is about

(a) 1.2
(b) 2.08
(c) 3.1
(d) 3.5

4. The structure of many compounds are explained on the formation of hybrid orbitals of the central atom. These involve s, p and d orbitals of the same atom and their appropriate mixing gives equivalent hybrid orbitals. Based on this information, answer the following three questions.

(i) dsp^2 hybridization leading to the square planar structure includes

(a) d_{xy} orbital (b) $d_{x^2-y^2}$ orbitals (c) d_{z^2} orbital (d) d_{xz} orbital

(ii) sp^3d hybridization leading to the trigonal bipyramidal structure includes

(a) d_{xy} orbital (b) d_{yz} orbital (c) d_{z^2} orbital (d) $d_{x^2-y^2}$ orbital

(iii) sp^3d hybridization leading to the square pyramidal structure includes

(a) d_{xy} orbital (b) d_{yz} orbital (c) d_{z^2} orbital (d) $d_{x^2-y^2}$ orbital.

5. VSEPR theory can predict the structures of inorganic compounds. The perfect structures are also distorted to some extent due to repulsion amongst the pairs of electrons. In general, the order of repulsion follows the order lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

Based on these information, answer the following three questions.

(i) In ClF_3, the chlorine orbitals undergo hybridization of the type

(a) sp^3 (b) dsp^2 (c) sp^3d (d) d^2sp^3

(ii) The shape of ClF_3 is

(a) square planar (b) trigonal planar (c) T-shape (d) tetrahedral

(iii) Which of the following statements is correct for ClF_3?

(a) All bond lengths Cl—F are identical

(b) All bond angles are identical

(c) Equatorial bonds are larger than apical bond

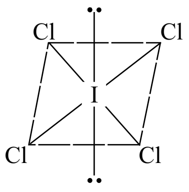
(d) Equatorial bonds are smaller than apical bond.

6. VSEPR theory helps understanding the structures of inorganic compounds. The regular geometry may be distorted due to repulsion between pairs of electrons. Based on this theory, answer the following three questions.

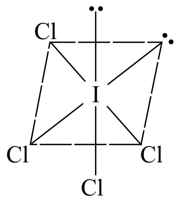
(i) The hybridization of iodine in ICl_4^- is

(a) sp^3 (b) dsp^2 (d) d^2sp^2 (d) d^2sp^3

(ii) The structure of ICl_4^- is



(a)



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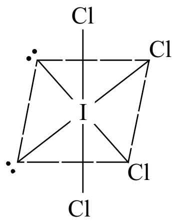

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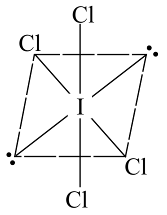
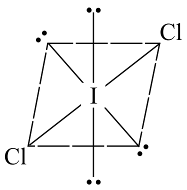
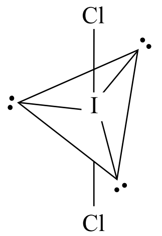


(d)

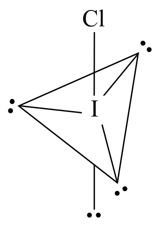
(iii) The structure of ICl_2^- is



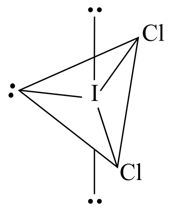
(a)



(b)



(c)

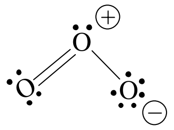
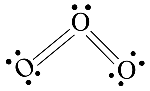


(d)

Assertion and Reason Type

The questions below consist of an '*Assertion*' in column 1 and the '*Reason*' in column 2. Use the following key to choose the appropriate answer.

(a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion.*
(b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
(c) If *assertion* is CORRECT, but *reason* in INCORRECT.
(d) If *assertion* is INCORRECT, but *reason* is CORRECT.

	Assertion (column I)	*Reason* (column II)
1.	In molecules Li_2, B_2, C_2 and N_2, the energy of σ2p molecular orbital is more than that of π2p orbitals.	σ2p orbitals is destabilized in comparison to π2p orbitals due to more strong electrostatic repulsion between electrons occupying σ2p and σ2s orbitals.
2.	In molecules O_2 and F_2, the energy of σ2p orbital is lesser than that of π2p orbitals.	The energy difference between 2s and 2p atomic orbitals in atoms is small so as to permit sp mixing in the formation of molecular orbitals.
3.	The bond angles in sp^3d hybrid orbitals have the same value.	The sp^3d hybridization leads to trigonal bipyramid geometry.
4.	The electronic structure of O_3 is 	 structure is not allowed because octet around O cannot be expanded.
5.	LiCl is predominantly a covalent compound.	Electronegativity difference between Li and Cl is too small.
6.	Band gap in germanium is small.	The energy spread of each germanium atomic energy level is infinitesimally small.
7.	Anhydrous $AlCl_3$ is covalent but in aqueous solution it is ionic.	Hydration energy is more than ionization energy.
8.	The density of water increases from 0°C to 4°C there after it decreases with increase in temperature	The density of liquid water is maximum at 4°C.
9.	The boiling point of *o*-nitrophenol is smaller than that of *p*-nitrophenol.	*o*-Nitrophenol involves intermolecular hydrogen bondings while *p*-nitrophenol involves intramolecular hydrogen bondings.
10.	$N(SiH_3)_3$ has a planar geometry while $N(CH_3)_3$ has a nonplanar geometry.	Nitrogen orbitals undergo sp^3 hybridization in both $N(CH_3)_3$ and $N(SiH_3)_3$ molecules.
11.	HF exists as gaseous form at room temperature.	Hydrogen bonding is present only when the substance exists as liquid or solid form.

Matrix Match Type

1. Match each of the diatomic molecule in Column I with its property/properties in Column II.

Column I	**Column II**
(a) B_2	(p) paramagnetic
(b) N_2	(q) undergoes oxidation
(c) O_2^-	(r) undergoes reduction
(d) O_2	(s) Bond order ≥ 2
	(t) Mixing of s and p orbitals

(2009)

2. Column I lists oxidation/reduction of O_2 and N_2. Column II lists some of the properties associated with these oxidation/reduction reactions. Match each entry of Column I with those listed in Column II.

Column I	**Column II**
(a) $N_2 \rightarrow N_2^+$	(p) Bond order increases
(b) $N_2 \rightarrow N_2^-$	(q) Bond order decreases
(c) $O_2 \rightarrow O_2^+$	(r) paramagnetism increases
(d) $O_2 \rightarrow O_2^-$	(s) paramagnetism decreases
	(t) no change in bond order

3. Column I lists some of hybridization schemes and Column II lists some of the compounds. Match each entry of Column I with the compounds mentioned in Column II.

Column I	**Column II**
(a) sp^3	(p) $Ni(CN)_4$
(b) dsp^2	(q) XeO_3
(c) dsp^3	(r) SO_3^{2-}
(d) d^2sp^3	(s) X_eF_2
	(t) XeF_4
	(u) XeO_2F_2

4. Column I lists some of the common geometries of inorganic species. Column II includes the list of inorganic species. Match correctly each entry of Column I with the examples listed in Column II.

Column I	**Column II**
(a) Linear	(p) CO_3^{2-}
(b) Bent	(q) I_3^-
(c) Tetrahedral	(r) O_3
(d) Planar	(s) XeF_2
	(t) OF_2
	(u) XeF_4
	(v) SO_3

ANSWERS

Straight Objective Type

1. (b)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (d)	**7.** (c)
8. (b)	**9.** (a)	**10.** (b)	**11.** (b)	**12.** (b)	**13.** (b)	**14.** (a)
15. (a)	**16.** (b)	**17.** (a)	**18.** (b)	**19.** (b)	**20.** (d)	**21.** (c)
22. (d)	**23.** (c)	**24.** (c)	**25.** (b)	**26.** (b)	**27.** (b)	**28.** (b)
29. (c)	**30.** (c)	**31.** (c)	**32.** (d)	**33.** (a)	**34.** (a)	**35.** (b)
36. (c)	**37.** (a)	**38.** (a)	**39.** (b)	**40.** (a)	**41.** (c)	**42.** (a)
43. (c)	**44.** (c)	**45.** (c)	**46.** (c)	**47.** (d)	**48.** (b)	**49.** (b)
50. (b)	**51.** (c)	**52.** (b)	**53.** (c)	**54.** (d)	**55.** (b)	**56.** (c)
57. (b)	**58.** (b)	**59.** (c)	**60.** (c)	**61.** (a)	**62.** (c)	**63.** (b)
64. (c)	**65.** (b)	**66.** (d)	**67.** (c)	**68.** (b)	**69.** (c)	**70.** (b)
71. (b)	**72.** (a)	**73.** (c)	**74.** (c)	**75.** (d)	**76.** (b)	**77.** (a)
78. (b)	**79.** (a)	**80.** (a)	**81.** (b)	**82.** (a)	**83.** (c)	**84.** (d)
85. (d)	**86.** (c)	**87.** (a)	**88.** (b)	**89.** (d)	**90.** (c)	**91.** (d)
92. (b)	**93.** (a)	**94.** (b)	**95.** (b)	**96.** (a)	**97.** (a)	**98.** (a)
99. (d)	**100.** (a)	**101.** (a)	**102.** (b)	**103.** (b)	**104.** (a)	**105.** (c)
106. (a)	**107.** (b)	**108.** (d)	**109.** (a)	**110.** (b)	**111.** (b)	

Multiple Correct Choice Type

1. (a), (c)
2. (a), (c)
3. (b), (d)
4. (a), (b), (c), (d)
5. (a), (c), (d)
6. (a), (b), (c), (d)
7. (a), (b), (c)
8. (a), (c), (d)
9. (a), (b)
10. (b), (d)
11. (a), (b), (c), (d)
12. (b), (d)
13. (b), (d)
14. (a), (b), (c)
15. (b), (d)
16. (a), (b), (c)
17. (a), (d)
18. (b), (c)
19. (b), (d)
20. (a), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (d) **(iii)** (a)
2. **(i)** (a) **(ii)** (c) **(iii)** (c)
3. **(i)** (b) **(ii)** (b) **(iii)** (b)
4. **(i)** (b) **(ii)** (c) **(iii)** (d)
5. **(i)** (c) **(ii)** (c) **(iii)** (d)
6. **(i)** (d) **(ii)** (a) **(iii)** (b)

Assertion-Reason Type

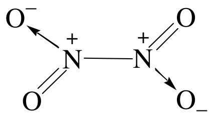
1. (a)
2. (c)
3. (d)
4. (a)
5. (c)
6. (c)
7. (a)
8. (a)
9. (c)
10. (c)
11. (c)

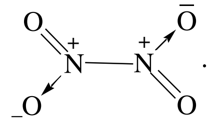
Matrix Match Type

1. (a) – (p), (r); (t) (b) – (s), (t); (c) – (p), (q); (d) – (p), (q), (s)
2. (a) – (q), (r); (b) – (q), (r); (c) – (p), (s); (d) – (q), (s)
3. (a) – (q), (r); (b) – (p); (c) – (s); (u) (d) – (t)
4. (a) – (q), (s); (b) – (r); (c) – (t); (d) – (p), (u), (v)

Hints and Solutions

Straight Objective Type

1. Carbon tetrachloride is a nonpolar compound.
2. CCl_4 has a regular tetrahedral structure.
3. Liquid HCl will not have hydrogen bond.
4. $CuSO_4 \cdot 5H_2O$ has eletrovalent, covalent and coordinate covalent bonds.
5. NO has odd number of electrons. It will contain one unpaired electrons.
6. The bond between two identical nonmetallic atoms has a pair of electrons equally shared between them.
7. F being most electronegative will yield strongest hydrogen bond.
8. The structure of N_2O_5 is  . It contains covalent and coordinate bond. In solid phase, it crystallises as $NO_2^+ NO_3^-$. The choice d will be correct in solid phase.
9. CO and CN^- involve the same number of electrons.
10. BF_3 will have zero dipole moment.
11. There are four hydrogen bonds around H_2O molecule.
12. The octet rule is not obeyed by H_2O.
13. The electronegativity increases in the order Cl < N < O < F. The same order exists for the strength of hydrogen bonds.
14. Choice a is correct.
15. F being most electronegative. It leads to maximum ionic character in HF.
16. Choice b is correct as the structure of carbon monoxide is $:C \overset{\leftarrow}{\equiv} O:$.
17. Large cation and small anion will have least distortion of ionic clouds of each other.
18. Interaction between two electronegative atoms leads to the formation of covalent bond.

19. The structure of N_2O_4 is  . It involves covalent and coordinates bond.

20. Small cation and large anion will have maximum distortion of ionic clouds of each other.

21. NF_3 has tetrahedral structure. It has nonzero dipole moment.

22. Statement d is not correct.

23. Structure c does not represent resonating structure.

24. H_2O_2 has —OH polar bond and —O—O— nonpolar bond.

25. If r is the bond distance, then the dipole moment of HCl will be

$(0.17\ e)\ r = (0.17 \times 1.6 \times 10^{-19}\ \text{C})\ r$

This is equal to 1.03 D (= $1.03 \times 3.33 \times 10^{-30}$ C m).

Hence $$r = \frac{1.03 \times 3.3356 \times 10^{-30}\ \text{C m}}{0.17 \times 1.6 \times 10^{-19}\ \text{C}} = 1.27 \times 10^{-10}\ \text{m} = 127\ \text{pm}$$

27. Hydration energy depends on the charge density (= charge/size) of position ion.

29. $CsBr_3$ may be represented as $Cs^+\ Br_3^-$.

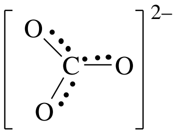
30. $KHF_2 \rightarrow K^+ + HF_2^-$

31. NO_2^+, BaO_2 and AlO_2^- are even-electron species whereas KO_2 is an odd-electron species.

32. The guiding rule for the bond length is triple bond < double bond < single bond

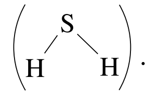
The given chemical species are

$C\equiv O$
triple bond

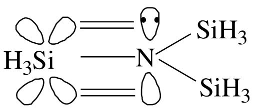

in between single and double bond

$O=C=O$
double bond

Hence, the increasing order of the C—O bond length is $CO < CO_2 < CO_3^{2-}$

33. The structure of H_2S is angular  . Because of the different values of electronegativity of S and H, the bond S—H is polar and hence the dipole moment of H_2S is nonzero.

34. Trisilylamine $N(SiH_3)_3$ is planar due to dπ-pπ bonding in which the lone pair in p orbital of nitrogen atom is extended to an empty orbital of Si.



Trimethylamine is tetrahedral due to sp^3 hybridization of nitrogen orbitals.

35. Sulphur dioxide involves sp^2 hybridization of sulphur atomic orbitals.

36. CH_3^+ involves sp^2 hybrid orbitals of carbon.

37. CO_2 is a linear molecule.

38. PCl_3 has a pyramidal shape.

39. NCO^- has a linear structure.

40. ClO_2^- has four paired electrons around Cl and thus it involves sp^3 hybrid orbitals.

41. There are four paired of electrons around oxygen in OF_2. Thus, the state of hybridization of oxygen is sp^3.

42. Choice A is correct.

43. NH_4^+ has a tetrahedral shape.

44. $(CH_3)_3\underline{C}OH$ involves sp^3 hybrid orbitals of $\underline{C}$ atom.

45. Oxygen in OF_2 has four paired electrons. The geometry of OF_2 is tetrahedral.

46. There are five paired electrons around S. It will involve dsp^3 hybridization.
47. Xe in XeF_2 has five paired electrons around it. Its hybridization is trigonal bipyramidal.
48. Presence of four paired electrons around the central atom leads to tetrahedron arrangement.
49. Presence of three paired electrons around the central atom leads to trigonal planar arrangement.
50. Presence of five pairs of electrons around the central atom leads to trigonal bipyramid arrangement.
51. Iodine in IF_5 has six paired of electrons. It leads to octahedron shape.
52. SO_2 has sp^2 hybridization of sulphur orbitals.
53. BF_3 has sp^2 hybridization of boron orbitals. Each BF bond is polar.
54. Molecular shapes of SF_4, CF_4 and XeF_4 are different with 1, 0, 2 lone pairs of electrons, respectively.
55. NO_2^+, NO_3^- and NH_4^+ involve sp, sp^2 and sp^3 hybridization.
56. Total number of valence electrons = 6 + 2 × 7 = 20. These are distributed as $:\underset{\cdot\cdot}{\ddot{Cl}}:\underset{\cdot\cdot}{\ddot{S}}:\underset{\cdot\cdot}{\ddot{Cl}}:$. There are four pairs of electrons around S. Hence, it involves sp^3 hybridization.
57. Ni in the complex exists as Ni^{2+} with electronic configuration $(3d)^8$. CN^- is a strong ligand. It pushes the unpaired electrons of Ni^{2+} to couple with each other and thus generates a vacant d orbital in Ni^{2+} so as to form dsp^2 hybridization and thus making $[Ni(CN)_4]^{2-}$ a square planar complex ion.
58. The valence electrons in the given species are as follows.

SO_4^{2-}	$6 + 4 \times 6 + 2 = 32$	SeO_4^{2-}	$6 + 4 \times 6 + 2 = 32$
SF_4	$6 + 4 \times 7 = 34$	SO_2Cl_2	$6 + 2 \times 6 + 2 \times 7 = 32$

The species SF_4 will not involve tetrahedral structure

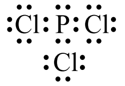
59. The valence electrons in the given species are as follows

CO_2	$4 + 2 \times 6 = 16$	SO_2	$6 + 2 \times 6 = 18$
N_2O	$2 \times 5 + 6 = 16$	H_2S	$2 + 6 = 8$

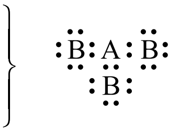
Only in SO_2, the electrons are distributed as $:\underset{\cdot\cdot}{\ddot{O}}:\ddot{S}:\underset{\cdot\cdot}{\ddot{O}}:$. There are three paired electrons on S and thus S involves sp^2 hybridization.

60. The number of valence electrons in ClO_2^- are 7 + 2 × 6 + 1 = 20. These are distributed as $:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{Cl}}:\underset{\cdot\cdot}{\ddot{O}}:$. There are four pairs of electrons around Cl and thus if involves sp^3 hybridization.
61. The number of pairs of electrons are:

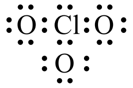
PCl_3 $\quad 5 + 3 \times 7 = 26$



SO_3 $\quad 6 + 3 \times 6 = 24$
NO^-_3 $\quad 5 + 3 \times 6 + 1 = 24$
BF_3 $\quad 3 + 3 \times 7 = 24$



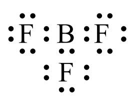
Only in PCl_3, there are four pair of electrons around P. Hence, it involves sp^3 hybridization.
62. In the species ClO_3^-, the number of paired electrons around Cl may be shown as follows.
Valence electrons 7 + 3 × 6 + 1 = 26.



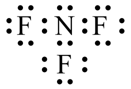
Four paired electrons around Cl. Hence, it involves sp^3 hybridization.
63. The number of valence electrons are as follows.

BF_3	$3 + 3 \times 7 = 24$	NF_3	$5 + 3 \times 7 = 26$

These electrons are distributed as follows.



Three unpaired electrons around B. Hence, it involves sp^2 hybridization.



Four unpaired electrons around N. Hence, it involves sp^3 hybridization.

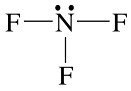
64. The number of valence electrons in OF_2 is 6 + 2 × 7 = 20. These are distributed as $:\ddot{\underset{..}{F}}:\ddot{\underset{..}{O}}:\ddot{\underset{..}{F}}:$. There are four paired of electrons around O. Hence, it involves sp^3 hybridization.

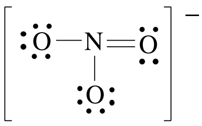
65. NH_3, H_2O and CH_4 involves sp^3 hybridization whereas BeF_2 involves sp hybridization (bond angle 180°). Amongst NH_3, H_2O and CH_4, the molecule H_2O is expected to have minimum bond angle due to larger repulsion between two lone pairs of electrons which forces bond angle to decreases from the regular tetrahedron structure.

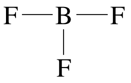
66. SO_2 involves sp^2 hybridization making angle near to 120°

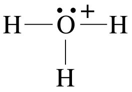
67. The number of valence electrons in PH_3 is 5 × 3 = 8. These are distributed as $\mathrm{H:\underset{\underset{H}{..}}{\ddot{P}}:H}$. There are four paired of electrons around P. Hence, it involves sp^3 hybridization. The bond angles are expected to be 109°.

69. Isostructural pairs have similar structures.

NF_3: Lewis structure,  ; tetrahedron structure, geometry-triangle pyramidal

NO_3^-: Lewis structure,  ; triangular planar

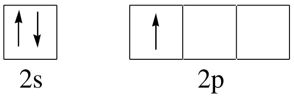
BF_3; Lewis structure,  ; triangular planar

H_3O^+; Lewis structure,  ; tetrahedron structure

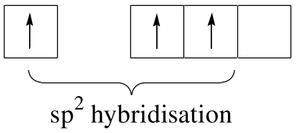
HN_3; Lewis structure, $\mathrm{H{-}\ddot{N}{=}N{\equiv}N:}$; linear

Thus, isostructural pairs are [NF_3, H_3O^+] and [NO_3^-, BF_3]

70. Outer electronic configuration of boron atom



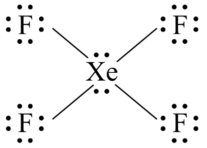
Electronic configuration of boron atom in BF_3



The geometry corresponding to sp^2 hybridisation is trigonal planar.

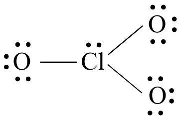
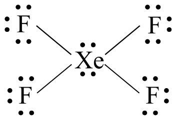
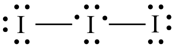
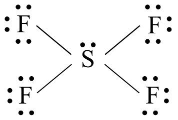
71. The structures of NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 are tetrahedral, square planar, triangle bipyramid and triangular planar, respectively. Hence, the central atoms respectively involve sp^3, dsp^2, dsp^3 and sp^2 hybrid orbitals.

73. The total number of valence electrons in XeF_4 are 36 (= 8 + 4 × 7). These are distributed as follows.



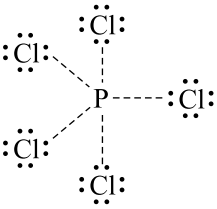
Thus, Xe contains six line pair of electrons around Xe out of which two are lone pairs. According VSEPR, these six pairs of electrons are distributed in the octahedral geometry.

74. For the given species, we have

Species	*Valence electrons*	*Lewis structure*	*Unpaired electrons*
ClO_3^-	$7 + 6 \times 3 + 1 = 26$		1
XeF_4	$8 + 4 \times 7 = 36$		2
I_3^-	$7 \times 3 + 1 = 22$		3
SF_4	$6 + 4 \times 7 = 34$		1

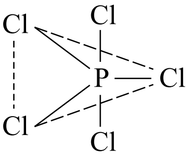
75. The species P_4 has a tetrahedron structure. Each P involves sp^3 hybrid orbital. Hence, p-character will be 75%.

76. The valence electrons in $PCl_5 = 5 + 5 \times 7 = 40$. The distribution of these electrons in PCl_5 is as follows.

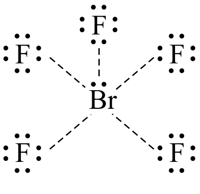


There are five lone pairs of electrons around P. Hence, the arrangement of these electrons around P will be trigonal bipyramidal,

The hybridization involved in this complex is dsp^3. Hence, the shape of PCl_5 is

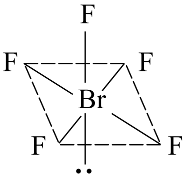


The valence electrons in $BrF_5 = 7 + 5 \times 7 = 42$. The distribution of these electrons in BrF_5 is as follows.



There are six lone pairs of electrons around Br. Hence, the arrangement of these electrons around Br will be octahedral. The hybridization involved in this complex is d^{2}sp^3.

Hence, the shape of BrF_5 is



77. *Molecular Structure of* OSF_4

The total number of valence electrons to be distributed are 40 (= 6 + 6 + 4 × 7). These are distributed as shown in Fig. 5.2a.

There are five pairs of electrons around S atom. These will assume trigonal bipyramidal geometry around S atom. The structure of OSF_4 is shown in Fig. 5.2b
The hybridisation involved is sp^3d of sulphur orbitals. There is no lone pair of electrons in OSF_4.

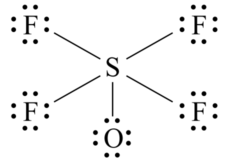


Fig. 5.2a

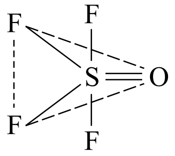


Fig. 5.2b

Structure of $XeOF_4$
The total number of valence electrons to be distributed are 42 = 8 + 6 + 4 × 7. These are distributed as shown in Fig. 5.3a.
There are six pair of electrons around the central Xe atom. These assume octahedral geometry. The structure of $XeOF_4$ is shown in Fig. 5.3b.

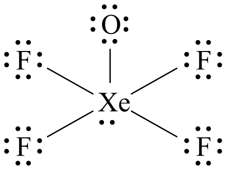


Fig. 5.3a

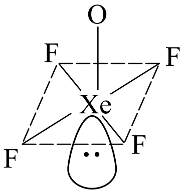
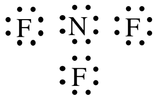


Fig. 5.3b

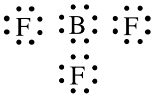
The hybridisation involved is sp^3d^2 of Xe orbitals. There is one lone pair of electrons around Xe atom.

78. NF_3 has 26 valence electrons. These electrons are distributed as



. There are four pairs of electrons around N, hence, it is sp^3 hybridized and thus will have dipole moment and thus polar in nature.

BF_3 has 24 valence electrons. These electrons are distributed as

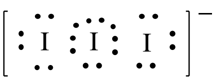


. There are three pairs of electrons around B, hence, it is sp^2 hybridized and its geometry will be trigonal planar. The net dipole moment of this molecule will be zero and hence nonpolar in nature.

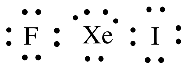
79. The valence electrons and their distributions are as follows.

NO_2^+	5 + 2 × 6 − 1 = 16		Central N is sp hybridized. Bond angle 180°
NO_2	5 + 2 × 6 = 17		Unpaired electron of N makes angle less than 180°
NO_2^-	5 + 2 × 6 + 1 = 18		N is sp^2 hybridized, bond angle 120°.

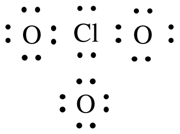
80. The number of paired electrons around the central atom are



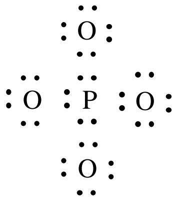
; valence electron = 22



; valence electron = 22



; valence electron = 26



valence electron = 32

Only I_3^- and XeF_2 have 5 paired electrons and hence they are isostructural.

81. Nitrogen in NO_3^- has three paired electrons. It involves sp^2 hybridization.

82. O_2^- has one unpaired electrons. It is paramagnetic.

83. Molecular oxygen is paramagnetic as it contains two unpaired electrons.

84. N_2 has no unpaired electrons.

85. O_2 is paramagnetic. It is not diamagnetic.

86. Same as Q.85.

87. O_2^{2-} will have largest bond length.

88. Bond order of O_2 is 2.

89. Bond order of N_2 is 3.

90. The number of molecular orbitals formed will be equal to the number of atomic orbitals mixed in the combination.

91. The correct order involves $E(\sigma 2p_z)$ prior to $E(\pi 2p_x)$.

92. The correct bond order is $O_2^- < O_2 < O_2^+$.

93. Lesser the bond order, larger the bond length. The choice a is correct.

94. N_2 involves one σ and two π bonds.

95. The bond order of the superoxide is 1.5 as it contains one more electron in the antibonding orbital as compared to oxygen (which has bond order of 2).

96. O_2 has two electrons in the antibonding molecular orbital.

97. The electronic configuration of B_2 is $KK(\sigma 2s)^2(\sigma^*2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$.

100. The electronic configurations of N_2 and O_2 are as follows.
N_2 : KK $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\sigma 2p_z)^2$
O_2 : KK $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi^*2p_x)^1$ $(\pi^*2p_y)^1$
In going from N_2 to N_2^+, one bonding electron is removed. This decreases bond order and hence increase in bond length. In going from O_2 to O^2_+, one antibonding electron is removed. This increases bond order and hence decrease in bond length

101. The bond order are as follows.
O_2^+ 2 ; O_2^+ 2.5 ; O_2^- 1.5 ; O_2^{2-} 1
Larger the bond order, larger the dissociation energy.

102. The bond orders are as follows.
N_2 3 ; N_2^+ 2.5 ; N_2^- 2.5, ; N_2^{2-} 2
Larger the bond order, lesser the bond length.

103. Calcium carbide is an ionic compound $(Ca^{2+}C^{2-})$ which produces acetylene on reacting with water. Thus, the structure of C^{2-} is $[C \equiv C]^{2-}$. It has one σ and two π bonds.

104. All the three species contain 10 valence electrons. Their molecular electronic configurations are represented as $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\sigma 2p_z)^2$

$$\text{Bond order} = \frac{\text{Bonding electrons} - \text{Antibonding electrons}}{2} = \frac{8-2}{2} = 3$$

105. The species O_2^- has one unpaired electron.

106. π-electronic charge lies above and below molecular plane.

107. The electronic configuration of O_2^- is $KK(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi^*2p_x)^2$ $(\pi^*2p_y)^1$. It contains one unpaired electron and is thus paramagnetic. Its bond order is BO = $\frac{1}{2}$[Number of (bonding – antibonding) electrons = $\frac{1}{2}$ (8 – 5) = $\frac{3}{2}$

The bond order of O_2 is $\quad \text{BO} = \frac{1}{2}(8-4) = 2$

108. Na_2O_2 is $(2Na^+)$ (O_2^{2-}). There is no unpaired electron either on Na^+ or O_2^{2-}. Hence, it must be diamagnetic.
O_3 and N_2O have even-numbered electrons and thus are diamagnetic.
KO_2 is (K^+) (O_2^-). The species O_2^- contains one unpaired electron. Hence, it must be paramagnetic.

109. The diatomic species have the following scheme of molecular orbitals in the increasing order of energy.

$$KK(\sigma\,2s)\ (\sigma\,{}^*2s)\ (\pi 2p_x)\ (\pi 2p_y)\ (\sigma 2p_z)\ (\pi^*2p_x)\ (\pi^*2p_y)\ (\sigma\,{}^*2p_z)$$

The species CO, NO^+, CN^- and N_2 have the same number (= 10) of valence electrons while NO^- has 12 electrons. Thus, NO^- will have different bond order.

110. In the given compounds, oxygen is present as O_2, O_2^+ and O_2^-, respectively. For these species, we have

O_2 KK $(\sigma 2s)^2$ $(\sigma{*}2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi{*}2p_x)^1$ $(\pi{*}2p_y)^1$

O_2^+ KK $(\sigma 2s)^2$ $(\sigma{*}2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi{*}2p_x)^1$

O_2^- KK $(\sigma 2s)^2$ $(\sigma{*}2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi{*}2p_x)^2$ $(\pi{*}2p_y)^1$

The bond orders of these species as given by the expression

BO = (1/2) [Number of (bonding – antibonding) electrons]

are as follows.

For O_2 $\quad \text{BO} = \frac{1}{2}(8 - 4) = 2$ $\qquad$ For O_2^+ $\quad \text{BO} = \frac{1}{2}(8 - 3) = 2.5$

For O_2^- $\quad \text{BO} = \frac{1}{2}(8 - 5) = 1.5$

Since bond length is inversely proportional bond order, the increasing order of bond length of O—O is

$$O_2[AsF_6] < O_2 < KO_2$$

111. The species CN^- and NO^+ are isoelectronic (valence electrons = 10). They are expected to have identical electronic configuration and hence identical bond order.

Multiple Correct Choice Type

1. Carbon dioxide, mercuric chloride and acetylene are linear molecules.

2. CN^- and NO^+ have the same number of electrons.

3. The species H_3O^+, NH_3 and CH_3^- have same number of electrons.

5. (a) It is present within the molecule.

(b) It occurs between two different/identical molecules.

6. (a) Hybrid orbitals are obtained by mixing orbitals centred on the same atom.

(b) The structure of CO molecule is $:\mathrm{C}\overset{\longleftarrow}{=}\mathrm{O}:$

(d) SO_2 does not have linear geometry.

7. (a) (Fluorine is the most electronegative element. A strong polarization of bonding electrons occurs in HF leading to hydrogen bonding even in the gaseous state.

(c) Due to the resonance, both bonds are identical.

8. (a) Be_2 would contain equal number of bonding and antibonding electrons.

(b) There are more bonding electrons than antibonding electrons.

(c) CH_3F involes lesser C—F distance but more charge separation as compared to those in CH_3Cl. Here, bond distance has more dominating effect causing dipole moment of CH_3Cl greater than that of CH_3F.

(d) Stronger the hydrogen bonding, weaker the base.

CHAPTER 6

ENERGETICS

Thermodynamics deals with the transfer of heat between a chemical system and its surroundings when a reaction or phase change takes place within the system. The entire formulation of thermodynamics is based on two fundamental laws which have been established on the basis of experimental behaviour of macroscopic aggregates of matter, collected over a long period of time.

FIRST LAW OF THERMODYNAMICS

The internal energy of a system can be changed by transferring heat to/from the system from/to the surroundings. It can also be changed by doing the mechanical work on/by the system by/on the surroundings. These facts are represented in the form of the first law of thermodynamics as

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad \text{or} \qquad \Delta U = q + w$$

Since heat given to the system and work done on the system raise the internal energy of the system, these two operations are assigned positive values. The converse of the two operations, viz., heat given out and work done by the system are assigned negative values.

The expression of work done by/on a gaseous system is given by

$$\mathrm{d}w = -\,p_{\mathrm{ext}}\,\mathrm{d}V$$

where p_{ext} is the external pressure against which the volume of gaseous system is changed by an amount dV. For a constant external pressure, we have

$$w = -\,p_{\mathrm{ext}}\,(V_2 - V_1)$$

where V_1 and V_2 are the initial and final volumes of the gaseous system.

If p_{ext} differs from the pressure of the gas by infinitesimal amount, the work is said to be carried out under reversible condition. In this case, the expression of work under constant temperature condition is given by

$$w = -\,nRT\,\ln\,(V_2/V_1)$$

Note that for $V_2 > V_1$, there occurs an expansion of the gas. The work is done by the system on the surroundings and it carries a negative sign.

For $V_1 > V_2$, there occurs compression of the gaseous system. The work is done by the surroundings on the system and it carries a positive sign.

INTERNAL ENERGY AND ENTHALPY

From the first law of thermodynamics, it can be shown that the heat transferred at constant volume changes the internal energy of the system, whereas that at constant pressure changes the enthalpy of the system.

The changes in internal energy and enthalpy of a system caused by change in temperature are given by

$$\Delta U = nC_{V,\,\mathrm{m}}\,(T_2 - T_1); \qquad \text{and} \qquad \Delta H = nC_{p,\,\mathrm{m}}\,(T_2 - T_1)$$

where $C_{V,\,\mathrm{m}}$ and $C_{p,\,\mathrm{m}}$ are the molar heat capacities at constant volume and constant pressure, respectively.

In the laboratory, the majority of chemical reactions are carried out under the condition of constant pressure, and thus the heat transferred in such a system is equal to the enthalpy change in a chemical reaction. Since the enthaply of a system can also change due to the variation in temperature and pressure, it is, therefore essential that the reactants and products in a chemical reaction must have the same temperature and pressure.

ENTHALPY CHANGE OF A CHEMICAL EQUATION

The enthalpy change of a thermochemical equation is

$$\Delta H = \sum_{\text{(products)}} \nu_j H_{m,j} - \sum_{\text{(reactants)}} \nu_i H_{m,i}$$

where $H_{m,i}$ refers to the molar enthalpy of species i in the balanced chemical equation and ν_i is the corresponding stoichiometric coefficient. The units of ΔH are kJ mol^{-1}.

Two types of reactions may be distinguished.

1. *Exothermic reactions* For these ΔH is negative, which implies negative q_p and hence release of heat when reactants are converted into products. In this case

$$\sum H(\text{products}) < \sum H(\text{reactants})$$

2. *Endothermic reactions* For these ΔH is positive, which implies positive q_p and hence absorption of heat when reactants are converted into products. In this case

$$\sum H(\text{products}) > \sum H(\text{reactants})$$

MOLAR ENTHALPIES OF FORMATIONS

It is not possible to determine the absolute value of enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation (the term standard indicates a pressure of 1 bar) of other substances can be determined.

The enthalpy of formation of every element in its stable states of aggregation at 1 bar and 25 °C is assigned a zero value.

For example, $\Delta_f H°$ (graphite) = 0, $\Delta_f H°(Br_2, l) = 0$, $\Delta_f H°$(S, rhombic) = 0, $\Delta_f H°(H_2, g) = 0$ and so on. The enthalpy change of a chemical equation can be computed by using the expression

$$\Delta_r H° = \sum_{\text{(products)}} \Delta_f H_i^\circ - \sum_{\text{(reactants)}} \Delta_f H_i^\circ$$

HESS'S LAW OF CONSTANT HEAT SUMMATION

Since the molar enthalpies of formation of reactants and products involved in a chemical equation have definite values, the enthalpy change of (or heat involved in) the chemical equation will have a definite value, irrespective of the fact whether the reaction is carried out in one step or more than one step. This fact is known as Hess's law of constant heat summation. For example,

(i) $\quad \text{C(graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -393.51 \text{ kJ mol}^{-1}$

(ii) $\quad \text{C(graphite)} + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad \Delta H_2 = -110.52 \text{ kJ mol}^{-1}$

$\quad CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad \Delta H_3 = -282.99 \text{ kJ mol}^{-1}$

Obviously, $\quad \Delta H_1 = \Delta H_2 + \Delta H_3$

TYPES OF REACTIONS AND CORRESPONDING ENTHALPY CHANGES

The enthalpy change in a reaction is suitably named according to the type of reaction in question. Two types of reaction are specifically defined as follows.

Enthalpy of Formation The enthalpy of formation of a substance is defined as the enthalpy change when 1 mol of a given substance is formed, starting from the elements in their stable states of aggregation. A few examples are

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta_f H°(H_2O, l) = -285.77 \text{ kJ mol}^{-1}$$

$$12\text{C(graphite)} + 11H_2(g) + \tfrac{11}{2} O_2(g) \rightarrow C_{12}H_{22}O_{11}(s) \qquad \Delta_f H°(C_{12}H_{22}O_{11}, s) = -2218 \text{ kJ mol}^{-1}$$

Enthalpy of Combustion The enthalpy of combustion of a given substance is defined as the enthalpy change when one mole of this substance combines with requisite amount of oxygen to form products in their stable states of aggregation. A few examples are

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_c H(CH_4,\ g) = -74.85\ \text{kJ mol}^{-1}$$

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l) \qquad \Delta_c H(C_{12}H_{22}O_{11},\ s) = -5644\ \text{kJ mol}^{-1}$$

Similarly, one can name the enthalpy change based on the type of reaction. A few examples are

Enthalpy of fusion : $H_2O(s) \xrightarrow[273.15\ K]{} H_2O(l)$ $\Delta_{fus}H = 6\ \text{kJ mol}^{-1}$

Enthalpy of vaporization : $H_2O(l) \xrightarrow[373.15\ K]{} H_2O(g)$ $\Delta_{vap}H = 40.6\ \text{kJ mol}^{-1}$

Enthalpy of sublimation : $I_2(s) \rightarrow I_2(g)$ $\Delta_{sub}H = 63.4\ \text{kJ mol}^{-1}$

Enthalpy of transition : $C(\text{graphite}) \rightarrow C(\text{diamond})$ $\Delta_{trs}H = 1.90\ \text{kJ mol}^{-1}$

Enthalpy of neutralization : $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta_{neut}H = -57.3\ \text{kJ mol}^{-1}$

Enthalpy of ionization : $HCN(aq) \rightarrow H^+(aq) + CN^-(aq)$ $\Delta_{ioniz}H = 45.17\ \text{kJ mol}^{-1}$

RELATION BETWEEN ΔH AND ΔU OF A CHEMICAL EQUATION

Since, $H = U + pV$, we have

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + (\Delta \nu_g)RT$$

where $\Delta\nu_g$ is the change in the stoichiometric number of gaseous molecules in converting reactants to products and is given as

$$\Delta \nu_g = \sum_{\text{(products)}} \nu_{g,i} - \sum_{\text{(reactants)}} \nu_{g,i}$$

For a reaction involving condensed phases $\Delta H \simeq \Delta U$

Bond Enthalpies Bond enthalpy of a given bond is defined as the average enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms in the gaseous phase. The bond enthalpy may be distinguished from bond dissociation enthalpy which is enthalpy required to dissociate a given bond of some specific molecule. It is possible to construct a table listing the average bond enthalpies of different types of bonds and with the help of this, one can estimate the enthalpy change of a chemical equation involving gaseous species. For example, for a reaction

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

we can write $\Delta H = +\varepsilon(\text{H—H}) + \varepsilon(\text{Cl—Cl}) - 2\varepsilon(\text{H—Cl})$

SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics identifies a state function, called the entropy, which provides a criterion for identifying reversible or irreversible nature of the given process undergone by a system. The entropy of the universe (system + surroundings) increases for irreversible processes whereas it remains constant for reversible processes.

The entropy function has been identified with the disorderliness of the system—larger the disorderliness, larger the entropy of the system. For example, for a substance in three states of matter we have

$$S(\text{gaseous state}) >> S(\text{liquid state}) > S(\text{solid state})$$

Expression of Entropy Function For a system which involves transferring infinitesimal heat at constant temperature, the entropy change of the system is given by

$$dS = dq_{rev}/T$$

For finite heat transferred at constant temperature, we have

$$\Delta S = q_{rev}/T$$

For example, for a pure substance we have

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_{\text{b}}} \quad \text{and} \quad \Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{m}}}$$

where the subscripts vap and fus represent vaporization and fusion, respectively.

Third Law of Thermodynamics According to third law of thermodynamics, every pure perfectly crystalline substance has zero entropy at 0 K, since these involve perfectly ordered arrangements of their constituent particles. However, the substance such as CO, NO, H_2 and ice do not have ordered arrangements at 0 K and thus have nonzero value of entropy. This is known as residual entropy.

Gibbs Function Gibbs function (or energy) or simply free energy is defined as $G = H - TS$

For a process occurring at constant T and p, the change in Gibbs function is given by $\Delta G = \Delta H - T\,\Delta S$
For a process to be spontaneous, the value of ΔG is negative. For a nonspontaneous reaction, ΔG is positive.
For a reaction at equilibrium, $\Delta G = 0$ and temperature at which the system occurs at equilibrium is given by

$$T_{\text{eq}} = \Delta H/\Delta S$$

Standard States of a Substance

For a pure gas, the standard state at a given temperature is the ideal gas at one bar pressure.
For a pure liquid, the standard state at a given temperature is the pure liquid at one bar pressure.
For a pure crystalline substance, the standard state at a given temperature is the pure crystalline substance at one bar pressure.
For a substance or ion in solution, the standard state at a given temperature is the unit molality of the species in ideal solution at one bar pressure.
The standard free energy change of a reaction is related to its equilibrium constant by the expression $\Delta_r G^\circ = -RT \ln K_p^\circ$.

PRESSURE-VOLUME WORK

An ideal gas can undergo expansion or compression under isothermal or adiabatic conditions. The expansion and compression may be carried out under reversible or irreversible conditions. We give below the expressions of p-V work under different conditions. In a reversible process, system as well as surrourolings can be restored back by following the reverse path. In an irreversible process, this is not possible.

Isothermal *p*-*V* Work In this case, temperature of the system remains constant, i.e. $\Delta T = 0$.

For irreversible condition: $w = -p_{\text{ext}}(V_2 - V_1)$; For reversible condition: $w = -nRT \ln (V_2/V_1)$

Adiabatic *p*-*V* Work In this case, heat can neither enter to or leave from the system, i.e. $q = 0$. From first law of thermodynamics, it follows that $\Delta U = w$

where ΔU is given by $\Delta U = C_V(T_2 - T_1)$

For a gas undergoing adiabatic irreversible volume change, the expression of work is given by

$$w = -p_{\text{ext}}(V_2 - V_1)$$

For an ideal gas undergoing adiabatic reversible expansion/compression, we also have

$$pV^\gamma = \text{constant}; \quad pT^{\gamma(1-\gamma)} = \text{constant}; \quad \text{and} \quad TV^{\gamma-1} = \text{constant}$$

where $\gamma = C_{p,\text{m}}/C_{V,\text{m}}$. The symbols $C_{p,\text{m}}$ and $C_{V,\text{m}}$ represent molar heat capacities at constant pressure and volume conditions, respectively.

For a monatomic ideal gas: $C_{V,\text{m}} = (3/2)R$; $C_{p,\text{m}} = (5/2)R$; and $\gamma = 5/3$

For a diatomic ideal gas: $C_{V,\text{m}} = (5/2)R$; $C_{p,\text{m}} = (7/2)R$; and $\gamma = 7/5$

Straight Objective Type

First Law of Thermodynamics

1. For a monatomic gas, the value of the ratio of $C_{p,\,\mathrm{m}}$ and $C_{V,\,\mathrm{m}}$ is
(a) 5/3 (b) 7/5 (c) 9/7 (d) 9/11

2. For a diatomic gas, the value of the ratio of $C_{p,\,\mathrm{m}}$ and $C_{V,\,\mathrm{m}}$ is
(a) 5/3 (b) 7/5 (c) 9/7 (d) 9/11

3. For a linear triatomic gas, the value of the ratio of $C_{p,\,\mathrm{m}}$ and $C_{V,\,\mathrm{m}}$ is
(a) 5/3 (b) 7/5 (c) 9/7 (d) 15/13

4. Molar heat capacity of water in equilibrium with ice at constant pressure is
(a) zero (b) infinity (c) 40.45 kJ $\mathrm{K^{-1}\ mol^{-1}}$ (d) 75.48 J $\mathrm{K^{-1}\ mol^{-1}}$
(1997)

5. For a nonlinear triatomic gas, the value of the ratio $C_{p,\,\mathrm{m}}$ and $C_{V,\,\mathrm{m}}$ is
(a) 7/5 (b) 9/7 (c) 7/6 (d) 17/13

6. Which of the following is an example of a closed system?
(a) Hot coffee in a thermos flask (b) A tree in a garden
(c) Water in a beaker (d) Mercury in a clinical thermometer

7. When a sample of an ideal gas expands from 6.0 L to 14.0 L against a constant pressure of 0.30 atm, the work involved is
(a) 243.19 J (b) – 243.19 J (c) 234.19 J (d) – 234.19 J

8. One litre-atmosphere is equal to
(a) 33.8 J (b) 66.6 J (c) 101.3 J (d) 135.1 J

9. A gas expands adiabatically from 1.0 L to 12.0 L against a constant pressure of 0.75 atm. The ΔU of the gas is
(a) – 853.9 J (b) 835.9 J (c) 853.9 J (d) – 835.9 J

10. Which of the following expressions is **not** correctly represented?
(a) $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$ (b) $\Delta U = \Delta q + \Delta w$ (c) $\Delta H = q_p$ (d) $\Delta S = q_{\mathrm{rev}}/T$

11. Two moles of an ideal gas undergoes isothermal reversible expression from 2 L to 8 L at 300 K. The enthalpy change of the gas is
(a) 11.4 kJ (b) – 11.4 kJ (c) zero (d) 4.8 kJ (2004)

12. One mole of a monatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from one litre to three litres. The final temperature of the gas is
(a) T (b) $T/3^{(5R/2)}$ (c) $T - 2\mathrm{K}/(1.5 \times 0.082)$ (d) $T + 2\mathrm{K}/(1.5 \times 0.082)$
(2005)

13. If for an ideal gas, the ratio of pressure and volume is constant and is equal to 1 atm $\mathrm{L^{-1}}$, the molar heat capacity at constant pressure would be
(a) (3/2) R (b) $2R$
(c) (5/2) R (d) zero (2006)

14. An ideal monatomic gas is taken round the cycle ABCD as shown in the Fig. 6.1. The work done during the cycle is
(a) pV (b) $2pV$
(c) $\frac{1}{2}pV$ (d) zero

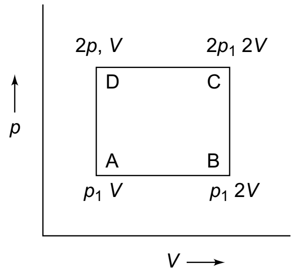


Fig. 6.1

15. Two identical containers A and B with frictionless pistons contain the same ideal gas at the same temperature and the same volume V. The mass of the gas in A is m_A and that in B is m_B. The gas in each cylinder is now allowed to expand isothermally to the same final volume $2V$. The changes in the pressure in A and B are found to be Δp and $1.5\ \Delta p$, respectively. Then
(a) $4m_\mathrm{A} = 9m_\mathrm{B}$ (b) $2m_\mathrm{A} = 3m_\mathrm{B}$ (c) $3m_\mathrm{A} = 2m_\mathrm{B}$ (d) $9m_\mathrm{A} = 4m_\mathrm{B}$

16. Two cylinders A and B fitted with pistons contain equal amounts of an ideal gas (diatomic) at 300 K. The piston of A is free to move, while that of B is held fixed. The same amount of heat is given to the gas in each cylinder. If the rise in temperature of the gas in A is 30 K, then the rise in temperature of the gas in B is

(a) 30 K (b) 18 K (c) 50 K (d) 42 K

17. Starting with the same initial conditions, an ideal gas expands from V_1 to V_2 in three different ways. The work done by the gas is W_1 if the process is reversibly isothermal, W_2 if purely isobaric and W_3 if reversibly adiabatic. Then

(a) $W_2 > W_1 > W_3$ (b) $W_2 > W_3 > W_1$ (c) $W_1 > W_2 > W_3$ (d) $W_1 > W_3 > W_2$

18. The work done, when a gas at p_1, V_1 changes to p_2 and V_2 adiabatically,

(a) remains the same irrespective of the nature of gas

(b) increases with increase in atomicity of gaseous molecules

(c) is the same as that for an isothermal change to the same state

(d) is zero

19. Which of the following expressions is applicable for the adiabatic expansion of a monatomic ideal gas?

(a) $pV^{5/3}$ = constant (b) $p^{5/3}V$ = constant (c) $pV^{7/5}$ = constant (d) $pV^{9/7}$ = constant

20. One mole of a monatomic gas ($\gamma = 1.66$) is mixed with 2 mol of a diatomic gas ($\gamma = 1.4$). For the mixture, the value of γ would be

(a) 1.36 (b) 1.46 (c) 1.53 (d) 1.54

21. When an ideal diatomic gas is heated at constant pressure, the fraction of the heat supplied which increases the internal energy of the gas is

(a) 2/5 (b) 3/5

(c) 3/7 (d) 5/7

22. p–V plots for two gases during adiabatic processes are shown in the Fig. 6.2. Plots 1 and 2 should correspond respectively to

(a) He and O_2 (b) O_2 and He

(c) He and Ar (d) O_2 and N_2

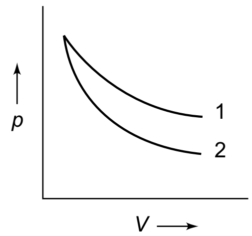


Fig. 6.2

23. In a given process on an ideal gas, dw = 0 and dq < 0. Then for the gas

(a) the temperature will decrease (b) the volume will increase

(c) the pressure will remain constant (d) the temperature will increase

24. 4 kg of ice at – 20 °C is mixed with 10 kg of water at 20 °C in an insulating vessel having a negligible heat capacity. Calculate the final mass of water remaining in the container. Given : Specific heat capacities of water and ice are 4.184 kJ K^{-1} kg^{-1} and 2.092 kJ K^{-1} kg^{-1}, respectively. Molar enthalpy of fusion of ice is 334.7 kJ kg^{-1}.

(a) 8 kg (b) 10 kg (c) 12 kg (d) 14 kg

25. An ideal gas expands isothermally from a volume V_1 to V_2 and then compressed to original volume V_1 adiabatically. Initial pressure is p_1 and final pressure is p_3. The total work done is w. Then

(a) $p_3 > p_1$; $w > 0$ (b) $p_3 < p_1$; $w_1 < 0$

(c) $p_3 > p_1$, $w < 0$ (d) $p_3 = p_1$, $w = 0$

Δ*H* and Δ*U* Relationship

26. The difference between heats of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ mol^{-1} is

(a) –7.43 (b) +3.72 (c) –3.72 (d) +7.43 (1991)

27. For the combustion reaction $2Ag(s) + \frac{1}{2}O_2(g) \rightarrow 2Ag_2O(s)$ at 298 K, which of the following alternatives is correct?

(a) $\Delta H = \Delta U$ (b) $\Delta H > \Delta U$

(c) $\Delta H < \Delta U$ (d) ΔH and ΔU bear no relation with each other

28. The word "standard" in standard molar enthalpy change implies

(a) temperature 298 K (b) pressure 1 bar

(c) temperature 298 K and pressure 1 bar (d) all temperatures and all pressures

29. For which of the following equations, will ΔH be equal to ΔU?
(a) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ (b) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
(c) $2NO_2(g) \rightarrow N_2O_4(g)$ (d) $4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$

30. Enthalpy of the system is given as
(a) $H + pV$ (b) $U + pV$ (c) $U - pV$ (d) $H - pV$

31. Enthalpy change of a reaction will be equal to
(a) $\Delta U + p\Delta V$ (b) $\Delta U + V\Delta p$ (c) $\Delta U + \Delta(pV)$ (d) $\Delta U + (\Delta \nu_g)\Delta(pV)$

32. The standard enthalpies of formation at 300 K for $CCl_4(l)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are -107, -242, -394 and -93 kJ mol^{-1}, respectively. The value of ΔU°_{300K} for the reaction
$CCl_4(l) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$ is
(a) -170 kJ mol^{-1} (b) -175 kJ mol^{-1} (c) -182.5 kJ mol^{-1} (d) -282.5 kJ mol^{-1}

33. The reaction $NH_2CN(s) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$ was carried out in a bomb caloriemeter. The heat released was 743 kJ mol^{-1}. The value of ΔH_{300K} for this reaction would be
(a) -740.5 kJ mol^{-1} (b) -741.75 kJ mol^{-1} (c) -743.0 kJ mol^{-1} (d) -744.25 kJ mol^{-1}

34. The enthalpy of vaporization of water at 100 °C is 40.63 kJ mol^{-1}. The value ΔU° for this process would be
(a) 37.53 kJ mol^{-1} (b) 39.08 kJ mol^{-1} (c) 42.19 kJ mol^{-1} (d) 43.73 kJ mol^{-1}

35. Given: $Ag_2O(s) \rightarrow 2Ag(s) + O_2(g)$; $\Delta H = 30.66$ kJ mol^{-1}. Which one of the following is correct?
(a) $\Delta H = \Delta U$ (b) $\Delta H > \Delta U$ (c) $\Delta H < \Delta U$ (d) $\Delta H = \Delta U - RT$

36. The enthalpy change for the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ at 1000 K is 176 kJ mol^{-1}. The value of ΔU for the reaction will be
(a) 176 kJ mol^{-1} (b) 184.3 kJ mol^{-1} (c) 167.7 kJ mol^{-1} (d) 180 kJ mol^{-1}

37. Identify the reaction in which $\Delta_r H < \Delta_r U$.
(a) $N_2O_4(g) + O_2(g) \rightarrow 2NO_3(g)$ (b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$
(c) $2H_2(g) + O_2(g) \rightarrow H_2O(g)$ (d) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

38. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy (ΔH) of the process is
(a) 40.0 1 atm (b) 42.3 L atm
(c) 44.0 L atm (d) not defined, because pressure is not constant
(2002)

Enthalpy of Formation

39. Which of the following equations corresponds to the definition of enthalpy of formation at 298 K?
(a) $C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(l) \rightarrow CH_3OH(g)$
(b) $C(\text{diamond}) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$
(c) $2C(\text{graphite}) + 4H_2(g) + O_2(g) \rightarrow 2CH_3OH(l)$
(d) $C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$

40. The molar enthalpies of combustion of $C_2H_2(g)$, $C(\text{graphite})$ and $H_2(g)$ are -1300, -394 and -286 kJ mol^{-1}, respectively. The standard enthalpy of formation of $C_2H_2(g)$ is
(a) -226 kJ mol^{-1} (b) -626 kJ mol^{-1} (c) 226 kJ mol^{-1} (d) 626 kJ mol^{-1}

41. Standard molar enthalpy of formation of CO_2 is equal to
(a) zero
(b) the standard molar enthalpy of combustion of gaseous carbon
(c) the sum of standard molar enthalpies of formation of CO and O_2
(d) the standard molar enthalpy of combustion of carbon(graphite) (1997)

42. Which of the following reactions corresponds to the definition of enthalpy of formation at 298 K?
(a) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ (b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
(c) $H_2(g) + \frac{1}{2}O_2(l) \rightarrow H_2O(l)$ (d) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$

43. For which one of the following equations is $\Delta_r H°$ equal to $\Delta_f H°$?

(a) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(1) + 2HCl(g)$ (b) $Xe(g) + 2F_2(g) \longrightarrow XeF_4(g)$

(c) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ (d) $N_2(g) + O_3(g) \longrightarrow N_2O_3(g)$ (2003)

Enthalpy of Combustion

44. The products of combustion of an aliphatic thiol (RSH) at 298 K are
(a) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$ (b) $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$
(c) $CO_2(l)$, $H_2O(l)$ and $SO_2(g)$ (d) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$ (1992)

45. Which of the following equations corresponds to the enthalpy of combustion at 298 K?

(a) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ (b) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

(c) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ (d) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

46. Which of the following reactions corresponds to the definition of enthalpy of combustion at 25 °C?
(a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ (b) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
(c) $CH_4(l) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ (d) $CH_4(l) + 2O_2(l) \rightarrow CO_2(l) + 2H_2O(l)$

Enthalpy of Reaction

47. For the equations

$$C(\text{diamond}) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta H_1$$
$$C(g) + 4H(g) \rightarrow CH_4(g) \qquad \Delta H_2$$

predict whether
(a) $\Delta H_1 = \Delta H_2$ (b) $\Delta H_1 > \Delta H_2$
(c) $\Delta H_1 < \Delta H_2$ (d) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

48. The expression $\Delta_{sub}H° = \Delta_{fus}H° + \Delta_{vap}H°$ is true at all
(a) temperatures (b) pressures
(c) temperatures and pressures (d) temperatures and 1 bar pressure conditions

49. Which of the following expressions is true?

(a) $\Delta_f H°(CO, g) = \frac{1}{2}\ \Delta_f H°(CO_2, g)$

(b) $\Delta_f H°(CO, g) = \Delta_f H°(C, \text{graphite}) + \frac{1}{2}\ \Delta_f H°(O_2, g)$

(c) $\Delta_f H°(CO, g) = \Delta_f H°(CO_2, g) - \frac{1}{2}\ \Delta_f H°(O_2, g)$

(d) $\Delta_f H°(CO, g) = \Delta_c H°(C, \text{graphite}) - \Delta_c H°(CO, g)$

50. The $\Delta_f H°$ for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, – 110.5 and – 241.8 kJ mol^{-1} respectively. The standard enthalpy change for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is
(a) 524.1 kJ mol^{-1} (b) 41.2 kJ mol^{-1} (c) – 262.5 kJ mol^{-1} (d) – 41.2 kJ mol^{-1} (2000)

51. In an endothermic reaction
(a) the enthalpy of reactants is more than that of products
(b) heat is given out of the system
(c) ΔH has a positive value
(d) ΔU has a negative value

52. Given:

$$HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq); \qquad \Delta H_1 = -41.84 \text{ kJ mol}^{-1}$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l); \qquad \Delta H_2 = -57.32 \text{ kJ mol}^{-1}$$

The enthalpy change for the reaction $HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq)$ would be
(a) (– 41.84 – 57.32) kJ mol^{-1} (b) (– 41.84 + 57.32) kJ mol^{-1}
(c) (41.84 + 57.32) kJ mol^{-1} (d) (41.84 – 57.32) kJ mol^{-1}

53. The reaction of cyanamide, $NH_2CN(s)$, with oxygen was run in a bomb calorimeter and ΔU at 300 K was found to be –743 kJ mol^{-1}. The value of ΔH at 300 K for the combustion reaction
$NH_2CN(s) + (3/2)\ O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$ would be
(a) – 741.75 kJ mol^{-1} (b) – 743 kJ mol^{-1} (c) – 744.25 kJ mol^{-1} (d) – 740.5 kJ mol^{-1}

54. The enthalpies of combustion of S(s), SO_2(g) and H_2(g) are – 298.2, – 98.7 and – 287.3 kJ mol^{-1}. If the enthalpy of reaction $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$ is – 130.2 kJ mol^{-1}, the enthalpy of formation of H_2SO_4(l) would be

(a) – 814.4 kJ mol^{-1} (b) – 650.3 kJ mol^{-1} (c) – 554.2 kJ mol^{-1} (d) – 435.5 kJ mol^{-1}

55. If $\Delta_f H°$(CO, g) = – 110.5 kJ mol^{-1} and $\Delta_f H°(CO_2, g)$ = – 393.5 kJ mol^{-1}, the mass of oxygen consumed in the reaction C(graphite) + O_2(g) → mixture of CO(g) + CO_2(g) for which $\Delta_r H$ = – 313.8 kJ mol^{-1} will be about

(a) 24.0 g (b) 25.5 g (c) 27.5 g (d) 29.0 g

56. The standard energy change for the reaction

$$\begin{array}{lccccc} & CH_4(g) + & 4CuO(s) \rightarrow & CO_2(g) + & 2H_2O(l) + & 4Cu(s) \\ \Delta_f H°/kJ\ mol^{-1} & -74.9 & -157.3 & -393.5 & -285.9 & \end{array}$$

is

(a) – 261.2 kJ mol^{-1} (b) 261.2 kJ mol^{-1} (c) – 130.6 kJ mol^{-1} (d) 130.6 kJ mol^{-1}

57. The enthalpy change in the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ is termed as

(a) enthalpy of reaction (b) enthalpy of fusion (c) enthalpy of formation (d) enthalpy of combustion

58. The standard enthalpy of combustion at 25 °C of H_2(g), cyclohexene(g) and cyclohexane(g) are – 241, – 3800 and – 3920 kJ mol^{-1}, respectively. The standard enthalpy of hydrogenation of cyclohexene will be

(a) 121 kJ mol^{-1} (b) – 1211 kJ mol^{-1} (c) – 121 kJ mol^{-1} (d) – 242 kJ mol^{-1}

59. The enthalpies of combustion of C(graphite) and C(diamond) are – 393.5 kJ mol^{-1} and – 395.3 kJ mol^{-1}, respectively. The enthalpy change of the reaction C(graphite) → C(diamond) is

(a) – 1.80 kJ mol^{-1} (b) 1.80 kJ mol^{-1} (c) 3.60 kJ mol^{-1} (d) – 360 kJ mol^{-1}

60. The enthalpy of formation of Al_2O_3(s) and Fe_2O_3(s) are – 1670 kJ mol^{-1} and – 834 kJ mol^{-1}, respectively. The enthalpy change of the reaction $Fe_2O_3(s) + Al(s) \rightarrow Al_2O_3(s) + 2Fe(s)$ would be

(a) 836 kJ mol^{-1} (b) 2504 kJ mol^{-1} (c) – 2504 kJ mol^{-1} (d) – 836 kJ mol^{-1}

Enthalpy of Neutralization

61. Given $\Delta_{ioniz}H°$(HCN) = 45.2 kJ mol^{-1} and $\Delta_{ioniz}H°(CH_3COOH)$ = 2.1 kJ mol^{-1}. Which one of the following facts is true?

(a) $pK_a(HCN) = pK_a(CH_3COOH)$ (b) $pK_a(HCN) > pK_a(CH_3COOH)$

(c) $pK_a(HCN) < pK_a(CH_3COOH)$ (d) $pK_a(HCN) = (45.17/2.07)pK_a(CH_3COOH)$

62. Enthalpy of neutralization of a strong acid and a strong base is

(a) – 57.32 kJ mol^{-1} (b) – 55.56 kJ mol^{-1} (c) – 54.0 kJ mol^{-1} (d) – 51.0 kJ mol^{-1}

63. The magnitude of enthalpy of neutralization of a weak acid and a strong base may be

(a) equal to 57.32 kJ mol^{-1} (b) greater than 57.32 kJ mol^{-1}

(c) lesser than 57.32 kJ mol^{-1} (d) greater or lesser than 57.32 kJ mol^{-1} depending upon acid

Bond Enthalpy

64. The bond enthalpies of H—H, Cl—Cl and H—Cl are 435, 243 and 431 kJ mol^{-1}, respectively. The enthalpy of formation of HCl(g) will be

(a) 92 kJ mol^{-1} (b) – 92 kJ mol^{-1} (c) 247 kJ mol^{-1} (d) 770 kJ mol^{-1}

65. The bond enthalpies of H—H and Cl—Cl are 430 and 242 kJ mol^{-1}. If $\Delta_f H$(HCl) is – 91 kJ mol^{-1}, the bond enthalpy of HCl would be

(a) – 214 kJ mol^{-1} (b) – 427 kJ mol^{-1} (c) 214 kJ mol^{-1} (d) 427 kJ mol^{-1}

66. The enthalpy of combustion of H_2(g) at 298 K to give H_2O(g) is – 249 kJ mol^{-1} and bond enthalpies of H—H and O=O are 433 kJ mol^{-1} and 492 kJ mol^{-1}, respectively. The bond enthalpy of O—H is

(a) 464 kJ mol^{-1} (b) – 464 kJ mol^{-1} (c) 232 kJ mol^{-1} (d) – 232 kJ mol^{-1}

67. The enthalpy of combustion of H_2(g) to give H_2O(g) is – 249 kJ mol^{-1} and bond enthalpies of H—H and O=O are 433 kJ mol^{-1} and 492 kJ mol^{-1}, respectively. The bond enthalpy of O—H is

(a) 464 kJ mol^{-1} (b) – 464 kJ mol^{-1} (c) 232 kJ mol^{-1} (d) – 232 kJ mol^{-1}

68. Given are the bond enthalpies: $\varepsilon(\mathrm{N{\equiv}N}) = 945\ \mathrm{kJ\ mol^{-1}}$, $\varepsilon(\mathrm{H{-}H}) = 436\ \mathrm{kJ\ mol^{-1}}$ and $\varepsilon(\mathrm{N{-}N}) = 391\ \mathrm{kJ\ mol^{-1}}$. The enthalpy change of the reaction $\mathrm{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}$ is

(a) $-\ 93\ \mathrm{kJ\ mol^{-1}}$ (b) $-\ 89\ \mathrm{kJ\ mol^{-1}}$ (c) $-\ 105\ \mathrm{kJ\ mol^{-1}}$ (d) $105\ \mathrm{kJ\ mol^{-1}}$

69. If $\varepsilon(\mathrm{C{=}C}) = 590\ \mathrm{kJ\ mol^{-1}}$ and $\varepsilon(\bar{\mathrm{C}}{-}\mathrm{C}) = 331\ \mathrm{kJ\ mol^{-1}}$, the enthalpy of polymerisation per mole of ethylene will be about

(a) $72\ \mathrm{kJ\ mol^{-1}}$ (b) $-\ 72\ \mathrm{kJ\ mol^{-1}}$ (c) $144\ \mathrm{kJ\ mol^{-1}}$ (d) $-\ 144\ \mathrm{kJ\ mol^{-1}}$

70. If $\varepsilon(\mathrm{C{-}H}) = 413.4\ \mathrm{kJ\ mol^{-1}}$, $\varepsilon(\mathrm{C{-}C}) = 347.7\ \mathrm{kJ\ mol^{-1}}$, $\varepsilon(\mathrm{C{=}C}) = 615.1\ \mathrm{kJ\ mol^{-1}}$, $\Delta_{\mathrm{sub}}H(\mathrm{C,\ graphite}) = 718.4\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{f}}H(\mathrm{H,\ g}) = 218\ \mathrm{kJ\ mol^{-1}}$, the enthalpy of formation of gaseous isoprene ($\mathrm{CH_2{=}C(CH_3)CH{=}CH_2}$) will be about

(a) $206.4\ \mathrm{kJ\ mol^{-1}}$ (b) $-\ 206.4\ \mathrm{kJ\ mol^{-1}}$ (c) $103.2\ \mathrm{kJ\ mol^{-1}}$ (d) $-\ 103.2\ \mathrm{kJ\ mol^{-1}}$

71. If $\Delta_{\mathrm{f}}H$ of $\mathrm{SF_6(g)}$, S(g) and F(g) are $-\ 1100$, 275 and 80 $\mathrm{kJ\ mol^{-1}}$, the S—F bond enthalpy will be about

(a) $103.1\ \mathrm{kJ\ mol^{-1}}$ (b) $206.2\ \mathrm{kJ\ mol^{-1}}$ (c) $251.8\ \mathrm{kJ\ mol^{-1}}$ (d) $309.2\ \mathrm{kJ\ mol^{-1}}$

72. The enthalpies of formation of OH(g), H(g) and O(g) are 42, 218 and 248 $\mathrm{kJ\ mol^{-1}}$. The value of bond enthalpy O—H is

(a) $424\ \mathrm{kJ\ mol^{-1}}$ (b) $-\ 424\ \mathrm{kJ\ mol^{-1}}$ (c) $212\ \mathrm{kJ\ mol^{-1}}$ (d) $-\ 212\ \mathrm{kJ\ mol^{-1}}$

73. Which of the following is expected to have largest bond dissociation enthalpy?

(a) HF (b) HCl (c) HBr (d) HI

Entropy and Free Energy Function

74. Which of the following statements regarding the entropy is not correct?

(a) S(monoclinic) > S(rhombic) (b) C(diamond) > C(graphite)

(c) $\mathrm{H_2O(g) > H_2O(l)}$ (d) $\mathrm{O_3(g) > O_2(g)}$

75. Which of the following results in a decrease in entropy?

(a) Crystallization of sucrose from solution (b) Rusting of iron

(c) Conversion of ice into water (d) Vaporisation of camphor

76. For an irreversible isothermal expansion of an ideal gas

(a) $\Delta S_{\mathrm{sys}} = \Delta S_{\mathrm{surr}}$ (b) $\Delta S_{\mathrm{sys}} = -\ \Delta S_{\mathrm{surr}}$ (c) $|\Delta S_{\mathrm{sys}}| > |\Delta S_{\mathrm{surr}}|$ (d) $|\Delta S_{\mathrm{sys}}| < |\Delta S_{\mathrm{urr}}|$

77. Which of the following species has zero entropy at 0 K?

(a) $\mathrm{H_2}$ (b) CO (c) NO (d) $\mathrm{O_2}$

78. The combustion reaction occurring in an automobile is $\mathrm{2C_8H_{18}(s) + 5O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)}$. This reaction is accompanied with

(a) $\Delta H = -\mathrm{ve}$, $\Delta S = +\mathrm{ve}$, $\Delta G = +\mathrm{ve}$ (b) $\Delta H = +\mathrm{ve}$, $\Delta S = -\mathrm{ve}$, $\Delta G = +\mathrm{ve}$

(c) $\Delta H = -\mathrm{ve}$, $\Delta S = +\mathrm{ve}$, $\Delta G = -\mathrm{ve}$ (d) $\Delta H = +\mathrm{ve}$, $\Delta S = +\mathrm{ve}$, $\Delta G = -\mathrm{ve}$

79. For the reaction $\mathrm{2A(g) + B(g) \rightarrow 2D(g)}$; $\Delta U^{\circ}_{300\mathrm{K}} = -\ 10.0\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\circ}_{300\mathrm{K}} = -\ 45\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The reaction

(a) will be spontaneous (b) will not be spontaneous

(c) will be at equilibrium (d) is endothermic

80. For a reversible reaction at temperature T, which of the following is correct?

(a) $T > \Delta H/\Delta S$ (b) $T < \Delta H/\Delta S$ (c) $T = \Delta H/\Delta S$ (d) $T = \Delta S/\Delta H$

81. For the chemical equation $\mathrm{2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)}$, the entropy change would be

(a) negative (b) positive (c) zero (d) independent of temperature

82. The enthalpy of vaporization of water at 100 °C is $40.63\ \mathrm{kJ\ mol^{-1}}$. Its entropy of vaporization would be

(a) $406.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ (b) $108.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$ (c) $606.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ (d) $4063\ \mathrm{kJ\ mol^{-1}}$

83. For a spontaneous process at all conditions of temperature, which of the following is correct?

(a) ΔH positive and ΔS positive (b) ΔH negative and ΔS positive

(c) ΔH positive and ΔS negative (d) ΔH negative and ΔS negative

84. For a spontaneous process, which of the following is correct?

(a) ΔS_{sys} positive (b) ΔS_{surr} positive (c) $\Delta S_{\mathrm{total}}$ positive (d) $\Delta S_{\mathrm{total}}$ negative

85. For a reversible isothermal expansion of an ideal gas

(a) $\Delta S_{\mathrm{sys}} = \Delta S_{\mathrm{surr}} = \mathrm{positive}$ (b) $\Delta S_{\mathrm{sys}} = -\ \Delta S_{\mathrm{surr}}$

(c) $\Delta S_{\mathrm{sys}} = \Delta S_{\mathrm{surr}} = \mathrm{negative}$ (d) $\Delta S_{\mathrm{sys}} = \Delta S_{\mathrm{surr}} = 0$

86. Which of the following is not expected to have zero entropy at 0 °C?
(a) Br_2 (b) CO (c) Cl_2 (d) He

87. The enthalpy of vaporization of water at 100 °C is 37.3 kJ mol^{-1}. Its entropy of vaporization will be
(a) 37300 kJ K^{-1} mol^{-1} (b) 50 J K^{-1} mol^{-1} (c) 0.0373 kJ K^{-1} mol^{-1} (d) 100 J K^{-1} mol^{-1}

88. For a spontaneous process, the change of Gibbs function is equal to the
(a) heat content of the system (b) entropy change of the system
(c) work of expansion (d) useful work

89. When an ideal gas is suddenly expanded adiabatically against vacuum
(a) $\Delta S = 0$ (b) $\Delta G = 0$ (c) $\Delta U = 0$ (d) $\Delta p = 0$

90. The term $R \ln K_p^\circ$ is equal to
(a) $-\Delta G$ (b) $-\Delta G^\circ$ (c) $-\Delta G/T$ (d) $-\Delta G^\circ/T$

91. Which of the following expressions is not correct?
(a) $\Delta G^\circ = -nFE^\circ$ (b) $\Delta G^\circ = -RT \ln K_{eq}^\circ$
(c) $E^\circ = (RT/n\mathrm{F}) \log K_p^\circ$ (d) $\Delta G = \Delta G^\circ + RT \ln Q_p$

92. For a reaction $A(g) \rightleftharpoons B(g)$ at equilibrium, the partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction $A \rightarrow B$ is
(a) $RT \ln 4$ (b) $-RT \ln 4$ (c) $RT \log 4$ (d) $-RT \log 4$

93. The standard enthalpy and entropy of vaporization of a liquid are 25 kJ mol^{-1} and 100 J K^{-1} mol^{-1}, respectively. The normal boiling point of the liquid is
(a) 200 K (b) 250 K (c) 400 K (d) 500 K (2004)

94. The reaction A → B proceeds through the following steps: $A \rightarrow C \rightarrow D \rightarrow B$
If ΔS (A → C) = 60 eu, ΔS(C → D) = 20 eu and ΔS(B → D) = 10 eu, entropy change for A → B would be
(a) 70 eu (b) –70 eu (c) 90 eu (d) –90 eu (2006)

95. For the process H_2O(1, 1 bar, 373 K) → H_2O(g, 1 bar, 373 K), the correct set of thermodynamic parameters is (2007)
(a) $\Delta G = 0$, $\Delta S = +ve$ (b) $\Delta G = 0$, $\Delta S = -ve$ (c) $\Delta G = +ve$, $\Delta S = 0$ (d) $\Delta G = -ve$, $\Delta S = +ve$

96. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given: $\Delta_r H_{298K} = -54.07$ kJ mol^{-1}, $\Delta_r, S^\circ_{298K} = 10$ J K^{-1} mol^{-1} and $R = 8.314$ J K^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$.)
(a) 5 (b) 10 (c) 95 (d) 100 (2007)

97. The entropy change in an adiabatic reversible expansion of an ideal is
(a) positive (b) negative
(c) zero (d) positive or negative depending upon the pressure of the gas

98. If $\Delta_f G^\circ(H_2O, l) = -237.19$ kJ mol^{-1} and $\Delta_f G^\circ(H_2O, g) = -228.59$ kJ mol^{-1}, the vapour pressure of water at 298 K would be about
(a) 0.01 atm (b) 0.02 atm (c) 0.03 atm (d) 0.05 atm

99. If $\Delta_f H^\circ$(OH, g) = 42.0 kJ mol^{-1}, $\Delta_f H^\circ$(H, g) = 218.0 k J mol^{-1} and $\Delta_f H^\circ$(O, g) = 148 kJ mol^{-1}, then the bond enthalpy of OH(g) is
(a) 424 kJ mol^{-1} (b) 212 kJ mol^{-1} (c) 260 kJ mol^{-1} (d) 290 kJ mol^{-1}

100. If the vaporization of benzene at it boiling point (353 K) is 31.064 kJ mol^{-1}, then the its entropy of vaporization will be
(a) 78 J K^{-1} mol^{-1} (b) 88 J K^{-1} mol^{-1} (c) 98 J K^{-1} mol^{-1} (d) 108 J K^{-1} mol^{-1}

Multiple Correct Choice Type

1. For the reaction $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$; ΔH = positive, which of the following fact(s) is/are correct?
(a) $\Delta H = \Delta U$ (b) $\Delta H < \Delta U$ (c) $\Delta H > \Delta U$ (d) $(RT)^{\Delta \nu g} = 1$ at 298 K

2. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2\,NH_3(g)$ which of the following fact(s) is/are correct?
(a) $\Delta H = \Delta U$ (b) $\Delta H < \Delta U$ (c) $\Delta H > \Delta U$ (d) $(RT)^{\Delta \nu g} < 1$ at 298 K

3. For the reaction $SO_3(g) \rightarrow SO_2(g) + O_2(g)$ which of the following fact(s) is/are correct?
(a) $\Delta H = \Delta U$ (b) $\Delta H < \Delta U$ (c) $\Delta H > \Delta U$ (d) $(RT)^{\Delta \nu g} > 1$ at 298 K

4. Which of the following statements is/are correct?
(a) Enthalpy of combustion of most species is an exothermic process.
(b) Amongst cyclopropane, cyclobutane and cyclopentane, the enthalpy of combustion per CH_2 group is maximum for cyclopropane.
(c) The enthalpy of formation of acetylene is positive.
(d) The entropy of all substances at 25 °C is positive.

5. Which of the following statements are correct?
(a) First law of thermodynamics is not adequate in predicting the direction of the process.
(b) In an exothermic reaction, the total enthalpy of products is greater than that of reactants.
(c) In an endothermic reaction, the total enthalpy of products is greater than that of reactants.
(d) The standard enthalpy of formation of diamond is zero at 298 K and 1 atm pressure.

6. Which of the following statements are correct?
(a) The standard enthalpy of formation of $Br_2(g)$ is taken to be zero at standard conditions of 298 K and 1 atm.
(b) The magnitude of enthalpy of neutralization of a weak acid is smaller than that of a strong acid.
(c) In the relation $\Delta H = \Delta U + (\Delta \nu_g)RT$, the units of $\Delta \nu_g$ is mol.
(d) The terms, bond enthalpy and bond dissociation enthalpy stand for one and the same thing.

7. Which of the following statements are correct?
(a) At 298 K, the enthalpy of combustion of CH_4 corresponds to the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

(b) For an exothermic reaction, ΔH is positive.
(c) For an endothermic reaction, ΔH is positive.
(d) The calorific value of a fat is greater than that of a carbohydrate.

8. Which of the following statements are correct?
(a) For a reaction involving condensed phases $\Delta H = \Delta U$.
(b) It is possible to calculate the value of ΔH for the reaction $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$ from the bond-enthalpy data alone.
(c) The enthalpy of combustion of diamond and enthalpy of formation of carbon dioxide has the same value.
(d) The reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is accompanied with decrease in entropy.

9. Which of the following statements are **not** correct?
(a) In an exothermic reaction, the total enthalpy of reactants is lesser than that of products.
(b) In an endothermic reaction, the total enthalpy of reactant is lesser than that of products.
(c) The standard molar enthalpy of formation of a substance is the enthalpy of formation of the substance at 1 atm pressure and at specified temperature.
(d) The conventional standard molar enthalpy of formation of an element in its stable state of aggregation at 273 K is taken to be zero.

10. Which of the following statements are **not** correct?
(a) The products of combustion of a hydrocarbon at 298 K are $H_2O(l)$ and $CO_2(g)$.
(b) The products of combustion of a hydrocarbon at 398 K are $H_2O(l)$ and $CO_2(g)$.
(c) The enthalpy of neutralization is about $-$ 52.5 kJ mol^{-1}.
(d) The magnitude of enthalpy of neutralization of a weak acid is smaller than that of a strong acid. The difference of the latter from the former is known as enthalpy of ionization of the weak acid.

11. Which of the following statements are correct?
(a) The heat released when the requisite amounts of ions in the gaseous state combine to given 1 mol of crystal lattice is known as lattice energy.
(b) Enthalpy of fusion of KCl is larger than that of naphthalene.
(c) The stable state of aggregation of carbon at 298 K and 1 bar pressure is diamond.
(d) The stable state of aggregation of sulphur at 298 K and 1 bar pressure is rhombic sulphur.

12. Identify the intensive quantities from the following: (1993)
(a) Enthalpy (b) Temperature (c) Volume (d) Refractive index

13. The following is (are) endothermic reaction(s) :
(a) Combustion of methane
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethylene
(d) Conversion of graphite to diamond (1999)

14. Among the following, the state function(s) is/are
(a) Internal energy
(b) Irreversible expansion work
(c) Reversible expansion work
(d) Molar enthalpy (2009)

15. An ideal gas is taken from the state A (pressure p, volume V) to the state B (pressure $p/2$, volume $2V$) along a straight line path in the p-V diagram. Select the correct statement(s) from the following:
(a) The work done by the gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along an isotherm.
(b) In the T-V diagram, the path AB becomes a part of a parabola.
(c) In the p-T diagram, the path AB becomes a part of a hyperbola.
(d) In going from A to B, the temperature T of the gas first increases to a maximum value and then decreases.

16. During the melting of a slab of ice at 273 K at atmospheric pressure,
(a) work is done by the ice-water system on the atmosphere.
(b) work is done on the ice-water system by the atmosphere.
(c) the internal energy of the ice-water system increases.
(d) the inernal energy of the ice-water system decreases.

17. An ideal gas is compressed reversily and adiabatically. Its
(a) temperature will increase
(b) internal energy will increase
(c) entropy will increase
(d) pressure will increase

18. For an ideal gas
(a) the change in internal energy in a constant pressure process from temperature T_1 to T_2 is equal to $nC_{V,\mathrm{m}}\ (T_2 - T_1)$,
(b) the change in internal energy of the gas and the work done by the gas are equal in magnitude in an adiabatic process
(c) the inernal energy does not change in an isothermal process
(d) no heat is added or removed in an adiabatic process.

19. Which of the following statements are correct ?
(a) The value of $C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$ for a mixture of 1 mol of a monatomic gas ($\gamma = 5/3$) and 1 mol of a diatomic gas ($\gamma = 7/5$) is 1.5.
(b) The work done by an ideal gas in expanding V_1 to V_2 is higher when the expansion is done isothermally as compared to that carried out adiabatically.
(c) The internal energy of an ideal gas does not change in the isothermal process.
(d) The fraction of heat utilized in increasing energy of a monatomic gas is 3/5 when the heat is supplied under constant pressure condition.

20. In thermodynamics, a process is called reversible when
(a) surroundings and system change into each other
(b) system and surroundings can be restored by following reverse path
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

21. Which one of the following statements is false?
(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states ae specified
(d) Heat is a state function

Linked Comprehension Type

1. Given:
$\Delta_f G^\circ(NH_4^+, aq) = -\ 79.31$ kJ mol^{-1}, $\Delta_f G^\circ(OH^-, aq) = -\ 157.24$ kJ mol^{-1} $\Delta_f G^\circ(NH_3, g) = -\ 16.45$ kJ mol^{-1} $\Delta_f G^\circ(H_2O, 1) = -\ 237.13$ kJ mol^{-1} and $K_b^\circ(NH_4OH) = 1.8 \times 10^{-5}$. Assume $T = 298$ K.

(i) $\Delta_r G^\circ$ for $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ is about

(a) 27.07 kJ mol^{-1} (b) 54.14 kJ mol^{-1} (c) – 27.07 kJ mol^{-1} (d) – 54.14 kJ mol^{-1}

(ii) $\Delta_f G^\circ(NH_4OH)$ is about

(a) 263.62 kJ mol^{-1} (b) –263.62 kJ mol^{-1} (c) 290.69 kJ mol^{-1} (d) – 54.14 kJ mol^{-1}

(iii) $\Delta_r G^\circ$ for $NH_3(g) + H_2O(l) = NH_4OH(aq)$ is about

(a) 10.04 kJ mol^{-1} (b) – 37.11 kJ mol^{-1} (c) 37.11 kJ mol^{-1} (d) – 10.04 kJ mol^{-1}

2. Given: $NH_3(g) + H_2O(l) = NH_4OH(aq)$: $\Delta_r G^\circ = -\ 10.04$ kJ mol^{-1}. $\Delta_f G^\circ(NH_4^+, aq) = -\ 79.31$ kJ mol^{-1} $\Delta_f G^\circ(OH^-, aq) = -\ 157.24$ kJ mol^{-1}. $\Delta_f G^\circ(NH_3, g) = -\ 16.45$ kJ mol^{-1}. $\Delta_f G^\circ(H_2O, 1) = -\ 237.13$ kJ mol^{-1}

(i) The value of K° for $NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(aq)$ at 298 K is about

(a) 57.53 (b) 115.06 (c) 172.56 (d) 230.12

(ii) $\Delta_r G^\circ$ for $NH_3(g) + H_2O(l) = NH_4^+\ (aq) + OH^-\ (aq)$ is about

(a) – 17.03 kJ mol^{-1} (b) – 34.06 kJ mol^{-1} (c) 34.06 kJ mol^{-1} (d) 17.03 kJ mol^{-1}

(iii) K° for $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$ is about

(a) 1.03×10^{-2} (b) 1.03×10^{-3} (c) 1.03×10^{-4} (d) 1.03×10^{-5}

3. An ideal gas has a molar heat capacity at constant pressure equal to $5R/2$. The gas is kept in a closed vessel of volume 8300cm^3, at a temperature of 300 K and a pressure of 1.6 MPa. To this system, 24.9 kJ of heat is supplied. Based on this information, answer the following three questions.

(i) The amount of gas is about

(a) 4.50 mol (b) 5.33 mol (c) 6.44 mol (d) 7.52 mol

(ii) The final temperature of the gas is about

(a) 350 K (b) 360 K (c) 375 K (d) 395 K

(iii) The final pressure of the gas is about

(a) 3.6 MPa (b) 4.5 MPa (c) 5.6 MPa (d) 6.5 MPa

4. At 27 °C, 2 mol of an ideal monatomic gas occupy a volume V. The gas expands adiabatically to a volume $2V$. Based on this information, answer the following three questions.

(i) The final temperature of the gas is about

(a) 150 K (b) 189 K (c) 232 K (d) 252 K

(ii) The change in internal energy of the gas is

(a) 2770 J (b) 1330 J (c) –1330 J (d) – 2770 J

(iii) The work done by the gas is

(a) – 2270 J (b) – 1540 J (c) – 1540 J (d) – 3240 J

5. Two moles of helium gas ($\gamma = 5/3$) is initially at 27 °C and occupies a volume of 20 L. The gas is first expanded at constant pressure unit the volume is doubled. This is followed by an adiabatic expansion until the temperature returns to its initial value. On this information, answer the following three questions.

(i) The final volume of the gas is

(a) 0.08 m^3 (b) 0.09 m^3 (c) 0.11 m^3 (d) 0.21 m^3

(ii) The final pressure of the gas is

(a) 44.1 kPa (b) 34.1 kPa (c) 30.1 kPa (d) 27.1 kPa

(iii) The work involved in the given processes is

(a) – 4980 J (b) – 7470 J (c) – 12450 J (d) – 16340 J

6. An ideal gas is taken through a cyclic process through four steps. The heats involved in these steps are $q_1 = 5960$ J, $q_2 = -\ 5585$ J, $q_3 = -\ 2980$ J and $q_4 = 3645$ J, respectively. The corresponding work involved as $w_1 = -\ 2200$ J, $w_2 = +825$ J, $w_3 = +1100$ J and w_4, respectively. Based on these information answer the following three questions.

(i) The work involved in the fourth step is

(a) 765 J (b) – 765 J (c) 456 J (d) – 456 J

(ii) The net energy change in the entire process is
(a) 1678 J (b) 2756 J (c) zero (d) – 2345 J

(iii) Which of the following steps is accompaned with a net decrease in the internal energy?
(a) (1st + 2nd) steps (b) (1st + 3rd) steps (c) (3rd + 4th) steps (d) (1st + 4th) steps

7. Given are the following data at 298 K.

$\Delta_{\text{comb}}H°(\text{glucose}) = -\ 2815.8\ \text{kJ mol}^{-1}$ $S°(O_2,\ g) = 205\ \text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_f G°(\text{glucose}) = -\ 900\ \text{kJ mol}^{-1}$ $S°(CO_2,\ g) = 213.6\ \text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_f G°(CO_2,\ g) = -\ 395\ \text{kJ mol}^{-1}$ $S°(H_2O,\ l) = 69.96\ \text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_f G°(H_2O,\ l) = -\ 237\ \text{kJ mol}^{-1}$

Using the above data, answer the following three questions.

(i) The value of $\Delta G°$ for the combustion of glucose is about
(a) – 2540 kJ mol^{-1} (b) – 2600 kJ mol^{-1} (c) – 2690 kJ mol^{-1} (d) – 2890 kJ mol^{-1}

(ii) The value of $\Delta S°$ for the combustion of glucose is about
(a) 236 J K^{-1} mol^{-1} (b) 256 J K^{-1} mol^{-1} (c) 276 J K^{-1} mol^{-1} (d) 296 J K^{-1} mol^{-1}

(iii) The entropy of glucose is about
(a) 215 J K^{-1} mol^{-1} (b) 225 J K^{-1} mol^{-1} (c) 245 J K^{-1} mol^{-1} (d) 255 J K^{-1} mol^{-1}

8. When 12.0 g of carbon reacted with oxygen to form a mixture of CO and CO_2 at 25°C and constant pressure, 315 kJ of heat was released. Given $\Delta_f H°(CO,\ g) = -\ 110\ \text{kJ mol}^{-1}$ and $\Delta_f H°(CO_2,\ g) = -\ 395\ \text{kJ mol}^{-1}$. Based on this data, answer the following three questions.

(i) Mass of carbon yielding CO is
(a) 6.0 g (b) 7.5 g (c) 9.0 g (d) 10.5 g

(ii) Mass of oxygen reacted with carbon yielding carbon dioxide is
(a) 15.0 g (b) 19.0 g (c) 21.0 g (d) 23.0 g

(iii) Mass of total oxygen reacted is
(a) 27.5 g (b) 29.9 g (c) 32 g (d) 35.2 g

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explanation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	**Statement–2**
1.	The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.	The volume occupied by the molecules of an ideal gas is zero.
2.	Nitric oxide has nonzero value of entropy at 0 K.	All pure crystalline substance is expected to have zero entropy at 0 K.
3.	The enthalpy of formation of diamond is zero.	The enthalpy of formation of an element is taken to be zero for the most stable form of the element at 298 K.
4.	The reaction accompained with $\Delta H < 0$ and $\Delta S > 0$ is spontaneous at all temperature.	The free energy change of the reaction will always be less than zero.
5.	The boiling of an egg is accompained with increase in its entropy.	There is a break down of hydrogen bonding in the constituents of an egg on heating and thus is accompained with more disorderliness.
6.	An adiabatic expansion of a gas in accompained with decrease in its internal energy.	The decreases of energy is due to the transfer of heat from the system to its surroundings.
7.	The enthalpy of reaction is related to energy of reaction by the expression $\Delta_r H = \Delta_r U + (\Delta \nu_g)RT$.	$\Delta\nu_g$ in the relation $\Delta_r H = \Delta_r U + (\Delta \nu_g)RT$ represents change in amount of gaseous species in a chemical reaction.

8.	The heat released in the neutralization of a weak acid with a strong base is always less than that released in the neutralization of a strong acid with a strong base.	Weak acid is partly ionized in solution while strong acid is completely ionized in solution.
9.	For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.	At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
10.	There is a natural asymmetry between converting work to heat and converting heat to work.	No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

Matrix Match Type

1. The entries in Column I is related with the $\gamma (= C_{p,\mathrm{m}}/C_{V,\mathrm{m}})$ values given in Column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Monatomic gas	(p) 9/7
(b) Diatomic gas	(q) 7/6
(c) Linear triatomic gas	(r) 5/3
(d) Nonlinear triatomic gas	(s) 15/3

2. The signs of $\Delta_r H$ and $\Delta_r S$ of chemical reactions are given in Column I. Match each of these entries with the correct characteristic of the reactions given in column II.

Column I	**Column II**
(a) ΔH = +ve ; ΔS = +ve	(p) Spontaneous at low temperature
(b) ΔH = +ve ; ΔS = –ve	(q) Spontaneous at high temperature
(c) ΔH = –ve ; ΔS = +ve	(r) Nonspontaneous at low temperature
(d) ΔH = –ve ; ΔS = –ve	(s) Nonspontaneous at high temperature

3. Column I lists a few physical processes and their expressions to compute these physical processes are listed in Column II. Match the correct choices.

Column I	**Column II**
(a) $\Delta_r G^\circ$	(p) $\Delta_r U + (\Delta \nu_g)RT$
(b) $\Delta_r H$	(q) $RT \ln(p_1/p_2)$
(c) $\Delta_r S$	(r) q_{rev}/T
(d) $w_{\mathrm{reversible}}$	(s) $- RT \ln K^\circ$
	(t) $- nFE^\circ$
	(u) $nC_{p,\mathrm{m}}\Delta T$

4. Column I list expansion of an ideal gas under different conditions and the corresponding expressions to be used are listed in Column II. Identify the correct choice.

Column I	**Column II**
(a) Reversible isothermal expansion	(p) $- p_{\mathrm{ext}}(V_2 - V_1)$
(b) Reversible adiabatic expansion	(q) $- nRT \ln (V_2/V_2)$
(c) Irreversible isothermal expansion against a constant pressure	(r) $C_V \Delta T$
(d) Irreversible adiabatic expansion	(s) $- nRT \ln (p_1/p_2)$
	(t) pV^γ = constant

5. Column I lists four thermodynamic quantities and their natural independent variables are listed in Column II. Identify the correct choices.

Column I	**Column II**
(a) U	(p) T
(b) H	(q) p
(c) A	(r) V
(d) G	(s) S

ANSWERS

Straight Objective Type

1. (a) **2.** (c) **3.** (d) **4.** (b) **5.** (c) **6.** (d) **7.** (b)
8. (c) **9.** (d) **10.** (b) **11.** (c) **12.** (c) **13.** (b) **14.** (a)
15. (c) **16.** (d) **17.** (a) **18.** (b) **19.** (a) **20.** (b) **21.** (c)
22. (b) **23.** (a) **24.** (c) **25.** (a) **26.** (a) **27.** (c) **28.** (b)
29. (b) **30.** (b) **31.** (c) **32.** (c) **33.** (b) **34.** (a) **35.** (b)
36. (c) **37.** (c) **38.** (c) **39.** (d) **40.** (c) **41.** (d) **42.** (a)
43. (b) **44.** (b) **45.** (c) **46.** (a) **47.** (b) **48.** (d) **49.** (d)
50. (b) **51.** (c) **52.** (b) **53.** (a) **54.** (a) **55.** (c) **56.** (a)
57. (a) **58.** (c) **59.** (b) **60.** (d) **61.** (b) **62.** (a) **63.** (c)
64. (b) **65.** (d) **66.** (a) **67.** (a) **68.** (a) **69.** (b) **70.** (c)
71. (d) **72.** (a) **73.** (a) **74.** (b) **75.** (a) **76.** (c) **77.** (d)
78. (c) **79.** (b) **80.** (c) **81.** (a) **82.** (b) **83.** (b) **84.** (c)
85. (b) **86.** (b) **87.** (d) **88.** (d) **89.** (c) **90.** (d) **91.** (c)
92. (a) **93.** (b) **94.** (a) **95.** (a) **96.** (b) **97.** (c) **98.** (c)
99. (a) **100.** (b)

Multiple Correct Choice Type

1. (a), (d) **2.** (b), (d) **3.** (c), (d) **4.** (a), (b), (c), (d)
5. (a), (c) **6.** (a), (c), (d) **7.** (c), (d) **8.** (a), (d)
9. (a), (d) **10.** (b), (c) **11.** (a), (b), (d) **12.** (b), (d)
13. (b), (c), (d) **14.** (a), (d) **15.** (a), (b), (d) **16.** (b), (c)
17. (a), (b), (d) **18.** (a), (b), (c), (d) **19.** (a), (c) **20.** (b), (c)
21. (a), (d)

Linked Comprehension Type

1. **(i)** (d) **(ii)** (b) **(iii)** (d)
2. **(i)** (a) **(ii)** (d) **(iii)** (b)
3. **(i)** (b) **(ii)** (c) **(iii)** (a)
4. **(i)** (b) **(ii)** (d) **(iii)** (a)
5. **(i)** (a) **(ii)** (c) **(iii)** (c)
6. **(i)** (b) **(ii)** (c) **(iii)** (a)
7. **(i)** (d) **(ii)** (b) **(iii)** (a)
8. **(i)** (c) **(ii)** (d) **(iii)** (a)

Assertion and Reason Type

1. (b) **2.** (b) **3.** (d) **4.** (a) **5.** (a) **6.** (c) **7.** (c)
8. (b) **9.** (d) **10.** (a)

Matrix Match Type

1. (a) – (r); (b) – (p); (c) – (s); (d) – (q)
2. (a) – (q), (r); (b) – (r), (s); (c) – (p), (q); (d) – (p), (s)
3. (a) – (s), (t); (b) – (p), (u); (c) – (r); (d) – (q)
4. (a) – (q), (s); (b) – (r), (t); (c) – (p); (d) – (p)
5. (a) – (r), (s); (b) – (q), (s); (c) – (p), (r); (d) – (p), (q)

Hints and Solutions

Straight Objective Type

1. For a monatomic gas, $C_{V,\,\mathrm{m}} = (3/2)R$ and $C_{p,\,\mathrm{m}} = (5/2)\,R$. Hence, $C_{p,\,\mathrm{m}}/C_{V,\,\mathrm{m}} = 5/3$.

2. For a diatomic gas, $C_{V,\,\mathrm{m}} = \frac{3}{2}R + R + R = (7/2)R$ and $C_{p,\,\mathrm{m}} = (9/2)R$. Hence $C_{p,\,\mathrm{m}}/C_{V,\,\mathrm{m}} = 9/7$.

3. For a linear triatomic molecule, $C_{V,\,\mathrm{m}} = \frac{3}{2}R + R + 4R = (13/2)R$ and $C_{p,\,\mathrm{m}} = (15/2)\,R$. Hence $C_{p,\,\mathrm{m}}/C_{V,\,\mathrm{m}} = 15/13$.

4. On adding heat, no change in temperature occurs. Hence, $C = q/T = \infty$.

5. For a linear triatomic molecule, $C_{V,\,\mathrm{m}} = \frac{3}{2}R + \frac{3}{2}R + 3R = 6R$, and $C_{p,\,\mathrm{m}} = 7R$. Hence $C_{p,\,\mathrm{m}}/C_{V,\,\mathrm{m}} = 7/6$.

6. A closed system can exchange heat and not matter.

7. $w = -\,p_{\mathrm{ext}}\Delta V = -\,(0.30\text{ atm})\,(14.0\text{ L} - 6.0\text{ L}) = -\,2.40\text{ atm L}\left(\dfrac{8.314\text{ J}}{0.082\text{ L atm}}\right) = -\,243.3\text{ J}$

8. $0.082\text{ L atm} = 8.314\text{ J}$. Hence, $1\text{ L atm} = \dfrac{8.314}{0.082}\text{ J} = 101.\,3\text{ J}$

9. $\Delta U = w = -\,p_{\mathrm{ext}}\Delta V = -\,(0.75\text{ atm})\,(12.0\text{ L} - 1.0\text{ L}) = 8.25\text{ L atm}$

$$\equiv -\,(8.25\text{ L atm})\left(\frac{8.314\text{ J}}{0.082\text{ L atm}}\right) = -\,835.9\text{ J}$$

10. Since q and w are not state function, the finite changes in these are not represented as Δq and Δw, respectively, but simply as q and w.

11. Since temperature remains constant, $\Delta H = 0$.

12. From first law of thermodynamics, we have $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

For adiabatic expansion, $\mathrm{d}q = 0$. Hence $\mathrm{d}U = \mathrm{d}w$ or $nC_{V,\mathrm{m}}\,\Delta T = -\,p\Delta V$

i.e. $$(1\text{ mol})\left(\frac{3}{2}R\right)(T_{\mathrm{f}} - T) = -\,(1\text{ atm})\,(3\text{ L} - 1\text{ L})$$

or $$T_{\mathrm{f}} = T - \frac{(1\,\text{atm})(2\,\text{L})}{(1\,\text{mol})(1.5\times0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1})} = T - \frac{2\,\text{K}}{1.5\times0.082}$$

13. By definition, $H = U + pV$

Hence $$C_{p,\mathrm{m}} = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

For the given ideal gas, we will have $pV = RT \Rightarrow \{(1\text{ atm L}^{-1})V\}\,V = RT$ or $V^2 = \dfrac{RT}{(1\text{ atm L}^{-1})}$

Hence $$2V\left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{(1\text{ atm L}^{-1})} \quad\text{or}\quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{2V(1\text{ atm L}^{-1})}$$

Also $$U = \frac{3}{2}RT \Rightarrow \left(\frac{\partial U}{\partial T}\right)_p = \frac{3}{2}R$$

With these, $$C_{p,\mathrm{m}} = \frac{3}{2}R + p\left\{\frac{R}{2V(1\,\text{atm}\,\text{L}^{-1})}\right\} = \frac{3}{2}R + \frac{R}{2} = 2R$$

14. The work done during the cyclic path is equal to the area enclosed by the path, which is, pV.

15. The initial pressures in the containers will be

$$p_A = \frac{n_A RT}{V} = m_A\left(\frac{RT}{MV}\right); \quad p_B = \frac{n_B RT}{V} = m_B\left(\frac{RT}{MV}\right)$$

After the isothermal expansions, the pressures will be

$$p'_A = \frac{n_A RT}{2V} = m_A\left(\frac{RT}{2MV}\right); \quad p'_B = \frac{n_B RT}{2V} = m_B\left(\frac{RT}{2MV}\right)$$

Now $-\Delta p_A = p_A - p'_A = m_A\left(\frac{RT}{2MV}\right)$ and $-\Delta p_B = p_B - p'_B = m_B\left(\frac{RT}{2MV}\right)$

It is given that $-\Delta p_A = \Delta P$ and $-\Delta p_B = 1.5\ \Delta P$.

Hence $-\Delta p_A = -\frac{\Delta p_B}{1.5}$ or $m_A\left(\frac{RT}{2MV}\right) = \frac{2}{3}\left(m_B\frac{RT}{2MV}\right)$ or $3m_A = 2m_B$

16. The heat given to the gas in cylinder A is at constant pressure, while to that in cylinder B is at constant volume. If such cylinder contains the amount n of a diatomic gas, then

Heat given to the gas in cylinder A = $nC_{p,\mathrm{m}}\ \Delta T = n\left(\frac{7}{2}R\right)(30\ \mathrm{K})$

If this much heat is given to the cylinder B, then

$$nC_{V,\mathrm{m}}\ \Delta T = n\left(\frac{7}{2}R\right)(30\ \mathrm{K}) \quad \text{or} \quad n\left(\frac{5}{2}R\right)\Delta T = n\left(\frac{7}{2}R\right)(30\ \mathrm{K}) \quad \text{or} \quad \Delta T = \frac{7}{5}(30\ \mathrm{K}) = 42\ \mathrm{K}$$

17. The work done by the gas during isothermal and adiabatic expansions are shown schematically by the areas under the corresponding $P - V$ lines. Obviously, $W_1 > W_3$.

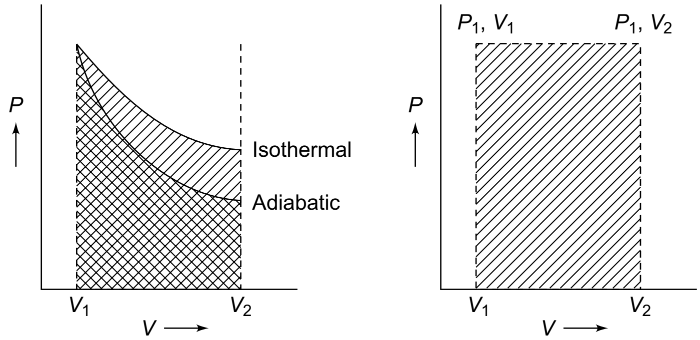


Fig. 6.3

The work done by the gas during isobaric expansion depends on the temperature of the gas in the final state. The work done by the gas can be more or less than W_1 (or W_3) depending upon the temperature in final state. Assuming that the final pressure of the gas is the same as the initial pressure we will have $W_2 > W_1$ (or W_3).

18. For adiabatic expansion

$$W = nC_{V,\mathrm{m}}\ (T_2 - T_1) = C_{V,\mathrm{m}}\left(\frac{p_2V_2}{R} - \frac{p_1V_1}{R}\right) = \frac{C_{V,\mathrm{m}}}{R}(p_2V_2 - p_1V_1) = \frac{C_{V,\mathrm{m}}}{C_{p,\mathrm{m}} - C_{V,\mathrm{m}}}(p_2V_2 - p_1V_1)$$

$$W = \frac{p_2V_2 - p_1V_1}{\gamma - 1}$$

The value of $\gamma(= C_p/C_V)$ decreases with an increase in the atomicity of gaseous molecules. Thus, W increases with an increase in the atomicity of gaseous molecules.

19. For a monoatomic gas, $C_V = (3/2)\ R$ and $C_p = (5/2)\ R$

Hence $\gamma = \dfrac{C_p}{C_V} = \dfrac{5}{3}$

Thus, for adiabatic expansion of a monoatomic gas $pV^\gamma = pV^{5/3}$ = constant.

20. $(C_{p,\mathrm{m}})_{\mathrm{mix}} = \left(\dfrac{1}{3\,\mathrm{mol}}\right)\left[(1\,\mathrm{mol})\left(\dfrac{5}{2}R\right)+(2\,\mathrm{mol})\left(\dfrac{7}{2}R\right)\right]$ and $(C_{V,\mathrm{m}})_{\mathrm{mix}} = \left(\dfrac{1}{3\,\mathrm{mol}}\right)\left[(1\,\mathrm{mol})\left(\dfrac{3}{2}R\right)+(2\,\mathrm{mol})\left(\dfrac{5}{2}R\right)\right]$

$$\gamma = \frac{(C_{p,\mathrm{m}})_{\mathrm{mix}}}{(C_{V,\mathrm{m}})_{\mathrm{mix}}} = \frac{19}{13} = 1.46$$

21. Heat used in increasing the internal energy = $C_V\,\Delta T$. Heat absorbed at constant pressure to increase the temperature by $\Delta T = C_p\ \Delta T$

Hence, Fraction of heat used in increasing the internal energy $\varphi = \dfrac{C_V\ \Delta T}{C_p\ \Delta T} = \dfrac{C_V}{C_p}$

For a diatomic gas, $C_{V,\mathrm{m}}$ = (5/2) R and $C_{p,\mathrm{m}}$ = (7/2) R. Hence $\varphi = \dfrac{(5/2)R}{(7/2)R} = \dfrac{5}{7}$

22. For an adiatomic process, pV^γ = constant. Also $\gamma\,(= C_{p,\mathrm{m}}/C_{V,\mathrm{m}})$ for a diatomic gas (= 7/5) is smaller than that of a monatomic gas (= 5/3). Hence, for given volume. $(V^\gamma)_{\text{diatomic gas}} < (V^\gamma)_{\text{monatomic gas}}$
Since at any instant, pV = constant, we will have $p_{\text{diatomic gas}} > p_{\text{monatomic gas}}$
Hence, the curve 1 is meant for a diatomic gas and the curve 2 for a monatomic gas.

23. From first law of thermodynamics, we get $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$
For an given data of an ideal gas, we get $\mathrm{d}U = (\ <0) + 0 = (\ <0)$
Since for an ideal gas, the internal energy changes only due to change in temperature, it may be concluded that $\Delta T < 0$, i.e. temperature decreases.

24. The conservation of heat gives $m_\mathrm{i}C_\mathrm{i}$ (20 K) + $m'_1\ \Delta_{\mathrm{fus}}H - m_\mathrm{W}C_\mathrm{W}$ (20 K) = 0
(4 kg) (2.092 kJ $\mathrm{J^{-1}\ kg^{-1}}$) (20 K) + m'_1 (334.7 kJ $\mathrm{kg^{-1}}$) – (10 kg) (4.184 kJ $\mathrm{K^{-1}\ kg^{-1}}$) (20 K) = 0
This gives

$$m'_1 = \left[\frac{(10)(4.184)(20)-(4)(2.092)(20)}{334.7}\right]\mathrm{kg} = \left(\frac{836.8-167.36}{334.7}\right)\mathrm{kg} = \left(\frac{669.44}{334.7}\right)\mathrm{kg} = 2.0\ \mathrm{kg}$$

Hence, mass of water in the container is m' = (10 kg) + (2 kg) = 12 kg.

25. In the Fig. 6.4, the curve ab represents isothermal expansion from p_1,V_1 to p_2,V_2. In adiabatic compression from V_2 to V_1, the temperature of the gas will be larger than the temperature at the state a.
Consequently, the pressure of the gas after the gas has undergone compression will be larger than that existing at the state a. Thus, the adiabatic compression will be represented by the curve bc. The total work done is given by $W = W_{\text{isothermal}} + W_{\text{adiabatic}}$
where $W_{\text{isothermal}}$ has a negative value as it involves expansion of the gas. Since the magnitude of work is given by the area under the curve, the total work will carry positive sign.

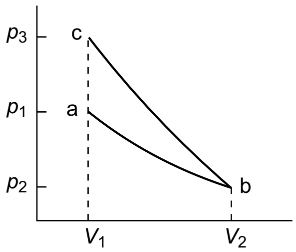


Fig. 6.4

26. $\Delta H - \Delta U = (\Delta\nu_\mathrm{g})RT = (-3)(8.314\times10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}})(298\ \mathrm{K}) = -7.43\ \mathrm{kJ\ mol^{-1}}$

27. For the given reaction, $\Delta\nu_\mathrm{g} = -1/2$. Hence $\Delta H - \Delta U = (\Delta\nu_\mathrm{g})\ RT$ = negative. Hence, $\Delta H < \Delta U$.

28. The 'standard' implies pressure equal to 1 bar.

29. For $\Delta H = \Delta U$, we must have $\Delta\nu_\mathrm{g} = 0$. Thus, choice b is correct.

30. By definition, $H = U + pV$.

31. $\Delta H = \Delta U + \Delta(pV)$

32. For the reaction $CCl_4(l) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$, we have

$$\Delta_r H = \Delta_f H(CO_2,\ g) + 4\Delta_f H(HCl,\ g) - \Delta_f H(CCl_4,\ l) - 2\Delta_f H(H_2O,\ g)$$

$$= (-394 - 4 \times 93 + 107 + 2 \times 242)\ \text{kJ mol}^{-1} = -175\ \text{kJ mol}^{-1}$$

$$\Delta_r U = \Delta_r H - (\Delta\nu_g)\ RT = -175 - (3)\ (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K}) = -182.5\ \text{kJ mol}^{-1}$$

33. We have

$$\Delta H = \Delta U + (\Delta\nu_g)RT = (-743\ \text{kJ mol}^{-1}) + (1/2)(8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})(300\ \text{K}) = -741.75\ \text{kJ mol}^{-1}$$

34. We have

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H^\circ = 40.63\ \text{kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - (\Delta\nu_g)\ RT = 40.63\ \text{kJ mol}^{-1} - (1)\ (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (373\ \text{K})$$

$$= (40.73 - 3.10)\ \text{kJ mol}^{-1} = 37.53\ \text{kJ mol}^{-1}$$

35. $\Delta\nu_g$ is positive. Hence, $\Delta H = \Delta U + (\Delta\nu_g)RT$ suggests that $\Delta H > \Delta U$.

36. $\Delta\nu_g = 1$. Hence

$$\Delta U = \Delta H - (\Delta\nu_g)RT = 1.76\ \text{kJ mol}^{-1} - (1)\ (8.314 \times 10^{3})\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (1000\ \text{K})$$

$$= (176 - 8.314)\ \text{kJ mol}^{-1} = 167.7\ \text{kJ mol}^{-1})$$

37. Since $\Delta_r H = \Delta_r U + (\Delta\nu_g)RT$, the reaction leading to $\Delta\nu_g < 0$ will have $\Delta_r H < \Delta_r U$

38. $\Delta H = \Delta U + \Delta(pV) = \Delta U + (p_2V_2 - p_1V_1) = 30.0\ \text{L atm} + [(4.0\ \text{atm})(5.0\ \text{L}) - (2.0\ \text{atm})(3.0\ \text{L})]$
$= 30.0\ \text{L atm} + 14.0\ \text{L atm} = 44.0\ \text{L atm}$

39. At 298 K, CH_3OH exists as liquid. Thus, choice d is correct.

40. We have

$$\begin{array}{lll}
\text{(i)} & C_2H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) & \Delta H_1 = -1300\ \text{kJ mol}^{-1} \\
\text{(ii)} & C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) & \Delta H_2 = -394\ \text{kJ mol}^{-1} \\
\text{(iii)} & H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H_3 = -286\ \text{kJ mol}^{-1} \\
\text{(iv)} & 2C(\text{graphite}) + H_2(g) \rightarrow C_2H_2(g) & \Delta H = ?
\end{array}$$

Equation (iv) can be obtained as follows

2 Eq. (ii) + Eq. (iii) – Eq. (i)

Hence, $\Delta H = (-2 \times 394 - 286 + 1300)\ \text{kJ mol}^{-1} = 226\ \text{kJ mol}^{-1}$

41. For $CO_2(g)$, the standard enthalpy of formation and standard enthalpy of combustion of gaseous carbon (graphite) represent one and the same equation.

42. In the enthalpy of formation, we have stoichiometric number of the desired species equal to one and it appears as the product. Moreover, the reactants must be at stable state of aggregation.

43. The reaction given in choice (b) represents either $\Delta_r H^\circ$ or $\Delta_f H^\circ$

44. At 298 K, the products are $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$.

45. At 298 K, H_2O exists as liquid. Thus, choice c is correct.

46. In the enthalpy of combustion, the stoichiometric number of the species being combusted is equal to one. The products are $CO_2(g)$ and $H_2O(l)$ when the temperature is 25 °C.

47. We have

$$\begin{array}{lll}
C(\text{diamond}) + 2H_2(g) \rightarrow CH_4(g) & & \Delta H_1 \\
4H(g) \rightarrow 2H_2(g) & & \Delta H = \text{negative} \\
\hline
C(\text{diamond}) + 4H(g) \rightarrow CH_4(g) & & \Delta H_2 = \Delta H_1 + \Delta H
\end{array}$$

Hence $\Delta H_2 < \Delta H_1$, i.e., $\Delta H_1 > \Delta H_2$.

48. The expression $\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ$ is true at all temperatures and 1 bar pressure.

49. We have

$$\begin{array}{ll}
C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) & \Delta_c H(C,\ \text{graphite}) \\
CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) & \Delta_c H(CO,\ g) \\
C(\text{graphite}) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) & \Delta_f H\ (CO,\ g)
\end{array}$$

Hence $\Delta_f H(CO,\ g) = \Delta_c H(C,\ \text{graphite}) - \Delta_c H^\circ(CO,\ g)$

50. For the given equation, we have

$$\Delta_r H = \Delta_f H(CO,\ g) + \Delta_f H(H_2O,\ g) - \Delta_f H(CO_2,\ g) - \Delta_f H(H_2,\ g)$$

$$= (-110.5 - 241.8 + 393.5 - 0)\ \text{kJ mol}^{-1} = 41.2\ \text{kJ mol}^{-1}$$

51. In an endothermic reaction, heat is added to the system. $H_{\text{products}} > H_{\text{reactants}}$ and thus ΔH is positive.

52. Given equation is obtained by subtracting second equation from the first. Hence

$$\Delta H = \Delta H_1 - \Delta H_2 = (-\ 41.84 + 57.32)\ \text{kJ mol}^{-1}$$

53. $\Delta H = \Delta U + (\Delta \nu_g)\ RT = -\ 743\ \text{kJ mol}^{-1} + \left(\frac{1}{2}\right)\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K}) = -\ 741.75\ \text{kJ mol}^{-1}$

54. Given data are:

$S(s) + O_2(g) \rightarrow SO_2\ (g)\ ;\qquad \Delta H = -\ 298.2\ \text{kJ mol}^{-1}$

$SO_2\ (g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow SO_3\ (g)\ ;\qquad \Delta H = -\ 98.7\ \text{kJ mol}^{-1}$

$H_2\ (g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow H_2O\ (l)\ ;\qquad \Delta H = -\ 287.3\ \text{kJ mol}^{-1}$

$SO_3\ (g) + H_2O(l) \rightarrow H_2SO_4(l)\ ;\qquad \Delta H = -\ 130.2\ \text{kJ mol}^{-1}$

The formation of $H_2SO_4(l)$ implies the reaction $H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)$
This reaction is obtained by adding the above four reactions. Hence

$$\Delta H = -\ (298.2 + 98.7 + 287.3 + 130.2)\ \text{kJ mol}^{-1} = -\ 814.4\ \text{kJ mol}^{-1}$$

55. Given: The data are

$C(\text{graphite}) + \frac{1}{2}\ O_2(g) \rightarrow CO(g) \quad : \Delta_f H^\circ = -\ 110.5\ \text{kJ mol}^{-1}$

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad : \Delta_f H^\circ = -\ 393.5\ \text{kJ mol}^{-1}$

$C(\text{graphite}) + O_2(g) \rightarrow$ a mixture of $CO(g)$ and $CO_2(g)$ $\ : \Delta_r H^\circ = -\ 313.8\ \text{kJ mol}^{-1}$

If x is the amount fraction of CO in the mixture, then the amount of O_2 consumed will be

$$\frac{x}{2} + (1 - x) = 1 - \frac{x}{2}$$

where x may be calculated from the expression

$$x\ (-\ 110.5\ \text{kJ mol}^{-1}) + (1 - x)\ (-\ 393.5\ \text{kJ mol}^{-1}) = -\ 313.8\ \text{kJ mol}^{-1}$$

which gives $x = 0.272$.

Mass of O_2 consumed $= \left\{\left(1 - \frac{0.272}{2}\right)\text{mol}\right\}\ (32\ \text{g mol}^{-1}) = 27.6\ \text{g}$

56. $\Delta_r H = \Delta_f H(CO_2) + 2\Delta_f H(H_2O) - \Delta H(CH_4) - 4\Delta_f H(CuO)$

$= (-\ 393.5 - 2 \times 285.9 + 74.9 + 4 \times 157.3)\ \text{kJ mol}^{-1}$

$= -\ 261.2\ \text{kJ mol}^{-1}$

57. The enthalpy change will be called enthalpy of reaction.

58. We have

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad ;\ \Delta H_1^\circ = -\ 241\ \text{kJ mol}^{-1}$

(ii) $C_6H_{10}(g) + \frac{17}{2}O_2(g) \rightarrow 6CO_2(g) + 5H_2O(g) \quad ;\ \Delta H_2^\circ = -\ 3800$ kJ mol–1

(iii) $C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g) \quad ;\ \Delta H_3^\circ = -\ 3920\ \text{kJ mol}^{-1}$

We have to determine $\Delta_r H$ for the reaction $C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$
This is given by

$$\Delta H^\circ = \Delta H^\circ_{(ii)} + \Delta H^\circ_{(i)} - \Delta H^\circ_{(iii)} = (-\ 3800 - 241 + 3920)\ \text{kJ mol}^{-1} \qquad = -\ 121\ \text{kJ mol}^{-1}$$

59. We have

(a) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);\qquad \Delta H_a = -\ 393.5\ \text{kJ mol}^{-1}$

(b) $C(\text{diamond}) + O_2(g) \rightarrow CO_2(g);\qquad \Delta H_2 = -\ 395.3\ \text{kJ mol}^{-1}$

The given transformation C(graphite) → C(diamond) is obtained by subtracting Eq. (b) from Eq. (a). Hence

$$\Delta H = \Delta H_b - \Delta H_a = [-\ 393.5 - (-\ 395.3)]\ \text{kJ mol}^{-1} = 1.80\ \text{kJ mol}^{-1}$$

60. $\Delta_r H = \Delta_f H(Al_2O_3,\ s) - \Delta_f H(Fe_2O_3,\ s) = (-\ 1670 + 834)\ \text{kJ mol}^{-1} = -\ 836\ \text{kJ mol}^{-1}$

61. Larger the value of $\Delta_{\text{ioniz}}H^\circ$, weaker the acid and larger the value of pK_a. Hence, pK_a(HCN) > pK_a(CH_3COOH).

62. One mole of H^+ combines with 1 mol of OH^- in a dilute solution involves – 57.32 k J mol^{-1} of enthalpy change.

63. A portion of heat is utilized in the ionization of weak acid. Hence, the magnitude of enthalpy of neutralization is less than 57.32 k J mol^{-1}.

64.

$$\begin{tikzcd}
\frac{1}{2}H_2(g) \arrow[d, "\frac{1}{2}\,\varepsilon(\text{H—H})"] & + & \frac{1}{2}Cl_2(g) \arrow[d, "\frac{1}{2}\,\varepsilon(\text{Cl—Cl})"] \arrow[r, "\Delta H"] & HCl\,(g) \\
H(g) & + & Cl(g) \arrow[ur, "-\,\varepsilon(\text{H—Cl})"'] &
\end{tikzcd}$$

We have

$$\Delta H = \tfrac{1}{2}\varepsilon\ (\text{H—H}) + \tfrac{1}{2}\varepsilon\ (\text{Cl—Cl}) - \varepsilon\ (\text{HCl}) = \left[\tfrac{1}{2}(435+243)-431\right]\text{kJ mol}^{-1} = -\ 92\ \text{kJ mol}^{-1}$$

65. We have

$$\begin{tikzcd}
\frac{1}{2}H_2(g) \arrow[d, "\frac{1}{2}\,\varepsilon(\text{H—H})"] & + & \frac{1}{2}Cl_2(g) \arrow[d, "\frac{1}{2}\,\varepsilon(\text{Cl—Cl})"] \arrow[r, "\Delta H"] & HCl\,(g) \\
H(g) & + & Cl(g) \arrow[ur, "-\,\varepsilon(\text{H—Cl})"'] &
\end{tikzcd}$$

$$\tfrac{1}{2}\ (\varepsilon_{\text{H—H}} + \varepsilon_{\text{Cl—Cl}}) - \varepsilon_{\text{H—Cl}} = \Delta H$$

$$\tfrac{1}{2}\ (430 + 242)\ \text{kJ mol}^{-1} - \varepsilon_{\text{H—Cl}} = -91\ \text{kJ mol}^{-1}$$

$$\varepsilon_{\text{HCl}} = \left[\tfrac{1}{2}(430+242)+91\right]\ \text{kJ mol}^{-1} = 427\ \text{kJ mol}^{-1}$$

66. We have

$$\begin{tikzcd}
H_2(g) \arrow[d, "\varepsilon_{\text{H—H}}"] & + & \frac{1}{2}O_2(g) \arrow[d, "\frac{1}{2}\,\varepsilon_{\text{O=O}}"] \arrow[r, "\Delta H"] & H_2O\,(g) \\
2H\,(g) & + & O\,(g) \arrow[ur, "-2\,\varepsilon_{\text{O—H}}"'] &
\end{tikzcd}$$

Hence $\quad \varepsilon_{\text{H-H}} + \tfrac{1}{2}\varepsilon_{\text{O=O}} - 2\varepsilon_{\text{O-H}} = \left(433+\tfrac{1}{2}\times 492\right)\text{kJ mol}^{-1} - 2\varepsilon_{\text{O-H}} = -\ 249\ \text{kJ mol}^{-1}$

$$\varepsilon_{\text{O-H}} = \tfrac{1}{2}\left[\left(433+\tfrac{1}{2}\times 492\right)+249\right]\text{kJ mol}^{-1} = 464\ \text{kJ mol}^{-1}$$

67. For the equation

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)\ ; \qquad \Delta H = -\ 249\ \text{kJ mol}^{-1}$$

Thus $\quad \varepsilon(\text{H} - \text{H}) + \dfrac{1}{2}\ \varepsilon(\text{O} = \text{O}) - 2\ \varepsilon(\text{O} - \text{H}) = -\ 249\ \text{kJ mol}^{-1}$

$$[433 + \frac{1}{2}(492)]\ \text{kJ mol}^{-1} - 2\ \varepsilon(\text{O} - \text{H}) = -\ 249\ \text{kJ mol}^{-1}$$

$$\text{Hence } \varepsilon(\text{O} - \text{H}) = \frac{1}{2}[\ +\ 249 + 433 + \frac{1}{2}\ (492)]\ \text{kJ mol}^{-1} = 464\ \text{kJ mol}^{-1}$$

68.

$$\begin{tikzcd}
N_2(g) + 3H_2(g) \arrow[d, "\varepsilon(\text{N}\equiv\text{N})"', "3\varepsilon(\text{H—H})"] \arrow[rr, "\Delta H"] & & 2NH_3(g) \\
2N(g) + 6H(g) \arrow[urr, "-6\varepsilon(\text{N—H})"'] & &
\end{tikzcd}$$

Hence, $\Delta H = \varepsilon(\text{N} \equiv \text{N}) + 3\ \varepsilon(\text{H} - \text{H}) - 6\ \varepsilon(\text{N} - \text{H})$

$$= (945 + 3 \times 436 - 6 \times 391)\ \text{kJ mol}^{-1} = -\ 93\ \text{kJ mol}^{-1}$$

69. In polymerization breaking one double bond generates two single bonds. Hence

$$\Delta H = \{590 - 2(331)\}\ \text{kJ mol}^{-1} = -\ 72\ \text{kJ mol}^{-1}$$

70. The formation reaction is

$$\begin{tikzcd}
5\text{C (graphite)} \arrow[d, "5\times 718.4\text{ kJ mol}^{-1}"] & + & 4\text{H}_2\text{(g)} \arrow[d, "8\times 218\text{ kJ mol}^{-1}"] \arrow[r, "\Delta_f H"] & \text{CH}_2{=}\text{C(CH}_3\text{)CH}{=}\text{CH}_2 \\
5\text{C (g)} & + & 8\text{ H (g)} \arrow[r, no head] & {} \arrow[u, "\begin{array}{l}-2\varepsilon(\text{C}{=}\text{C})\\-2\varepsilon(\text{C—C})\\-8\varepsilon(\text{C—H})\end{array}"']
\end{tikzcd}$$

Hence $\Delta_f H = 5 \times 718.4 + 8 \times 218 - 2 \times 615.1 - 2 \times 347.7 - 8 \times 413.4)\ \text{kJ mol}^{-1}$

$= 103.2\ \text{kJ mol}^{-1}$

71. We have

$\text{S(rhombic)} \rightarrow \text{S(g)}$; $\Delta_f H = 275\ \text{kJ mol}^{-1}$

$F_2(g) \rightarrow F(g)$; $\Delta_f H = 80\ \text{kJ mol}^{-1}$

$\text{S(rhombic)} + 3F_2(g) \rightarrow SF_6(s)$; $\Delta_f H = -\ 1100\ \text{kJ mol}^{-1}$

We have to determine the value of $\dfrac{\Delta H}{6}$ for $SF_6(g) \rightarrow S(g) + 6F(g)$

which is equal to $\dfrac{1}{6}\ [275 + 6 \times 80 + 1100] = 309.2\ \text{kJ mol}^{-1}$

72. We have to calculate ΔH for the equation $OH(g) \rightarrow H(g) + O(g)$

$$\Delta H = \Delta_f H(\text{H, g}) + \Delta_f H(\text{O, g}) - \Delta_f H(\text{OH, g}) = (218 + 248 - 42)\ \text{kJ mol}^{-1} = 424\ \text{kJ mol}^{-1}$$

73. H—F bond is the strongest.

74. At room temperature, C(graphite) is more stable that C(diamond).

75. Decrease in disorderliness would result into the decrease in entropy.

76. For an irreversible process $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ = positive. Hence $|\Delta S_{\text{sys}}| > |\Delta S_{\text{surr}}|$

77. H_2, CO and NO have residual entropies.

78. The combustion reaction is an exothermic process. Hence, ΔH = –ve. The reaction occurs with $\Delta \nu_g$ positive. Hence, ΔS = +ve. Since $\Delta G = \Delta H - T\Delta S$ = –ve – T (+ve) = –ve.

79. $\Delta H^\circ = \Delta U^\circ + (\Delta \nu_g)RT = -\ 10.0\ \text{kJ mol}^{-1} + (-\ 1)\ (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K}) = -\ 12.49\ \text{kJ mol}^{-1}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -\ 12.49\ \text{kJ mol}^{-1} - (300\ \text{K})\ (-\ 45 \times 10^{-3})\ \text{kJ K}^{-1}\ \text{mol}^{-1}\ \text{J}$

$= (-\ 12.45 + 13.5)\ \text{kJ mol}^{-1}$= positive

81. $\Delta \nu_g$ is negative, entropy change will also be negative.

82. $\Delta S = \Delta H/T = 40.63 \times 10^3\ \text{J mol}^{-1}/373\ \text{K} = 108.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

83. For a spontaneous process, ΔG is negative. Since $\Delta G = \Delta H - T\Delta S$, ΔG will always be negative if and only if ΔH is negative and ΔS is positive.

85. In the reversible isothermal reaction, temperature of the system and surroundings are taken to be identical. Since heat absorbed by the system is equal to the heat lost by surroundings, ΔS_{sys} and ΔS_{surr} will have equal value but carry opposite sign.

86. CO has residual entropy due to orientations CO and OC in the crystal lattice.

87. $\Delta S = \Delta H/T = (37300\ \text{J mol}^{-1})/(373\ \text{K}) = 100\ \text{J K}^{-1}\ \text{mol}^{-1}$

89. Adiabatically implies $q = 0$. Expansion against vacuum implies $w = 0$. Hence, $\Delta U = q + w = 0$.

92. $K_p = p_B/p_A = 1/4$. Since $\Delta G^\circ = -\ RT \ln K_p^\circ$, we will have $\Delta G^\circ = RT \ln 4$

93. $T = \Delta H/\Delta S = (25 \times 10^3\ \text{J mol}^{-1})/(100\ \text{J K}^{-1}\ \text{mol}^{-1}) = 250\ \text{K}$

94. $\Delta S(A \rightarrow B) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) + \Delta S(D \rightarrow B) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) - \Delta S(B \rightarrow D)$

$= (60 + 20 - 10)\ \text{eu} = 70\ \text{eu}$

96. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = [-\ 54.07 \times 10^3 - (298)\ (10)]\ \text{J mol}^{-1} = -\ 57050\ \text{J mol}^{-1}$

$$K^\circ = \frac{-\Delta G^\circ}{2.303\,RT} = \frac{57050\ \text{J mol}^{-1}}{5705\ \text{J mol}^{-1}} = 10$$

97. In an adiabatic reversible expansion of an ideal gas is always equal to zero, becuase the entropy change due to the temperature change is equal and opposite of the entropy change due to volume (or pressure) change.

98. $\Delta_r G^\circ$ for the reaction $H_2O(l) \rightleftharpoons H_2O(g)$ is

$$\Delta_r G^\circ = \Delta_f G^\circ(H_2O,\ g) - \Delta_f G^\circ(H_2O,\ l) = (-\ 228.59 + 273.19)\ \text{kJ mol}^{-1} = 8.6\ \text{kJ mol}^{-1}$$

$$p_{H_2O(g)}/\text{atm} = K^\circ = \text{antilog}\ (-\ \Delta G^\circ/2.303\ RT)$$

$$= \text{antilog}\ \{-\ 8.6 \times 10^3/(2.303 \times 8.314 \times 298)\} = \text{antilog}\ (-\ 1.507)$$

$$= 0.03$$

99. The reaction to be considered is $OH(g) \rightarrow O(g) + H(g)$

$$\Delta H^\circ = \Delta_f H^\circ(O,g) + \Delta_f H^\circ(H,g) - \Delta_f H^\circ(OH,g) = (248 + 218 - 42)\ \text{kJ mol}^{-1}$$

$$= 424\ \text{kJ mol}^{-1}$$

100. At the boiling point of benzene, $\Delta G = 0$. Hence the exspression $\Delta G = \Delta H - T\Delta S$ gives

$$\Delta S = \frac{\Delta H}{T} = \frac{31064\ \text{J mol}^{-1}}{353\ \text{K}} = 88\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Multiple Correct Choice Type

1. For the given reaction, $\Delta\nu_g = 0$. Hence $\Delta H = \Delta U$.

2. For the given reaction, $\Delta\nu_g = -2$. Since $\Delta H = \Delta U + (\Delta\nu_g)RT$, it follows that $\Delta H < \Delta U$. Also $(RT)^{-2} < 1$.

3. For the given reaction, $\Delta\nu_g = +1$. Hence, $\Delta H > \Delta U$ and $(RT)^1 > 1$.

4. Cyclopropane is the most stained.

5. (b) In an exothermic reaction, the total enthalpy of products is smaller than that of reactants.
(d) It is graphite which is more stable and thus has standard enthalpy of formation equal to zero.

6. (a) It is $Br_2(l)$ which has a zero value.
(c) $\Delta\nu_g$ is the change in the stoichiometric number of gaseous species and thus a unitless quantity.
(d) Bond dissociation energy refers to a diatomic molecule whereas bond enthalpy refers to the average of enthalpies required to break a given bond in different molecules.

7. (a) At 298 K, $H_2O(l)$ is stable species and not $H_2O(g)$.
(b) For an exothermic reaction, ΔH is negative.

8. (a) For a reaction involving condensed phases (solids or liquids), $\Delta\nu_g$ is zero.
(b) Bond enthalpy data refers to gaseous species only.
(c) Enthalpy of combustion of graphite and enthalpy of formation of carbon dioxide refer to one and the same chemical equation.
(d) The reaction is accompained with decrease in the gaseous species and, hence, decresase in entropy.

12. Temperature and refractive index remain the same if the system of any substance is divided into two or more parts.

14. Internal energy and molar enthalpy are state functions.

15. Figure 6.5 displays the straight-line path along with the corresoponding isothermal path.
Since the work done by the gas is equal to the area under the curve (such as shown in Fig. 6.5, by the shaded portion for the isothermal path), it is obvious that the gas does more work along the straight-line path as compared to that for the isothermal path.

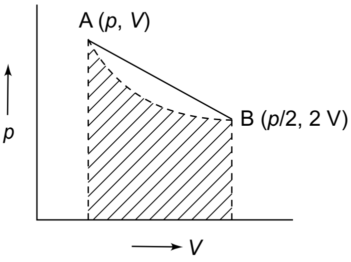


Fig. 6.5

As the volume is increased from V to $2V$, the difference of pressure between the straight line path and isothermal path initiallly increases and then decreases after attaining a maximum value. The same trend is observed in the case of temperature ($p \propto T$, V constant).

Now the slope of straight-line path is slope = $\dfrac{p - p/2}{V - 2V} = -\dfrac{1}{2}\dfrac{p}{V}$

Hence $p = -2V$ (slope)

Substituting this in the ideal gas equation $pV = nRT$, we get $[-\,2V\text{ (slope)}]\ V = nRT$

or $V^2 = \dfrac{nR}{-2\text{(slope)}}T$ or $V^2 = \text{(constant)}\ T$

which is the equation of a parabola.

Similarly, eliminating V from ideal gas equation, we get

$$p\left[-\frac{p}{2\text{(slope)}}\right] = nRT \quad\text{or}\quad p^2 = [-2\ \text{(slope)}nRT]\ T = \text{(constant)}\ T$$

which is again an equation of parabola.

16. Melting of the ice slab is accompanied with a decrease in volume and hence positive work is done on the ice-water system by the atmosphere. Melting of the ice slab is accomplished by the absorption of heat and hence it involves the increase in the internal energy of the ice-water system.

17. In an adiabatic compression, ΔT, ΔU and Δp are positive whereas ΔS is zero.

19. We have $C_{p,\mathrm{m}}\text{(mixture)} = \dfrac{1}{2}(C_{p1} + C_{p2}) = \dfrac{1}{2}\left(\dfrac{5}{2}R + \dfrac{7}{2}R\right) = 3\ R$

$$C_{V,\mathrm{m}}\text{(mixture)} = \frac{1}{2}(C_{V1} + C_{V2}) = \frac{1}{2}\left(\frac{3}{2}R + \frac{5}{2}R\right) = 2\ R$$

$$\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} = 3R/2R = 3/2$$

The choice b is incorrect as may be seen from the areas under the isothermal and adiabatic curves shown in Fig. 6.6.

The choice c is correct as the internal energy of an ideal gas depends only on temperature.

The choice d is also incorrect as shown in the following.

Heat used in increasing intermal energy = $C_V\ \Delta T$

Heat absorbed at constant pressure = $C_p\ \Delta T$

Fraction of heat used in increasing internal energy is $\phi = \dfrac{C_V\,\Delta T}{C_p\,\Delta T} = \dfrac{C_V}{C_p}$

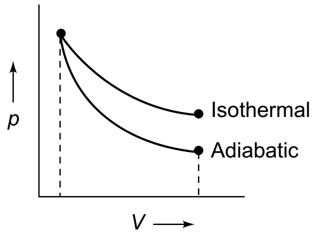


Fig. 6.6

For one mole of the gas $\phi = \dfrac{C_{V,\mathrm{m}}}{C_{p,\mathrm{m}}} = \dfrac{(5/2)R}{(7/2)R} = \dfrac{5}{7}$

Linked Comprehension Type

1. **(i)** $\Delta_r G^\circ = -RT\ln K_b^\circ = -2.303\ RT\ln K_b^\circ = -(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})\log(1.8\times 10^{-5})$

$= -[(2.303)(8.314)(298)(-4.75)]\ \text{J mol}^{-1} = 27030\ \text{J mol}^{-1} = 27.07\ \text{kJ mol}^{-1}$

(ii) $\Delta_r G^\circ = \Delta_f G^\circ(\text{NH}_4^+,\ \text{aq}) + \Delta_f G^\circ(\text{OH}^-,\ \text{aq}) - \Delta_f G^\circ(\text{NH}_4\text{OH},\ \text{aq})$

Hence $\Delta_f G^\circ(\text{NH}_4\text{OH},\ \text{aq}) = (-79.31 - 157.24 - 27.07)\ \text{kJ mol}^{-1} = -263.62\ \text{kJ mol}^{-1}$

(iii) $\Delta_r G^\circ = \Delta_f G^\circ(\text{NH}_4\text{OH},\ \text{aq}) - \Delta_f G^\circ(\text{NH}_3,\ \text{g}) - \Delta_f G^\circ(\text{H}_2\text{O},\ \text{l})$

$= (-263.62 + 16.45 + 237.13)\ \text{kJ mol}^{-1} = -10.04\ \text{kJ mol}$

2. **(i)** $$\log K_b^\circ = -\frac{\Delta_r G^\circ}{2.303RT} = \frac{(10.04\times 10^3\ \text{J mol}^{-1})}{(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})} = 1.76 \quad\Rightarrow\quad K_b^\circ = 10^{1.76} = 57.54$$

(ii) $\Delta_r G^\circ = \Delta_f G^\circ(\text{NH}_4^+,\ \text{aq}) + \Delta_f G^\circ(\text{OH}^-,\ \text{aq}) - \Delta_f G^\circ(\text{NH}_3,\ \text{g})$

$= (-79.31 - 157.24 + 16.45 + 237.13)\ \text{kJ mol}^{-1} = 17.03\ \text{kJ mol}^{-1}$

(iii) $$\log K_b^\circ = -\frac{\Delta_r G^\circ}{2.303RT} = -\frac{(17030\ \text{J mol}^{-1})}{(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})} = -2.985$$

$K_b^\circ = 10^{-2.985} = 1.04\times 10^{-3}$

3. **(i)** $$n = \frac{pV}{RT} = \frac{(1.6\times 10^3\ \text{kPa})(8300\ \text{cm}^3)}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})} = 5.33\ \text{mol}$$

(ii) $$\Delta T = \frac{q}{nC_{V,\text{m}}} = \frac{q}{n\left[C_{p,\text{m}} - R\right]} = \frac{q}{n(3R/2)} = \frac{2q}{3nR} = \frac{2(24.9\times 10^3\ \text{J})}{3(5.33\ \text{mol})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})} = 375.2\ \text{K}$$

$T_f = T_i + \Delta T = 300\ \text{K} + 375.2\ \text{K} = 675.2\ \text{K}$

(iii) $$p_f = \frac{T_f}{T_i}p_i = \left(\frac{675.2}{300}\right)(16.\ \text{MPa}) = 3.6\ \text{MPa}$$

4. **(i)** $$T_2 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1 = \left(\frac{V}{2V}\right)^{(5/3)-1} (300\ \text{K}) = \frac{300\ \text{K}}{2^{1/3}} \simeq 189\ \text{K}$$

(ii) $\Delta U = nC_{V,\text{m}}(T_2 - T_1) = (2\ \text{mol})\ (\frac{3}{2}\times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (189\ \text{K} - 300\ \text{K}) = -2770\ \text{J}$

(iii) Since $\Delta U = \Delta q + \Delta w$ and $\Delta q = 0$, we get $\Delta U = \Delta w = -2770\ \text{J}$

5. **(i)** The pressure of the gas is $$p_1 = \frac{nRT_1}{V_1} = \frac{(2\ \text{mol})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{(0.02\ \text{m}^3)} = 14.9\times 10^4\ \text{Pa}$$

In the isobaric expansion, the temperature of the gas becomes

$$T_2 = V_2\left(\frac{T_1}{V_1}\right) = (0.04\ \text{m}^3)\left(\frac{300\ \text{K}}{0.02\ \text{m}^3}\right) = 600\ \text{K}$$

The final volume of the gas after it has undergone adiabatic expansion computed by the expression $T_3V_3^{\gamma-1} = T_2V_2^{\gamma-1}$ is

$$V_3 = V_2\left(\frac{T_2}{T_3}\right)^{1/(\gamma-1)} = (0.04\ \text{m}^3)\left(\frac{600\ \text{K}}{300\ \text{K}}\right)^{1/\{(5/3)-1\}} = (0.04\ \text{m}^3)\ 2^{3/2} = (0.04\ \text{m}^3)(2)(1.414) = 0.113\ \text{m}^3$$

(ii) The final pressure computed by the expression $p_3V_3 = p_1V_1$ is

$$p_3 = \frac{p_1V_1}{V_3} = \frac{(24.9\times10^4\,\text{Pa})(0.02\,\text{m}^3)}{(0.113\,\text{m}^3)} = 4.41 \times 10^4 \text{ Pa}$$

(iii) In isobaric expansion, $w_1 = -p_{\text{ext}}(V_2 - V_1) = -(24.9 \times 10^4 \text{ Pa})\{(0.04 - 0.02)\text{ m}^3\} = -4980 \text{ J}$
In adiabatic expansion $w_2 = \Delta U = nC_{V,\text{m}}\,\Delta T = (2 \text{ mol})(\frac{3}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K} - 600 \text{ K})$
$= -7470 \text{ J}$
Total work done by the gas is $w = w_1 + w_2 = -4980 \text{ J} - 7470 \text{ J} = -12450 \text{ J}$

6. **(i)** From the first law of thermodynamics, we have

$\Delta U_1 = q_1 + w_1 = 5960 \text{ J} - 2200 \text{ J} = 3760 \text{ J};\quad \Delta U_2 = q_2 + w_2 = -5585 \text{ J} + 825 \text{ J} = -4760 \text{ J}$

$\Delta U_3 = q_3 + w_3 = -2980 \text{ J} + 1100 \text{ J} = -1880 \text{ J};\quad \Delta U_4 = 3645 \text{ J} + w_4$

Since the process is cyclic, the net ΔU ($= \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4$) will be equal to zero.
Hence $3760 \text{ J} - 4760 \text{ J} - 1880 \text{ J} + (3645 \text{ J} + w_4) = 0$
This gives $w_4 = -765 \text{ J}$

(ii) $\Delta U_{\text{net}} = 0$. See part (i)

(iii) Step 1st and 2nd taken together will accompany with a net decrease in the internal energy of the gas.

7. **(i)** The combustion reaction is $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta_cG^\circ = 6\Delta_fG^\circ(CO_2, g) + 6\Delta_fG^\circ(H_2O, l) - \Delta_fG^\circ(\text{glucose})$

$= [6(-395) + 6(-237) - (-900)] \text{ kJ mol}^{-1} = -2892 \text{ kJ mol}^{-1}$

(ii) Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we get

$$\Delta S^\circ = \frac{1}{T}(\Delta H^\circ - \Delta G^\circ) = \frac{1}{298\,\text{K}}(-2815.8 + 2892) \text{ kJ mol}^{-1} = 0.256 \text{ kJ K}^{-1} \text{ mol}^{-1} = 256 \text{ J K}^{-1} \text{ mol}^{-1}$$

(iii) The entropy change for the combustion reaction is

$\Delta_cS^\circ = 6S^\circ(CO_2, g) + 6S^\circ(H_2O, l) - S^\circ(C_6H_{12}O_6, s) - 6S^\circ(O_2, g)$

Hence

$S^\circ(\text{glucose}) = 6S^\circ(CO_2, g) + 6S^\circ(H_2O, l) - 6S^\circ(O_2, g) - \Delta_cS^\circ$
$= [6(213.6) + 6(69.96) - 6(205) - 256] \text{ J K}^{-1} \text{ mol}^{-1} = 215.4 \text{ J K}^{-1} \text{ mol}^{-1}$

8. The reactions to be considered are

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^\circ = -110 \text{ kJ mol}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -395 \text{ kJ mol}^{-1}$

(i) If x is the amount of C giving CO, then

$[x(-110) + (1.0 \text{ mol} - x)(-395)] \text{ kJ mol}^{-1} = -315 \text{ kJ}$

$$x = \frac{-315+395}{395-110} \text{ mol} = \frac{80}{285} \text{ mol} \simeq 0.28 \text{ mol}$$

Mass of C reacted to give CO = (0.28 mol) (32 g mol^{-1}) $\simeq$ 9.0 g

(ii) Amount of C yielding CO_2 = 1.0 mol – 0.28 mol = 0.72 mol
Mass of O_2 reacted yielding CO_2 = (0.72 mol)(32 g mol^{-1}) $\simeq$ 23 g

(iii) Mass of O_2 reacted yielding CO $= \left(\frac{0.28\,\text{mol}}{2}\right)(32 \text{ g mol}^{-1}) = 4.5 \text{ g}$

Mass of total O_2 reacted = 23 g + 4.5 g = 27.5 g

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The enthaplies of the following reactions are shown alongwith.

$$\begin{array}{ll} \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g) & \Delta H = 42.09 \text{ kJ mol}^{-1} \\ H_2(g) \rightarrow 2H(g) & \Delta H = 435.89 \text{ kJ mol}^{-1} \\ O_2(g) \rightarrow 2O(g) & \Delta H = 495.05 \text{ kJ mol}^{-1} \end{array}$$

Calculate the O — H bond energy for the hydroxyl radical. (1981)

Solution We have to calculate the enthalpy of the reaction $OH(g) \rightarrow O(g) + H(g)$
From the given reactions, this can be obtained as follows.

$$\begin{array}{lll} & -\left[\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) + \rightarrow OH(g)\right] & \Delta H = -42.09 \text{ kJ mol}^{-1} \\ & +\frac{1}{2}[H_2(g) \rightarrow 2H(g)] & \Delta H = \frac{1}{2} \times 435.89 \text{ kJ mol}^{-1} \\ & +\frac{1}{2}[O_2(g) \rightarrow 2O(g)] & \Delta H = \frac{1}{2} \times 495.05 \text{ kJ mol}^{-1} \\ \hline \text{Add} & OH(g) \rightarrow H(g) + O(g) & \Delta H = 423.38 \text{ kJ mol}^{-1} \end{array}$$

2. The standard enthalpies of formation at 298 K for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are – 106.7, – 241.8, –393.7 and – 92.5 kJ mol^{-1}, respectively. Calculate ΔH°_{298K} for the reaction

$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$ (1982)

Solution The enthalpy change of the given reaction will be given as

$$\begin{aligned} \Delta H^\circ &= \Delta_f H^\circ(CO_2, g) + 4\Delta_f H^\circ(HCl, g) - \Delta_f H^\circ(CCl_4, g) - 2\Delta_f H^\circ(H_2O, g) \\ &= (-393.7 - 4 \times 92.5 + 106.7 + 2 \times 241.8) \text{ kJ mol}^{-1} = -173.4 \text{ kJ mol}^{-1}. \end{aligned}$$

3. The standard molar enthalpies of combustion of $C_2H_2(g)$, C(graphite) and $H_2(g)$ are – 1299.63, – 393.51, –285.85 kJ mol^{-1}, respectively. Calculate the standard enthalpy of formation of $C_2H_2(g)$.

Solution Given data are :

$$\begin{array}{lll} \text{(i)} & C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) & \Delta H^\circ = -1299.63 \text{ kJ mol}^{-1} \\ \text{(ii)} & C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ = -393.51 \text{ kJ mol}^{-1} \\ \text{(iii)} & H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H^\circ = -285.85 \text{ kJ mol}^{-1} \end{array}$$

(1983)

Solution We have to determine ΔH for the reaction $2C(\text{graphite}) + H_2(g) \rightarrow C_2H_2(g)$
This equation can be obtained by the following manipulation: Eq. (ii) + Eq. (iii) – Eq. (i)
Hence, $\Delta H^\circ = \Delta H^\circ_{(ii)} + \Delta H^\circ_{(iii)} - \Delta H^\circ_{(i)} = (-2 \times 393.51 - 285.85 + 1299.63) \text{ kJ mol}^{-1} = 226.76 \text{ kJ mol}^{-1}$.

(1984)

4. Given the following standard enthalpies of reactions.

(i) Enthalpy of formation of water = – 285.8 kJ mol^{-1}
(ii) Enthalpy of combustion of acetylene = – 1 299.6 kJ mol^{-1}
(iii) Enthalpy of combustion of ethylene = – 1 410.8 kJ mol^{-1}

Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume (25 °C).

Solution The given data are :

$$\begin{array}{lll} \text{(i)} & H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H^\circ = -285.8 \text{ kJ mol}^{-1} \\ \text{(ii)} & C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) & \Delta H^\circ = -1299.6 \text{ kJ mol}^{-1} \\ \text{(iii)} & C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) & \Delta H^\circ = -1410.8 \text{ kJ mol}^{-1} \end{array}$$

We have to find ΔU of the reaction $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

This equation can be obtained by the manipulation Eq. (ii) + Eq. (i) – Eq. (iii)

Hence, $\Delta H^\circ = \Delta H^\circ_{(ii)} + \Delta H^\circ_{(i)} - \Delta H^\circ_{(iii)} = (-1299.6 - 285.8 + 1410.8)\ \text{kJ mol}^{-1} = -174.6\ \text{kJ mol}^{-1}$

Now for the given reaction $\Delta\nu_g = -1$. Hence, using the expression $\Delta H^\circ = \Delta U^\circ + (\Delta\nu_g)RT$ we get

$$\Delta U^\circ = \Delta H^\circ - (\Delta\nu_g)RT = -174.6\ \text{kJ mol}^{-1} - (-1)(8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1})(298\ \text{K})$$
$$= (-174.6 + 2.48)\ \text{kJ mol}^{-1} = -172.12\ \text{kJ mol}^{-1}.$$

5. The bond dissociation enthalpy of gaseous H_2, Cl_2 and HCl are 435, 243 and 431 kJ mol^{-1}, respectively. Calculate the enthalpy of formation of HCl gas. (1985)

Solution The given data are

(i) $H_2(g) \rightarrow 2H(g)$ $\Delta H = 435\ \text{kJ mol}^{-1}$
(ii) $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H = 243\ \text{kJ mol}^{-1}$
(iii) $HCl(g) \rightarrow H(g) + Cl(g)$ $\Delta H = 431\ \text{kJ mol}^{-1}$

We have to find ΔH for the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$

This equation can be obtained by the manipulation $\frac{1}{2}$ Eq. (i) + $\frac{1}{2}$ Eq. (ii) – Eq. (iii)

Hence, carrying out the corresponding manipulation on ΔHs, we get

$$\Delta H = +\tfrac{1}{2}\Delta H_{(i)} + \tfrac{1}{2}\Delta H_{(ii)} - \Delta H_{(iii)} = \left(\tfrac{1}{2}\times 435 + \tfrac{1}{2}\times 243 - 431\right)\ \text{kJ mol}^{-1} = -92\ \text{kJ mol}^{-1}.$$

6. The standard molar enthalpies of formation of ethane, carbon dioxide and liquid water are – 88.3, – 393.7 and – 285.8 kJ mol^{-1}, respectively. Calculate the standard molar enthalpy of combustion of ethane. (1986)

Solution The given data are :

(i) $2C(\text{graphite}) + 3H_2(g) \rightarrow C_2H_6(g)$ $\Delta H^\circ = -88.3\ \text{kJ mol}^{-1}$
(ii) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.7\ \text{kJ mol}^{-1}$
(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ = -285.8\ \text{kJ mol}^{-1}$

We have to find ΔH° for the reaction $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l)$

This equation can be obtained by the manipulations –Eq. (i) + 2 Eq. (ii) + 3 Eq. (iii)

Carrying out the corresponding manipulations on ΔH s, we get

$$\Delta H^\circ = -\Delta H^\circ_{(i)} + 2\Delta H^\circ_{(ii)} + 3\Delta H^\circ_{(iii)} = (88.3 - 2 \times 393.7 - 3 \times 285.8)\ \text{kJ mol}^{-1}$$
$$= -1556.5\ \text{kJ mol}^{-1}.$$

7. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cm^3 of the mixture. Given:

$\Delta_f H(Al_2O_3, s) = -1669\ \text{kJ mol}^{-1}$; $\Delta_f H(Fe_2O_3, s) = -833\ \text{kJ mol}^{-1}$
Density of Fe_2O_3 = 5.2 g cm^{-3}; Density of Al = 2.7 g cm^{-3} (1988)

Solution The reaction involved is $Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s)$

The enthalpy change of this reaction is

$$\Delta H = \Delta_f H(Al_2O_3, s) - \Delta_f H(Fe_2O_3, s) = (-1669 + 833)\ \text{kJ mol}^{-1} = -836\ \text{kJ mol}^{-1}$$

Total mass of the reactants = Molar mass of Fe_2O_3 + 2 Molar mass of Al = 160 g + (2 × 27) g = 214 g

$$\text{Heat evolved per unit mass of the reactants} = \frac{836\ \text{kJ}}{214\ \text{g}} = 3.906\ \text{kJ g}^{-1}$$

$$\text{Total volume of the reactants} = \frac{160\ \text{g}}{5.2\ \text{g cm}^{-3}} + 2\,\frac{27}{2.7\ \text{g cm}^{-3}} = 50.77\ \text{cm}^3$$

$$\text{Heat evolved per unit volume of the reactants} = \frac{836\ \text{kJ}}{50.77\ \text{cm}^3} = 16.47\ \text{kJ cm}^{-3}.$$

8. The standard enthalpy of combustion at 25 °C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ mol^{-1}, respectively. Calculate the standard enthalpy of hydrogenation of cyclohexene. (1989)

Solution The given data are:

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ = -241\ \text{kJ mol}^{-1}$

(ii) $C_6H_{10}(g) + \frac{17}{2}O_2(g) \rightarrow 6CO_2(g) + 5H_2O(l)$ $\Delta H^\circ = -3800\ \text{kJ mol}^{-1}$

(iii) $C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H^\circ = -3920\ \text{kJ mol}^{-1}$

We have to calculate the enthalpy change for the reaction $C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$
This equation can be obtained by the manipulations Eq. (ii) + Eq. (i) – Eq. (iii)
Carrying out the corresponding manipulations on ΔH s, we get

$$\Delta H^\circ = \Delta H^\circ_{(ii)} + \Delta H^\circ_{(i)} - \Delta H^\circ_{(iii)} = (-3800 - 241 + 3920)\ \text{kJ mol}^{-1} = -121\ \text{kJ mol}^{-1}.$$

9. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ mol^{-1}. (1989)

Solution Energy available from 100 g glucose = 1560 kJ

Energy utilized by athlete = $\frac{1}{2} \times 1560$ kJ

Energy unutilized by athlete = $\frac{1}{2} \times 1560$ kJ

Enthalpy of evaporation of water = 44 kJ mol^{-1}

Amount of water to be converted into vapours from unused energy = $\dfrac{78\ \text{kJ}}{44\ \text{kJ mol}^{-1}} = 17.73$ mol

Mass of water perspired = 17.73×18 g = 319.14 g.

10. Using the data given below, calculate the bond enthalpy of C—C and C—H bonds.

$\Delta_c H^\circ(\text{ethane}) = -1556.5\ \text{kJ mol}^{-1}$; $\Delta_c H^\circ(\text{propane}) = -2117.5\ \text{kJ mol}^{-1}$

$C(\text{graphite}) \rightarrow C(g)$; $\Delta H = 719.7\ \text{kJ mol}^{-1}$

Bond enthalpy of H—H = 435.1 kJ mol^{-1}

$\Delta_f H^\circ(H_2O, l) = -284.5\ \text{kJ mol}^{-1}$; $\Delta_f H^\circ(CO_2, g) = -393.3\ \text{kJ mol}^{-1}$

Solution From the enthalpy of combustion of ethane and propane, we write (1990)

(1) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_c H = 3\Delta_f H(H_2O, l) + 2\Delta_f H(CO_2, g) - \Delta_f H(C_2H_6, g)$

Thus, $\Delta_f H(C_2H_6, g) = -\Delta_c H + 3\Delta_f H(H_2O, l) + 2\Delta_f H(CO_2, g) = (1556.5 - 3 \times 284.5 - 2 \times 393.3)\ \text{kJ mol}^{-1}$
$= -83.6\ \text{kJ mol}^{-1}$

(2) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta_c H = 3\Delta_f H(CO_2, g) + 4\Delta_f H(H_2O, l) - \Delta_f H(C_3H_8, g)$

Thus $\Delta_f H(C_3H_8, g) = -\Delta_c H + 3\Delta_f H(CO_2, g) + 4\Delta_f H(H_2O, l) = (2217.5 - 3 \times 393.5 - 4 \times 284.5)\ \text{kJ mol}^{-1}$
$= -101.0\ \text{kJ mol}^{-1}$

To calculate the $\varepsilon_{C—H}$ and $\varepsilon_{C—C}$, we carry out the following manipulations.

(i) $2C(\text{graphite}) + 3H_2(g) \rightarrow C_2H_6(g)$ $\Delta H = -83.6\ \text{kJ mol}^{-1}$
$2C(g) \rightarrow 2C(\text{graphite})$ $\Delta H = -2 \times 719.7\ \text{kJ mol}^{-1}$
$6H(g) \rightarrow 3H_2(g)$ $\Delta H = -3 \times 435.1\ \text{kJ mol}^{-1}$

Add

$2C(g) + 6H(g) \rightarrow C_2H_6(g)$ $\Delta H_{(i)} = (-83.6 - 2 \times 719.7 - 3 \times 435.1)\ \text{kJ mol}^{1}.$
$= -2828.3\ \text{kJ mol}^{-1}$

(ii) $3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$ $\Delta H = -101.0\ \text{kJ mol}^{-1}$
$3C(g) \rightarrow 3C(\text{graphite})$ $\Delta H = -3 \times 719.7\ \text{kJ mol}^{-1}$
$8H(g) \rightarrow 4H_2(g)$ $\Delta H = -4 \times 435.1\ \text{kJ mol}^{-1}$

Add

$3C(g) + 8H(g) \rightarrow C_3H_8(g)$ $\Delta H_{(ii)} = (-101 - 3 \times 719.7 - 4 \times 435.1)\ \text{kJ mol}^{-1}$
$= -4000.5\ \text{kJ mol}^{-1}$

Now $\Delta H_{(\mathrm{i})} = -\varepsilon_{\mathrm{C—C}} - 6\varepsilon_{\mathrm{C—H}} = -2828.3\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_{(\mathrm{ii})} = -2\varepsilon_{\mathrm{C—C}} - 8\varepsilon_{\mathrm{C—H}} = -4000.5\ \mathrm{kJ\ mol^{-1}}$

Solving for $\varepsilon_{\mathrm{C—C}}$ and $\varepsilon_{\mathrm{C—H}}$, we get $\varepsilon_{\mathrm{C—H}} = 414.0\ \mathrm{kJ\ mol^{-1}}$ and $\varepsilon_{\mathrm{C—H}} = 344.3\ \mathrm{kJ\ mol^{-1}}$.

11. A gas mixture consisting of 3.67 litres of ethylene and methane on complete combustion at 25 °C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1423 and – 891 kJ mol^{-1}, respectively, at 25 °C. (1991)

Solution The combustion reactions are

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Let *V* be the volume of $C_2H_4(g)$ in the gaseous mixture of 3.67 L. From the chemical equations, we find that

Volume of $CO_2(g)$ produced due to the combustion of $C_2H_4(g) = 2V$

Volume of $CO_2(g)$ produced due to the combustion of $CH_4(g) = 3.67\ \mathrm{L} - V$

Equating the latter with 6.11 L – 2 *V*, we get

$3.67\ \mathrm{L} - V = 6.11\ \mathrm{L} - 2V$ or $V = 2.44\ \mathrm{L}$

Hence, in the original mixture, we have

$$\text{Volume of } C_2H_4(g) \text{ per litre of the mixture} = \left(\frac{2.44\ \mathrm{L}}{3.67\ \mathrm{L}}\right)(1\ \mathrm{L}) = 0.665\ \mathrm{L}$$

$$\text{Volume of } CH_4(g) \text{ per litre of the mixture} = 1.0\ \mathrm{L} - 0.665\ \mathrm{L} = 0.335\ \mathrm{L}$$

Now,
$$\text{Volume of 1 mol of any gas at 25 °C} = (22.414\ \mathrm{L})\left(\frac{298\ \mathrm{K}}{273\ \mathrm{K}}\right) = 24.467\ \mathrm{L}$$

Hence,
$$\text{Heat released due to the combustion of } C_2H_4(g) = (1423\ \mathrm{kJ})\left(\frac{0.665\ \mathrm{L}}{24.467\ \mathrm{L}}\right) = 38.68\ \mathrm{kJ}$$

$$\text{Heat released due to the combustion of } CH_4(g) = (891\ \mathrm{kJ})\left(\frac{0.335\ \mathrm{L}}{24.467\ \mathrm{L}}\right) = 12.20\ \mathrm{kJ}$$

Total heat released = (38.68 + 12.20) kJ = 50.88 kJ.

12. Determine the enthalpy of the reaction $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$ at 25 °C using the given enthalpy of combustion values under standard conditions:

Compound:	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
$\Delta_cH/\mathrm{kJ\ mol^{-1}}$:	– 285.8	– 890.0	– 1560.0	– 393.5

The standard enthalpy of formation of $C_3H_8(g)$ is – 103.8 kJ mol^{-1}. (1992)

Solution The given data are:

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8\ \mathrm{kJ\ mol^{-1}}$

(ii) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.0\ \mathrm{kJ\ mol^{-1}}$

(iii) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H = -1560.0\ \mathrm{kJ\ mol^{-1}}$

(iv) $C(\mathrm{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5\ \mathrm{kJ\ mol^{-1}}$

(v) $3C(\mathrm{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$ $\Delta H = -103.8\ \mathrm{kJ\ mol^{-1}}$

We have to determine ΔH of the reaction $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$

This equation can be obtained by the following manipulations.

– Eq. (v) – Eq. (iii) – Eq. (ii) + 3 Eq. (iv) + 5 Eq. (i)

Carrying out the corresponding manipulations on ΔH s, we get

$$\Delta H = (103.8 + 1560 + 890 - 3 \times 393.5 - 5 \times 285.8)\ \mathrm{kJ\ mol^{-1}} = -55.7\ \mathrm{kJ\ mol^{-1}}.$$

13. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as the required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Enthalpies of combustion : CH_4 = 809 kJ mol^{-1}; C_4H_{10} = 2 878 kJ mol^{-1}. (1993)

Solution The combustion reactions are

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$

$$\text{Calorific value of } CH_4 = \frac{809}{16}\ \text{kJ g}^{-1}; \qquad \text{Calorific value of } C_4H_{10} = \frac{2878}{58}\ \text{kJ g}^{-1}$$

$$\text{Mass of } C_4H_{10} \text{ having the same calorific output as that of } CH_4 = \left(\frac{809}{16}\right)\left(\frac{58}{2878}\right)\ \text{g}$$

$$\text{Amount of } C_4H_{10} \text{ having the same calorific output as that of } CH_4 = \frac{809}{16\times 2878}\ \text{mol}$$

Now, $\frac{1}{16}$ mol CH_4 requires the supply x L h^{-1} of CH_4

$$\frac{809}{16\times 2878}\ \text{mol } C_4H_{10} \text{ requires the supply of } \frac{x\,\text{L h}^{-1}}{(1/16)}\left(\frac{809}{16\times 2878}\right) = (0.28\,x)\ \text{L h}^{-1} \text{ of } C_4H_{10}$$

$$\text{The corresponding supply of } O_2 = (0.28\,x)\left(3\times\frac{13}{2}\right)\ \text{L h}^{-1} = (5.48\,x)\ \text{L h}^{-1}$$

14. The polymerisation of ethylene to linear polyethylene is represented by the reaction (1994)

$$n\,CH_2{=}CH_2 \rightarrow (\!-CH_2-CH_2-\!)_n$$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C and C—C at 298 K are +590 and +331 kJ mol^{-1}, respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Solution In polymerisation, 1 double bond (C=C) is replaced by two single C—C bonds. For the polymerisation of 1 mol of ethylene, 1 mol of C=C bonds are replaced by 2 mol of C—C bonds. Hence

$$\Delta H = -2\,\varepsilon_{C-C} + \varepsilon_{C=C} = \{-2(331) + 590\}\ \text{kJ mol}^{-1} = -72\ \text{kJ mol}^{-1}.$$

15. When 12.0 g of carbon(graphite) reacted with oxygen to form CO and CO_2 at 25 °C and constant pressure, 313.8 kJ of heat was released and no carbon remained. If $\Delta_f H°(CO, g) = -110.5$ kJ mol^{-1} and $\Delta_f H°(CO_2, g) = -393.5$ kJ mol^{-1}, calculate the mass of oxygen consumed.

Solution We have

$$\text{Amount of carbon} = \frac{12.0\ \text{g}}{12.0\ \text{g mol}^{-1}} = 1\ \text{mol}$$

The equations to be considered are

$$C(\text{graphite}) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H° = -110.5\ \text{kJ mol}^{-1}$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = -393.5\ \text{kJ mol}^{-1}$$

Let the amount x of carbon be converted into CO and the remaining (i.e. 1.0 mol − x) into CO_2. We will have

$$[x(-110.5) + (1.0\ \text{mol} - x)(-393.5)]\text{kJ mol}^{-1} = -313.8\ \text{kJ}$$

which gives $$x = \frac{-313.8 + 393.5}{393.5 - 110.5}\ \text{mol} = 0.282\ \text{mol}$$

Now, $$\text{Amount of oxygen needed} = \left[\frac{0.282}{2} + (1.0 - 0.282)\right]\text{mol} = 0.859\ \text{mol}$$

$$\text{Mass of oxygen needed} = (0.859\ \text{mol})\ (32\ \text{g mol}^{-1}) = 27.5\ \text{g}$$

16. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. Bond energy of I_2 is 240 kJ mol^{-1}. (1995)

Solution The dissociation reaction is $I_2 \rightarrow 2I$

Bond energy per single bond is $\varepsilon = \dfrac{240\ \text{kJ mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}} = 3.985 \times 10^{-22}\ \text{kJ} = 3.985 \times 10^{-19}\ \text{J}$

Energy of 1 photon of wavelength 4500 Å is $E = \dfrac{hc}{\lambda} = \dfrac{(6.626 \times 10^{-34}\ \text{J s})\,(3 \times 10^{8}\ \text{m s}^{-1})}{(4500 \times 10^{-10}\ \text{m})} = 4.417 \times 10^{-19}\ \text{J}$

Of the energy 4.417×10^{-19} J, the energy consumed to break I_2 molecules is 3.985×10^{-19} J. The remaining energy is used in imparting kinetic energy to the two iodine atoms. Hence

$$\text{Kinetic energy per iodine atom} = \frac{(4.417 - 3.985) \times 10^{-19}\ \text{J}}{2} = 2.16 \times 10^{-20}\ \text{J}.$$

17. A natural gas may be assumed to be a mixture of methane and ethane only. On complete combustion of 10 L of the gas at STP, the heat evolved was 474.6 kJ. Assuming $\Delta_c H(CH_4, g) = -894$ kJ mol^{-1} and $\Delta_c H(C_2H_6, g) = -1\,560$ kJ mol^{-1}, calculate the percentage of volume of each gas in the mixture.

Solution Let V be the volume of CH_4 in 10 L mixture. We have

$$\text{Amount of methane} = \frac{V}{22.414\ \text{L mol}^{-1}} \qquad \text{Amount of ethane} = \frac{10.0\ \text{L} - V}{22.414\ \text{L mol}^{-1}}$$

Setting the expression of heat evolved, we will get

$$\left(\frac{V}{22.414\ \text{L mol}^{-1}}\right)(894\ \text{kJ mol}^{-1}) + \left(\frac{10.0\ \text{L} - V}{22.414\ \text{L mol}^{-1}}\right)(1\,560\ \text{kJ mol}^{-1}) = 474.6\ \text{kJ}$$

Solving for V, we get

$$V = \frac{22.414 \times 474.6 - 10 \times 1560}{1560 - 894}\ \text{L} = 7.45\ \text{L}$$

$$\text{Volume per cent of methane} = \frac{7.45\ \text{L}}{10\ \text{L}} \times 100 = 74.5$$

$$\text{Volume per cent of ethane} = 100 - 74.5 = 25.5.$$

18. A person takes 15 breaths per minute. The volume of air inhaled in each breath is 450 mL and contains 21% of oxygen by volume. The exhaled air contains 16.1% of oxygen by volume. Both inhaled and exhaled air are at 298 K. If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day and how much of heat is evolved. Given: $\Delta_c H(C_{12}H_{22}O_{11}, s) = -5\,645$ kJ mol^{-1}.

Solution We have

$$\text{Oxygen inhaled by body in one breath} = \frac{21.0}{100} \times 450\ \text{mL} - \frac{16.1}{100} \times 450\ \text{mL} = 22.05\ \text{mL}$$

$$\text{Oxygen inhaled by body in one day} = (15 \times 22.05\ \text{mL})\,(60 \times 24) = 476\,280\ \text{mL} \equiv 476.28\ \text{L}$$

$$\text{Amount of oxygen inhaled by the body per day} = \frac{pV}{RT} = \frac{(1\ \text{atm})\,(476.28\ \text{L})}{(0.0821\ \text{atm L K}^{-1}\ \text{mol}^{-1})\,(298\ \text{K})} = 19.467\ \text{mol}$$

Now according the combustion reaction of sucrose $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

we have Amount of sucrose combusted = $\frac{1}{12} \times 19.467$ mol = 1.622 mol

Mass of sucrose combusted = (1.622 mol) (342 g mol^{-1}) = 554.7 g

Quantity of heat evolved = ($-5\,645$ kJ mol^{-1}) (1.622 mol) = $-9\,156.2$ kJ.

19. Calculate the standard energy change (ΔU) at 298 K for the following reaction.

$$CH_4(g) + 4\ CuO(s) \rightarrow CO_2(g) + 2H_2O(l) + 4Cu(s)$$

Given : $\Delta_f H^\circ(CO_2,\ g) = -393.5\ \text{kJ mol}^{-1}$; $\Delta_f H^\circ(H_2O,\ l) = -285.9\ \text{kJ mol}^{-1}$

$\Delta_f H^\circ(CH_4,\ g) = -74.9\ \text{kJ mol}^{-1}$ and $\Delta_f H^\circ(CuO,\ s) = -157.3\ \text{kJ mol}^{-1}$

Solution For the given reaction, we will have

$$\Delta H^\circ = \Delta_f H^\circ(CO_2,\ g) + 2\Delta_f H^\circ(H_2O,\ l) - \Delta_f H^\circ(CH_4,\ g) - 4\Delta_f H^\circ(CuO,\ s)$$

$$= (-393.5 - 2 \times 285.9 + 74.9 + 4 \times 157.3)\ \text{kJ mol}^{-1} = -261.2\ \text{kJ mol}^{-1}$$

Since for the given reaction, $\Delta\nu_g = 0$, we will have $\Delta U^\circ = \Delta H^\circ = -261.2\ \text{kJ mol}^{-1}$.

20. Compute the heat of reaction (at constant volume) of the following reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(l) + 4NO(g)$$

Given : Standard enthaplies of formation at 298 K for $NH_3(g)$, $H_2O(l)$ and $NO(g)$ are -46.2, -285.9 and $90.4\ \text{kJ mol}^{-1}$, respectively.

Solution For the given reaction, we have

$$\Delta H = 6\Delta_f H^\circ(H_2O,\ l) + 4\ \Delta_f H^\circ(NO,\ g) - 4\ \Delta_f H^\circ(NH_3,\ g)$$

$$= (-6 \times 285.9 + 4 \times 90.4 + 4 \times 46.2)\ \text{kJ mol}^{-1} = -1169.0\ \text{kJ mol}^{-1}.$$

Moreover, for the reaction $\Delta\nu_g = -5$. Hence

$$\Delta U^\circ = \Delta H^\circ - (\Delta\nu_g)\ RT = -1169.0\ \text{kJ mol}^{-1} - (-5)\ (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (298\ \text{K})$$

$$= (-1169.0 + 12.39)\ \text{kJ mol}^{-1} = -1156.6\ \text{kJ mol}^{-1}.$$

21. Calculate ΔH° and ΔU° for the reaction $4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$ at 298 K from the data given below.

$\Delta_f H^\circ(NH_3,\ g) = -\ 46.2\ \text{kJ mol}^{-1}$; $\Delta_f H^\circ(H_2O,\ g) = -241.8\ \text{kJ mol}^{-1}$ $\Delta_f H^\circ(NO,\ g) = 90.4\ \text{kJ mol}^{-1}$

Solution The enthalpy change of the given reaction is given as

$$\Delta H^\circ = 6\ \Delta_f H^\circ(H_2O,\ g) + 4\ \Delta_f H^\circ(NO,\ g) - 4\ \Delta_f H^\circ(NH_3,\ g)$$

$$= [6\ (-241.8) + 4(90.4) - 4(-46.2)]\ \text{kJ mol}^{-1} = -904.4\ \text{kJ mol}^{-1}$$

Now, for the given chemical equation $\Delta\nu_g = +6 + 4 - 4 - 5 = +1$

Hence, $\Delta U^\circ = \Delta H^\circ - (\Delta\nu_g)\ RT = -904.4\ \text{kJ mol}^{-1} - (+1)(8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})(298\ \text{K})$

$$= -906.9\ \text{kJ mol}^{-1}.$$

22. The $\Delta_f H^\circ(KF,\ s)$ is – 563 kJ mol^{-1}. The ionization enthalpy of K(g) is 419 kJ mol^{-1} and the enthalpy of sublimation of potassium is 88 kJ mol^{-1}. The electron affinity of F(g) is 322 kJ mol^{-1} and F—F bond enthalpy is 158 kJ mol^{-1}. Calculate the lattice enthalpy of KF(s).

The given data are as follows.

(i) $K(s) + \frac{1}{2}\ F_2(g) \rightarrow KF(s)$ $\Delta_f H^\circ = -\ 563\ \text{kJ mol}^{-1}$

(ii) $K(g) \rightarrow K^+(g) + e^-$ $\Delta_{\text{ioniz}} H^\circ = 419\ \text{kJ mol}^{-1}$

(iii) $K(s) \rightarrow K(g)$ $\Delta_{\text{sub}} H^\circ = 88\ \text{kJ mol}^{-1}$

(iv) $F(g) + e^- \rightarrow F^-(g)$ $\Delta_{\text{ea}} H^\circ = -\ 322\ \text{kJ mol}^{-1}$

(v) $F_2(g) \rightarrow 2F(g)$ $\Delta_{\text{diss}} H^\circ = 158\ \text{kJ mol}^{-1}$

(vi) $K^+(g) + F^-(g) \longrightarrow KF(s)$ $\Delta H^\circ = ?$

Solution Equation (vi) can be generated by the following manipulations.

$$\text{Eq. (i)} - \text{Eq. (ii)} - \text{Eq. (iii)} - \text{Eq. (iv)} - \tfrac{1}{2}\ \text{Eq. (v)}$$

Carrying out the corresponding manipulations on ΔH° s, we get

$$\Delta H^\circ = (-\ 563 - 419 - 88 + 322 - 79)\ \text{kJ mol}^{-1} = -\ 827\ \text{kJ mol}^{-1}.$$

23. Using the bond-enthalpy data, compute ΔH° for the reaction $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

Given: $\varepsilon(C{-}H) = 414\ \text{kJ mol}^{-1}$; $\varepsilon(O{-}H) = 460\ \text{kJ mol}^{-1}$; $\varepsilon(C{=}C) = 619\ \text{kJ mol}^{-1}$;

$\varepsilon(O{=}O) = 499\ \text{kJ mol}^{-1}$; $\varepsilon(C{=}O) = 724\ \text{kJ mol}^{-1}$

Solution The given reaction may be visualized to take place as shown in the following.

$$\begin{tikzcd}
C_2H_4(g) + 3O_2(g) \arrow[rr, "\Delta H"] \arrow[dr, "\Delta H_1"'] & & 2CO_2(g) + 2H_2O(g) \\
& 2C(g) + 4H(g) + 6O(g) \arrow[ur, "\Delta H_2"'] &
\end{tikzcd}$$

Obviously, $\Delta H = \Delta H_1 + \Delta H_2$

Now $\Delta H_1 = \varepsilon(\mathrm{C{=}C}) + 4\varepsilon(\mathrm{C{-}H}) + 3\varepsilon(\mathrm{O{=}O}) = (619 + 4 \times 414 + 3 \times 499)\ \mathrm{kJ\ mol^{-1}}$

$= 3772\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_2 = -\,4\varepsilon(\mathrm{C{=}O}) - 4\varepsilon(\mathrm{O{-}H}) = (-\,4 \times 724 - 4 \times 460)\ \mathrm{kJ\ mol^{-1}}$

$= -\,4736\ \mathrm{kJ\ mol^{-1}}$

Hence, $\Delta H = (3772 - 4736)\ \mathrm{kJ\ mol^{-1}} = -\,964\ \mathrm{kJ\ mol^{-1}}$.

24. Using the bond enthalpy data given below, compute the enthalpy of formation of gaseous isoprene $CH_2{=}C(CH_3)CH{=}CH_2$.

$\varepsilon(\mathrm{C{-}H}) = 413.4\ \mathrm{kJ\ mol^{-1}}$; $\varepsilon(\mathrm{C{-}C}) = 347.7\ \mathrm{kJ\ mol^{-1}}$; $\varepsilon(\mathrm{C{=}C}) = 615.1\ \mathrm{kJ\ mol^{-1}}$

Enthalpy of sublimation of C(graphite) = 718.4 kJ $\mathrm{mol^{-1}}$

Enthalpy of formation of H(g) = 218.0 kJ $\mathrm{mol^{-1}}$

Solution We have to compute the enthalpy change of the following reaction:

$$5C(\text{graphite}) + 4H_2(g) \rightarrow CH_2{=}C(CH_3)CH{=}CH_2(g)$$

The provided data are

$C{-}H(g) \rightarrow C(g) + H(g)$ $\quad \Delta H = 413.4\ \mathrm{kJ\ mol^{-1}}$

$C{-}C(g) \rightarrow 2C(g)$ $\quad \Delta H = 347.7\ \mathrm{kJ\ mol^{-1}}$

$C{=}C(g) \rightarrow 2C(g)$ $\quad \Delta H = 615.1\ \mathrm{kJ\ mol^{-1}}$

$C(\text{graphite}) \rightarrow C(g)$ $\quad \Delta H = 718.4\ \mathrm{kJ\ mol^{-1}}$

$\frac{1}{2}\ H_2(g) \rightarrow H(g)$ $\quad \Delta H = 218.0\ \mathrm{kJ\ mol^{-1}}$

The given reaction may be thought to occur through the following alternative path.

$$\begin{tikzcd}
5C(\text{graphite}) + 4H_2(g) \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2(g) \\
& 5C(g) + 8H(g) \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

Obviously,

$\Delta H_1 = \Delta H_2 + \Delta H_3$

where $\Delta H_2 = (5 \times 718.4 + 8 \times 218.0)\ \mathrm{kJ\ mol^{-1}} = 5336\ \mathrm{kJ\ mol^{-1}}$

and $\Delta H_3 = -\,2\varepsilon(\mathrm{C{-}C}) - 2\varepsilon(\mathrm{C{=}C}) - 8\varepsilon(\mathrm{C{-}H})$

$= [-2 \times 347.7 - 2 \times 615.1 - 8 \times 413.4]\ \mathrm{kJ\ mol^{-1}} = -\,5232.8\ \mathrm{kJ\ mol^{-1}}$

Hence, $\Delta H_1 = (5336 - 5232.8)\ \mathrm{kJ\ mol^{-1}} = 103.2\ \mathrm{kJ\ mol^{-1}}$

25. Find the bond enthalpy of S—S bond from the following data :

$C_2H_5{-}S{-}C_2H_5(g)$ $\quad \Delta_f H^\circ = -\,147.2\ \mathrm{kJ\ mol^{-1}}$

$C_2H_5{-}S{-}S{-}C_2H_5(g)$ $\quad \Delta_f H^\circ = -\,201.9\ \mathrm{kJ\ mol^{-1}}$

$S(g)$ $\quad \Delta_f H^\circ = 222.8\ \mathrm{kJ\ mol^{-1}}$

Solution We are given that

(i) $4C(\text{graphite}) + 5H_2(g) + S(s) \rightarrow C_2H_5{-}S{-}C_2H_5(g)$ $\quad \Delta H = -\,147.2\ \mathrm{kJ\ mol^{-1}}$

(ii) $4C(\text{graphite}) + 5H_2(g) + 2S(s) \rightarrow C_2H_5{-}S{-}S{-}C_2H_5(g)$ $\quad \Delta H = -\,201.9\ \mathrm{kJ\ mol^{-1}}$

Subtracting Eq. (i) from Eq. (ii), we get $C_2H_5—S—C_2H_5(g) + S(s) \rightarrow C_2H_5—S—S—C_2H_5(g)$

$$\Delta H = (-\ 201.9 + 147.2)\ \text{kJ mol}^{-1} = -\ 54.7\ \text{kJ mol}^{-1}$$

Adding to this, the following equation

$$S(g) \rightarrow S(s) \qquad \Delta H = -\ 222.8\ \text{kJ mol}^{-1}$$

we get $C_2H_5—S—C_2H_5(g) + S(g) \rightarrow C_2H_5—S—S—C_2H_5(g)$

$$\Delta H = (-\ 54.7 - 22.8)\ \text{kJ mol}^{-1} = -\ 277.5\ \text{kJ mol}^{-1}.$$

In the last equation, 277.5 kJ heat is evolved because of the S—S bond formation. Hence, the bond enthalpy of S—S bond is 277.5 kJ mol^{-1}.

26. Calculate the bond enthalpies of C—H, C—C and C═C bonds from the following data.

$$\Delta_f H°(CH_4,\ g) = -\ 74.9\ \text{kJ mol}^{-1}; \quad \Delta_f H°(C_2H_6,\ g) = -\ 84.7\ \text{kJ mol}^{-1}$$

$$\Delta_f H°(C_2H_4,\ g) = 52.3\ \text{kJ mol}^{-1}; \quad \Delta_{sub} H°(C,\ \text{graphite}) = 718.4\ \text{kJ mol}^{-1}$$

Dissociation enthalpy of $H_2(g) = 435.9$ kJ mol^{-1}

Bond enthalpy of C—H *bond* To compute C—H bond enthalpy, we determine the ΔH value of the reaction

$$CH_4(g) \rightarrow C(g) + 4H(g) \qquad \Delta H° = \ ? \tag{1}$$

This equation can be obtained by the addition of the following reactions.

$$CH_4(g) \rightarrow C(\text{graphite}) + 2H_2(g) \qquad \Delta H° = 74.9\ \text{kJ mol}^{-1}$$
$$C(\text{graphite}) \rightarrow C(g) \qquad \Delta H° = 718.4\ \text{kJ mol}^{-1}$$
$$2H_2(g) \rightarrow 4H(g) \qquad \Delta H° = 2 \times 435.9\ \text{kJ mol}^{-1}$$

Carrying out the corresponding manipulations on $\Delta H°$s, we get

$$\Delta H° = (74.9 + 718.4 + 2 \times 435.9)\ \text{kJ mol}^{-1} = 1665.1\ \text{kJ mol}^{-1}$$

Now, since $\Delta H° = 4\varepsilon(C—H)$, we get $\varepsilon(C—H) = \dfrac{1665.1}{4}\ \text{kJ mol}^{-1} = 416.3\ \text{kJ mol}^{-1}$

Bond enthalpy of C—C *bond from* $\Delta_f H°(C_2H_6)$: For the reaction

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g) \tag{2}$$

we will have $\Delta H° = \varepsilon(C—C) + 6\varepsilon(C—H)$

Equation (2) can be obtained by the following manipulations.

$$C_2H_6(g) \rightarrow 2C(\text{graphite}) + 3H_2(g) \qquad \Delta H° = 84.7\ \text{kJ mol}^{-1}$$
$$2C(\text{graphite}) \rightarrow 2C(g) \qquad \Delta H° = 2 \times 718.4\ \text{kJ mol}^{-1}$$
$$3H_2(g) \rightarrow 6H(g) \qquad \Delta H° = 3 \times 435.9\ \text{kJ mol}^{-1}$$

Carrying out the corresponding manipulations on $\Delta H°$s, we get

$$\Delta H° = (84.7 + 2 \times 718.4 + 3 \times 435.9)\ \text{kJ mol}^{-1} = 2829.2\ \text{kJ mol}^{-1}$$

Hence, $\varepsilon(C—C) = \Delta H° - 6\varepsilon(C—H) = (2829.2 - 6 \times 416.3)\ \text{kJ mol}^{-1} = 331.4\ \text{kJ mol}^{-1}$

Bond enthalpy of C═C *from* $\Delta_f H°(C_2H_4)$:

For the reaction $C_2H_4(g) \rightarrow 2C(g) + 4H(g)$ (3)
we will have $\Delta H° = \varepsilon(C═C) + 4\varepsilon(C—H)$
Equation (3) can be obtained from the following manipulations.

$$C_2H_4(g) \rightarrow 2C(\text{graphite}) + 2H_2(g) \qquad \Delta H° = -\ 52.3\ \text{kJ mol}^{-1}$$
$$2C(\text{graphite}) \rightarrow 2C(g) \qquad \Delta H° = 2 \times 718.4\ \text{kJ mol}^{-1}$$
$$2H_2(g) \rightarrow 2H(g) \qquad \Delta H° = 2 \times 435.9\ \text{kJ mol}^{-1}$$

Carrying out the corresponding manipulations on $\Delta H°$s, we get

$$\Delta H° = (-\ 52.3 + 2 \times 718.4 + 2 \times 435.9)\ \text{kJ mol}^{-1} = 2256.3\ \text{kJ mol}^{-1}$$

Now $\varepsilon(C = C) = \Delta H° - 4\ \varepsilon(C—H) = (2\,256.3 - 4 \times 416.3)\ \text{kJ mol}^{-1} = 591.1\ \text{kJ mol}^{-1}$

27. Compute the resonance energy of gaseous benzene from the following data.

$\varepsilon(\mathrm{C—H}) = 416.3\ \mathrm{kJ\ mol^{-1}}$; $\varepsilon(\mathrm{C—C}) = 331.4\ \mathrm{kJ\ mol^{-1}}$; $\varepsilon(\mathrm{C{=}C}) = 591.1\ \mathrm{kJ\ mol^{-1}}$;

$\Delta H^\circ_{\mathrm{sub}}(\mathrm{C,\ graphite}) = 718.4\ \mathrm{kJ\ mol^{-1}}$; $\Delta H^\circ_{\mathrm{diss}}(\mathrm{H_2,\ g}) = 435.9\ \mathrm{kJ\ mol^{-1}}$;

$\Delta_f H^\circ(\mathrm{benzene,\ g}) = 82.9\ \mathrm{kJ\ mol^{-1}}$

Solution To compute resonance energy, we compare the calculated value of $\Delta_f H^\circ$(benzene, g) with the given one. To calculate $\Delta_f H^\circ$(benzene, g), we add the following reactions.

$6\mathrm{C(g)} + 6\mathrm{H(g)} \rightarrow \mathrm{C_6H_6(g)}$ $\Delta H^\circ = -\,(3\varepsilon_{\mathrm{C–C}} + 3_{\mathrm{C=C}} + 6\varepsilon_{\mathrm{C–H}})$

$6\mathrm{C(graphite)} \rightarrow 6\mathrm{C(g)}$ $\Delta H^\circ = 6 \times 718.4\ \mathrm{kJ\ mol^{-1}}$

Add $3\mathrm{H_2(g)} \rightarrow 6\mathrm{H(g)}$ $\Delta H^\circ = 3 \times 435.9\ \mathrm{kJ\ mol^{-1}}$

$6\mathrm{C(graphite)} + 3\mathrm{H_2(g)} \rightarrow \mathrm{C_6H_6(g)}$

The corresponding enthalpy change is

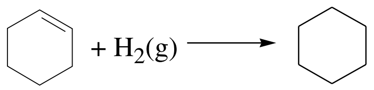
$$\begin{aligned}\Delta_f H^\circ &= -(3\varepsilon_{\mathrm{C—C}} + 3\varepsilon_{\mathrm{C=C}} + 6\varepsilon_{\mathrm{C—H}}) + [6 \times 718.4 + 3 \times 435.9]\ \mathrm{kJ\ mol^{-1}}\\ &= [-(3\times 331.4 + 3\times 591.1 + 6\times 416.3 + 6\times 718.4 + 3\times 435.9]\ \mathrm{kJ\ mol^{-1}}\\ &= 352.8\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The given $\Delta_f H^\circ$ is $\Delta_f H^\circ(\mathrm{benzene,\ g}) = 82.9\ \mathrm{kJ\ mol^{-1}}$

This means benzene becomes more stable by (352.8 – 82.9) $\mathrm{kJ\ mol^{-1}}$, i.e., 269.7 $\mathrm{kJ\ mol^{-1}}$. This is its resonance energy.

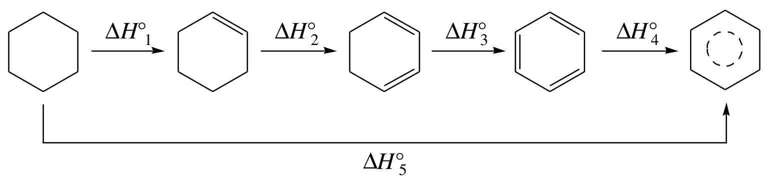
28. The standard molar enthalpies of formation of cyclohexane(l) and benzene(l) at 25 °C are – 156 and + 49 $\mathrm{kJ\ mol^{-1}}$, respectively. The standard enthalpy of hydrogenation of cyclohexene(l) at 25 °C is – 119 $\mathrm{kJ\ mol^{-1}}$. Use these data to estimate the magnitude of the resonance energy of benzene.

Solution The reaction corresponding to the hydrogenation of cyclohexene(l) is



$\Delta H^\circ = -119\ \mathrm{kJ\ mol^{-1}}$

This implies that the generation of one double bond in cyclohexane requires 119 $\mathrm{kJ\ mol^{-1}}$ of enthalpy. To calculate the resonance energy, we may proceed as follows.



Now $\Delta H^\circ_1 = \Delta H^\circ_2 = \Delta H^\circ_3 = 119\ \mathrm{kJ\ mol^{-1}}$

ΔH°_4 = resonance energy

$\Delta H^\circ_5 = \Delta_f H^\circ(\mathrm{benzene}) - \Delta_f H^\circ(\mathrm{cyclohexane}) = [49 - (-\,156)]\ \mathrm{kJ\ mol^{-1}} = 205\ \mathrm{kJ\ mol^{-1}}$

According to Hess's law, we have

$$\Delta H^\circ_4 = \Delta H^\circ_5 - (\Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3) = (205 - 3 \times 119)\ \mathrm{kJ\ mol^{-1}} = -\,152\ \mathrm{kJ\ mol^{-1}}$$

29. The enthalpy change involved in the oxidation of glucose is – 2880 $\mathrm{kJ\ mol^{-1}}$. Twenty-five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose. (1997)

Solution We are given that $\mathrm{C_6H_{12}O_6(s)} + 6\mathrm{O_2(g)} \rightarrow 6\mathrm{CO_2(g)} + 6\mathrm{H_2O(l)}$ $\Delta H = -\,2880\ \mathrm{kJ\ mol^{-1}}$

Enthalpy consumed in muscular work = (2880 kJ)(25/100) = 720 kJ

$$\text{Amount of glucose in 120 g} = \left(\frac{120\ \mathrm{g}}{180\ \mathrm{g\ mol^{-1}}}\right) = 0.6667\ \mathrm{mol}$$

Enthalpy available for muscular work from 120 g of glucose = (720 $\mathrm{kJ\ mol^{-1}}$) (0.6667 mol) = 480 kJ

$$\text{Distance to which a person can move} = \left(\frac{1\ \mathrm{kg}}{100\ \mathrm{kJ}}\right)(480\ \mathrm{kJ}) = 4.80\ \mathrm{km}$$

30. Compute the enthalpy of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Enthalpy of vaporization of liquid methyl alcohol = 38 kJ/mol. Enthalpy of gaseous atoms from the elements in their standard states; H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

Average bond enthalpy: C—H, 415 kJ/mol; C—O, 356 kJ/mol, and O—H, 463 kJ/mol (1997)

Solution The given data are as follows.

(1) $CH_3OH(l) \rightarrow CH_3OH(g)$ $\Delta H_1 = 38\ \text{kJ mol}^{-1}$

(2) $\frac{1}{2}H_2(g) \rightarrow H(g)$ $\Delta H_2 = 218\ \text{kJ mol}^{-1}$

(3) $C(\text{graphite}) \rightarrow C(g)$ $\Delta H_3 = 715\ \text{kJ mol}^{-1}$

(4) $\frac{1}{2}O_2(g) \rightarrow O(g)$ $\Delta H_4 = 249\ \text{kJ mol}^{-1}$

(5) $C—H(g) \rightarrow C(g) + H(g)$ $\Delta H_5 = 415\ \text{kJ mol}^{-1}$

(6) $C—O(g) \rightarrow C(g) + O(g)$ $\Delta H_6 = 356\ \text{kJ mol}^{-1}$

(7) $O—H(g) \rightarrow O(g) + H(g)$ $\Delta H_7 = 463\ \text{kJ mol}^{-1}$

We have to calculate the enthalpy of formation of liquid methyl alcohol, i.e.,

(8) $C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$ $\Delta H_8 = ?$

First of all, we calculate the enthalpy of reaction

(9) $CH_3OH(g) \rightarrow C(g) + 4H(g) + O(g)$

from the data on bond enthalpies. This is given as

$$\Delta H_9 = 3\,\Delta H_5 + \Delta H_6 + \Delta H_7 = (3 \times 415 + 356 + 463)\text{kJ mol}^{-1} = 2064\ \text{kJ mol}^{-1}$$

Equation (8) can be generated as follows

Eq. (3) + 4. Eq. (2) + Eq. (4) – Eq. (9) – Eq. (1)

Hence, $\Delta H = \Delta H_3 + 4\Delta H_2 + \Delta H_4 - \Delta H_9 - \Delta H_1 = (715 + 4 \times 218 + 249 - 2064 - 38)\ \text{kJ mol}^{-1} = -266\ \text{kJ mol}^{-1}$

31. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene(g) are – 393.5, – 285.8 and 20.42 kJ mol^{-1}, respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ mol^{-1}. (1998)

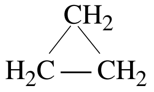
Solution For the reaction

(i) $CH_3CH{=\!=}CH_2(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

$$\Delta_r H = 3\Delta_f H(CO_2, g) + 3\Delta_f H(H_2O, l) - \Delta_f H(CH_3CH{=\!=}CH_2)$$

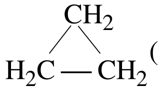
$$= [3(-393.5) + 3(-285.8) - (20.42)]\ \text{kJ mol}^{-1} = -2058.32\ \text{kJ mol}^{-1}$$

To the reaction (i), if we add the reaction



$\rightarrow CH_3CH = CH_2(g)$ $\Delta_r H = -33.0\ \text{kJ mol}^{-1}$

we get



$(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

Hence, $\Delta_c H(\text{cyclopropane}) = (-2058.32 - 33.0)\ \text{kJ mol}^{-1} = -2091.32\ \text{kJ mol}^{-1}$

32. Estimate the average S—F bond enthalpy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are: – 1100, 275 and 80 kJ mol^{-1} respectively. (1999)

Solution To calculate the average S—F bond enthalpy, we determine the enthalpy change for the following reaction.

$$\underset{\Delta_f H^\circ\ 275\ \text{kJ mol}^{-1}}{S(g)} + \underset{80\ \text{kJ mol}^{-1}}{6F(g)} \rightarrow \underset{-1100\ \text{kJ mol}^{-1}}{SF_6(g)}$$

$$\Delta_r H^\circ = \Delta_f H^\circ(SF_6, g) - [\Delta_f H^\circ(S, g) + 6\,\Delta_f H^\circ(F, g)] = [-1100 - (275 + 6 \times 80)]\ \text{kJ mol}^{-1}$$

$$= -1855\ \text{kJ mol}^{-1}$$

Hence, $$\varepsilon(S-F) = \frac{-\Delta_f H^\circ(SF_6, g)}{6} = \frac{1855\ \text{kJ mol}^{-1}}{6} = 309.2\ \text{kJ mol}^{-1}$$

33. A sample of argon gas at 1 atm pressure and 27 °C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{V,\mathrm{m}}$ for argon is 12.48 J K^{-1} mol^{-1}. (2000)

Solution: For a reversible expansion of an ideal gas, we have

$$T_2\,V_2^{\gamma-1} = T_1\,V_1^{\gamma-1} \qquad \text{where} \qquad \gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$$

For a monatomic gas (assumed to be ideal),

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_{V,\mathrm{m}} + R}{C_{V,\mathrm{m}}} = 1 + \frac{R}{C_{V,\mathrm{m}}} = 1 + \frac{8.314}{12.48} = 1.6662$$

Hence,
$$T = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1 = \left(\frac{1.25}{2.50}\right)^{0.6662} (300\ \mathrm{K}) = 189.0\ \mathrm{K}$$

The enthalpy change in the given process would be $\Delta H = nC_{p,\mathrm{m}}\,\Delta T$

where
$$n = \frac{pV}{RT} = \frac{(101.325\ \mathrm{kPa})\,(1.25\ \mathrm{dm}^3)}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(300\ \mathrm{K})} = 0.0508\ \mathrm{mol}$$

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R = (12.48 + 8.314)\ \mathrm{J\ K^{-1}\ mol^{-1}} = 20.794\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta T = T_2 - T_1 = (189.0 - 300)\ \mathrm{K} = -\,111\ \mathrm{K}$$

Hence
$$\Delta H = nC_{p,\mathrm{m}}\,\Delta T = (0.0508\ \mathrm{mol})\,(20.794\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(-\,111\ \mathrm{K}) = -\,117.25\ \mathrm{J}$$

34. Show that the reaction $CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy change is – 0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are – 394.4 and – 137.2 kJ mol^{-1}, respectively. (2000)

Solution For the given reaction, we have

$$\begin{array}{lccccc} & CO(g) & + & \frac{1}{2}O_2(g) \rightarrow & CO_2(g) & \Delta_r S^\circ = -\,0.094\ \mathrm{kJ\ K^{-1}\ mol^{-1}} \\ \Delta_f G^\circ & -\,137.2\ \mathrm{kJ\ mol^{-1}} & & & -\,394.4\ \mathrm{kJ\ mol^{-1}} & \end{array}$$

The standard free-energy change of the reaction is

$$\Delta_r G^\circ = \Delta_f G^\circ(CO_2, g) - \Delta_f G^\circ(CO, g) = (-\,394.4) + 137.2)\ \mathrm{kJ\ mol^{-1}} = -\,257.2\ \mathrm{kJ\ mol^{-1}}$$

Since $\Delta_r G^\circ$ is negative, the reaction is spontaneous. The enthalpy change of the reaction is

$$\Delta_r H^\circ = \Delta_r G^\circ - T\Delta_r S^\circ = (-\,257.2 + (300)\,(-\,0.094)\ \mathrm{kJ\ mol^{-1}} = -\,285.4\ \mathrm{kJ\ mol^{-1}}$$

Since $\Delta_r H^\circ$ is negative, the reaction is exothermic.

35. Diborane is a potential rocket fuel which undergoes combustion according to the reaction

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane.

$2B(s) + (3/2)\,O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -\,1273\ \mathrm{kJ\ mol^{-1}}$.

$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)$ $\Delta H = -\,286\ \mathrm{kJ\ mol^{-1}}$

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = 44\ \mathrm{kJ\ mol^{-1}}$

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ $\Delta H = 36\ \mathrm{kJ\ mol^{-1}}$ (2000)

Solution

The given reaction can be obtained as follows.

$$\begin{array}{lll} & B_2H_6(g) \rightarrow 2B(s) + 3H_2(g) & \Delta H = -\,36\ \mathrm{kJ\ mol^{-1}} \\ & 2B(s) + (3/2)\,O_2(g) \rightarrow B_2O_3(s) & \Delta H = -\,1273\ \mathrm{kJ\ mol^{-1}} \\ & 3[H_2O(l) \rightarrow H_2O(g)] & \Delta H = 3 \times 44\ \mathrm{kJ\ mol^{-1}} \\ & 3[H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)] & \Delta H = -\,3 \times 286\ \mathrm{kJ\ mol^{-1}} \\ \hline \text{Add} & B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g) & \Delta H = -\,2035\ \mathrm{kJ\ mol^{-1}} \end{array}$$

UNSOLVED PROBLEMS

1. The $\Delta_f H°(CaBr_2, s) = -675\ kJ\ mol^{-1}$. The first and second ionization energies of Ca are 590 and 1145 kJ mol^{-1}. The enthalpy of formation of Ca is 178 kJ mol^{-1}. The bond enthalpy of Br_2 is 193 kJ mol^{-1} and enthalpy of vaporization of Br_2 is 31 kJ mol^{-1}. The electron affinity of Br(g) is 325 kJ mol^{-1}. Calculate the lattice energy of $CaBr_2(s)$.
2. Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 41.84 kJ of heat at (a) constant pressure and (b) constant volume conditions. Given: $\Delta_f H°$ (HgO, s) $= -90.8\ kJ\ mol^{-1}$ and $M(Hg) = 200.6\ g\ mol^{-1}$.
3. The enthalpies of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ are -1410.8, -1559.8 and -285.9 kJ mol^{-1}, respectively. What is the enthalpy of hydrogenation of ethylene?
4. Using the bond enthalpy data given below, calculate the enthalpy of formation of acetone(g).

$\varepsilon(C—H) = 413.4\ kJ\ mol^{-1}$; $\varepsilon(C—C) = 347.0\ kJ\ mol^{-1}$; $\varepsilon(C{=}O) = 728.0\ kJ\ mol^{-1}$;

$\varepsilon(O{=}O) = 495.0\ kJ\ mol^{-1}$; $\varepsilon(H—H) = 435.8\ kJ\ mol^{-1}$; $\Delta_{sub}H(C) = 718.4\ kJ\ mol^{-1}$;

5. Using the bond enthalpy data given below, estimate the enthalpy of formation of propanoic acid.

Bond	*Bond enthalpy* ε/kJ mol^{-1}	*Enthalpy of formation of gaseous atoms*	$\Delta_f H$/kJ mol^{-1}
C—H	413.38	C(g)	718.39
C—C	347.69	H(g)	217.94
C═O	728.02	O(g)	247.52
C—O	351.46		
O—H	462.75		

6. Find ΔH for the reaction at 298 K; $C_6H_6(l) + 7\frac{1}{2}\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ given that ΔU for this reaction is $-3268\ kJ\ mol^{-1}$.
7. The measured $\Delta H°$ for the combustion of $C_6H_6(g)$ to $CO_2(g)$ and $H_2O(g)$ is $-3170\ kJ\ mol^{-1}$. Calculate $\Delta H°$ for this reaction using bond enthalpies and then calculate the resonance energy of benzene. Given:

$\varepsilon(C—C) = 346\ kJ\ mol^{-1}$; $\varepsilon(C{=}C) = 615\ kJ\ mol^{-1}$; $\varepsilon(C—H) = 413\ kJ\ mol^{-1}$;

$\varepsilon(C{=}O) = 728\ kJ\ mol^{-1}$; $\varepsilon(O—H) = 463\ kJ\ mol^{-1}$; $\varepsilon(O{=}O) = 495\ kJ\ mol^{-1}$;

8. The enthalpy of combustion of liquid C_8H_{18} to carbon dioxide and water at 298 K is 1303 kJ mol^{-1}. Calculate ΔU for this combustion process.
9. The solution of $CaCl_2\cdot 6H_2O$ in a large volume of water is endothermic to the extent of 14.64 kJ mol^{-1}. What is the enthalpy of solution of anhydrous $CaCl_2$ in a large volume of water? Given that ΔH for the reaction $CaCl_2(s) + 6H_2O(l) \rightarrow CaCl_2\cdot 6H_2O(s)$ is $-97.49\ kJ\ mol^{-1}$.
10. What mass of butane be burnt to heat 10 L water from 30°C to 100°C? Enthalpy of combustion of butane is $-2879\ kJ\ mol^{-1}$. Assume ρ and C_p of water to be 1 g cm^{-3} and 4.184 J K^{-1} g^{-1} respectively.
11. From the following data, calculate the bond enthalpies of C—C and C≡N bonds.

Enthalpy of formation of CH_3CN = 87.86 kJ mol^{-1}; Enthalpy of dissociation of nitrogen = 945.58 kJ mol^{-1}

Enthalpy of formation of C_2H_6 = -83.68 kJ mol^{-1}; Enthalpy of dissociation of hydrogen = 435.14 kJ mol^{-1}

Enthalpy of sublimation of graphite = 719.65 kJ mol^{-1} C—H bond enthalpy = 414.22 kJ mol^{-1}

12. The enthalpy of formation of $H_2O(l)$ is $-285.77\ kJ\ mol^{-1}$ and enthalpy of neutralization of a strong acid and a strong base is $-56.07\ kJ\ mol^{-1}$. What is the enthalpy of formation of OH^- ions?
13. From the data

,Reaction	$\Delta H°$/kJ mol^{-1}
$\frac{1}{2}\ H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow OH(g)$	42.09
$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(g)$	-241.84
$H_2(g) \rightarrow 2H(g)$	435.88
$O_2(g) \rightarrow 2O(g)$	495.04

at 25°C, calculate $\Delta H°$ for the reactions

(a) $OH(g) \rightarrow H(g) + O(g)$ (b) $H_2O(g) \rightarrow 2H(g) + O(g)$ (c) $H_2O(g) \rightarrow H(g) + OH(g)$

Also compute $\Delta U°$ of these reactions.

14. Using the bond enthalpy data, estimate the enthalpy of formation of acetic acid.

Bond	*Bond enthalpy* ε/kJ mol^{-1}
C—H	413.4
C—C	347.7
C═O	728.0
C—O	351.5
O—H	462.8

Enthalpy of atomization $\Delta H°$/kJ mol^{-1}	
C	718.4
H	218.0
O	247.5

The observed $\Delta_f H°$ for a acetic acid is -438.2 kJ mol^{-1}, compute the resonance energy of acetic acid.

15. The bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are 436.0 kJ mol^{-1} and 941.8 kJ mol^{-1} and the enthalpy of formation of $NH_3(g)$ is -46.0 kJ mol^{-1}. What is the enthalpy of atomization of $NH_3(g)$? What is the average bond enthalpy of N—H bond?

16. Calculate the enthalpy of formation of $I_2O_5(g)$ from the following data:

(a) $I_2O_5(s) + nH_2O(l) \rightarrow 2HIO_3(aq)$ $\Delta H = 3.6$ kJ mol^{-1}

(b) $KI(aq) + 3HClO(aq) \rightarrow HIO_3(aq) + 2HCl(aq) + KCl(aq)$ $\Delta H = -322.4$ kJ mol^{-1}

(c) $NaOH(aq) + HClO(aq) \rightarrow NaOCl(aq) + H_2O(l)$ $\Delta H = -44.4$ kJ mol^{-1}

(d) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H = -57.3$ kJ mol^{-1}

(e) $2NaOH(aq) + Cl_2(g) \rightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$ $\Delta H = -99.8$ kJ mol^{-1}

(f) $2KI(aq) + Cl_2(g) \rightarrow 2KCl(aq) + I_2(s)$ $\Delta H = -223.9$ kJ mol^{-1}

(g) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.0$ kJ mol^{-1}

(h) $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$ $\Delta H = -92.3$ kJ mol^{-1}

(i) $HCl(g) + nH_2O(l) \rightarrow HCl(aq)$ $\Delta H = -75.2$ kJ mol^{-1}

17. The enthalpy changes for the following reactions at 25 °C are

$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$ $\Delta H = -411.0$ kJ mol^{-1}

$H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)$ $\Delta H = -811.3$ kJ mol^{-1}

$2Na(s) + S(s) + 2O_2(g) \rightarrow Na_2SO_4(s)$ $\Delta H = -1382.8$ kJ mol^{-1}

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$ $\Delta H = -93.3$ kJ mol^{-1}

From these data, find the heat change of reaction at constant volume for the process

$$2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$$

18. (a) Values of $\Delta H°_{298K}$ for the reaction $N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g)$ is found to be 108.8 kJ mol^{-1}. Calculate the bond enthalpy of N═N bond. Given: ε(N—N) = 163.2 kJ mol^{-1}, ε (N—H) = 390.8 kJ mol^{-1} and ε(H—H) = 435.9 kJ mol^{-1}.

(b) If $\Delta_f H°(N_2H_4, g) = 95$ kJ mol^{-1}, calculate $\Delta_f H°(N_2H_2, g)$.

(c) Calculate $\Delta_f H°(N_2H_4, g)$ and $\Delta_f H°(N_2H_2, g)$ from the bond enthalpies data and compare with those of part (b). Given: ε(N≡N) = 942.2 kJ mol^{-1}.

(d) Compute $\Delta U°$ for the reaction of part (a) at 298 K.

ANSWERS

1. – 2162 kJ mol^{-1}
2. 93.72 g
3. – 136.9 kJ mol^{-1}
4. – 192.3 kJ mol^{-1}
5. – 346.66 kJ mol^{-1}
6. 3271.9 kJ mol^{-1}
7. – 2440.5 kJ mol^{-1}, 729.5 kJ mol^{-1}
8. 1314.15 kJ mol^{-1}
9. – 82.84 kJ mol^{-1}
10. 59.027 g
11. 343.08 kJ mol^{-1}, 891.2 kJ mol^{-1}
12. – 229.7 kJ mol^{-1}
13. 423.37, 925.24, 501.87, 425.85, 930.20 and 504.35 kJ mol^{-1}
14. – 326.8 kJ mol^{-1}, –111.4 kJ mol^{-1}
15. – 1170.9 kJ mol^{-1}, +390.3 kJ mol^{-1}
16. – 163.1 kJ mol^{-1}
17. 60.92 kJ mol^{-1}
18. (a) 400.1 kJ mol^{-1}, (b) 203.8 kJ mol^{-1}, (c) 87.9 kJ mol^{-1}, 196.7 kJ mol^{-1}, (d) 108.4 kJ mol^{-1}

CHAPTER 7

CHEMICAL EQUILIBRIA

SECTION I CHEMICAL EQUILIBRIUM

Many reactions are known in which the reactants are not completely converted into products. The reaction proceeds to a certain extent and the resulting mixture contains both reactants and products. At the final stage, when the properties of the system remain constant with time, the reaction is said to be at equilibrium. A stage of equilibrium can be reached starting from either reactants or products or any arbitrary amounts of reactants and products taken together. At equilibrium, the processes of conversion of reactant(s) into product(s) and vice versa do not cease but both of them occur simultaneously at equal rates and thus at equilibrium, the system involves dynamic equilibrium.

Law of Mass Action According to the law of mass action, the rate of a reaction at constant temperature is directly proportional to the product of molar concentrations of reacting species, each raised to a power equal to the corresponding stoichiometric coefficient appearing in the balanced chemical equation.

Taking the example of the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
we can write

Rate of forward reaction, $r_f \propto [N_2]\ [H_2]^3 = k_f\,[N_2]\ [H_2]^3$

Rate of backward reaction, $r_b \propto [NH_3]^2 = k_b\,[NH_3]^2$

At equilibrium, both these rates are equal. Hence, we have

$$k_f\,[N_2]\ [H_2]^3 = k_b\,[NH_3]^2$$

or

$$K_{eq} = \frac{k_f}{k_b} = \frac{[NH_{3]}]^2}{[N_2][H_2]^3} \tag{1}$$

The constant K_{eq} (also written as K_c) is known as *equilibrium constant* of the reaction. Its value depends only on temperature and is independent of individual concentrations of NH_3, N_2 and H_2. We may start with any arbitrary concentrations of NH_3, N_2 and H_2, but at equilibrium, Eq.(1) will always yield a constant value, equal to the equilibrium constant.

Equilibrium Constant K_p For reactions involving gaseous species, the concentration of each species will be directly proportional to its partial pressure. According to the ideal gas equation, the expression relating these two is

$$p = cRT$$

Hence, the equilibrium constant of a gaseous reaction can also be written in terms of partial pressures. For example, the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is given as $K_p = \dfrac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$ (2)

In the expression of K_p, the partial pressures are expressed in "atm" unit and the K_p carries the appropriate unit. In IUPAC (International Union of Pure and Applied Chemistry), the partial presses are expressed in "bar" unit (1 atm = 101.325 kPa = 1.01325 bar).

In thermodynamics, the equilibrium constant carries no unit as the pressures are expressed in terms of standard unit of 1 atm or 1 bar. In fact, the expression of K_p involves the term $p/p°$, where p is the pressure of the gaseous substance and $p°$ is the standard unit pressure. This type of equilibrium constant is known as standard (or thermodynamic) equilibrium constant and is represented as K_p°.

Equilibrium Constant in Units Other than Partial Pressures

Equilibrium constant of a reaction is also expressed in units other than that of partial pressure. For example, if the concentrations are used, one gets the constant K_c. Equation (1) is the expression of K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The standard equilibrium constant K_c° involves the use of $c/c°$, where $c°$ is the standard unit concentration of 1 mol L^{-1}.

Likewise, one can define the constants K_x and K_n where the subscripts x and n stand for mole fraction and amount of substance, respectively. For the reaction mentioned above, we have

$$K_x = \frac{x_{NH_3}^2}{x_{N_2}\, x_{H_2}^3} \quad \text{and} \quad K_n = \frac{n_{NH_3}^2}{n_{N_2}\, n_{H_2}^3}$$

Relations Between Equilibrium Constants The various equilibrium constants are related to each other through the following expressions.

Equilibrium constants K_p and K_c are related to each other through the expression

$$K_p = K_c\,(RT)^{\Delta\nu_g} \tag{3}$$

where $\Delta\nu_g$ is the change in the stoichiometric numbers of gaseous molecules during the conversion of reactants to products and is defined as $\Delta\nu_g = \Sigma\nu_g(\text{product}) - \Sigma\nu_g(\text{reactant})$ (4)

The equilibrium constants K_p and K_c are quite often used to deal with the reactions at equilibrium. If K_p is expressed in terms of "atm" unit, the value of R to be used is 0.082 L atm K^{-1} mol^{-1}.

The expressions involving standard equilibrium constants are as follows.

$$K_p^\circ = K_c^\circ\,(c°\,RT/p°)^{\Delta\nu_g}; \quad K_p^\circ = K_x\,(p_{total}/p°)^{\Delta\nu_g}, \quad \text{and} \quad K_p^\circ = K_n^\circ\,(n°/n_{total})^{\Delta\nu_g}\,(p_{total}/p°)^{\Delta\nu_g}$$

where $n° = 1$ mol.

Simultaneous Equilibrium Reactions with a Common Species

Consider the following reactions occurring simultaneously in a system

$$X(g) \rightleftharpoons A(g) + B(g) \quad \text{and} \quad Y(g) \rightleftharpoons A(g) + C(g)$$

Let the reactions be initiated with the partial pressures a and b of X and Y, respectively. Let the partial pressures x and y of X and Y, respectively, are transformed into the respective products at equilibrium. We will have

$$\underset{a-x}{X(g)} \rightleftharpoons \underset{x+y}{A(g)} + \underset{x}{B(g)}; \qquad K_{p1} = \frac{p_A\,p_B}{p_X} = \frac{(x+y)x}{a-x}$$

$$\underset{b-y}{Y(g)} \rightleftharpoons \underset{x+y}{A(g)} + \underset{y}{C(g)}; \qquad K_{p2} = \frac{p_A\,p_C}{p_Y} = \frac{(x+y)y}{b-y}$$

Equilibrium Constant of a Reaction Involving Condensed Phases The expression of the equilibrium constant of a reaction involving condensed (solid or liquid) and gaseous states is obtained by considering the concentrations or partial pressures of only the gaseous species. The concentration of condensed phases being constant are merged with the equilibrium constant.

Variation of K_p° with Temperature The equilibrium constant K_p° of a reaction at equilibrium varies with change in temperature and the relation governing this change is

$$\ln K_p^\circ = -\frac{\Delta_r H°}{RT} + I$$

where I is a constant and $\Delta_r H°$ is the standard enthalpy change of the reaction.

For an exothermic reaction, $\Delta_r H^\circ$ is negative and thus an increase in temperature causes a decrease in the value of equilibrium constant.

For an endothermic reaction, $\Delta_r H^\circ$ is positive and thus an increase in temperature causes an increase in the value of equilibrium constant.

Degree of Dissociation The degree of dissociation of a substance implies the fraction of the substance present in the dissociated form. The equilibrium constant can be expressed in terms of the degree of dissociation (symbol: α) of the substance. Consider the reaction

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

If n is the amount of NH_3 taken to start with, then we will have

$$\begin{array}{lccc} & 2NH_3(g) & \rightleftharpoons\ N_2(g) & +\ 3H_2(g) \\ \text{At equilibrium} & n(1-\alpha) & n(\alpha/2) & n(3\alpha/2) \end{array}$$

Total amount of the substance $= n(1-\alpha) + n(\alpha/2) + n(3\alpha/2) = n(1+\alpha)$

Partial pressure of NH_3, $p_{NH_3} = x_{NH_3} P = \dfrac{n(1-\alpha)}{n(1+\alpha)}P = \dfrac{1-\alpha}{1+\alpha}P$

Partial pressure of N_2, $p_{N_2} = x_{N_2} P = \dfrac{n(\alpha/2)}{n(1+\alpha)}P = \dfrac{\alpha}{2(1+\alpha)}P$

Partial pressure of H_2, $p_{H_2} = x_{H_2} P = \dfrac{n(3\alpha/2)}{n(1+\alpha)}P = \dfrac{3\alpha}{2(1+\alpha)}P$

Finally, the expression of K_p is

$$K_p = \frac{p_{N_2}\,p^3_{H_2}}{p^2_{NH_3}} = \left[\frac{\alpha}{2(1+\alpha)}P\right]\left[\frac{3\alpha}{2(1+\alpha)}P\right]^3\left[\frac{1+\alpha}{1-\alpha}\frac{1}{P}\right]^2 = \frac{27\alpha^4 P^2}{16\left(1-\alpha^2\right)^2}$$

Thermodynamics of a Reaction at Equilibrium The standard free energy of reaction at equilibrium is related to K_p° of the reaction by the expression $\Delta_r G^\circ = -RT \ln K_p^\circ$.

Le Chatelier's Principle When a reaction at equilibrium is subjected to a change in temperature, pressure or concentration of one (or more) of the reacting species, then the system adjusts to a new equilibrium stage as dictated by the change of the variable. These changes can be predicted qualitatively by the general principle known as Le Chatelier's principle. This principle states that *if a system at equilibrium is subjected to a change, the system adjusts to a new equilibrium stage in such a way so as to oppose or reduce the said change.*

The effects predicted by Le Chatelier's principle are as follows.

1. Pressure increase (or decrease)	Reaction will shift in the direction where the number of gaseous species is reduced (or increased), thus lowering (or increasing) the pressure.
2. Heat added (or removed) or temperature is raised (or lowered)	The equilibrium will be shifted in the endothermic (or exothermic) direction, i.e. it is shifted to high (or low) enthalpy side.
3. One of the components of the system is added.	The reaction proceeds in such a direction so as to reduce the amount of this component.

The addition of an inert gas at equilibrium keeping the pressure constant causes the system to move in the direction of larger number of gaseous molecules, whereas the addition of an inert gas keeping the volume constant does not affect the equilibrium position. These effects are in agreement with the Le Chatelier's principle.

Straight Objective Type

Equilibrium Constant K_p

1. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 present
(d) temperature (1981)

2. For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the pressure of $CO_2(g)$ depends on
(a) the mass of $CaCO_3(s)$
(b) the mass of CaO(s)
(c) the masses of both $CaCO_3(s)$ and CaO(s)
(d) temperature of the system.

3. For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the addition of more of CaO(s) causes
(a) the decrease in the concentration of $CO_2(g)$
(b) the increase in the concentration of $CO_2(g)$
(c) no change in the concentration of $CO_2(g)$
(d) the increase in the concentration of $CaCO_3(s)$

4. Predict which of the following facts for the equilibrium reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ holds good?
(a) K_p of the reaction is changed with increase in pressure of the system
(b) K_p of the reaction remains unaffected with increase in pressure of the system
(c) More of $NH_3(g)$ is decreased with increase in pressure
(d) Less of $H_2(g)$ is formed as compared to $N_2(g)$

5. The concentration of a pure solid or liquid phase is not included in the expression of equilibrium constant because
(a) solid and liquid concentrations are independent of their quantities
(b) solids and liquids react slowly
(c) solids and liquids at equilibrium do not interact with gaseous phase
(d) the molecules of solids and liquids cannot migrate to the gaseous phase

6. In the system $AB(s) \rightleftharpoons A(g) + B(g)$, doubling the quantity of AB(s) would
(a) increase the amount of A to double its value
(b) increase the amount of B to double its value
(c) increase the amounts of both A and B to double their values
(d) cause no change in the amounts of A and B

7. For the reaction $2NO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons N_2O_5(g)$ if the equilibrium constant is K_p, then the equilibrium constant for the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ would be
(a) K_p^2
(b) $2/K_p$
(c) $1/K_p^2$
(d) $1/\sqrt{K_p}$

8. When two reactants, A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction
(a) is zero
(b) decreases with time
(c) is independent of time
(d) increases with time (2000)

9. The decomposition reaction $4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$ is started with pure HNO_3. If p is the total pressure at equilibrium, then
(a) $K_p = (p_{O2})^7/(p - 7p_{O2})^4$
(b) $K_p = 1024(p_{O2})^7/(p-7p_{O2})^4$
(c) $K_p = 7p_{O2}/(p - 4p_{O2})$
(d) $K_p = (p - p_{O2})^7/(p - 7p_{O2})^4$

10. If α is the degree of dissociation of the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ and p is total equilibrium pressure, then K_p of the reaction is given by
(a) $K_p = \dfrac{\alpha^3 p}{(1+\alpha)(1-\alpha)^2}$
(b) $K_p = \dfrac{\alpha^3 p}{(2+\alpha)(1-\alpha)^2}$
(c) $K_p = \dfrac{(1+\alpha)\,p}{\alpha^2\,(1-\alpha)^2}$
(d) $K_p = \dfrac{(2+\alpha)\,p}{(1+\alpha)(1-\alpha)^2}$

11. For a reversible reaction, the concentration of the reactants are doubled, the equilibrium constant will
(a) also be doubled (b) be halved (c) become one fourth (d) remain the same

12. The equilibrium constant K_p for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one half of its volume, the value of K_p for the reaction at the same temperature will be
(a) 8 (b) 16 (c) 32 (d) 64

13. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2p)/(1 - x^2)$, where p = pressure, x = extent of decomposition. Which one of the following statements is true? (2001)
(a) K_p increases with increase of p (b) K_p increases with increase of x
(c) K_p increases with decrease of x (d) K_p remains constant with change in p and x

14. Consider the following equilibrium in a closed container:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
(a) neither K_p nor α changes (b) both K_p and α change
(c) K_p changes, but α does not change (d) K_p does not change, but α changes (2001)

15. The following equilibrium are given:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\quad K_1 \qquad N_2 + O_2 \rightleftharpoons 2NO;\quad K_2 \qquad H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;\quad K_3$$

The equilibrium constant of the reaction $2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$ in terms of K_1, K_2 and K_3 is
(a) $K_1\ K_2/K_3$ (b) $K_1\ K^2{}_3/K_2$ (c) $K_2\ K_3^3/K_1$ (d) $K_1\ K_2\ K_3$ (2003)

16. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by
(a) temperature and pressure (b) temperature only
(c) pressure only (d) temperature, pressure and catalyst (1999)

17. When two reactants, A and B are mixed to give products C and D, the reaction quotient, Q, at the final stages of the reaction
(a) is zero (b) decreases with time
(c) is independent of time (d) increases with time

18. Which of the following expression is true for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, where α is the degree of dissociation of N_2O_4 and P is the equilibrium vapour pressure?
(a) $\alpha = \sqrt{(4P + K_p)/K_p}$ (b) $\alpha = \sqrt{K_p/(4P + K_p)}$
(c) $\alpha = \sqrt{(4P - K_p)/K_p}$ (d) $\alpha = \sqrt{K_p/(4P - K_p)}$

19. The standard free energy of formation of $NH_3(g)$ is -16.6 kJ mol^{-1}. The expression of K_p° for the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3$ at 298 K will be
(a) K_p° = antilog $\{-16.6/(8.314 \times 298)\}$ (b) K_p° = antilog $\{16.6/(8.314 \times 298)\}$
(c) K_p° = antilog $\{16.6 \times 10^3/(8.314 \times 298)\}$ (d) K_p° = antilog $\{16.6 \times 10^3/(2.303 \times 8314 \times 298)\}$

20. The reaction $A(g) \rightleftharpoons B(g) + C(g)$ was initiated with the amount a of A(g). At equilibrium, it is found that the amount of A(g) remaining is $a - x$ at a total pressure of p. The equilibrium constant K_p of the reaction can be computed from the expression
(a) $\frac{x^2}{a^2 + x^2}P$ (b) $\frac{x^2}{a^2 - x^2}P$ (c) $\frac{a + x^2}{x^2}P$ (d) $\frac{a^2 - x^2}{x^2}P$

21. For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$, the degree of dissociation in terms K_p is

(a) $\alpha = \left(1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right)^{-1/2}$ (b) $\alpha = \left(1 - \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right)^{-1/2}$

(c) $\alpha = \left(1 + \frac{3\sqrt{3}}{4}\frac{K_p}{p}\right)^{-1/2}$ (d) $\alpha = \left(1 - \frac{3\sqrt{3}}{4}\frac{K_p}{p}\right)^{-1/2}$

22. For the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, the degree of dissociation at equilibrium pressure p and temperature T is given by

(a) $\alpha = (\rho\, p\, M_{COCl_2}/RT) + 1$ (b) $\alpha = (\rho\, p\, M_{COCl_2}/RT) - 1$

(c) $\alpha = (p\, M_{COCl_2}/\rho RT) + 1$ (d) $\alpha = (p\, M_{COCl_2}/\rho RT) - 1$

where ρ is the density of the gases at equilibrium.

23. An exothermic reaction proceeding towards equilibrium is associated with

(a) the absorption of heat
(b) an increase in the enthalpy of reaction
(c) a decrease in the value of equilibrium constant with increase in temperature
(d) a decrease in the value of equilibrium constant with the variation of pressure at a constant temperature.

24. An endothermic reaction proceeding towards equilibrium is associated with

(a) the release of heat
(b) a decrease in the enthalpy of reaction
(c) a decrease in the value of K_p° with increase in temperature
(d) an increase in the value of K_p° with increase in temperature

25. For a reaction at equilibrium

(a) K_p° varies linearly with temperature with a positive slope
(b) K_p° varies linearly with inverse of temperature with a positive slope
(c) $\ln K_p^\circ$ varies linearly with a temperature
(d) $\ln K_p^\circ$ varies linearly with inverse of temperature

Relation Between K_p and K_c

26. For the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and K_c cannot be correlated unless pressure of the system is given

27. For the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and K_c cannot be correlated unless pressure of the system is provided

28. For the reaction $4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and Kc cannot be correlated unless pressure of the system is provided

29. The equilibrium constants K_p and K_c for a gaseous reactions are related to each other by the expression

(a) $K_p = K_c(RT)^{-\Delta\nu_g}$ (b) $K_p = K_c(RT)^{\Delta\nu_g}$ (c) $K_p = K_c(R)^{-\Delta\nu_g}$ (d) $K_p = K_c(R)^{\Delta\nu_g}$

30. The K_p of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ was found to be 11.45 kPa at 298 K. Its K_c would be

(a) 4.62×10^{-2} M (b) 4.62×10^{-3} M (c) 4.62×10^{-4} M (d) 4.62×10^{-5} M

31. For the reversible reaction, $N_2(g) + 3H_2(g) = 2NH_3(g)$ at 500 °C, the value of K_p° is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c°, with concentration in mol L^{-1}, is
(a) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$ (b) $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
(c) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$ (d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$ (2000)

32. For which of the following reactions, $K_p > K_c$?
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ (d) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

33. For a reaction, $2N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the value of $\Delta\nu_g$ is
(a) + 2 (b) – 3 (c) + 3 (d) – 2

34. The K_c° of the reaction $2X_2(g) + Y_2(g) \rightleftharpoons 2X_2Y(g)$ is 10 at 300 K. Its K_p° value will be
(a) 3.0 (b) 9.0 (c) 0.16 (d) 0.41

35. In the expression $K_p^\circ = K_c^\circ\,(c^\circ\, RT/p^\circ)^{\Delta\nu_g}$, p° is expressed in kPa. The value of R to be used is
(a) 0.082 L atm K^{-1} mol^{-1} (b) 8.314 kPa dm^3 K^{-1} mol^{-1}
(c) 1.987 cal K^{-1} mol^{-1} (d) 8.314×10^7 ergs K^{-1} mol^{-1}

Calculations of Equilibrium Constant

36. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the relation connecting the degree of dissociation (α) of $N_2O_4(g)$ with the equilibrium constant K_p is

(a) $\alpha = \dfrac{K_p/p}{4 + K_p/p}$ (b) $\alpha = \dfrac{K_p}{4 + K_p}$ (c) $\alpha = \left(\dfrac{K_p/p}{4 + K_p/p}\right)^{1/2}$ (d) $\alpha = \left(\dfrac{K_p}{4 + K_p}\right)^{1/2}$

37. In a system $A(s) \rightleftharpoons 2B(g) + 3C(g)$ if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to
(a) two times the original value (b) one half of its original value
(c) $2\sqrt{2}$ times its original value (d) $1/2\sqrt{2}$ times the original value

38. The equilibrium constant of the reaction $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is 4×10^{-3} atm$^{-1/2}$. The equilibrium constant of the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ would be
(a) 250 atm (b) 4×10^3 atm (c) 0.25×10^4 atm (d) 6.25×10^4 atm

39. The equilibrium constant K_c of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ is 50. If 1 mol of A_2 and 2 mol of B_2 are mixed, the amount AB at equilibrium would be
(a) 0.467 mol (b) 0.934 mol (c) 1.401 mol (d) 1.866 mol

40. For the reaction $A(g) + 2B(g) \rightleftharpoons 2C(g)$, one mole of A and 1.5 mol of B are taken in a 2.0-L vessel. At equilibrium, the concentration of C was found to be 0.35 M. The equilibrium constant K_c of the reaction would be
(a) 0.295 M^{-1} (b) 0.673 M^{-1} (c) 1.178 M^{-1} (d) 2.36 M^{-1}

41. If 0.2 mol of $H_2(g)$ and 2.0 mol of S(s) are mixed in a 1.0 – L vessel at 90 °C, the partial pressure of $H_2S(g)$ formed according to the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$, $K_p = 6.8 \times 10^{-2}$, would be
(a) 0.19 atm (b) 0.38 atm (c) 0.6 atm (d) 6.8×10^{-2} atm/(0.2×2)

42. The equilibrium constant K_c for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ is 16. If 1 mol of each of all the four gases is taken in 1 dm^3 vessel, the equilibrium concentration of NO would be
(a) 0.4 M (b) 0.6 M (c) 1.4 M (d) 1.6 M

43. For the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ a reaction mixture containing NO(g) and $Cl_2(g)$ at partial pressures of 0.373 atm and 0.310 atm, respectively, is taken. The total pressure of the system at equilibrium was found to be 0.544 atm. The value of K_p for the reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ would be
(a) 1.838 atm (b) 0.544 atm (c) 0.04 atm (d) 0.016 atm

44. For the decomposition reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$, the $K_p = 2.9 \times 10^{-5}$ atm^3. The total pressure of gases at equilibrium when 1.0 mol of $NH_2COONH_4(s)$ was taken to start with would be
(a) 0.0194 atm (b) 0.0388 atm (c) 0.0582 atm (d) 0.0766 atm

45. One mole of N_2O_4(g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4(g) decomposes to NO_2(g). The resultant pressure is
(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm (1996)

46. One mole of N_2 is mixed with three moles of H_2 in a 4-litre container. If 0.25% of N_2 is converted into NH_3 by the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the equilibrium constant K_c of the reaction would be about
(a) 1.50×10^{-3} mol^{-2} L^2 (b) 1.50×10^{-4} mol^{-2} L^2
(c) 1.50×10^{-5} mol^{-2} L^2 (d) 1.50×10^{-6} mol^{-2} L^2

47. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100 °C is 50. If a one-litre flask containing one mole of A_2 is connected to a two-litre flask containing two moles of B_2, the amount of AB at equilibrium would be about
(a) 0.93 mol (b) 1.87 mol (c) 2.80 mol (d) 3.74 mol

48. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_2(g) + NO(g)$. If one mole of each of all the four gases in a one-litre container are introduced, the equilibrium concentration of NO would be about
(a) 0.4 mol L^{-1} (b) 0.6 mol L^{-1} (c) 1.4 mol L^{-1} (d) 1.6 mol L^{-1}

49. If at 37°C and 1 atm pressure, 25% of N_2O_4 is dissociated to $2NO_2$, the equilibrium constant K_p will be about
(a) 0.27 atm (b) 0.40 atm (c) 0.54 atm (d) 0.67 atm

50. HgO(s) dissociates according to the equation $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2} O_2(g)$. The dissociation pressure is 0.51 atm at 693 K. The K_p of the reaction is about
(a) 0.04 atm$^{3/2}$ (b) 0.14 atm$^{3/2}$ (c) 0.24 atm$^{3/2}$ (d) 0.34 atm$^{3/2}$

51. If 66% of N_2O_4(g) is dissociated into NO_2(g) at 27 °C and 1 atm pressure, the volume occupied by 11.5 g of N_2O_4 would be about
(a) 3 L (b) 4 L (c) 5 L (d) 6 L

52. The values of K_c° for the reactions $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ and $NO(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g)$ are 2.4×10^{30} and 1.55, respectively. The value of K_c° for the reaction $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g)$ will be about
(a) 10^{-11} (b) 10^{-13} (c) 10^{-15} (d) 10^{15}

53. The reaction, $N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2} O_2(g)$, is started with initial pressure of N_2O_5(g) equal to 600 mmHg. The fraction of N_2O_5(g) decomposed when the total pressure of system is 960 mmHg is about
(a) 0.05 (b) 0.10 (c) 0.20 (d) 0.41

54. In the study of the water gas reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, a mixture of CO_2 and H_2 initially containing 40 mol % H_2 was brought to equilibrium in a closed vessel. At equilibrium, there was 15% of H_2. The value of K_p is about
(a) 0.6 (b) 0.8 (c) 1.0 (d) 1.2

55. The value of $K_c^\circ = 85$ for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$. A mixture of these gases contains $[SO_2] = 0.04$ M, $[NO_2] = 0.50$ M, $[NO] = 0.30$ M and $[SO_3] = 0.02$ M, then
(a) the mixture is at equilibrium
(b) the reaction proceeds to right to attain equilibrium
(c) the reaction proceeds to left to attain equilibrium
(d) the reaction may proceed to right or left depending upon the volume of the vessel.

56. A mixture of 0.40 atm of NO(g) and 0.30 atm of Cl_2(g) is prepared at 500 K. The reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ takes place. The total pressure at equilibrium is 0.6 atm. The K_p of the reaction is about
(a) 1.11 atm^{-1} (b) 3.3 atm^{-1} (c) 5 atm^{-1} (d) 4.4 atm^{-1}

57. In an equilibrium reaction, the rate constants of the forward and backward reactions are 3.2 mol^{-1} dm^3 s^{-1} and 0.12 mol^{-1} dm^3 s^{-1}, respectively. The equilibrium constant of the reaction is
(a) 0.25 (b) 0.37 (c) 3.7 (d) 26.7

58. For the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, $\Delta H = -$ 536 kJ mol^{-1}. The energy of activation of forward reaction is 208 kJ mol^{-1}, the energy of activation of the backward reaction is
(a) 328 kJ mol^{-1} (b) 744 kJ mol^{-1} (c) 536 kJ mol^{-1} (d) not known

59. HI was heated in a sealed vessel at 440 °C till the equilibrium is reached. HI was found to be 22% decomposed. The standard equilibrium constant for the dissociation of HI is

(a) 0.282 (b) 0.080 (c) 0.199 (d) 0.0199

60. For the reaction $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$, $K_p = 0.05$ atm. The value of $\Delta G°$ of the reaction at 627 °C would be

(a) 11.19 mol^{-1} (b) 22.40 kJ mol^{-1} (c) 33.57 kJ mol^{-1} (d) 27.98 kJ mol^{-1}

61. The equilibrium constant of the reaction $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ is 1.60. If 0.4 mol of each of H_2 and CO_2 are enclosed in a 1.0-L vessel, the equilibrium concentration of $H_2O(g)$ will be

(a) 0.26 M (b) 0.24 M (c) 0.22 M (d) 0.20 M

62. In a system $A(s) \rightleftharpoons B(g) + 2C(g)$, doubling the equilibrium concentration of B will cause the equilibrium concentration of C to change to

(a) two times its original value (b) one-half its original value

(c) $\sqrt{2}$ times the original value (d) $1\sqrt{2}$ times the original value.

63. In a system $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, doubling the mass of CaO will cause the equilibrium concentration of CO_2 to

(a) become half of its initial value (b) remain unchanged

(c) become twice of its initial value (d) become one third of its initial value

64. The reaction $A(g) + 2B(g) \rightleftharpoons AB_2(g)$ is studied by starting with equal amounts of A and B in a constant-volume container. Which of the following expressions will be true at equilibrium?

(a) [A] = [B] (b) $[AB_2]$ = [B] (c) [B] < [A] (d) [A] < [B]

65. The reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ was initiated with 2 mol of PCl_5. If at equilibrium, the amount of PCl_5 was found to be 0.88 mol at a pressure of 1 bar. the value of K_p for the reaction is

(a) 0.40 bar (b) 0.46 bar (c) 0.52 bar (d) 0.58 bar

66. N_2O_4 dissociates as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. When 0.46 g of N_2O_4 was introduced into a 1 dm^3 flask maintained at 300 K, the equilibrium pressure was found to be 20.785 kPa. The degree of dissociation of N_2O_4 is

(a) 0.47 (b) 0.57 (c) 0.67 (d) 0.77

67. The reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; $K°_{p1} = 4.0$ and $A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$; $K°_{p2}$ = ? were studied in the same vessel starting from the equal amounts of $A_2(g)$ and $B_2(g)$. At equilibrium, the partial pressure of AB(g) and $AB_3(g)$ were found to be 0.2 atm and 0.1 atm, respectively. The value of $K°_{p2}$ will be

(a) 159 atm^{-2} (b) 209 atm^{-2} (c) 259 atm^{-2} (d) 304 atm^{-2}

68. Given are the informations

$$H_2(g) + \frac{1}{2}S_2(g) = H_2S(g); \qquad K°_{p1} = 0.80$$

$$3H_2(g) + SO_2(g) = H_2S(g) + 2H_2O(g); \qquad K°_{p2} = 1.8 \times 10^4$$

The value of $K°_p$ for the reaction $4H_2(g) + 2SO_2(g) = S_2(g) + 4H_2O(g)$ is found to be

(a) 4.44×10^{-5} (b) 2.25×10^4 (c) 5.07×10^8 (d) 4.26×10^6

Le-Chatelier Principle

69. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if

(a) temperature is increased and pressure is kept constant

(b) temperature is reduced and pressure is increased

(c) both temperature and pressure are increased

(d) both temperature and pressure are reduced (1981)

70. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25 °C in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct?

(a) Concentrations of SO_2, Cl_2 and SO_2Cl_2 are not changed (b) More chlorine is formed

(c) Concentration of SO_2 is reduced (d) More SO_2Cl_2 is formed (1989)

71. Given the following reaction at equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas is added at constant volume. Predict which of the following facts will be affected?

(a) More of $NH_3(g)$ is produced

(b) Less of $NH_3(g)$ is produced

(c) No affect on the degree of advancement of the reaction at equilibrium

(d) K_p of the reaction is increased

72. Given the following reaction at equilibrium. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected?
(a) More $NH_3(g)$ is produced
(b) Less $NH_3(g)$ is produced
(c) No affect on the equilibrium
(d) K_p of the reaction is decreased

73. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -$ve. The formation of $NH_3(g)$ is favoured at
(a) high pressure and low temperature
(b) low pressure and high temperature
(c) low pressure and low temperature
(d) high pressure and high temperature

74. For the reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$, $\Delta H = -\ 180\ \text{kJ mol}^{-1}$. Which of the following facts does not hold good?
(a) The pressure changes at constant temperature do not affect the equilibrium constant
(b) The volume changes at constant temperature do not affect the equilibrium constant
(c) The dissociation of NO is favoured more at high temperature
(d) The dissociation of NO is favoured less at high temperature

75. For the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$, $\Delta H = 93.6\ \text{kJ mol}^{-1}$. Which of the following facts does not hold good?
(a) The pressure changes at constant temperature does not affect the equilibrium constant
(b) The volume changes at constant temperature does not affect the equilibrium constant
(c) The dissociation of NH_3 is more favoured at high temperature
(d) The dissociation of NH_3 is less favoured at high temperature

76. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(1)$, which of the following statements is true?
(a) The pressure changes do not affect the equilibrium
(b) More of ice melts if pressure on the system is increased
(c) More of liquid freezes if pressure on the system is increased
(d) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system

77. Solids $CaCO_3$ and CaO and gaseous CO_2 are placed in a vessel and allowed to reach equilibrium

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -180\ \text{kJ mol}^{-1}$$

The quantity of CaO in the vessel could be increased by
(a) adding more of $CaCO_3$
(b) removing some of CO_2
(c) lowering the temperature
(d) reducing the volume of the vessel

78. For a given equilibrium reaction, an increase in temperautre will
(a) increase the rate of the exothermic reaction more than that of the endothermic reaction.
(b) increase the rate of the endothermic reaction more than that of the exothermic reaction.
(c) increase both rates equally.
(d) decreases both rates equally.

79. For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, $\Delta H = -$ve. An increase in temperature would cause
(a) an increase in the value of K_{eq}
(b) a decrease in the value of K_{eq}
(c) no change in the value of K_{eq}
(d) a change in K_{eq} which cannot be qualitatively predicted

80. For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, $\Delta H = +$ve. An increase in temperature would cause
(a) an increase in the value of K_{eq}
(b) a decrease in the value of K_{eq}
(c) no change in the value of K_{eq}
(d) a change in K_{eq} which cannot be qualitatively predicted

81. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -\ 93.6\ \text{kJ mol}^{-1}$. The concentration of H_2 at equilibrium will increase if
(a) the temperature is lowered
(b) the volume of the system is decreased
(c) N_2 is added at constant volume
(d) NH_3 is removed

82. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -\ 93.6\ \text{kJ mol}^{-1}$. The amount (i.e. number of mole) of H_2 at equilibrium will increase if
(a) volume is increased
(b) volume is decreased
(c) O_2 is added at constant volume
(d) NH_3 is removed.

83. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_c^\circ = 66.9$ at 350 °C and $K_c^\circ = 50.0$ at 448 °C. The reaction has
(a) ΔH = +ve
(b) ΔH = −ve
(c) ΔH = zero
(d) ΔH whose sign cannot be predicted

84. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by
(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g) (1998)

85. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by
(a) temperature and pressure
(b) temperature only
(c) pressure only
(d) temperature, pressure and catalyst.

86. In the reaction, $2SO_3(g) \rightleftharpoons 2SO_2(g) + 2A(g)$, an inert gas is introduced at constant temperature and volume. The dissociation of SO_3 is
(a) increased
(b) decreased
(c) unaffected
(d) affected but cannot be predicted

87. In the reaction $2A(g) + B_2(g) \rightleftharpoons 2AB(g)$, $\Delta H < 0$. The yield of AB(g) is increased when
(a) temperature is increased keeping pressure constant
(b) temperature is decreased and pressure is increased.
(c) both temperature and pressure are increased
(d) both temperature and pressure are decreased

88. For the reaction $A_2(g) \rightleftharpoons 2A(g)$, the formation of A(g) is favoured at
(a) high temperature and low pressure
(b) high temperature and high pressure
(c) low temperature and high pressure
(d) low temperature and low pressure

89. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 93.6$ kJ, the concentration of NH_3 at equilibrium will increacse if
(a) the temperature is lowered
(b) the volume is increased
(c) H_2 is removed from the system
(d) an inert gas at constant pressure is added.

90. For the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $\Delta H > 0$. The concentration of NO(g) in the reaction at equilibrium is increased when
(a) temperature is increased
(b) temperature is decreased
(c) inert gas is introduced in the container
(d) a catalyst is introduced.

91. Ammonium chloride dissolves in water with absorption of heat. Which of the following is correct?
(a) The solubility of ammonium chloride decreases with increase in temperature
(b) The solubility of ammonium chloride increases with increase in temperature
(c) At higher temperature, ammonium chloride in solution exists as ammonia and hydrochloric acid
(d) At lower temperature, ammonium chloride in solution exists in the molecular form

92. The quantities of products in a reaction at equilibrium is increased if an inert gas is added under the condition of
(a) constant volume provided $\Delta\nu_g$ (change in the gaseous species) of the reaction is positive.
(b) constant pressure provided $\Delta\nu_g$ of the reaction is positive.
(c) constant volume provided $\Delta\nu_g$ of the reaction is negative.
(d) constant pressure provided $\Delta\nu_g$ of the reaction is negative.

93. The quantities of products in a reaction at equilibrium is decreased if an inert gas is added under the conditon of
(a) constant volume provided $\Delta\nu_g$ (change in the gaseous species) of the reaction is positive.
(b) constant pressure provided $\Delta\nu_g$ of the reaction is positive.
(c) constant volume provided $\Delta\nu_g$ of the reaction of negative.
(d) constant pressure provided $\Delta\nu_g$ of the reaction is negative.

94. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium:
(a) K_p does not change significantly with pressure
(b) α does not change with pressure
(c) concentration of NH_3 does not change with pressure
(d) concentration of H_2 is less than that of nitrogen (1984)

95. Haber-Bosch process for the manufacture of NH_3 is based on the reaction

$$N_2(g) + 3H_2(g) \xrightleftharpoons{\text{catalyst}} 2NH_3(g); \qquad \Delta_r H^\circ = -\,46.0 \text{ kJ mol}^{-1}; \qquad K_p^\circ = 14$$

Which of the following information regarding the above reaction is correct?

(a) On adding N_2, the equilibrium is shifted to right side with an increase in entropy.

(b) The equilibrium constant K_p° increases with increase in temperature.

(c) At equilibrium, $2G_m(NH_3) = G_m(N_2) + 3G_m(H_2)$ where G_m represents the molar Gibbs function of the species enclosed within the brackets.

(d) The use of catalyst helps increasing the rate of forward reaction more than that of backward reaction thereby increasing the yield of NH_3. (2006)

Multiple Correct Choice Type

1. For the gas phase reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6 \qquad \Delta H = -136.8 \text{ kJ mol}^{-1}$ carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by

(a) increasing the temperature (b) decreasing the pressure

(c) removing some H_2 (d) adding some C_2H_6

2. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium

(a) addition of $NaNO_2$ favours reverse reaction (b) addition of $NaNO_3$ favours forward reaction

(c) increasing temperature favours forward reaction (d) increasing pressure favours reverse reaction

3. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperatrue is favoured by

(a) introducing an inert gas at constant volume (b) introducing chlorine gas at constant volume

(c) introducing an inert gas at constant pressure (d) increasing the volume of the container

4. For an equilibrium reaction, which of the following statements is true?

(a) If the reaction quotient of the reaction is greater than K_{eq}, the reaction moves in the backward direction

(b) If the reaction quotient of the reaction is lesser than K_{eq}, the reaction moves in the forward direction

(c) If the reaction quotient of the reaction is equal to K_{eq}, the reaction is at equilibrium

(d) There is no correlation between the reaction quotient and K_{eq} in predicting the direction in which the reaction proceeds

5. For an equilibreium reaction, which of the following statements is/are correct?

(a) If the reaction quotient of a reaction is greater thatn K_{eq}, the reaction has a tendency to move in the backward direction.

(b) If the reaction quotient of a reaction is greater than K_{eq}, the reaction has a tendency to the move in the forward direction.

(c) The addition of an inert gas at constant volume does not affect the extent of reaction.

(d) The addition of an inert gas at constant pressure does not affect the extent of the reaction.

6. Consider the reaction $L(g) + M(g) \rightleftharpoons N(g) + O(g); \qquad \Delta H = \text{positive}$

When this reaction attains equilibrium it is found that $K_p = K_c$. The value of equilibrium constant K_c can be changed by

(a) adding L(g) (b) removing M(g) (c) decreasing temperature (d) increasing temperature

7. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium

(a) addition of $NaNO_2$ favours reverse reaction. (b) addition of $NaNO_3$ favours forward reaction.

(c) increasing temperature favours forward reaction. (d) increasing pressure favours reverse reaction.

8. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by

(a) adding a suitable catalyst. (b) removing $H_2(g)$.

(c) decreasing the volume of the container. (d) increasing the amount of CO(g).

9. There is no effect on the reaction at equilibrium if an inert gas is added under the condition of

(a) constant volume provided $\Delta\nu_g$ (change in the gaseous species) of the reaction is positive.

(b) constant pressure provided $\Delta\nu_g$ of the reaction is positive.

(c) constant volume provided $\Delta\nu_g$ of the reaction is negative.

(d) constant pressure provided $\Delta\nu_g$ of the reaction is negative.

Linked Comprehension Type

1. Given: $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$; $K° = 2.79 \times 10^{-3}$

$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$; $K° = 8.46 \times 10^{-7}$

(i) The solubility of AgCl in 1 M NH_3 is about

(a) 0.053 M (b) 2.79×10^{-3} M (c) 0.53 M (d) 0.279 M

(ii) The solubility of AgCl in 1 M NH_4OH is about

(a) 9.2×10^{-2} M (b) 9.2×10^{-4} M (c) 8.46×10^{-7} M (d) 0.2 M

(iii) The equilibrium constant of the reaction $NH_3 + H_2O = NH_4OH$ is about

(a) 3.3×10^3 (b) 3.03×10^{-4} (c) 57.43 (d) 1.74×10^{-2}

2. Given: $4NO_2(g) + O_2(g) = 2N_2O_5(g)$.

$\Delta_f H°/\text{kJ mol}^{-1}$ 33.2 11.3

(i) The standard enthalpy of reaction is

(a) -21.9 kJ mol^{-1} (b) 21.9 kJ mol^{-1} (c) -110.2 kJ mol^{-1} (d) 110.2 kJ mol^{-1}

(ii) On increasing temperature, the reaction

(a) is shifted towards right side (b) is shifted towards left side

(c) is not affected (d) gets affected but cannot be predicted

(iii) The yield of N_2O_5 is larger at

(a) low temperature and low pressure (b) low temperature and high pressure

(c) high temperature and low pressure (d) high temperature and high pressure

3. Given:

$4NO_2(g) + O_2(g) = 2N_2O_5(g)$

$\Delta_f G°/\text{kJ mol}^{-1}$ 51.3 115.1

(i) The standard change in Gibbs function is

(a) 166.4 kJ mol^{-1} (b) -166.4 kJ mol^{-1} (c) -25 kJ mol^{-1} (d) 25.0 kJ mol^{-1}

(ii) The value of K_p° of the reaction at 298 K is

(a) 4.15×10^{-5} (b) 4.15×10^{-4} (c) 4.15×10^{-3} (d) 4.15×10^{-2}

(iii) The value of K_c° of the reaction at 298 K is

(a) 6.11 (b) 6.1 (c) 0.061 (d) 0.61

4. Given is the following information.

$2SO_3(g) = 2SO_2(g) + O_2(g)$

$\Delta_f H°/\text{kJ mol}^{-1}$ -395.7 -296.8

(i) The enthalpy change of the reaction is

(a) 98.9 kJ mol^{-1} (b) 197.8 kJ mol^{-1} (c) -98.9 kJ mol^{-1} (d) -197.8 kJ mol^{-1}

(ii) On increasing temperature, the reaction is

(a) shifted to the right side (b) shifted to the left side

(c) no affected (d) affected but cannot be predicted

(iii) Decomposition of SO_3 is favoured at

(a) low temperature and low pressure (b) low temperature and high pressure

(c) high temperature and low pressure (d) high temperature and high pressure

5. Given is the following information.

$2SO_3(g) = 2SO_2(g) + O_2(g)$

$\Delta_f G°/\text{kJ mol}^{-1}$ -371.1 -300.2

(i) The change in free energy of the reaction is

(a) 70.9 kJ mol^{-1} (b) -70.9 kJ mol^{-1} (c) 141.8 kJ mol^{-1} (d) -141.8 kJ mol^{-1}

(ii) The value of K_p° at 298 K is

(a) 7.2×10^{24} (b) 1.4×10^{-25} (c) 2.7×10^{12} (d) 3.7×10^{-13}

(iii) The value of K_c° at 298 K is

(a) 6.6×10^{13} (b) 5.7×10^{-27} (c) 2.9×10^{23} (d) 1.5×10^{-14}

6. PCl_5 dissociates according to the equation $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The reaction is initiated with 0.03 mol of PCl_5 at a constant pressure of 100 kPa and temperature of 500 K. The volume of the system at equilibrium was found to be 2.08 dm^3. Based on this information, answer the following three questions.

(i) The degree of dissociation of PCl_5 is

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

(ii) The equilibrium constant of the reaction is

(a) 60 kPa (b) 70 kPa (c) 80 kPa (d) 90 kPa

(iii) The free energy change of the reaction is

(a) 910 J mol^{-1} (b) 928 J mol^{-1} (c) 952 J mol^{-1} (d) 998 J mol^{-1}

7. The standard free energies of formation of $N_2O_4(g)$ and $NO_2(g)$ are 97.89 and 51.31 kJ mol^{-1}, respectively. For the reaction $N_2O_4(g) \rightleftharpoons NO_2(g)$ at 300 K and 1 atm pressure, answer the following three questions. Take p° = 100 Pa.

(i) The value of K_p° for the reaction is

(a) 0.10 (b) 0.12 (c) 0.15 (d) 0.18

(ii) The value of K_c° for the reaction is

(a) 6.1×10^{-3} (b) 6.8×10^{-3} (c) 7.5×10^{-3} (d) 8.5×10^{-3}

(iii) The value of K_x for the reaction is

(a) 0.168 (b) 0.148 (c) 0.128 (d) 0.108

8. The value of $K_p^\circ = 1.8$ at 500 K for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. The equilibrium pressure is 100 kPa. Based on this information, answer the following three questions. Take p° = 100 kPa

(i) The degree of dissociation of $PCl_5(g)$ is

(a) 0.6 (b) 0.7 (c) 0.8 (d) 0.85

(ii) The density of the reaction at equilibrium is

(a) 2.8 g dm^{-3} (b) 2.4 g dm^{-3} (c) 1.9 g dm^{-3} (d) 1.5 g dm^{-3}

(iii) The standard free energy change of the reaction at equilibrium is

(a) – 1.20 kJ mol^{-1} (b) – 1.80 kJ mol^{-1} (c) – 2.44 kJ mol^{-1} (d) – 2.98 kJ mol^{-1}

9. $COCl_2$ gas dissociates as $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

The density of the gas mixture at equilibrium is.1.2 g dm^{-3} when T = 700 K and p = 100 kPa. Based on this information, answer the following three questions.

(i) The degree of dissociation of $COCl_2(g)$ is

(a) 0.25 (b) 0.30 (c) 0.36 (d) 0.42

(ii) The equilibrium constant K_p° for the reaction is

(a) 0.214 (b) 0.294 (c) 0.364 (d) 0.394

(iii) The standard free energy change of the reaction is

(a) 8.0 kJ mol^{-1} (b) 8.98 kJ mol^{-1} (c) 9.8 kJ mol^{-1} (d) 10.5 kJ mol^{-1}

Assertion and Reason Type

In the following questions, two statements are given. For each question, select the correct choice from the following.

(a) Statement-1 is True. Statement-2 is True. Statement-2 is correct explanation for Statement-1.
(b) Statement-1 is True. Statement-2 is True. Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True. Statement-2 is False.
(d) Statement-1 is False. Statement-2 is True.

	Statement–1	**Statement–2**
1.	(a) For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the values of K_p° and K_c° are identical.	The reaction has the same number of gaseous species on either sides of equilibrium.
2.	The formation of NH_3 ($\Delta_f H^\circ = -46.11$ kJ mol^{-1}) is favoured at high pressure and low temperature.	The formation of NH_3 is accompanied with decreases in gaseous molecules and release of heat.
3.	The value of K_p is greater than that of K_c for a reaction involving $\Delta \nu_g$ = +ve.	The relation between K_p and K_c is $K_c = K_p (RT)^{\Delta \nu_g}$.
4.	The addition of an inert gas at constant volume does not affect the equilibrium of a reaction provided $\Delta \nu_g = 0$.	Addition of NH_3 at constant volume increases the pressure of the gaseous mixture of a reaction at equilibrium.

5.	The value of K_p of a reaction at equilibrium may carry the appropriate unit but K_p° is a unitless.	The expression of K_p merely involves pressure terms while K_p° involves the ratio of pressure and the standard unit pressure.
6.	The expression of K_c of a reaction at equilibrium does not include concentration terms of solid or liquid appeared in the reaction.	The concentration of solid or liquid is taken to be unity.
7.	K_x like K_p° of a reaction at equilibrium is independent of pressure of the system.	The reaction between K_p° and K_x is $K_p^\circ = K_x (p_{\text{total}}/p^\circ)^{\Delta\nu_g}$.
8.	The reaction proceeds in the forward direction if the reaction quotient is less than its K_p°.	The reaction involves larger reactants than those prevailing at equilibrium.
9.	The degree of dissociation of a species giving more number of gaseous products is independent of pressure of the system.	K_p° value of a reaction at equilibrium is independent of pressure of the system.
10.	The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ has the same value of K_p° as that of $\frac{1}{2}\,N_2O_4\,(g) \rightleftharpoons NO_2(g)$	The expression of equilibrium constant involves pressure terms raised to a power equal to the stoichiometric number of gaseous species in the balanced chemical equation of the reaction.
11.	The equilibrium constant of a reaction is affected by the temperature of the system.	The equilibrium reaction is associated with the absorption or release of heat.
12.	The vapour pressure of a liquid is equal to the equilibrium constant of the the reaction liquid $\rightleftharpoons$ vapour	The equilibrium constant of the reaction liquid $\rightleftharpoons$ vapour does not include the concentration of liquid phase.
13.	The enthalpy of a reaction at equilibrium can be determined from the variation of its equilibrium constant (K_p) with temperature.	The expression connecting equilibrium constant K_p and temperature is $\log K_p^\circ = -\Delta_r H/RT + I$
14.	The degree of dissociation $2N_2O_4 \rightleftharpoons 2NO_2$ is not affected by the variation of volume of the system.	K_p of the reaction is independent of the pressure of the system.

Matrix Match Type

1. **Column I** includes a few reactions at equilibrium. Match each of these reactions with the correct choice given in **Column II**.

Column I	**Column II**
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) $K_p^\circ > K_c^\circ$
(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	(q) $K_p^\circ < K_c^\circ$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(r) $K_p^\circ = K_c^\circ$
(d) $H_2O(l) \rightleftharpoons H_2O(g)$	(s) $K_p^\circ = p_{\text{eq}}$

2. **Column I** includes a few reactions at equilibrium. Match each of these reactions with the correct choice for the degree of dissociation given in **Column II**

Column I	Column II
(a) $XY_3(g) \rightleftharpoons XY(g) + Y_2(g)$	(p) $2\sqrt{K_p}\,/\,(1 + 2\sqrt{K_p}\,)$
(b) $2XY(g) \rightleftharpoons X_2(g) + Y_2(g)$	(q) $\sqrt{K_p/(4p + K_p)}$
(c) $X_2Y_4(g) \rightleftharpoons 2XY_2(g)$	(r) $\sqrt{4K_p/(3\sqrt{3}p + 4K_p)}$
(d) $XY_3(g) \rightleftharpoons \frac{1}{2}X_2(g) + \frac{3}{2}Y_2(g)$	(s) $\sqrt{K_p/(p + K_p)}$

3. Column I lists some of the characteristics of chemical reactions at equilibrium. Column II lists the conditions for shifting the equilibrium towards the forward direction. Match the correct choice for each entry in **Column I** with those mentioned in **Column II**.

Column I	Column II
(a) $\Delta\nu_g$ = + ve; $\Delta_r H°$ = + ve	(p) Increasing p and T
(b) $\Delta\nu_g$ = + ve; $\Delta_r H°$ = – ve	(q) Increasing p and decreasing T
(c) $\Delta\nu_g$ = – ve; $\Delta_r H°$ = + ve	(r) Decreasing p and increasing T
(d) $\Delta\nu_g$ = – ve; $\Delta_r H°$ = – ve	(s) Decreasing p and T

4. Column I lists and addition of gaseous species to a reaction at equilibrium. Column II mentions some consequences regarding the shifting of direction of the reactions. Match the correct choice for each entry in **Column I** with those mentioned in **Column II**

Column I	Column II
(a) Inert gaseous species at constant volume	(p) Forward direction
(b) Inert gaseous species at constant pressure	(q) Reverse direction
(c) Gaseous reactant	(r) No effect
(d) Gaseous product	(s) Larger number of species
	(t) Lesser number of species

ANSWERS

Straight Objective Type

1. (d)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (c)
8. (d)	**9.** (b)	**10.** (b)	**11.** (d)	**12.** (b)	**13.** (d)	**14.** (d)
15. (c)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (d)	**20.** (b)	**21.** (a)
22. (d)	**23.** (c)	**24.** (d)	**25.** (d)	**26.** (a)	**27.** (b)	**28.** (c)
29. (b)	**30.** (b)	**31.** (d)	**32.** (c)	**33.** (b)	**34.** (d)	**35.** (b)
36. (c)	**37.** (d)	**38.** (d)	**39.** (d)	**40.** (d)	**41.** (b)	**42.** (d)
43. (d)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (b)	**48.** (d)	**49.** (a)
50. (b)	**51.** (c)	**52.** (c)	**53.** (d)	**54.** (d)	**55.** (b)	**56.** (c)
57. (d)	**58.** (b)	**59.** (d)	**60.** (b)	**61.** (c)	**62.** (d)	**63.** (b)
64. (c)	**65.** (b)	**66.** (c)	**67.** (c)	**68.** (c)	**69.** (b)	**70.** (a)
71. (c)	**72.** (b)	**73.** (a)	**74.** (d)	**75.** (c)	**76.** (b)	**77.** (b)
78. (b)	**79.** (b)	**80.** (a)	**81.** (b)	**82.** (a)	**83.** (b)	**84.** (d)
85. (a)	**86.** (c)	**87.** (b)	**88.** (a)	**89.** (a)	**90.** (a)	**91.** (b)
92. (b)	**93.** (d)	**94.** (a)	**95.** (c)			

Multiple Correct Choice Type

1. (a), (b), (c), (d) **2.** (c), (d) **3.** (c), (d), (e) **4.** (a), (b), (c)
5. (a), (c) **6.** (c), (d) **7.** (c), (d) **8.** (b), (d)
9. (a), (c)

Linked Comprehension Type

1. **(i)** (a) **(ii)** (b) **(iii)** (c)
2. **(i)** (c) **(ii)** (b) **(iii)** (b)
3. **(i)** (d) **(ii)** (a) **(iii)** (d)
4. **(i)** (b) **(ii)** (a) **(iii)** (c)
5. **(i)** (c) **(ii)** (b) **(iii)** (b)
6. **(i)** (b) **(ii)** (c) **(iii)** (b)
7. **(i)** (c) **(ii)** (a) **(iii)** (b)
8. **(i)** (c) **(ii)** (a) **(iii)** (c)
9. **(i)** (d) **(ii)** (a) **(iii)** (b)

Reason and Assertion Type

1. (a) **2.** (a) **3.** (c) **4.** (d) **5.** (a) **6.** (c) **7.** (d)
8. (a) **9.** (d) **10.** (d) **11.** (a) **12.** (a) **13.** (c) **14.** (d)

Matrix Match Type

1. (a)-(r); (b)-(p); (c)-(q); (d)-(s) **2.** (a)-(s); (b)-(p); (c)-(q); (d)-(r)
3. (a)-(r); (b)-(s); (c)-(p); (d)-(q) **4.** (a)-(r); (b)-(s); (c)-(p); (d)-(q)

Hints and Solutions

Straight Objective Type

1. The equilibrium constant of a reaction is independent of total pressure, catalyst and concentrations of species. It depends only on temperature.

2. Masses of solid species do not affect equilibrium constant. Only temperature affects equilibrium constant.

3. Same as Q.2.

4. The equilibrium constant of a reaction is independent of pressure of the system. Since the reaction involves increase in the gaseous species, increasing pressure will favour the formation of more of NH_3(g).

5. The choice a is correct.

6. Increasing the quantity of AB(s) will cause no change in the amounts of A(g) and B(g).

7. Since the new reaction is obtained by reversing the old reaction followed by the multiplication by 2, the equilibrium constant of the new reaction will be $1/K_p^2$.

8. In the initial stages, more reactants and lesser products are present. Hence, $Q < K_{eq}$. and it will increase with time.

9.

$$\begin{array}{lclclcl} 4HNO_3(g) & \rightleftharpoons & 4NO_2(g) & + & 2H_2O(g) & + & O_2(g) \\ P - 4p(O_2) & & 4p(O_2) & & 2p(O_2) & & p(O_2) \end{array}$$

Equilibrium pressure $P + 3p(O_2) = p$ (given) $\Rightarrow$ $P = p - 3p(O_2)$

$$K_p = \frac{[4p(O_2)]^4\,[2p(O_2)]^2\;p(O_2)}{[\{p - 3p(O_2)\} - 4p(O_2)]^4} = \frac{1024\,[p(O_2)]^7}{[p - 7\,p(O_2)]^4}$$

10.

$$\begin{array}{lclcl} 2H_2S(g) & \rightleftharpoons & 2H_2(g) & + & S_2(g) \\ n(1 - \alpha) & & n\alpha & & n\alpha/2 \end{array}$$

Total amount of gases $= n(1 + \alpha/2) = n(2 + \alpha)/2$

$$p(\mathrm{H_2S}) = \frac{2(1-\alpha)}{2+\alpha}p;\quad p(\mathrm{H_2}) = \frac{2\alpha}{2+\alpha}p;\quad p(\mathrm{S_2}) = \frac{\alpha}{2+\alpha}p$$

$$K_p = \frac{\{2(\alpha)\,p/(2+\alpha)\}^2\,\{\alpha p/(2+\alpha)\}}{\{2(1-\alpha)\,p/(2+\alpha)\}^2} = \frac{\alpha^3 p}{(2+\alpha)(1-\alpha)^2}$$

11. The equilibrium constant is independent of individual concentrations.

12. The equilibrium constant is independent of volume of the container.

14. K_p of an equilibrium reaction depends only on temperature. However, the degree of dissociation will change in accordance with Le-Chatelier's principle.

15. The given reaction can be obtained as follows.

$$\begin{array}{l} -\ [\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}] \\ +\ [\mathrm{N_2 + O_2 \rightleftharpoons 2NO}] \\ +\ 3[\mathrm{H_2} + \frac{1}{2}\,\mathrm{O_2 \rightleftharpoons H_2O}] \\ \hline \mathrm{2NH_3} + \frac{5}{2}\,\mathrm{O_2 \rightleftharpoons 2NO + 3H_2O} \end{array}$$

Hence $K = K_2\,K_3^3/\mathrm{K}_1$

16. The given reaction will be exothermic in nature due to the formation of three X-Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species. Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

17. For the reaction A + B → C + D, the reaction quotient is defined as $Q = \dfrac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$

In the final stage of the reaction, the reaction is at equilibrium and thus the value of Q remains constant with time.

18. We have

$$\mathrm{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

$n(1-\alpha)$ $\quad n(2\alpha)$; Total amount of gases = $n(1+\alpha)$

$$K_p = \frac{p^2_{\mathrm{NO_2}}}{p_{\mathrm{N_2O_4}}} = \frac{[\{2\alpha/(1+\alpha)\}P]^2}{\{(1-\alpha)/(1+\alpha)\}P} = \frac{4\alpha^2 P}{1-\alpha^2} \quad \text{or} \quad \alpha = \sqrt{K_p/(4p+K_p)}$$

19. We have $\Delta G^\circ = -RT\ln K_p^\circ = -2.303\,RT\log K_p^\circ$

This gives $K_p^\circ = \text{antilog}\,(-\Delta G^\circ/2.303\,RT) = \text{antilog}\,\{16\,600/(2.303 \times 8.314 \times 298)\}$

20. We have

$$\mathrm{A(g) \rightleftharpoons B(g) + C(g)}$$

$a - x \quad x \quad x$; Total amount = $a + x$

$$p_{\mathrm{A}} = \left(\frac{a-x}{a+x}\right)P;\quad p_{\mathrm{B}} = p_{\mathrm{C}} = \frac{x}{a+x}P$$

$$K_p = \frac{p_{\mathrm{B}}\,p_{\mathrm{C}}}{p_{\mathrm{A}}} = \frac{\{x/(a+x)\}^2P^2}{\{(a-x)/(a+x)\}P} = \frac{x^2P}{a^2-x^2}$$

21. We have

$$\mathrm{NH_3(g)} \rightleftharpoons \frac{1}{2}\,\mathrm{N_2(g)} + \frac{3}{2}\,\mathrm{H_2(g)}$$

$n(1-\alpha)$ $\quad n(\alpha/2)$ $\quad n(3\alpha/2)$; Total amount = $n(1+\alpha)$

$$p_{\mathrm{NH_3}} = \{(1-\alpha)/(1+\alpha)\}P;\quad p_{\mathrm{N_2}} = \{\alpha/2(1+\alpha)\}P;\quad p_{\mathrm{H_2}} = \{3\alpha/2\,(1+\alpha)\}\,P$$

$$K_p = \frac{p^{1/2}_{\mathrm{N_2}}\,p^{3/2}_{\mathrm{H_2}}}{p_{\mathrm{NH_3}}} = \left[\frac{\alpha}{2(1+\alpha)}P\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}P\right]^{3/2}\left[\frac{1+\alpha}{1-\alpha}\,\frac{1}{P}\right] = \frac{3\sqrt{3}\,\alpha^2}{4\,(1-\alpha^2)}P$$

Hence $4\ K_p\ (1 - \alpha^2) - 3\sqrt{3}\ \ \alpha^2\ P = 0$

$$\alpha^2\ (4K_p + 3\sqrt{3}\ P) = 4\ K_p \quad \text{or} \quad \alpha^2\left(1+\frac{3\sqrt{3}}{4}\frac{P}{K_p}\right) = 1 \text{ or } \alpha = \left(1+\frac{3\sqrt{3}P}{4K_p}\right)^{-1/2}$$

22. We have

$$\underset{n(1\,-\,\alpha)}{COCl_2(g)} \rightleftharpoons \underset{n\alpha}{CO(g)} + \underset{n\alpha}{Cl_2(g)}$$

; Total amount of gases = $n\ (1 + \alpha)$

From ideal gas equation, we have

$$pV = n(1 + \alpha)\ RT = \frac{m(COCl_2)}{M(COCl_2)}\ (1 + \alpha)\ RT$$

$$\text{or} \qquad \alpha = \frac{V}{M(COCl_2)}\frac{pM(COCl_2)}{RT} - 1 = \frac{pM(COCl_2)}{\rho RT} - 1$$

23. Exothermic reaction implies the release of heat. Hence, heating will decrease the value of K_p.

24. Endothermic reaction implies the absorption of heat. Hence, heating will increase the value of K_p

25. The expression of variation of K_p is given by $\ln K_p^\circ = \dfrac{\Delta_r H^\circ}{RT} + I$

Hence $\ln K_p^\circ$ varies linearly with $1/T$.

26. Since $\Delta\nu_g = 0$, we will have $K_p = K_c$

27. For the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$, $\Delta\nu_g = 3$. Since $K_p = K_c\ (RT)^{\Delta\nu_g}$ and $(RT)^{\Delta\nu_g} > 1$, it follows that $K_p > K_c$.

28. For the reaction $4NO_2\ (g) + O_2\ (g) \rightleftharpoons 2N_2O_5(g)$, $\Delta\nu_g = -3$. Since $K_p = K_c\ (RT)^{\Delta\nu_g}$ and $(RT)^{\Delta\nu_g} < 1$, it follows that $K_p < K_c$.

29. The expression is $K_p = K_c\ (RT)^{\Delta\nu_g}$.

30. We have

$$K_p = K_c\ (RT)^{\Delta\nu_g}$$

$$(11.45\ \text{kPa}) = K_c[(8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\ (298\ \text{K})]^1$$

$$K_c = \frac{11.45}{8.314\times 298}\ \text{mol dm}^{-3} = 4.62 \times 10^{-3}\ \text{mol dm}^{-3}$$

31. We have $K_p = K_c\ (RT)^{\Delta\nu_g}$

$$1.44 \times 10^{-5}\ \text{atm}^{-2} = K_c\ \{(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (773\ \text{K})\}^{-2}$$

$$K_c = [(1.44 \times 10^{-5})/(0.082 \times 773)^{-2}]\ \text{mol}^{-2}\ \text{L}^2$$

32. $K_p = K_c\ (RT)^{\Delta\nu_g}$. If $\Delta\nu_g$ = +ve than $K_p > K_c$ and for $\Delta\nu_g$ = – ve, $K_p < K_c$

33. $\Delta\nu_g = \nu_g(\text{products}) - \nu_g(\text{reactants}) = 2 - (2 + 3) = -3$

34. $$K_p^\circ = K_c^\circ\left(\frac{c^\circ RT}{p^\circ}\right)^{\Delta\nu_g} = (10)\left[\frac{(1\ \text{mol dm}^{-3})\ (8.314\ \text{kPa dm}^3\ \text{K}^{-1}\text{mol}^{-1})(300\ \text{K})}{(101.325\ \text{kPa})}\right]^{-1} = 0.41$$

35. Since p° = 101.325 kPa and $c^\circ = 1\ \text{mol dm}^{-3}$, the value of R to be used is $8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$.

36. We have

$$\underset{c(1\,-\,\alpha)}{N_2O_4(g)} \rightleftharpoons \underset{2c\alpha}{2NO_2(g)}$$

$$x_{N_2O_4} = \frac{c(1-\alpha)}{c(1-\alpha)} = \frac{1-\alpha}{1+\alpha} \quad \text{and} \quad x_{NO_2} = \frac{2c\alpha}{c(1+\alpha)} = \frac{2\alpha}{1+\alpha}$$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\ p \quad \text{and} \quad p_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right) p$$

Hence $$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{[2\alpha p/(1+\alpha)]^2}{p(1-\alpha)/(1+\alpha)}$$

or $K_p(1 - \alpha^2) = 4\alpha^2 p$ or $\alpha^2(K_p + 4p) = K_p$

or $$\alpha = \left(\frac{K_p}{K_p + 4p}\right)^{1/2} = \left[\frac{K_p/p}{\left(K_p/p\right) + 4}\right]^{1/2}$$

37. For the reaction $A(s) \rightleftharpoons 2B(g) + 3C(g)$, we have $K_p = p_B^2\, p_C^3$
If the concentration of C at equilibrium is increased by a factor of 2, we will have

$$\left(\frac{p_B}{n}\right)^2 (2p_C)^3 = p_B^2\, p_C^2$$

or $n = \sqrt{8} = 2\sqrt{2}$, i.e. the concentration of B will change to $1/2\sqrt{2}$ times the original value.

38. Since the new reaction is obtained by reversing the old reaction and multiplying by 2, we get
$K_p = 1/(4 \times 10^{-3}\ \text{atm}^{-1/2})^2 = 6.25 \times 10^4$ atm

39. Since $\Delta\nu_g = 0$, we have

$$K_c = K_n = \frac{n_{AB_2}}{(n_{A_2})(n_{B_2})} = \frac{2x}{(1\ \text{mol} - x)(2\ \text{mol} - x)} = 50$$

Solving for x, we get about 0.93 mol. Hence, $n_{AB_2} = 2x = 1.86$ mol

40. We have

$$\begin{array}{ccccc} A(g) & + & 2B(g) & \rightleftharpoons & 2C(g) \\ 1\ \text{mol} - x & & 1.5\ \text{mol} - 2x & & 2x \end{array}$$

It is given that $[C] = 2x/2.0\ \text{L} = 0.35\ \text{mol L}^{-1}$. This gives $x = 0.35$ mol. Hence

$$K_c = \frac{[C]^2}{[A][B]^2} = \frac{(0.70\ \text{mol/2L})^2}{(0.65\ \text{mol/2L})\left\{(1.5\ \text{mol} - 0.70\ \text{mol/2L})\right\}^2} = \left(\frac{0.49}{4}\right)\left(\frac{2}{0.65}\right)\left(\frac{4}{0.64}\right)\ \text{M}^{-1}$$

$$\simeq \frac{3}{1.3}\ \text{M}^{-1} \simeq 2.36\ \text{M}^{-1}$$

41. We have

$$\begin{array}{ccccc} H_2(g) & + & S(s) & \rightleftharpoons & H_2S(g) \\ 0.2\ \text{mol} - x & & & & x \end{array}$$

Since $\Delta\nu_g = 0$, we have $$K_p = K_n = \frac{x}{0.2\ \text{mol} - x} = 6.8 \times 10^{-2}$$

This gives $$x = \frac{0.0136\ \text{mol}}{1.068} = 0.0127\ \text{mol}$$

The partial pressure of $H_2S(g)$ will be

$$p = \frac{nRT}{V} = \frac{(0.0127\ \text{mol})(0.083\ \text{L atm K}^{-1}\ \text{mol}^{-1})(363\ \text{K})}{(1\ \text{L})} \simeq 0.38\ \text{atm}.$$

42. We have
$$\begin{array}{ccccccc} SO_2(g) & + & NO_2(g) & \rightleftharpoons & SO_3(g) & + & NO(g) \\ 1\ \text{mol} - x & & 1\ \text{mol} - x & & 1\ \text{mol} + x & & 1\ \text{mol} + x \end{array}$$

$$K_c = K_n = \left(\frac{1\ \text{mol} + x}{1\ \text{mol} - x}\right)^2 = 16$$

This gives $x = (3/5)\ \text{mol} = 0.6$ mol.
Hence, $[NO] = 1.6\ \text{mol L}^{-1}$

43. We have
$$\begin{array}{ccccc} 2NO(g) & + & Cl_2(g) & \rightleftharpoons & 2NOCl(g) \\ 0.373\ \text{atm} - 2x & & 0.310\ \text{atm} - x & & 2x \end{array}$$

$p_{\text{total}} = (0.373\ \text{atm} - 2x) + (0.310\ \text{atm} - x) + 2x = 0.544$ atm

Hence, $x = 0.139$ atm

$$K_p = \frac{(p_{\mathrm{NOCl}})^2}{(p_{\mathrm{NO}})^2\left(p_{\mathrm{Cl_2}}\right)} = \frac{(2 \times 0.139\ \text{atm})^2}{(0.095\ \text{atm})^2\ (0.171\ \text{atm})} \simeq 50.0\ \text{atm}^{-1}$$

For the reaction

$$2\mathrm{NOCl(g)} \rightleftharpoons 2\mathrm{NO(g)} + \mathrm{Cl_2(g)} \qquad K_p' = \frac{1}{K_p} = \frac{1}{50\ \text{atm}^{-1}} = 0.02\ \text{atm}$$

44. We have

$$\underset{}{\mathrm{NH_2COONH_4(s)}} \rightleftharpoons \underset{2p}{2\mathrm{NH_3(g)}} + \underset{p}{\mathrm{CO_2(g)}}$$

$$K_p = (2p)^2\ p = 4p^3 = 2.9 \times 10^{-5}\ \text{atm}^3$$

This gives $p = 0.19$ atm

$$p_{\text{total}} = 2p + p = 3p = 0.057\ \text{atm}$$

45. The reaction is

$$\underset{1\ \text{mol} - x}{\mathrm{N_2O_4(g)}} \rightleftharpoons \underset{2x}{2\mathrm{NO_2(g)}}$$

Total amount of gases = 1 mol + x

Since 20% by mass of N_2O_4 is decomposed, $x = 0.2$ mol. Hence

$$p_{300\mathrm{K}} = \frac{1.2\ \text{mol}}{1\ \text{mol}} \times 1\ \text{atm} = 1.2\ \text{atm}.$$

Since temperature is doubled, pressure will also be doubled, i.e., 2.4 atm.

46.

$$\begin{array}{llcll} & \mathrm{N_2\,(g)} & + & \mathrm{3H_2\,(g)} & \rightleftharpoons\ \mathrm{2NH_3\,(g)} \\ t = 0 & 1\ \text{mol} & & 3\ \text{mol} & 0 \\ t_{\text{eq}} & (1 - 0.0025)\ \text{mol} & & (3 - 0.0075)\text{mol} & 0.005\ \text{mol} \end{array}$$

$$K_c = \frac{(0.005/4)^2}{(0.9975/4)(2.9925/4)^3}\left(\text{mol L}^{-1}\right)^2 = 1.50 \times 10^{-5}\ (\text{mol L}^{-1})^{-2}$$

47.

$$\begin{array}{llcll} & \mathrm{A_2(g)} & + & \mathrm{B_2(g)} & \rightleftharpoons\ \mathrm{2AB\,(g)} \\ t = 0 & 1\ \text{mol} & & 2\ \text{mol} & \\ t_{\text{eq}} & 1\ \text{mol} - x & & 2\ \text{mol} - x & 2x \end{array}$$

$$K_p = K_n = \frac{(2x)^2}{(1\,\text{mol} - x)\,(2\,\text{mol} - x)} = 50$$

Solving for x, we get $x = 0.93$ mol. Thus $2x = 1.86$ mol

48.

$$\begin{array}{llcllcl} & \mathrm{SO_2\,(g)} & + & \mathrm{NO_2\,(g)} & \rightleftharpoons\ \mathrm{SO_3\,(g)} & + & \mathrm{NO(g)} \\ t = 0 & 1\ \text{mol} & & 1\ \text{mol} & 1\ \text{mol} & & 1\ \text{mol} \\ t_{\text{eq}} & 1\ \text{mol} - x & & 1\ \text{mol} - x & 1\ \text{mol} + x & & 1\ \text{mol} + x \end{array}$$

$$K_c = \frac{(1\,\text{mol} + x)^2}{(1\,\text{mol} + x)^2} = 16$$

Solving for x, we get $x = 0.6$ mol. Hence, [NO] = 1.6 mol

49.

$$\begin{array}{lll} & \mathrm{N_2O_4} & \rightleftharpoons\ \mathrm{2NO_2} \\ t = 0 & n & 0 \\ \mathrm{t_{eq}} & n(1 - \alpha) & n(2\alpha) \end{array}$$

Total amount of species = $n\ (1 + \alpha)$

$$p_{\mathrm{N_2O_4}} = \frac{1-\alpha}{1+\alpha}\ (1\ \text{atm}) \quad \text{and} \quad p_{\mathrm{NO_2}} = \frac{2\alpha}{1+\alpha}\ (1\ \text{atm}).\ \text{Hence} \qquad K_p = \frac{[2\alpha/(1+\alpha)]^2}{(1-\alpha)/(1+\alpha)}\ \text{atm}.$$

It is given that $\alpha = 0.25$. Hence, $K_p = \dfrac{(0.5/1.25)^2}{(0.75/1.25)}$ atm = 0.267 atm

50. Partial pressure of Hg(g) = 0.51 atm/1.5 = 0.34 atm

Partial pressure of O_2(g) = (0.34/2) atm = 0.17 atm

$$K_p = (0.34)\ (0.17)^{1/2}\ \text{atm}^{3/2} = 0.14\ \text{atm}^{3/2}$$

51. Molar mass of N_2O_4 = 92 g mol^{-1}

Amount of N_2O_4 = 11.5 g/92 g mol^{-1} = 0.125 mol

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
$t = 0$	0.125 mol		
t_{eq}	(1 – 0.66) 0.125 mol = 0.0425 mol		(2 × 0.66) 0.125 mol = 0.165 mol

Total amount of gases = (0.0425 + 0.165) mol = 0.2075 mol

$$V = \frac{nRT}{p} = \frac{(0.2075\ \text{mol})(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{1\ \text{atm}} = 5.1\ \text{L}$$

52. The given reaction may be obtained by subtracting half of the first reaction from the second. Hence

$$K_c^\circ = \frac{1.55}{\left(2.4\times10^{30}\right)^{1/2}} = 1.0 \times 10^{-15}$$

53.

$N_2O_5(g)$	$\rightleftharpoons$	$2NO_2(g)$	+	$\frac{1}{2}\ O_2(g)$
600mmHg$-p$		$2p$		$p/2$

Pressure at any time = (600 mmHg – p) + ($2p$) + ($p/2$) = 600 mmHg + 1.5 p

Hence, 600 mmHg + 1.5 p = 960 mmHg $\Rightarrow$ p = 240 mmHg

$$x(N_2O_5) = \frac{240\ \text{mmHg}}{600\ \text{mmHg}} = 0.40$$

54.

	$CO_2(g)$ +	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
$t = 0$	0.6 mol	0.4 mol				
t_{eq}	0.35 mol	0.15 mol		0.25 mol		0.25 mol

$$K_p = \frac{(0.25)^2}{(0.35)(0.15)} = 1.2$$

55. For the given concentrations, we have

$$\frac{[NO][SO_3]}{[SO_2][NO_2]} = \frac{(0.30)(0.02)}{(0.04)(0.50)} = 0.3$$

This value is less than the equilibrium constant. Hence, to attain equilibrium, the reaction will proceed to right side.

56.

	$2NO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$2NOCl\ (g)$
$t = 0$	0.4 atm		0.3 atm		
t_{eq}	0.4 atm – $2p$		0.3 atm – p		$2p$

Total pressure at equilibrium, 0.7 atm – p = 0.6 atm (given).

Hence, p = 0.1 atm

$$K_p = \frac{p_{NOCl}^2}{p_{NO}^2\ p_{Cl_2}} = \frac{(0.2\ \text{atm})^2}{(0.2\ \text{atm})^2\ (0.2\ \text{atm})} = 5\ \text{atm}^{-1}$$

57. $K_{eq} = k_f/k_b = 3.2/0.12 = 26.7$

58. $E_{a(b)}$ = (208 + 536) kJ mol^{-1} = 744 kJ mol^{-1}.

59.

$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
0.78 mol		0.11 mol		0.11 mol

Since $\Delta\nu_g = 0$, $K_p = K_n = (0.11\ \text{mol})^2/(0.78\ \text{mol})^2 = 0.02$

60. $\Delta G^\circ = -RT\ \text{lm}\ K_p^\circ = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (900\ \text{K})\ \ln(0.05) = 22400\ \text{J mol}^{-1}$

61. $$\begin{array}{lcllcl} H_2(g) & + & CO_2(g) & \rightleftharpoons & H_2O(g) & + & CO(g) \\ 0.4\text{ mol} - x & & 0.4\text{ mol} - x & & x & & x \end{array}$$

$$\frac{x^2}{(0.4\,\text{mol} - x)^2} = 1.6.\quad \text{This gives } x = 0.22 \text{ mol}$$

62. $[B]_1\,[C]_1^2 = [B]_2\,[C]_2^2$. It is given that $[B]_2 = 2\,[B]_1$. Hence, $[C]_2 = [C]_1/\sqrt{2}$.

63. $K_p = p\,(CO)_2$. Thus, the concentration of CO_2 remains unaffected.

64. $$\begin{array}{lcll} A(g) & + & 2B(g) & \rightleftharpoons AB_2(g) \\ n - x & & n - 2x & \end{array}$$

Hence, $[B] < [A]$.

65. $$\begin{array}{llll} PCl_5(g) & \rightleftharpoons & PCl_3(g) & + \; Cl_2(g) \\ (2 - 1.12)\text{ mol} & & 1.12\text{ mol} & \quad 1.12\text{ mol} \\ = 0.88\text{ mol} & & & \end{array}$$

Total amount = $(0.88 + 2 \times 1.12)$ mol = 3.12 mol

$$PCl_5 = \left(\frac{0.88}{3.12}\right) 1\text{ bar} = 0.28\text{ bar}; \qquad p_{PCl_3} = p_{Cl_2} = \left(\frac{1.12}{3.12}\right) 1\text{ bar} = 0.36\text{ bar}$$

$$K_p = \frac{p_{PCl_3}\,p_{Cl_2}}{p_{Pcl_5}} = \frac{0.36^2}{0.28}\text{ bar} = 0.46\text{ bar}$$

66. $$\begin{array}{lcl} N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ n(1 - \alpha) & & 2n\alpha \end{array}$$

Total amount = $n(1 - \alpha) + 2n\alpha = n(1 + \alpha)$

From $pV = nRT$, we get

$$n = \frac{pV}{RT} = \frac{(20.785\,\text{kPa})(1\,\text{dm}^3)}{(8.314\,\text{kPa dm}^3\,\text{K}^{-1}\,\text{mol}^{-1}(300\,\text{K})} = \frac{2.5}{300}\text{ mol}$$

Equating this with $n(1 + \alpha)$, we get

$$n(1 + \alpha) = \frac{2.5}{300}\text{ mol} \quad \text{where } n = \frac{m_{N_2O_4}}{M_{N_2O_4}} = \frac{0.46\text{ g}}{92\text{ g mol}^{-1}} = 0.005\text{ mol}$$

Thus $$\alpha = \left(\frac{2.5}{300} \times \frac{1}{0.005} - 1\right) = 1.67 - 1 = 0.67$$

67. We have

$$\begin{array}{lclcl} A_2(g) & + & B_2(g) & \rightleftharpoons & 2AB(g); \\ a & & b & & 0.2\text{ atm} \end{array} \qquad K_{p1} = \frac{p_{AB}^2}{p_{A_2}\,p_{B_2}} = \frac{(0.2\,\text{atm})^2}{ab} = 4.0$$

$$\begin{array}{lclcl} A_2(g) & + & 3B_2(g) & \rightleftharpoons & 2AB_3(g); \\ a & & b & & 0.1\text{ atm} \end{array} \qquad K_{p2} = \frac{p_{AB_3}^2}{p_{A_2}\,p_{B_2}^3} = \frac{(0.1\,\text{atm})^2}{ab^3} = ?$$

$$\text{Total amount of } A_2 = a + \frac{0.2\,\text{atm}}{2} + \frac{0.1\,\text{atm}}{2} = a + 0.15\text{ atm}$$

$$\text{Total amount of } B_2 = b + \frac{0.2\,\text{atm}}{2} + \frac{3 \times 0.1\,\text{atm}}{2} = b + 0.25\text{ atm}$$

It is given that $a + 0.15$ atm $= b + 0.25$ atm or $a = b + 0.1$ atm

From K_{p1}, we get

$$ab = \frac{(0.2\,\text{atm})^2}{K_{p_1}} = \frac{(0.2\,\text{atm})^2}{4.0} = 0.01\text{ atm}^2$$

Thus $(b + 0.1\ \text{atm})(b) = 0.01\ \text{atm}^2$ i.e. $b_2 + (0.1\ \text{atm})\, b - 0.01\ \text{atm}^2 = 0$

This gives $b = \dfrac{-0.1\,\text{atm} \pm \sqrt{(0.1\,\text{atm})^2 + 4(0.01\,\text{atm}^2)}}{2} = \dfrac{-0.1\,\text{atm} \pm 0.223\,\text{atm}}{2} = 0.062$ atm (acceptable solution)

Hence $a = b + 0.1\ \text{atm} = 0.162\ \text{atm}$

Finally, $K_{p2} = \dfrac{(0.1\,\text{atm})^2}{ab^3} = \dfrac{(0.1\,\text{atm})^2}{(0.162\,\text{atm})\,(0.062\,\text{atm})^3} = 259\ \text{atm}^{-2}$

68. The given reaction is obtained as follows.

$$\begin{array}{rl}
2 \times [3H_2(g) + SO_2(g) = H_2S(g) + 2H_2O(g)]; & K^\circ_{p2} \\
-\,2 \times [H_2(g) + \frac{1}{2} S_2(g) = H_2S(g)]; & K^\circ_{p1} \\
\hline
4H_2(g) + 2\,SO_2(g) = S_2(g) + 4H_2O(g); & K^\circ_{p}
\end{array}$$

Hence $K^\circ_p = K^{\circ 2}_{p2}/K^{\circ 2}_{p1} = (1.8 \times 10^4)^2/(0.8)^2 \simeq 5.0 \times 10^8$

69. The reaction is $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -$ve. Since the reaction is exothermic, more of SO_3 will be formed if temperature is lowered.
Since the reaction involves decrease in the gaseous phase, increase in pressure will cause the formation of more of SO_3.

70. Adding inert gas at constant volume increases pressure of the system. Since K_p is independent of pressure, the equilibrium will not be affected. Thus, none of the given choices is correct.

71. The addition of an inert gas at constant volume does not affect equilibrium.

72. The addition of an inert gas at constant pressure increases volume of the system. The equilibrium shifts towards more number of gaseous species.

73. High pressure will favour more of NH_3 as the forward direction involves decrease in gaseous species.
Low temperature will favour more of NH_3 as the forward direction is exothermic.

74. Pressure changes do not affect equilibrium constant and hence equilibrium concentrations are not changed.
Since the reaction is exothermic, increasing temperature shifts the equilibrium towards the reactant side. Hence, lesser of NO is dissociated.

75. We can write the given reaction as $2NH_3(g) + Q \rightleftharpoons N_2(g) + 3H_2(g)$.
Increasing temperature implies heat is added. This will shift the equilibrium to right side, i.e. more of NH_3 is dissociated.

76. Since the reaction $H_2O(s) \rightleftharpoons H_2O(l)$ involves ΔV = negative, increasing pressure shifts the reaction to right side.

77. Since $K_p = 1/p_{CO_2}$, adding $CaCO_3(s)$ does not affect equilibrium.
Since reaction is exothermic, lowering temperature will shift the reaction to right side. Hence, the quantity of CaO(s) will be lowered.
Removing $CO_2(g)$ will favour equilibrium to left side. Hence, the quantity of CaO(s) will be increased.
Reducing volume will increase pressure. To maintain K_p or p_{CO_2} to a constant value, the equilibrium will shift to right side.

78. The rate of endothermic reaction (where heat is absorbed) will increase more than that of exothermic reaction.

79. The reaction willl shift to the reactant side with increase in temperature. Since the concentrations of reactants appear in the denominator and those of products appear in the numerator, the value of equilibrium constant will decrease.

80. Increase in temperature shifts the reaction to the right side. Consequently, the value of equilibrium constant is increased.

81. The choices a, c and d will decrease the concentration of H_2. The choice b is correct since decreasing volume will cause the reaction to move in the direction of increasing volume, i.e., towards the larger number of gaseous species.

82. We have $K_c = \dfrac{(n_{NH_3}/V)^2}{(n_{N_2}/V)(n_{H_2}/V)^3} = \dfrac{(n_{NH_3})^2}{(n_{N_2})(n_{H_2})^3}V^2$

Increasing volume will cause an increase in n_{H_2}.

83. Since K_c decreases with increase in temperature, the reaction must be exothermic. Hence $\Delta H = -$ve.

84. Since $\Delta\nu_g = 0$, only increasing the amount of CO(g) will increase the equilibrium amount of CO_2(g).

85. Both temperature and pressure affect the equilibrium concentration of X_3Y.

86. At constant volume, the concentrations will not change. Hence, $[SO_3]$ remains unaffected.

87. For $\Delta H < 0$, the reaction is exothermic and hence lowering temperature will increase the formation of products. The reaction involves $\Delta\nu_g = -$ve and hence increase of pressure will also increase the formation of products.

88. The dissociation of A_2 to 2A is endothermic and involves increase in the value of $\Delta\nu_g$. Hence, high temperature and low pressure will favour the dissociation of A_2.

89. The reaction is exothermic. Hence lowering temperature will increase the concentration of NH_3 at equilibrium.

90. Since $\Delta H > 0$, the reaction is endothermic. Hence increase in temperature favours the formation of NO.

91. Heating the solution implies the absorption of heat and this, in turn, leads to increase in the solubility.

92. The addition of inert gas at constant volume does not affect the equilibrium position. The addition at constant pressure causes the increase in volume and thus the equilibrium shifts towards larger number of gaseous molecules. $\Delta\nu_g$ is positive if ν_g(products) > ν_g(reactants), thus the equilibrium will shifts to product side.

93. See Q.91. In this case, $\Delta\nu_g$ will be negative if ν_g(reactants) > ν_g(products).

94. K_p depends only on temperature. The dissociation of NH_3 is $2NH_3 \rightleftharpoons N_2 + 3H_2$. Since $\Delta\nu_g \neq 0$, α will depend on the pressure.

95. At equilibrium, ΔG of the reaction is zero.

Multiple Correct Choice Type

1. The reaction is exothermic and involves decrease in the number of gaseous species. The equilibrium concentration of the reactant C_2H_4 can be increased by increasing temperature and decreasing pressure. It can also be increased by removing H_2 (one of the reactants) and adding some C_2H_6 (i.e. product).

2. The reaction is $2NaNO_3(s) \rightleftharpoons 2NaNO_2(s) + O_2(g)$.

Since $NaNO_3$ and $NaNO_2$ are solids, addition of these species do not affect equilibrium.

Since the reaction involves heating, the forward reaction will be favoured by increasing temperature.

Since the reaction involves increase in the gaseous species, increasing pressure favours reverse reaction.

3. Introducing an inert gas at constant volume will not affect the equilibrium. Introducing Cl_2(g) at constant volume will move the equilibrium in the reverse direction.

Introducing an inert gas at constant pressure will increase the volume of container. The equilibrium will shift in the direction of more number of gaseous species, i.e. forward direction. Introducing PCl_5(g) will also favour forward direction.

4. The choice d is not correct.

5. If the reaction quotient is greater than the equilibrium constant, this implies that the products are more than those at equilibrium. Hence, the reaction proceeds in the backward direction.

The addition of inert gas affects the equilibrium only at constant pressure.

6. Since $K_p = K_c$, it implies that $\Delta\nu_g = 0$. In such a case, only temperature changes can change the value of the equilibrium constant.

7. The reaction is $2NaNO_3(s) \rightleftharpoons 2NaNO_2(s) + O_2(g)$; $\Delta H = +$ ve

Since the reaction proceeds on heating, increase in temperature will cause the reaction to proceed towards the forward direction.

Also since $\Delta\nu_g = +$ ve, increasing pressure will shift the reaction in a direction where there occurs decrease in pressure, i.e. towards the reverse direction.

8. At constant volume, the equilibrium is affected.

Linked Comprehension Type

1. **(i)** $K^\circ = \dfrac{[\mathrm{Ag(NH_3)_2^+}][\mathrm{Cl^-}]}{[\mathrm{NH_3}]^2} = \dfrac{(s)(s)}{(1\,\mathrm{M})} = 2.79 \times 10^{-3}$; $s = \sqrt{2.79 \times 10^{-3}}$ M = 0.053 M

(ii) $K^\circ = \dfrac{[\mathrm{Ag(NH_3)_2^+}][\mathrm{Cl^-}]}{[\mathrm{NH_4OH}]^2} = \dfrac{(s)(s)}{(1\,\mathrm{M})^2}$ = 8.46×10^{-7}; $s = \sqrt{8.46 \times 10^{-7}}$ M = 9.2×10^{-4} M

(iii) Subtracting the given reactions, we get

$$2\mathrm{NH_3} + 2\mathrm{H_2O} \rightarrow 2\mathrm{NH_4OH} \qquad K^\circ = \frac{2.79 \times 10^{-3}}{8.46 \times 10^{-7}} = 3298$$

For $\mathrm{NH_3} + \mathrm{H_2O} \rightarrow \mathrm{NH_4OH}$, $\qquad K^\circ = \sqrt{3298} = 57.43$

2. **(i)** $\Delta_r H^\circ = 2\Delta_f H^\circ(\mathrm{N_2O_5}, \mathrm{g}) - 4\Delta_f H^\circ(\mathrm{NO_2}, \mathrm{g}) = (2 \times 11.3 - 4 \times 33.2)\ \mathrm{kJ\ mol^{-1}} = -\ 110.2\ \mathrm{kJ\ mol^{-1}}$

(ii) Since the reaction is exothermic, the reaction will proceed to left side on increasing temperature.

(iii) Since $\Delta H^\circ = -$ ve and $\Delta\nu_g = -\ 3$, the yield of $\mathrm{N_2O_5}$ will increase on increasing temperature and high pressure. At high pressure, the equilibrium will shift in a direction of lesser gaseous molecules as this direction will tend to decrease pressure.

3. **(i)** $\Delta_f G^\circ = 2\Delta_r G^\circ(\mathrm{N_2O_5}, \mathrm{g}) - 4\Delta_r G^\circ(\mathrm{NO_2}, \mathrm{g}) = (2 \times 115.1 - 4 \times 51.3)\ \mathrm{kJ\ mol^{-1}} = 25.0\ \mathrm{kJ\ mol^{-1}}$

(ii) $K_p^\circ = \text{antilog}\left(-\dfrac{\Delta G^\circ}{2.303\,RT}\right) = \text{antilog}\left(-\dfrac{25 \times 10^3}{2.303 \times 8.314 \times 298}\right) = \text{antilog}\ (-\ 4.38) = 4.15 \times 10^{-5}$

(iii) $K_c^\circ = K_p^\circ\ (RT)^{-\Delta\nu_g} = (4.15 \times 10^{-5})\ (0.082 \times 298)^3 = 0.61$

4. **(i)** $\Delta_r H^\circ = 2\Delta_f H^\circ(\mathrm{SO_2}, \mathrm{g}) - 2\Delta_f H^\circ(\mathrm{SO_3}, \mathrm{g}) = [2\ (-\ 296.8) - 2(-\ 395.7)]\ \mathrm{kJ\ mol^{-1}} = 197.8\ \mathrm{kJ\ mol^{-1}}$

(ii) Since the reaction is endothermic, increasing temperature will cause the reaction to shift towards right side.

(iii) Since $\Delta H^\circ = +$ ve and $\Delta\nu_g = +\ 1$, the decomposition of $\mathrm{SO_3}$ will be favoured on increasing temperature and decreasing pressure.

5. **(i)** $\Delta_r G^\circ = 2\Delta_f G^\circ(\mathrm{SO_2}, \mathrm{g}) - 2\Delta_f G^\circ(\mathrm{SO_3}, \mathrm{g}) = [2\ (-\ 300.2) - 2\ (-\ 371.1)]\ \mathrm{kJ\ mol^{-1}} = 141.8\ \mathrm{kJ\ mol^{-1}}$

(ii) $K_p^\circ = \text{antilog}\left(-\dfrac{\Delta G^\circ}{2.303\,RT}\right) = \text{antilog}\left(-\dfrac{141.8 \times 10^3}{2.303 \times 8.314 \times 298}\right) = 1.41 \times 10^{-25}$

(iii) $K_c^\circ = K_p^\circ\ (RT)^{-\Delta\nu_g} = (1.41 \times 10^{-25})\ (0.082 \times 298)^{-1} = 5.77 \times 10^{-27}$

6. **(i)** We have

$$\underset{n(1-\alpha)}{\mathrm{PCl_5(g)}} \rightleftharpoons \underset{n\alpha}{\mathrm{PCl_3(g)}} + \underset{n\alpha;}{\mathrm{Cl_2(g)}} \qquad \text{Total amount} = n(1 + \alpha)$$

From the given T, p and V, we get

$$n' = \frac{pV}{RT} = \frac{(100\ \mathrm{kPa})(2.08\ \mathrm{dm^3})}{(8.314\ \mathrm{kPa\ dm^3\ K^{-1}\ mol^{-1}})(500\ \mathrm{K})} = 0.05\ \mathrm{mol}$$

Hence $\quad n(1 + \alpha) = 0.05 \quad$ or $\quad \alpha = \dfrac{0.05\ \mathrm{mol}}{n} - 1 = \dfrac{0.05}{0.03} - 1 = 0.667$

(ii) $x_{\mathrm{PCl_5}} = \dfrac{1-\alpha}{1+\alpha}\,p$; $\qquad p_{\mathrm{PCl_3}} = p_{\mathrm{Cl_2}} = \dfrac{\alpha}{1+\alpha}\,p$

$$K_p = \frac{p_{\mathrm{PCl_3}}\,p_{\mathrm{Cl_2}}}{p_{\mathrm{PCl_5}}} = \frac{\alpha^2 p}{1-\alpha^2} = \frac{(2/3)^2(100\ \mathrm{kPa})}{1-(2/3)^2} = 80\ \mathrm{kPa}$$

(iii) The value of standard equilibrium constant is

$$K_p^\circ = \frac{\alpha^2}{1-\alpha^2}\left(\frac{p}{100\ \text{Pa}}\right) = 0.8$$

Hence $\Delta G^\circ = -RT\ln K_p^\circ = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (500\ \text{K})\ (2.303)\ \log\ (0.8)$

$= 927.8\ \text{J mol}^{-1}$

7. **(i)** The free change of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is

$\Delta_rG^\circ = 2\Delta_fG^\circ(NO_2,\ g) - \Delta_fG^\circ(N_2O_4,\ g) = (2 \times 51.31 - 97.89)\ \text{kJ mol}^{-1} = 4.73\ \text{kJ mol}^{-1}$

$$K_p^\circ = \text{antilog}\left(-\frac{\Delta_rG}{2.303\,RT}\right) = \text{antilog}\left[-\frac{4.73\times10^3\ \text{J mol}^{-1}}{(2.303)\ (8.314\ \text{J K}^{-1})(300\ \text{K})}\right]$$

$= \text{antilog}\ (-\ 0.823) = 0.150$

(ii) $$K_c^\circ = K_p^\circ\left(\frac{c^\circ RT}{p^\circ}\right)^{-\Delta\nu_g} = (0.150)\left[\frac{(1\ \text{mol dm}^{-3})\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{101.325\ \text{kPa}}\right]^{-1}$$

$$= (0.150)\left(\frac{101.325}{2494}\right) = 6.1 \times 10^{-3}$$

(iii) $$K_x = K_p^\circ\left(\frac{p_{\text{total}}}{p^\circ}\right)^{-\Delta\nu_g} = (0.150)\left(\frac{101.325}{100}\right)^{-1} = 0.148$$

8. **(i)** We have

$$\underset{n(1-\alpha)}{PCl_5(g)} \rightleftharpoons \underset{n\alpha}{PCl_3(g)} + \underset{n\alpha}{Cl_2(g)} \qquad ;\ \text{Total amount} = n(1+\alpha)$$

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha}P; \qquad p_{PCl_3} = p_{Cl_2} = \frac{\alpha}{1-\alpha}P$$

$$K_p = \frac{[\{\alpha/(1-\alpha)\}P]^2}{\{(1-\alpha)/(1+\alpha)\}]P} = \frac{\alpha^2P}{1-\alpha^2}; \qquad K_p^\circ = \frac{\alpha^2}{1-\alpha^2}\left(\frac{p}{p^\circ}\right)$$

Hence $\alpha = K_p^\circ/\{(P/p^\circ) + K_p^\circ\} = 1.8/(1 + 1.8) = 0.8$

(ii) From ideal gas equation, we find that

$$V = \frac{n(1-\alpha)RT}{p} = n(1+\alpha)\left[\frac{(8.314\ \text{kPa dm}^3\ \text{K}^{-1}\text{mol}^{-1})(500\,\text{K})}{(100\ \text{kPa})}\right]$$

$$= n(1+\alpha)\ (41.57\ \text{dm}^3\ \text{mol}^{-1}) = \frac{m}{M_{PCl_5}}\ (1+\alpha)\ (41.57\ \text{dm}^3\ \text{mol}^{-1})$$

$$\rho = \frac{m}{V} = \frac{M_{PCl_5}}{(1+\alpha)\,(41.57\ \text{dm}^3\ \text{mol}^{-1})} = \frac{(208.5\ \text{g mol}^{-1})}{(1.8)\,(41.57\ \text{dm}^3\ \text{mol}^{-1})} = 2.79\ \text{g dm}^{-3}$$

(iii) $\Delta_rG^\circ = -RT\ln K_p^\circ = -2.303\ RT\log K_p^\circ = -(2.303)\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (500\ \text{K})\ \log\ (1.80)$

$= -2444\ \text{J mol}^{-1} = -2.44\ \text{kJ mol}^{-1}$

9. **(i)** We have

$$\underset{n(1-\alpha)}{COCl_2} \rightleftharpoons \underset{n\alpha}{CO} + \underset{n\alpha}{Cl_2} \qquad ;\ \text{Total amount} = n(1+\alpha)$$

Volume of the gaseous mixture, $V = \dfrac{n(1+\alpha)\,RT}{p} = \dfrac{m(1+\alpha)\,RT}{M_{COCl_2}\,p}$

Density of the gaseous mixture is $\rho = \dfrac{m}{V} = \dfrac{M_{\mathrm{COCl_2}}\,p}{(1+\alpha)\,RT}$

Hence
$$\alpha = \frac{M_{\mathrm{COCl_2}}\,p}{\rho RT} - 1 = \frac{(99\ \mathrm{g\ mol^{-1}})(100\ \mathrm{kPa})}{(1.2\ \mathrm{g\ dm^{-3}})(8.314\ \mathrm{kPa\ dm^3K^{-1}\ mol^{-1}})(700\ \mathrm{K})} - 1$$
$$= 1.42 - 1 = 0.42$$

(ii) $p_{\mathrm{COCl_2}} = \left(\dfrac{1-\alpha}{1+\alpha}\right) p;\qquad p_{\mathrm{CO}} = p_{\mathrm{Cl_2}} = \dfrac{\alpha}{1+\alpha}\,p$

$$K^\circ_p = \frac{p_{\mathrm{CO}}\,p_{\mathrm{Cl_2}}}{p_{\mathrm{COCl_2}}} = \frac{[\{\alpha/(1+\alpha)\}\,(p/p^\circ)]^2}{\{(1-\alpha)/(1+\alpha)\}\,(p/p^\circ)} = \frac{\alpha^2}{1-\alpha^2}\,\frac{p}{p^\circ} = \left(\frac{0.42^2}{1-0.42^2}\right)\left(\frac{100\ \mathrm{kPa}}{100\ \mathrm{kPa}}\right) = 0.214$$

(iii) $\Delta G^\circ = -RT\ln K^\circ_p = -(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (700\ \mathrm{K})\ (2.303)\ \log\,(0.214) = 8975\ \mathrm{J\ mol^{-1}} = 8.98\ \mathrm{kJ\ mol^{-1}}$

Matrix Match Type

2. $2\mathrm{XY(g)} \rightleftharpoons \mathrm{X_2(g)} + \mathrm{Y_2(g)}$

$n(1-\alpha)\qquad n(\alpha/2)\qquad n(\alpha/2);$ Total amount $= n$

$$p_{\mathrm{XY}} = (1-\alpha)p;\quad p_{\mathrm{X_2}} = p_{\mathrm{Y_2}} = \frac{\alpha}{2}\,p$$

$$K_p = \frac{p_{\mathrm{X_2}}\,p_{\mathrm{Y_2}}}{p^2_{\mathrm{XY}}} = \frac{\{(\alpha/2)p\}^2}{\{(1-\alpha)p\}^2} = \frac{\alpha^2}{4(1-\alpha)^2}$$

This gives $\dfrac{\alpha}{1-\alpha} = \sqrt{K_p} \Rightarrow \alpha = \dfrac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

$\mathrm{X_2Y_4(g)} \rightleftharpoons 2\mathrm{XY_2(g)}$

$n(1-\alpha)\qquad n(2\alpha);$ Total amount $= n(1+\alpha)$

$$p_{\mathrm{X_2Y_4}} = \frac{1-\alpha}{1+\alpha}\,p;\quad p_{\mathrm{XY_2}} = \frac{2\alpha}{1+\alpha}\,p$$

$$K_p = \frac{p^2_{\mathrm{XY_2}}}{p_{\mathrm{X_2Y_4}}} = \frac{[\{2\alpha/(1+\alpha)p\}]^2}{[(1-\alpha)/(1+\alpha)]p} = \frac{4\alpha^2 p}{1-\alpha^2}\qquad \text{or}\qquad \alpha = \sqrt{\frac{K_p}{4p+K_p}}$$

$\mathrm{XY_3(g)} \rightleftharpoons \dfrac{1}{2}\,\mathrm{X_2(g)} + \dfrac{3}{2}\,\mathrm{Y_2(g)}$

$n(1-\alpha)\qquad n(\alpha/2)\qquad n(3\alpha/2);$ Total amount $= n(1+\alpha)$

$$p_{\mathrm{XY_3}} = \frac{1-\alpha}{1+\alpha}\,p;\quad p_{\mathrm{X_2}} = \frac{\alpha}{2(1+\alpha)}\,p;\quad p_{\mathrm{Y_2}} = \frac{3\alpha}{2(1+\alpha)}\,p$$

$$K_p = \frac{p^{1/2}_{\mathrm{X_2}}\,p^{3/2}_{\mathrm{Y_2}}}{p_{\mathrm{XY_3}}} = \frac{[\alpha p/\{2(1+\alpha)\}]^{1/2}\,[3\alpha p/\{2(1+\alpha)\}]^{3/2}}{(1-\alpha)p/(1+\alpha)} = \frac{3\sqrt{3}\,\alpha^2 p}{4\,(1-\alpha^2)}\qquad \text{or}\qquad \alpha = \sqrt{\frac{4K_p}{3\sqrt{3}\,p+4K_p}}$$

$\mathrm{XY_3} \rightleftharpoons \mathrm{XY} + \mathrm{Y_2}$

$n(1-\alpha)\qquad n\alpha\qquad n\alpha;$ Total amount $= n(1+\alpha)$

$$p_{\mathrm{XY_3}} = \frac{1-\alpha}{1+\alpha}\,p;\quad p_{\mathrm{XY}} = p_{\mathrm{Y_2}} = \frac{\alpha}{1+\alpha}\,p$$

$$K_p = \frac{p_{\mathrm{XY}}\,p_{\mathrm{Y_2}}}{p_{\mathrm{XY_3}}} = \frac{[\{\alpha/(1+\alpha)\}p]^2}{\{(1-\alpha)/(1+\alpha)\}p} = \frac{\alpha^2}{1-\alpha^2}\,p\qquad \text{or}\qquad \alpha = \sqrt{\frac{K_p}{p+K_p}}$$

ANNEXURE I

Subjective Problems for Practice

SOLVED PROBLEMS

1. One mole of nitrogen is mixed with three moles of hydrogen in a 4-litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

calculate the equilibrium constant K_c. What will be the value of K_c for the following equilibrium?

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \qquad (1981)$$

Solution From the given data, we write

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
$t = 0$	1 mol		3 mol		0
t_{eq}	(1 − 0.0025)mol		(3 − 0.0075) mol		0.005 mol

Hence,
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.005\ \text{mol}/4\,\text{L})^2}{\{(1-0.0025)\ \text{mol}/4\,\text{L}\}\ \{(3-0.0075)\ \text{mol}/4\,\text{L}\}^3} = 1.49 \times 10^{-5}\ (\text{mol L}^{-1})^{-2}$$

The equilibrium constant for the reaction $\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

would be, $K_c' = \sqrt{K_c} = 3.86 \times 10^{-3}\ (\text{mol L}^{-1})^{-1}$

2. One mole of N_2 and 3 mol of PCl_5 placed in a 100-litre vessel are heated to 227 °C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and K_p for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad (1984)$$

Solution If α is the degree of dissociation of $PCl_5(g)$, we will have

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
$t = 0$	3 mol		0		0
t_{eq}	3 mol(1 − α)		(3 mol)α		(3 mol)α

Total amount of gases in the vessel

$$n = n(N_2) + n(PCl_5) + n(PCl_3) + n(Cl_2) = 1\ \text{mol} + 3\ \text{mol}(1-\alpha) + (3\ \text{mol})\alpha + (3\ \text{mol})\alpha$$

$$= 4\ \text{mol} + (3\ \text{mol})\alpha \qquad (1)$$

From the given value of equilibrium pressure, we find that

$$\text{Total amount of gases, } n = \frac{pV}{RT} = \frac{(2.05\ \text{atm})(100\ \text{L})}{(0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})(500\,\text{K})} = 5.0\ \text{mol} \qquad (2)$$

Equating Eqs (1) and (2), we get

$$4\ \text{mol} + (3\ \text{mol})\alpha = 5\ \text{mol} \quad \text{or} \quad \alpha = \frac{1\ \text{mol}}{3\ \text{mol}} = 0.333$$

Now $n(PCl_5) = 3\ \text{mol}\ (1 - 0.333) = 2\ \text{mol}$ and $n(PCl_3) = n(Cl_2) = (3\ \text{mol})\ (0.333) = 1\ \text{mol}$

$$p(PCl_5) = \frac{n(PCl_5)}{n}\,p_{eq} = \frac{2}{5} \times 2.05\ \text{atm} = 0.82\ \text{atm};$$

$$p(PCl_3) = p(Cl_2) = \frac{1}{5} \times 2.05\ \text{atm} = 0.41\ \text{atm}$$

Hence, $$K_p = \frac{p(\mathrm{PCl_3})\cdot p(\mathrm{Cl_2})}{p(\mathrm{PCl_5})} = \frac{(0.41\ \mathrm{atm})^2}{0.82\ \mathrm{atm}} = 0.205\ \mathrm{atm}$$

3. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100 °C is 50. If a one-litre flask containing one mole of A_2 is connected to a two-litre flask containing two moles of B_2, what amount of AB will be formed at 373 K? (1985)

Solution We have

$$\begin{array}{lccccc} & A_2(g) & + & B_2(g) & \rightleftharpoons & 2AB(g) \\ t = 0 & 1\ \mathrm{mol} & & 2\ \mathrm{mol} & & \\ t_{\mathrm{eq}} & 1\ \mathrm{mol} - x & & 2\ \mathrm{mol} - x & & 2x \end{array}$$

Since for the given reaction, $\Delta\nu_g = 0$, we will have

$$K_p = K_n = \frac{n^2_{\mathrm{AB}}}{n_{A_2} n_{B_2}} = \frac{(2x)^2}{(1\ \mathrm{mol} - x)(2\ \mathrm{mol} - x)} = 50$$

or $$46\, x^2 - 50\ (3\ \mathrm{mol})\ x + 100\ \mathrm{mol}^2 = 0 \qquad \text{which gives } x = 0.934\ \mathrm{mol}$$

Hence, $$n(\mathrm{AB}) = 2x = 1.868\ \mathrm{mol}.$$

4. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction

$$\mathrm{SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)}$$

If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2? (1987)

Solution We have

$$\begin{array}{lccccccc} & \mathrm{SO_2(g)} & + & \mathrm{NO_2(g)} & \rightleftharpoons & \mathrm{SO_3(g)} & + & \mathrm{NO(g)} \\ t = 0 & 1\ \mathrm{mol} & & 1\ \mathrm{mol} & & 1\ \mathrm{mol} & & 1\ \mathrm{mol} \\ t_{\mathrm{eq}} & 1\ \mathrm{mol} - x & & 1\ \mathrm{mol} - x & & 1\ \mathrm{mol} + x & & 1\ \mathrm{mol} + x \end{array}$$

Hence, $$K_c = \frac{[\mathrm{SO_3}][\mathrm{NO}]}{[\mathrm{SO_2}][\mathrm{NO_2}]} = \frac{\{(1\ \mathrm{mol} + x)/1\ \mathrm{L}\}^2}{\{(1\ \mathrm{mol} - x)/1\ \mathrm{L}\}^2} = 16$$

or $$\frac{1\ \mathrm{mol} + x}{1\ \mathrm{mol} - x} = 4 \qquad \text{or} \qquad x = \frac{3}{5}\ \mathrm{mol} = 0.6\ \mathrm{mol}$$

Hence, $$[\mathrm{NO_2}] = 0.4\ \mathrm{mol\ L^{-1}} \qquad \text{and} \qquad [\mathrm{NO}] = 1.6\ \mathrm{mol\ L^{-1}}.$$

5. N_2O_4 is 25% dissociated at 37 °C and 1 atm pressure. Calculate (i) K_p and (ii) the precentage dissociation at 0.1 atm and 37 °C. (1988)

Solution If α is the degree of dissociation of N_2O_4, we will have

$$\begin{array}{lccc} & \mathrm{N_2O_4} & \rightleftharpoons & 2\ \mathrm{NO_2} \\ t = 0 & n & & \\ t_{\mathrm{eq}} & n(1 - \alpha) & & n(2\alpha) \end{array}$$

Total amount of gases $= n\ (1 + \alpha)$

Now $$p_{\mathrm{N_2O_4}} = \frac{1-\alpha}{1+\alpha}\, p \qquad \text{and} \qquad p_{\mathrm{NO_2}} = \frac{2\alpha}{1+\alpha}\, p$$

and $$K_p = \frac{(p_{\mathrm{NO_2}})^2}{p_{\mathrm{N_2O_4}}} = \frac{[2\alpha\, p/(1+\alpha)]^2}{(1-\alpha)\, p/(1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2}\, p$$

It is given that when $p = 1$ atm, $\alpha = 0.25$. Hence,

$$K_p = \frac{4(0.25)^2}{1-(0.25)^2}\ (1\ \mathrm{atm}) = 0.267\ \mathrm{atm}$$

Now when $p = 0.1$ atm, we will have

$$0.267\ \text{atm} = \frac{4\alpha^2}{1-\alpha^2}\ (0.1\ \text{atm})$$

Solving for α, we get $\quad \alpha^2 = \frac{2.67}{6.67} = 0.4 \quad$ or $\quad \alpha = 0.63$

Hence, 63% of N_2O_4 is dissociated at 0.1 atm and 37 °C.

6. The equilibrium constant K_p of the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial partial pressures of 1 atm and 2 atm, respectively, is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. (1989)

Solution Since to start with SO_2 is not present, it is expected that some of SO_3 will decompose to give SO_2 and O_2 at equilibrium. If $2x$ is the partial pressure of SO_3 that is decreased at equilibrium, we would have

	$2SO_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2SO_3(g)$
$t = 0$	0	2 atm	1 atm
t_{eq}	$2x$	2 atm + x	1 atm − $2x$

Hence, $$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2\,(p_{O_2})} = \frac{(1\ \text{atm} - 2x)^2}{(2x)^2\,(2\,\text{atm} + x)} = 900\ \text{atm}^{-1}$$

Assuming $x \ll 2$ atm, we get

$$\frac{(1\ \text{atm} - 2x)^2}{(2x)^2\,(2\,\text{atm})} = 900\ \text{atm}^{-1} \quad \text{or} \quad \frac{(1\ \text{atm} - 2x)^2}{(2x)^2} = 1800 \quad \text{or} \quad \frac{1\ \text{atm}}{2x} - 1 = 42.43$$

or $$x = \frac{1}{2 \times 43.43}\ \text{atm} = 0.0115\ \text{atm}$$

Hence, $p(SO_2) = 2x = 0.023$ atm; $p(O_2) = 2$ atm $+ x = 2.0115$ atm and $p(SO_3) = 1$ atm $- 2x = 0.977$ atm

7. For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, hydrogen gas is introduced into a five-litre flask at 327 °C containing 0.2 mol of CO(g) and a catalyst until the pressure is 4.92 atm. At this point, 0.1 mol of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p and K_c. (1990)

Solution We have

	$CO(g)$ +	$2H_2(g)$ $\rightleftharpoons$	$CH_3OH(g)$
$t = 0$	0.2 mol		
t_{eq}	0.1 mol	?	0.1 mol

Total amount of gas at equilibrium,

$$\frac{pV}{RT} = \frac{(4.92\ \text{atm})\,(5\,\text{L})}{(0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})\,(600\ \text{K})} = 0.5\ \text{mol}$$

Hence, Amount of H_2 at equilibrium = 0.5 mol − 0.2 mol = 0.3 mol

Now $$K_c = \frac{[CH_3OH]}{[CO]\,[H_2]^2} = \frac{(0.1\,\text{mol}/5\,\text{L})}{(0.1\,\text{mol}/5\,\text{L})(0.3\,\text{mol}/5\,\text{L})^2} = 27.78\ (\text{mol L}^{-1})^{-2}$$

$$K_p = \frac{p_{CH_3OH}}{p_{CO}\,(p_{H_2})^2} = \frac{(0.1/0.5) \times 4.92\ \text{atm}}{\{(0.1/0.5) \times 4.92\ \text{atm}\}\ \{(0.3/0.5) \times 4.92\ \text{atm}\}^2} = 0.115\ \text{atm}^{-2}.$$

8. 0.15 mol of CO taken in a 2.5 L flask is maintained at 705 K along with a catalyst so that the following reaction takes place $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$. Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mol of methanol is formed. Calculate (a) K_p and K_c and (b) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (1993)

Solution We have

	$CO(g)$	+ $2H_2(g)$ $\rightleftharpoons$	$CH_3OH(g)$
$t = 0$	0.15 mol		
t_{eq}	0.15 mol − x	$(n_{H_2})_0 - 2x$	x

It is given that 0.08 mol of CH_3OH is formed at equilibrium. Hence,

$$n_{CH_3OH} = x = 0.08 \text{ mol} \qquad \text{and} \qquad n_{CO} = 0.15 \text{ mol} - x = 0.07 \text{ mol}$$

From the total pressure of 8.5 atm at equilibrium, we calculate the total amount of gases, i.e. CO, H_2 and CH_3OH at equilibrium.

$$n_{total} = \frac{pV}{RT} = \frac{(8.5 \text{ atm})(2.5 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1})(705 \text{ K})} = 0.367\,6 \text{ mol}$$

Now, the amount of H_2 at equilibrium is given as

$$n_{H_2} = n_{total} - n_{CO} - n_{CH_3OH} = (0.3676 - 0.07 - 0.08) \text{ mol} = 0.2176 \text{ mol}$$

Hence, $$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(0.08 \text{ mol}/2.5 \text{ L})}{(0.07 \text{ mol}/2.5 \text{ L})(0.2176 \text{ mol}/2.5 \text{ L})^2} = 150.85 \ (\text{mol L}^{-1})^{-2}$$

Now $$K_p = K_c(RT)^{\Delta\nu_g} = (150.85 \text{ mol}^{-2} \text{ L}^2) \{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(705 \text{ K})\}^{-2} = 0.045\,13 \text{ atm}^{-2}$$

Since $n_{H_2} = (n_{H_2})_0 - 2x$, we have

$$(n_{H_2})_0 = n_{H_2} + 2x = (0.2176 + 2 \times 0.08) \text{ mol} = 0.3776 \text{ mol}$$

Total amount of CO and H_2 in the reacting system before the reaction sets in is given as

$$n_0 = (n_{CO})_0 + (n_{H_2})_0 = (0.15 + 0.3776) \text{ mol} = 0.5276 \text{ mol}$$

Hence, $$p_0 = \frac{n_0RT}{V} = \frac{(0.5276 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(705 \text{ K})}{(2.5 \text{ L})} = 12.20 \text{ atm}$$

Alternatively, p_0 may be calculated as given below.

$$\frac{p_0}{n_0} = \frac{p_1}{n_1} \qquad \text{or} \qquad p_0 = \left(\frac{8.5 \text{ atm}}{0.367\,6 \text{ mol}}\right)(0.527\,6 \text{ mol}) = 12.20 \text{ atm.}$$

9. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure P. (1994)

Solution Let n be the initial amount of AB_2. We will have

	$2AB_2(g)$	$\rightleftharpoons$	$2AB(g)$	$+ \ B_2(g)$
$t = 0$	n		0	0
t_{eq}	$n(1-x)$		nx	$nx/2$

Total amount of gases at equilibrium $\quad n_{total} = n_{AB_2} + n_{AB} + n_{B_2} = n(1 - x) + nx + nx/2 = n(1 + x/2)$

The partial pressures of the species at equilibrium would be

$$p_{AB_2} = \frac{n_{AB_2}}{n_{total}}P = \frac{n(1-x)}{n(1+x/2)}P = \frac{1-x}{1+x/2}P \simeq P; \quad p_{AB} = \frac{n_{AB}}{n_{total}}P = \frac{nx}{n(1+x/2)}P = \frac{x}{1+x/2}P \simeq xP$$

$$p_{B_2} = \frac{n_{B_2}}{n_{total}}P = \frac{nx/2}{n(1+x/2)}P = \frac{x/2}{1+x/2}P \simeq \frac{x}{2}P$$

Now $$K_p = \frac{(p_{AB})^2\,p_{B_2}}{(p_{AB_2})^2} = \frac{(xP)^2\,\{(x/2)P\}}{P^2} = \frac{x^3}{2}P \quad \text{or} \quad x = \left(\frac{2K_p}{P}\right)^{1/3}.$$

10. For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2\,CN^-$, the equilibrium constant at 25 °C is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$. (1994)

Solution We have

$$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2\,CN^-; \qquad K_{eq} = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = 4.0 \times 10^{-19} \text{ M}^2$$

For the reaction $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$ we will have,

$$K'_{eq} = \frac{1}{K_{eq}} = \frac{1}{4.0 \times 10^{-19} \text{ M}^2} = 0.25 \times 10^{19} \text{ M}^{-2}$$

The very large value of K'_{eq} implies almost complete conversion of Ag^+ ion. The very small concentration of Ag^+ ions will be left so as to satisfy the equilibrium constant. Let it be x. Hence

$$\begin{array}{lcccc} & Ag^+ & + \quad 2CN^- & \rightleftharpoons & Ag(CN)_2^- \\ t = 0 & 0.03\ \text{M} & 0.1\ \text{M} & & \\ t_{\text{eq}} & x & (0.1 - 2\times 0.03)\text{M} & & 0.03\ \text{M} \end{array}$$

Substituting these concentrations in the expression of K_{eq}, we get

$$\frac{(x)\,(0.04\ \text{M})^2}{(0.03\ \text{M})} = 4.0 \times 10^{-19}\ \text{M}^2 \quad \text{or} \quad x = [Ag^+] = \frac{(4.0\times 10^{-19})\,(0.03)}{(0.04)^2}\ \text{M} = 7.5 \times 10^{-18}\ \text{M}.$$

11. $HgO(s)$ dissociates according to the equation $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2}O_2(g)$. The dissociation pressure is 0.51 atm at 693 K. Calculate K_p for the reaction.

Solution We have

$$\text{Partial pressure of } Hg(g) = \frac{0.51\ \text{atm}}{1 + 1/2} = 0.34\ \text{atm; Partial pressure of } O_2(g) = 0.17\ \text{atm}$$

Hence, $K_p = p_{Hg}\,(p_{O_2})^{1/2} = (0.34\ \text{atm})\ (0.17\ \text{atm})^{1/2} = 0.14\ \text{atm}^{3/2}$.

12. The following data for the reaction $2Na(g) \rightleftharpoons Na_2(g)$ at equilibrium have been observed.

Equilibrium pressure = 1 atm; Mass per cent of Na = 71.3; Mass per cent of Na_2 = 28.7

Calculate K_p for the reaction.

Solution We have

$$\text{Amount of Na} = \frac{71.3}{23}\ \text{mol} = 3.1\ \text{mol}; \quad \text{Amount of } Na_2 = \frac{28.7}{46}\ \text{mol} = 0.624\ \text{mol}$$

$$\text{Mole fraction of Na} = \frac{3.1}{3.1 + 0.624} = 0.832; \quad \text{Mole fraction of } Na_2 = 1 - 0.832 = 0.168$$

Hence, $$K_p = \frac{p_{Na_2}}{(p_{Na})^2} = \frac{x_{Na_2}\,p}{(x_{Na}\,p)^2} = \frac{0.168\ \text{atm}}{(0.832\ \text{atm})^2} = 0.24\ \text{atm}^{-1}.$$

13. At 70 °C and 1 atm, N_2O_4 is 66% dissociated into NO_2. What volume will 10 g N_2O_4 occupy under these conditions?

Solution We have

$$\text{Molar mass of } N_2O_4 = 92\ \text{g mol}^{-1}; \quad \text{Amount of } N_2O_4 = \frac{10\ \text{g}}{92\ \text{g mol}^{-1}} = \frac{10}{92}\ \text{mol}$$

$$\begin{array}{lccc} & N_2O_4(g) & \rightleftharpoons & 2\ NO_2(g) \\ t = 0 & \dfrac{10}{92}\ \text{mol} & & \\ t_{\text{eq}} & \left(\dfrac{10}{92}\ \text{mol}\right)(1 - 0.66) & & \left(\dfrac{10}{92}\ \text{mol}\right)\ (2 \times 0.66) \end{array}$$

$$\text{Total amount of gases at equilibrium} = \left(\frac{10}{92}\ \text{mol}\right)\ (1 + 0.66)$$

Hence, $$V = \frac{nRT}{p} = \left(\frac{10 \times 1.66}{92}\ \text{mol}\right)\left[\frac{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (343\ \text{K})}{1\ \text{atm}}\right] = 5.08\ \text{L}.$$

14. The values of K_c° for the reactions $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ and $NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ are 2.4×10^{30} and 1.4, respectively at 300 K. Calculate the value of K_c for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br(g) \rightleftharpoons NOBr(g)$.

Solution The given reaction can be obtained by subtracting one half of the reaction

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K'_c = 2.4 \times 10^{30}$$

from the reaction $NO(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g) \qquad K_c'' = 1.4$

Hence, K_c of the new reaction would be

$$K_c = \frac{K_c''}{\sqrt{K_c'}} = \frac{1.4}{\sqrt{2.4 \times 10^{30}}} = 9.04 \times 10^{-16}.$$

15. For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ show that the degree of dissociation of NH_3 is given as

$$\alpha = \left(1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right)^{-1/2}$$

where p is the equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400 °C, determine the value of K_c.

Solution Let α be the degree of dissociation of $NH_3(g)$. We will have

$$\begin{array}{llll} & NH_3(g) & \rightleftharpoons \quad \frac{1}{2}N_2(g) & + \quad \frac{3}{2}H_2(g) \\ t = 0 & n & & \\ t_{eq} & n(1-\alpha) & n\alpha/2 & n(3\alpha/2) \end{array}$$

Total amount of gases $= n(1 + \alpha)$

Now Partial pressure of $NH_3 = \dfrac{1-\alpha}{1+\alpha}\,p$; Partial pressure of $N_2 = \dfrac{\alpha/2}{1+\alpha}\,p$

Partial pressure of $H_2 = \dfrac{(3/2)\alpha}{1+\alpha}\,p$

Hence,
$$K_p = \frac{(p_{N_2})^{1/2}\,(p_{H_2})^{3/2}}{p_{NH_3}} = \frac{\left(\dfrac{\alpha/2}{1+\alpha}p\right)^{1/2}\left(\dfrac{3\alpha/2}{1+\alpha}p\right)^{3/2}}{\left(\dfrac{1-\alpha}{1+\alpha}p\right)} = \left(\frac{3\sqrt{3}}{4}p\right)\left(\frac{\alpha^2}{1-\alpha^2}\right)$$

or
$$4(1-\alpha^2)K_p - 3\sqrt{3}\,\alpha^2 p = 0 \qquad \text{or} \qquad \alpha^2(4K_p + 3\sqrt{3}\,p) = 4K_p$$

or
$$\alpha = \left(\frac{4K_p}{4K_p + 3\sqrt{3}\,p}\right)^{1/2} = \left(\frac{1}{1 + 3\sqrt{3}\,p/4K_p}\right)^{1/2} = \left(1 + \frac{3\sqrt{3}\,p}{4K_p}\right)^{-1/2}$$

Now for the equilibrium reaction, $\Delta\nu_g = +1$. Hence using the expression $K_p = K_c(RT)^{\Delta\nu_g}$, we get

$$K_c = K_p(RT)^{-\Delta\nu_g} = (78.1\ \text{atm})\ \{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (673\ \text{K})\}^{-} = 1.413\ \text{mol L}^{-1}.$$

16. H_2S dissociates according to the equation $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ If α is the degree of dissociation of H_2S, show that K_p of the reaction is given as $K_p = \dfrac{\alpha^3 p}{2(1-\alpha)^2\,(1+\alpha/2)}$

At 1125 °C, the value of the α is found to be 0.31 when the equilibrium pressure is 1 atm. Determine the values of K_p and K_c.

Solution We have

$$\begin{array}{lll} 2H_2S(g) & \rightleftharpoons \quad 2H_2(g) & + \quad S_2(g) \\ n(1-\alpha) & n\alpha & n(\alpha/2); \end{array}$$

Total amount of gases $= n(1 + \alpha/2)$

Hence,
$$p_{H_2S} = \frac{1-\alpha}{1+\alpha/2}\,p; \qquad p_{H_2} = \frac{\alpha}{1+\alpha/2}\,p; \qquad p_{S_2} = \frac{\alpha/2}{1+\alpha/2}\,p$$

Thus,
$$K_p = \frac{(p_{H_2})^2\,(p_{S_2})}{(p_{H_2S})^2} = \frac{\left(\dfrac{\alpha}{1+\alpha/2}p\right)^2\left(\dfrac{\alpha/2}{1+\alpha/2}p\right)}{\left(\dfrac{1-\alpha}{1+\alpha/2}p\right)^2} = \frac{\alpha^3 p}{2(1-\alpha)^2\,(1+\alpha/2)}$$

Substituting the given value of α, we get

$$K_p = \frac{(0.31)^3\,(1\,\text{atm})}{2(1-0.31)^2\,(1+0.31/2)} = 2.71 \times 10^{-2}\ \text{atm}$$

For the given reaction, $\Delta\nu_g = +1$

Hence, $$K_c = K_p\,(RT)^{-\Delta\nu_g} = (2.71 \times 10^{-2}\ \text{atm})\ \{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (1380\ \text{K})\}^{-1}$$

$$= 2.39 \times 10^{-4}\ \text{mol L}^{-1}.$$

17. $COCl_2$ gas dissociates according to the equation $COCl_2 \rightleftharpoons CO + Cl_2$. When $COCl_2$ is heated to 724 K at 1 atm, the density of gas mixture at equilibrium was found to be 1.162 g L^{-1}. Calculate (a) the degree of dissociation and (b) K_p of the reaction.

Solution (a) Let n be the initial amount of $COCl_2$ and α be its degree of dissociation. We will have

$$\begin{array}{lcccc} & COCl_2 & \rightleftharpoons & CO & + & Cl_2 \\ t = 0 & n & & & & \\ t_{eq} & n(1-\alpha) & & n\alpha & & n\alpha \end{array}$$

Total amount of gases $= n(1-\alpha) + n\alpha + n\alpha = n(1+\alpha)$

Now, the volume of the flask would be $V = \dfrac{n\,(1+\alpha)\,RT}{p}$

The density of the mixture would be

$$\rho = \frac{n\,M_{COCl_2}}{V} = \frac{n\,M_{COCl_2}\,p}{n\,(1+\alpha)\,RT} = \frac{p\,M_{COCl_2}}{(1+\alpha)\,RT} \quad \text{or} \quad \alpha = \frac{pM_{COCl_2}}{\rho RT} - 1$$

Substituting the given values, we get

$$\alpha = \frac{(1\,\text{atm})\,(99\,\text{g mol}^{-1})}{(1.162\,\text{g L}^{-1})\,(0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1})\,(724\,\text{K})} - 1 = 1.433 - 1 = 0.433$$

(b) The partial pressures of the species involved in the reactions are

$$p_{COCl_2} = \frac{1-\alpha}{1+\alpha}\,p; \qquad p_{CO} = \frac{\alpha}{1+\alpha}\,p; \qquad p_{Cl_2} = \frac{\alpha}{1+\alpha}\,p$$

Hence, $$K_p = \frac{p_{CO}\,p_{Cl_2}}{p_{COCl_2}} = \frac{\alpha^2}{1-\alpha^2}\,p \quad \text{which gives} \quad K_p = \frac{(0.433)^2}{1-(0.433)^2}\ (1\ \text{atm}) = 0.231\ \text{atm}$$

18. N_2O_4 dissociates according to the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. When 0.578 g of N_2O_4 was introduced into a one litre flask maintained at 308 K, the equilibrium pressure was 0.238 atm. Calculate (a) the degree of dissociation, and (b) K_p of the reaction.

Solution We have

$$\text{Initial amount of } N_2O_4,\ n = \frac{0.578\ \text{g}}{92\ \text{g mol}^{-1}} = 0.00628\ \text{mol}$$

If α is the degree of dissociation of N_2O_4, we will have

$$\begin{array}{lcc} & N_2O_4(g) \rightleftharpoons & 2NO_2(g) \\ t = 0 & n & \\ t_{eq} & n(1-\alpha) & n(2\alpha); \end{array}$$

Total amount of gases $= n(1-\alpha) + 2n\alpha = n(1+\alpha)$

Now using the expression $pV = n\,(1+\alpha)\,RT$, we get

$$\alpha = \frac{pV}{nRT} - 1 = \frac{(0.238\,\text{atm})\,(1\,\text{L})}{(0.00628\,\text{mol})\,(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})\,(308\,\text{K})} - 1 = 0.5$$

Now $$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\,p = \frac{0.5}{1.5} \times 0.238\ \text{atm} = 0.0793\ \text{atm}$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha}\ p = \frac{2\times 0.5}{1.5} \times 0.238 \text{ atm} = 0.159 \text{ atm}$$

Hence, $$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} = \frac{(0.159 \text{ atm})^2}{(0.793 \text{ atm})} = 0.319.$$

19. $PCl_5(g)$ dissociates according to the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. At 523 K, $K_p = 1.78$ atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

Solution Let α be the degree of dissociation of PCl_5. We will have

$$\begin{array}{ccccc} PCl_5(g) & \rightleftharpoons & PCl_3(g) & + & Cl_2(g) \\ n(1-\alpha) & & n\alpha & & n\alpha \end{array}$$

Total amount of gases= $n\ (1 + \alpha)$

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha}\ p;\quad p_{PCl_3} = \frac{\alpha}{1+\alpha}\ p;\quad p_{Cl_2} = \frac{\alpha}{1+\alpha}\ p$$

Hence, $$K_p = \frac{p_{PCl_3}\ p_{Cl_2}}{p_{PCl_5}} = \frac{\alpha^2}{1-\alpha^2}\ p = \frac{\alpha^2}{1-\alpha^2} \qquad (\text{since } p = 1 \text{ atm})$$

or $$\alpha = \sqrt{\frac{K_p}{1+K_p}} = \sqrt{\frac{1.78}{1+1.78}} = 0.8$$

Now, the volume of mixture is

$$V = \frac{n(1+\alpha)\ RT}{p} = \frac{n(1+0.8)\ (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\ (523 \text{ K})}{(1 \text{ atm})} = (77.29\ n) \text{ L mol}^{-1}$$

Finally, the density of mixture is $$\rho = \frac{m}{V} = \frac{n M_{PCl_5}}{V} = \frac{n(208.5 \text{ g mol}^{-1})}{(77.29 n) \text{ L mol}^{-1}} = 2.70 \text{ g L}^{-1}.$$

20. Sulphur trioxide dissociates on heating $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$. A sample of 0.63 g of SO_3 is placed in a 1.0 L container and heated to a temperature of 1100 K. The equilibrium total pressure at this temperature is 1.0 atm. Calculate (a) degree of dissociation of SO_3 and (b) K_p and K_c of the reaction.

Solution If α is the degree of dissociation of SO_3, we get

$$\begin{array}{ccccc} 2\ SO_3(g) & \rightleftharpoons & 2SO_2(g) & + & O_2(g) \\ n(1-\alpha) & & n\alpha & & n(\alpha/2) \end{array}$$

Total amount of gases = $n\ (1 + \alpha/2)$

Using ideal gas equation, we get

$$pV = n\ (1 + \alpha/2)RT$$

$$(1 \text{ atm})(1.0 \text{ L}) = \left(\frac{0.63}{80} \text{ mol}\right)\left(1+\frac{\alpha}{2}\right)\ (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(1100 \text{ K})$$

This gives $$\alpha = 2\left[\frac{80}{0.63\times 0.0821\times 1100} - 1\right] = 2\ [1.406 - 1] = 0.81$$

Now $$p_{SO_3} = \frac{1-\alpha}{1+\alpha/2}\ p = \frac{0.19}{1.405}\ (1 \text{ atm}) = 0.135 \text{ atm};\quad p_{SO_2} = \frac{\alpha}{1+\alpha/2}\ p = \frac{0.81}{1.405}\ (1 \text{ atm}) = 0.577 \text{ atm}$$

$$p_{O_2} = \frac{\alpha/2}{1+\alpha/2}\ p = \frac{0.405}{1.405}\ (1 \text{ atm}) = 0.288 \text{ atm}$$

Hence, $$K_p = \frac{(p_{SO_2})^2\ (p_{O_2})}{(p_{SO_3})^2} = \frac{(0.577 \text{ atm})^2\ (0.288 \text{ atm})}{(0.135 \text{ atm})^2} = 5.26 \text{ atm}$$

Finally, since $K_p = K_c(RT)^{\Delta \nu g}$, we get

$$K_c = K_p(RT)^{-\Delta \nu g} = (5.26\ \text{atm})[(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (1100\ \text{K})]^{-1} = 5.82 \times 10^{-2}\ \text{mol L}^{-1}.$$

21. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 348 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Solution Let n be the amount of N_2O_4 at $t = 0$ and let α be the degree of dissociation of N_2O_4 at equilibrium. Then

$$\begin{array}{lccc} & N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ t = 0 & n & & 0 \\ t_{eq} & n(1-\alpha) & & n(2\alpha) \end{array}$$

Total amount at equilibrium= $n(1 + \alpha)$.

Using the ideal gas equation, we get

$$pV = n(1+\alpha)\,RT = \frac{m}{M}(1+\alpha)\,RT$$

or $$pM = \rho\,(1+\alpha)\,RT \quad \text{or} \quad \alpha = \frac{pM}{\rho RT} - 1$$

Substituting the given data, we get

$$\alpha = \frac{(1\ \text{atm})\,(92\ \text{g mol}^{-1})}{(1.84\ \text{g dm}^{-3})\,(0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})\,(348\ \text{K})} - 1 = 1.752 - 1 = 0.752$$

Hence, $$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{[2\alpha\, p/(1+\alpha)]^2}{(1-\alpha)\,p/(1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2}\,p = \frac{4(0.752)^2}{1-0.752^2}\,(1\ \text{atm}) = 5.206\ \text{atm}.$$

22. At 300 K, the equilibrium constant K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.174 atm. What would be the average molar mass of an equilibrium mixture of N_2O_4 and NO_2 formed by the dissociation of pure N_2O_4 at a total pressure of 1 atm at this temperature?

Solution We have

$$\begin{array}{ccc} N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ c(1-\alpha) & & c(2\alpha) \end{array}$$

Total amount of gases = $c(1 - \alpha) + c(2\alpha) = c(1 + \alpha)$

Now $$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P; \qquad p_{NO_2} = \frac{2\alpha}{1+\alpha}P. \quad \text{Hence,} \quad K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{4\alpha^2}{1-\alpha^2}P$$

Substituting $P = 1$ atm and $K_p = 0.174$ atm, we get $\dfrac{4\alpha^2}{1-\alpha^2} = 0.174$

Solving for α, we get $\alpha = \sqrt{\dfrac{0.174}{4.174}} = 0.204$

Now $$x_{N_2O_4} = \frac{p_{N_2O_4}}{P} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.204}{1+0.204} = 0.661$$

$$x_{NO_2} = \frac{p_{NO_2}}{P} = \frac{2\alpha}{1+\alpha} = \frac{2(0.204)}{1+0.204} = 0.339$$

$$\begin{aligned} M_{\text{apparent}} &= x_{N_2O_4}M_{N_2O_4} + x_{NO_2}M_{NO_2} = (0.661)\,(92.0\ \text{g mol}^{-1}) + (0.339)\,(46.0\ \text{g mol}^{-1}) \\ &= 76.5\ \text{g mol}^{-1} \end{aligned}$$

23. The equilibrium constant for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is 0.3 atm at 1000 K. One mole of SO_2 and two moles of O_2 are placed in a vessel that is maintained at a pressure of 4 atm. How much SO_3 is present at equilibrium?

Solution We have

$$\begin{array}{lccc} & 2SO_3(g) & \rightleftharpoons \quad 2SO_2(g) & + \quad O_2(g) \\ t = 0 & 0 & 1\ \text{mol} & 2\ \text{mol} \\ t_{eq} & 2x & 1\ \text{mol} - 2x & 2\ \text{mol} - x \end{array}$$

Total amount of gases at equilibrium = $2x + (1\ \text{mol} - 2x) + (2\ \text{mol} - x) = 3\ \text{mol} - x$

Now $$p_{SO_3} = \frac{2x}{3\,\text{mol} - x}P; \qquad p_{SO_2} = \frac{1\,\text{mol} - 2x}{3\,\text{mol} - x}P; \qquad p_{O_2} = \frac{2\,\text{mol} - x}{3\,\text{mol} - x}P$$

$$K_p = \frac{p_{SO_3}^2\, p_{O_2}}{p_{SO_3}^2} = \frac{(1\,\text{mol} - 2x)^2\,(2\,\text{mol} - x)\,P}{(2x)^2\,(3\,\text{mol} - x)}$$

At $P = 4$ atm, we get $$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3\,(3\,\text{mol} - x)}{(2\,\text{mol} - x)} \qquad (1)$$

To start with, we may assume $x \ll 2$ mol. With this, Eq. (1) becomes

$$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3 \times 3}{2} \quad \text{or} \quad \frac{1\,\text{mol} - 2x}{x} = \sqrt{0.45} = 0.671 \quad \text{or} \quad x = \frac{1\,\text{mol}}{2.671} = 0.374\ \text{mol}$$

Substituting this value of x in the right hand side of Eq. (1), we get

$$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3 \times 2.626}{1.626} = 0.484\,5 \quad \text{or} \quad \frac{1\,\text{mol} - 2x}{x} = 0.696 \quad \text{or} \quad x = \frac{1\,\text{mol}}{2.696} = 0.371\ \text{mol}$$

Repeating again with this new value of x, we again get $x = 0.371$ mol.

Hence, the concentration of SO_3 at equilibrium is 2×0.371 mol = 0.742 mol.

24. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fractions of N_2 and O_2. (1997)

Solution Let there be 100 mol of the three gases at equilibrium. We will have

$$\underbrace{N_2(g) + O_2(g)}_{98.2\ \text{mol}} \rightleftharpoons \underbrace{2NO(g)}_{1.8\ \text{mol}}$$

Let x be the amount of N_2 in the mixture. Then

$$\begin{array}{cccc} N_2(g) & + \quad O_2(g) & \rightleftharpoons & 2NO(g) \\ x & 98.2\ \text{mol} - x & & 1.8\ \text{mol} \end{array}$$

Using the equilibrium constant, we get

$$\frac{[NO]^2}{[N_2][O_2]} = 2.1 \times 10^{-3} \qquad \text{i.e.} \qquad \frac{(1.8\ \text{mol})^2}{x(98.2\ \text{mol} - x)} = 2.1 \times 10^{-3}$$

Solving for x, we get $x = 78.56$ mol

In the original air sample. We will have

Amount of N_2 = (78.56 + 0.9) mol = 79.46 mol
Amount of O_2 = (98.2 – 78.56 + 0.9) mol = 20.54 mol
Mole fraction of N_2 = 0.79 and Mole fraction of O_2 = 0.21

25. For the reaction, $N_2O_5(g) = 2NO_2(g) + 0.5\ O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at constant volume and temperature, if the initial pressure is 600 mmHg and the pressure at any time is 960 mmHg. Assuming ideal gas behaviour. (1998)

Solution If p is the partial pressure of N_2O_5 that has decomposed,

$$\begin{array}{lll} N_2O_5(g) & \rightleftharpoons\ 2NO_2(g) & +\ \tfrac{1}{2}O_2(g) \\ 600\ \text{mmHg}-p & \quad 2p & \quad p/2 \end{array}$$

Pressure at any time = $(600\ \text{mmHg} - p) + 2p + p/2 = 600\ \text{mmHg} + (3/2)p$

Equating this to 960 mmHg, we get $p = (2/3)\ (960 - 600)\ \text{mmHg} = 244\ \text{mmHg}$

The mole fraction of N_2O_5 decomposed would be $x = \dfrac{244\ \text{mmHg}}{600\ \text{mmHg}} = 0.407$

26. When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27 °C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27 °C. (ii) What would happen to equilibrium when more solid NH_4HS is introduced into the flask? (1999)

Solution The reaction along with the given data is

	$NH_4HS(s)\ \rightleftharpoons$	$NH_3(g)$ +	$H_2S(g)$
$t = 0$	3.06 g (= 0.06 mol)	0	0
t_{eq}	0.7×0.06 mol	0.3×0.06 mol = 0.018 mol	0.3×0.06 mol = 0.018 mol

(i) The equilibrium constant K_c is

$$K_c = [NH_3]\ [H_2S] = \left(\frac{0.018\ \text{mol}}{2\ \text{L}}\right)\left(\frac{0.018\ \text{mol}}{2\ \text{L}}\right) = 8.1 \times 10^{-5}\ (\text{mol/L})^2$$

The equilibrium constant K_p is

$$K_p = K_c\ (RT)^{\Delta \text{vg}} = (8.1 \times 10^{-5}\ \text{mol}^2/\text{L}^2)\ [(0.082\ \text{atm L mol}^{-1}\ \text{K}^{-1})\ (300\ \text{K})]^2$$

$$= 4.90 \times 10^{-2}\ \text{atm}^2$$

(ii) There will not be any effect on the equilibrium by introducing more of solid NH_4HS as the equilibrium constant is independent of the quantity of solid.

27. (a) the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is carried out at 298 K and 20 bar. Five moles of each of N_2O_4 and NO_2 are taken initially. Determine Δ_rG and K_p° at 298 K. Given: $\Delta_fG^\circ\ (N_2O_4) = 100\ \text{kJ mol}^{-1}$ and $\Delta_fG^\circ\ (NO_2) = 50\ \text{kJ mol}^{-1}$.

(b) The reaction proceeds at a initial pressure of 20 bar. Determine the direction in which the reaction proceeds to achieve equilibrium. Also determine the amounts of N_2O_4 and NO_2 when the reaction attains equilibrium. (2004)

Solution (a) Initially we have

$$p(NO_2) = x_{NO_2}\ p = \left(\frac{5\ \text{mol}}{10\ \text{mol}}\right)(20\ \text{bar}) = 10\ \text{bar}$$

$$p(N_2O_4) = x_{N_2O_4}\ p = \left(\frac{5\ \text{mol}}{10\ \text{mol}}\right)(20\ \text{bar}) = 10\ \text{bar}$$

$$Q_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{(10\ \text{bar})^2}{(10\ \text{bar})} = 10\ \text{bar}$$

For the given reaction,

$$\Delta_r G^\circ = 2\Delta_f G^\circ(\mathrm{NO_2}) - \Delta_f G^\circ(\mathrm{N_2O_4}) = 2\ (50\ \mathrm{kJ\ mol^{-1}}) - 100\ \mathrm{kJ\ mol^{-1}} = 0$$

From the expression

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_p^\circ$$

we get $\Delta_r G = 0 + (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (298\ \mathrm{K})\ \ln (10) = (8.314 \times 298 \times 2.303)\ \mathrm{J\ mol^{-1}}$

$= 5705.8\ \mathrm{J\ mol^{-1}}$

The value of K_p° of the reaction is given by $\Delta_r G^\circ = -RT \ln K_p^\circ$.
Since $\Delta_r G^\circ = 0$, $K_p^\circ = 1$
Since initially $Q_p^\circ > K_p^\circ$, the reaction will proceed in the reverse direction.

(b) We will have

$$\mathrm{N_2O_4(g)} \rightleftharpoons \mathrm{2NO_2(g)}$$

$5\ \mathrm{mol} + x$ $\qquad$ $5\ \mathrm{mol} - 2x$; total amount $= 10\ \mathrm{mol} - x$

where x is the amount of N_2O_4 formed at equilibrium.

$$p_{\mathrm{N_2O_4}} = \frac{5\ \mathrm{mol} + x}{10\ \mathrm{mol} - x}\ (20\ \mathrm{bar}) \quad \text{and} \quad p_{\mathrm{NO_2}} = \frac{5\ \mathrm{mol} - 2x}{10\ \mathrm{mol} - x}\ (20\ \mathrm{bar})$$

Since $K_p^\circ = 1$, we get

$$\frac{p_{\mathrm{NO_2}}^2}{p_{\mathrm{N_2O_4}}} = 1\ \mathrm{bar} \quad \text{or} \quad p_{\mathrm{NO_2}}^2 = (1\ \mathrm{bar})\ p_{\mathrm{N_2O_4}}$$

or $$\left[\frac{5\ \mathrm{mol} - 2x}{10\ \mathrm{mol} - x}(20)\right]^2 = \frac{5\ \mathrm{mol} + x}{10\ \mathrm{mol} - x}\ (20)$$

or $$20\ (5\ \mathrm{mol} - 2x)^2 = (5\ \mathrm{mol} + x)\ (10\ \mathrm{mol} - x)$$

or $$500\ \mathrm{mol^2} + 80\ x^2 - 400\ x\ \mathrm{mol} = 50\ \mathrm{mol^2} + 5\ x\ \mathrm{mol} - x^2$$

or $$81x^2 - 405\ x\ \mathrm{mol} + 450\ \mathrm{mol^2} = 0$$

or $$x = \frac{(405\ \mathrm{mol}) \pm \sqrt{(405\ \mathrm{mol})^2 - 4\ (81)\ (450\ \mathrm{mol^2})}}{2 \times 81}$$

This gives $x = 3.333$ mol or $x = 1.667$ mol
Since $2x$ cannot be more than 5 mol, we get

$$x = 1.667\ \mathrm{mol}$$

Hence, $n(\mathrm{N_2O_4}) = 5\ \mathrm{mol} + x = 6.667\ \mathrm{mol}$ and $n(\mathrm{NO_2}) = 5\ \mathrm{mol} - 2x = 1.667\ \mathrm{mol}$

UNSOLVED PROBLEMS

1. A mixture of 0.373 atm of NO(g) and 0.310 atm of Cl_2(g) is prepared at 500 K. The reaction

$$\mathrm{2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)}$$

takes place. The total pressure at equilibrium is 0.544 atm. Determine K_p for the reaction.

2. The decomposition of ammonium carbamate at 30 °C is represented as

$$\mathrm{NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)} \qquad K_p = 2.9 \times 10^{-5}\ \mathrm{atm^3}$$

What is the total pressure of gases in equilibrium with NH_2COONH_4(s) at 30 °C?

3. 25 mol of H_2 and 18 mol of I_2(g) were heated in a 1- L sealed tube at 465 °C when at equilibrium 30.8 mol of HI were formed. Calculate the degree of dissociation of HI if the reaction was started with pure HI.

4. For the reaction $\mathrm{I_2(g) \rightleftharpoons 2\ I(g)}$, $K_c^\circ = 1.0 \times 10^{-2}$. What volume of the vessel should be taken so that at equilibrium 1.0 mol of I_2 and 0.5 mol of I are present at equilibrium?

5. 0.39 mol SO_2, 0.156 mol O_2 and 0.657 mol SO_3 are introduced simultaneously into a 1.90-L reaction vessel at 1000 K. (a) Is the mixture at equilibrium? (b) If not, in which direction (forward or backward) would the reaction proceed? (c) Calculate the amounts of species at equilibrium. Given :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c^\circ = 2.8 \times 10^2$$

6. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, at equilibrium, the partial pressures of N_2O_4 and NO_2 were found to be 0.28 atm and 1.1 atm, respectively. If the volume of the container is doubled, calculate the equilibrium pressures of the two gases when the system reaches a new equilibrium state.

7. NO_2 is placed in a container at 1000 K with an initial pressure of 1.0 atm. At equilibrium the total pressure is 1.493 atm. Find K_p for the reaction.

8. Show that K_p for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is given by the expression

$$K_p = \frac{\alpha^3 p}{(2+\alpha)(1-\alpha)^2}$$

where α is the degree of dissociation and p is the total equilibrium pressure. Calculate K_c° of the reaction if α at 298 K and 1 atm pressure is 0.055.

9. $PCl_5(g)$ dissociates according to the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. At 250 °C, $K_p^\circ = 1.78$. Find the density of the equilibrium mixture at a total pressure of 2 atm.

10. For the reaction $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$, $K_p^\circ = 1.45 \times 10^{-5}$ at 1625 K. What is the dissociation pressure of $CaSO_4$ in mmHg at 1625 K?

11. At 3000 K and 1 atm, CO_2 is 40% dissociated into CO and O_2. (a) What will be the degree of dissociation if the pressure is raised to 2 atm? (b) What will be the degree of dissociation when a mixture of 50% CO_2 and 50% O_2 is heated at 3000 K, the pressure being 1 atm?

12. What amount (i.e. number of moles) of phosphorus pentachloride must be added to 1.0-L vessel at 250 °C to obtain a concentration of 0.1 mol of chlorine per litre? Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $K_p^\circ = 1.80$.

13. Calculate the total pressure at 4000 °C that must be applied to a mixture of three parts of hydrogen and one part of nitrogen to give a mixture containing 10% ammonia at equilibrium.

Given: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_p = 1.60 \times 10^{-4}\ \text{bar}^{-2}$ at 400 °C.

14. The equilibrium constant for the reaction $2SO_3 \rightleftharpoons 2SO_2 + O_2$ is 0.30 atm at 1000 K. One mol of SO_2 and 2 mol of O_2 are placed in a vessel that is maintained at a pressure of (a) 2 atm and (b) 8 atm. How much SO_3 is present at equilibrium?

15. At 460 °C, $K_c = 85.0$ for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$. A mixture of these gases has the following concentrations of the reactants and products :

$[SO_2] = 0.04$ M; $[NO_2] = 0.50$ M; $[NO] = 0.30$ M; $[SO_3] = 0.02$ M

Is this system at equilibrium? If not, in which direction must the reaction proceed to reach equilibrium. What will be the molar concentrations of the four gases at equilibrium?

16. 0.1 mol each of SO_2 and SO_3 are mixed in a 2.0 dm³ flask at 300 K. Equilibrium is attained as

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The equilibrium pressure is 281.68 kPa. Calculate (a) the mole fraction of O_2 at equilibrium, (b) K_p, and (c) the percentage dissociation of SO_3 if initially the flask contained 0.1 mol of SO_3 and none of O_2 and SO_2.

17. In a study of the water gas reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, a mixture of CO_2 and H_2 initially containing 42.4 mol % H_2 was brought to equilibrium in a closed vessel at 1259 K. The system was then found to contain 15.2 mol % H_2. Calculate K_p of the reaction.

18. Solid NH_4HS dissociates according to the equation $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$. The dissociation pressure of solid NH_4HS is 66.87 kPa at 298 K. Calculate K_p° for this reaction. What fraction of NH_4HS dissociates if 0.1 mol of NH_4HS is introduced into a 1 dm³ flask that contains NH_3 at 20.265 kPa and 298 K?

19. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g L^{-1} at 298 K. What is the value of K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$?

20. The dissociation pressure of HgO (reaction : $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2} O_2(g)$) is 51.56 kPa at 693 K . What is the value of K_p for this dissociation reaction?

21. The value of the K_p° for the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$ is 8.32 at 1 atm and 600 °C. Calculate K_p° for the reactions

(a) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$; (b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ and (c) $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$

22. If the decomposition reaction $4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$ is started with pure HNO_3, then show that

$$K_p = \frac{1024\,(p_{O_2})^7}{\left(p - 7p_{O_2}\right)^4}$$

where p is the total pressure at equilibrium.

23. A 2-L flask maintained at 700 K contains 0.1 mol of CO and a catalyst for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the equilibrium total pressure is 7 atm at which point 0.06 mol of methanol is formed. Calculate K_p° of the reaction. What would be the final pressure if the same amounts of CO and H_2 are used, but no catalyst is present such that no reaction occurs.

24. It is required to pass CO and H_2O vapours at 10 atm and 5 atm, respectively, into a reaction chamber at 973 K and to withdraw CO_2 and H_2 at partial pressures of 15 atm each. Is this theoretically possible? K_p° for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 0.71.

25. NOCl(g) was introduced in a 1 L vessel and heated so as to attain equilibrium

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

At equilibrium, [NOCl] = 0.1 M. Now more of NOCl is introduced till a new equilibrium is reached such that [NOCl] = 0.8 M. How are the concentrations of NO and Cl_2 get affected?

ANSWERS

1. 50.08 atm^{-1}
2. 0.0582 atm
3. 0.245
4. 25 L
5. No, forward, 0.079 mol O_2, 0.236 mol SO_2 and 0.811 mol SO_3
6. $p(NO_2)$ = 0.64 atm and $p(N_2O_4)$ = 0.095 atm
7. 2.026×10^3 atm
8. 3.7×10^{-6}
9. 5.76 g dm^{-3}
10. 34.95 mmHg
11. (a) 0.335, (b) 0.271
12. 0.341 mol
13. 23.1 bar
14. (a) 0.672 mol, (b) 0.802 mol
15. No, right direction
16. 0.115, 3.08×10^{-3} kPa^{-1}, 72.6
17. 1.602
18. 0.109,0.1
19. 0.023
20. 0.14
21. 0.01445, 69.22, 0.1202
23. 0.088, 10.44 atm
24. No
25. The concentrations of each of NO and Cl_2 becomes four times.

SECTION II || IONIC EQUILIBRIUM IN AQUEOUS SOLUTIONS

Ionization of a Weak Electrolyte

A weak electrolyte in a solution involves an equilibrium between the undissociated species and the corresponding dissociated species. For example, for acetic acid, we have

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The equilibrium constant of the above reaction is given as $K_{eq} = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$

Since water is present in large amount, its concentration remains constant. Hence, a new constant, known as *ionization* or *dissociation constant*, is defiend as

$$K_a = K_{eq}[H_2O] = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

The extent of dissociation of a weak electrolyte is usually represented by the physical quantity known as *degree of dissociation*. This is defined as the fraction of the total substance present in the form of ions. If α is the degree of dissociation, it means that the amount α out of 1 mol of the substance is present in the form of ions and the remaining fraction, namely $1 - \alpha$, is present in the form of undissociated species.

For example for acetic acid, we can write

$$\begin{array}{lcccc} & CH_3COOH + H_2O & \rightleftharpoons & CH_3COO^- & + \; H_3O^+ \\ \text{Fraction of substance} & 1-\alpha & & \alpha & \alpha \end{array}$$

If c is the concentration of acetic acid, then we will have

$$\begin{array}{lcccc} & CH_3COOH + H_2O & \rightleftharpoons & CH_3COO^- & + \; H_3O^+ \\ \text{Concentration} & c(1-\alpha) & & c\alpha & c\alpha \end{array}$$

Thus, $$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad (5)$$

For a weak electrolyte, $\alpha \ll 1$ and hence can be ignored in comparison to 1. Thus, the above expression becomes

$$K_a = c\,\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \qquad (6)$$

On dilution, c decreases and α increases. In the limit when $c \to 0$ (infinite dilution), α approaches 1, i.e. at infinite dilution, the entire weak electrolyte is present in the dissociated form. This fact is known as the **Ostwald dilution law**.

Ionization of Pure Water Pure water also ionizes as shown in the following reaction.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Its equilibrium constant is $K_{eq} = \dfrac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$

The concentration of water remains constant since it is very poorly ionized. Keeping this in mind, the following two new constants are defined.

$$K_{ioniz} = K_{eq}[H_2O] = \frac{[H_3O^+][OH^-]}{[H_2O]} \quad \text{and} \quad K_w = K_{ioniz}[H_2O] = [H_3O^+]\,[OH^-]$$

The constants K_{ioniz} and K_w are known as *ionization constant* and *ionic product of water*, respectively. At 25 °C, $K_w = 1.0 \times 10^{-14}\ M^2$.

pH Scale The concentration of H_3O^+ in an aqueous solution is conveniently expressed in terms of pH, defined as

$$pH = -\log\{[H_3O^+]/\text{mol dm}^{-3}\}$$

Similarly, we have the expressions of pOH and pK_w^o:

$$pOH = -\log\{[OH^-]/\text{mol dm}^{-3}\}; \qquad pK_w^o = -\log(K_w/\text{mol}^2\ \text{dm}^{-6})$$

Obviously, $pK_w^o = pH + pOH$

The value of pK_w is 14 at 25 °C. The nature of the solution (whether acidic or alkaline) can be defined in terms of $[H^+]$ (or pH) and $[OH^-]$ (or pOH). We have

Neutral solution $[H_3O^+] = [OH^-]$; $pH = pOH$
Acidic solution $[H_3O^+] > [OH^-]$; $pH < pOH$
Alkaline solution $[H_3O^+] < [OH^-]$; $pH > pOH$

At 25 °C, the above criteria are

Neutral solution $[H_3O^+] = [OH^-] = 10^{-7}$ M : $pH = pOH = 7$
Acidic solution $[H_3O^+] > 10^{-7}$ M; $pH < 7$ and $[OH^-] < 10^{-7}$ M; $pOH > 7$
Alkaline solution $[H_3O^+] < 10^{-7}$ M; $pH > 7$ and $[OH^-] > 10^{-7}$ M; $pOH < 7$

Solubility Product For a sparingly soluble salt, undissolved solid salt exists in equilibrium with its characteristic ions in the solution. For example

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq);\ CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq);\ Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Such an equilibrium is characterized by a constant known as the *solubility product constant*. It is defined as the product of ionic concentrations present in a saturated solution, each raised to a power equal to the corresponding stoichiometric coefficient of ion in the balanced chemical equation for the solution process. A few examples are

$$K_{sp}(AgCl) = [Ag^+][Cl^-];\ K_{sp}(CaF_2) = [Ca^{2+}][F^-]^2;\ K_{sp}(Ca_3(PO_4)_2) = [Ca^{2+}]^3[PO_4^{3-}]^2$$

The numerical value of solubility product constant of a salt at a given temperature (usually recorded at 25 °C) provides the maximum solubility of the salt in water.

For example, if x is the solubility of CaF_2 in the solution, we will have

$$CaF_2(s \rightleftharpoons \underset{x}{Ca^{2+}} + \underset{2x}{2F^-};\quad \text{Hence,}\quad K_{sp} = [Ca^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$$

For $Ca_3(PO_4)_2$, we will have $Ca_3(PO_4)_2 \rightleftharpoons \underset{3x}{3Ca^{2+}} + \underset{2x}{2PO_4^{3-}}$; $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 = 108x^5$

For a solution of a salt at specified concentration, the product of the concentrations of ions, each raised to a power equal to the stoichiometric number, is known as ionic product. For a saturated solution

Ionic product = Solubility product

and for an unsaturated solution Ionic product < Solubility product

If the ionic product exceeds the solubility product, then the solution is holding more salt that can dissolve in it. Such a solution is unstable and leads to the pecipitation of the salt. This precipitation continues till the ionic product becomes equal to the solubility product.

Common Ion Effect In a solution, if an electrolyte containing an ion already present in equilibrium is added, it affects the equilibrium in accordance with Le Chatelier's principle. For example, the addition of NH_4Cl in NH_4OH solution suppresses the ionization of the latter.

Acid-Base Equilibria According to Bronsted and Lowry, proton donor is an acid whereas proton acceptor is a base. Thus, acid and base pair exist together in a solution. For example,

$$\underset{\text{acid}_1}{CH_3COOH} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{base}_1}{CH_3COO^-} + \underset{\text{acid}_2}{H_3O^+}$$

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{base}_1}{Cl^-} + \underset{\text{acid}_2}{H_3O^+};\quad \underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_1}{NH_4^+} + \underset{\text{base}_2}{OH^-}$$

An acid with a strong tendency to donate a proton will have its conjugate base with least tendency to accept the proton and vice versa. Table 7.1 records some common conjugate acid-base pairs showing the interdependent relationship of their strengths.

Table 7.1 Common Conjugate Acid-Base Pairs

Increasing order ⟶

Acid		*Conjugate base*	
Name	*Formula*	*Formula*	*Name*
Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
Sulphuric acid	H_2SO_4	HSO_4^-	Hydrogen sulphate ion
Hydroiodic acid	HI	I^-	Iodide ion
Hydrobromic acid	HBr	Br^-	Bromide ion
Hydrochloric acid	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogen sulphate ion	HSO_4^-	SO_4^{2-}	Sulphate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Nitrous acid	HNO_2	NO_2^-	Nitrite ion
Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion
Carbonic acid	H_2CO_3	HCO_3^-	Bicarbonate ion
Hydrogen sulphide	H_2S	HS^-	Hydrogen sulphide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Water	H_2O	OH^-	Hydroxide ion
Ammonia	NH_3	NH_2^-	Amide ion

Increasing order ⟶

All acids which are stronger than H_3O^+ are completely ionized in aqueous solution. Similarly, all bases which are stronger than OH^- are completely ionized in aqueous solution. This fact is known as the *levelling effect*. The strongest acid and base which can exist in water are H_3O^+ and OH^-, respectively. The levelling effect is also observed in non-aqueous medium. For example, the strongest acid and base in NH_3 are NH_4^+ and NH_2^- ions, respectively.

According to Lewis, an electron-pair acceptor is an acid whereas an electron-pair donor is a base.

Hydrolysis of Salts A salt containing a strong conjugate acid (or/and strong conjugate base) undergoes hydrolysis reaction in which the species reacts with water to give undissociated weak base (or acid) and form H_3O^+ (or OH^-) ions. For example

$$\underset{\text{strong conjugate base}}{CH_3COO^-} + H_2O \rightleftharpoons \underset{\text{weak acid}}{CH_3COOH} + OH^-; \quad \underset{\text{strong conjugate acid}}{NH_4^+} + H_2O \rightleftharpoons \underset{\text{weak base}}{NH_4OH} + H_3O^+$$

Thus, an aqueous solution of such a salt is either acidic or alkaline depending upon the conjugate ion. For example, a solution of sodium acetate is alkaline whereas that of ammonium chloride is acidic. A hydrolysis reaction can be treated like any other equilibrium reaction. For example, the hydrolysis constants for acetate and ammonium ions are

$$K_h(CH_3COO^-) = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{[H_3O^+][OH^-]}{[CH_3COO^-][H_3O^+]/[CH_3COOH]} = \frac{K_w}{K_a}$$

$$K_h(NH_4^+) = \frac{[NH_4OH][H_3O^+]}{[NH_4^+]} = \frac{[H_3O^+][OH^-]}{[NH_4^+][OH^-]/[NH_4OH]} = \frac{K_w}{K_b}$$

where K_a and K_b are the ionization constants of acetic acid and ammonium hydroxide, respectively.

For a salt of a weak acid and a weak base, such as ammonium acetate, the hydrolysis constant is given as

$$K_h = \frac{K_w}{K_a\,K_b}$$

The pH of sodium acetate and ammonium chloride solutions can be obtained considering the hydrolysis reactions. For example, for sodium acetate solution, we have

$$K_h = \frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{[OH^-]^2}{[salt]} \quad \text{or} \quad [OH^-] = \left(\frac{K_w\,[salt]}{K_a}\right)^{1/2}$$

or $$pOH = \tfrac{1}{2}pK_w^o - \tfrac{1}{2}pK_a^o - \tfrac{1}{2}\log\,([salt]/M)$$

Similarly, for ammonium chloride solution, we have

$$pH = \tfrac{1}{2}pK_w^o - \tfrac{1}{2}pK_b^o - \tfrac{1}{2}\log\,([salt]/M)$$

For a salt formed from a weak acid and a weak base, such as ammonium acetate, we have

$$NH_4^+ + Ac^- + H_2O \rightleftharpoons NH_4OH + HAc$$

$$K_h = \frac{[NH_4\,OH][HAc]}{[NH_4^+][Ac^-]} = \frac{[NH_4OH]}{[NH_4^+][OH^-]}\,\frac{[HAc]}{[Ac^-][H^+]}[H^+][OH^-] = \frac{K_W}{K_aK_b}$$

To determine the pH of such a solution, we set $[NH_4OH] = [HAc]$ and $[NH_4^+] = [Ac^-]$

Thus get $$\frac{[HAc]^2}{[Ac^-]^2} = \frac{K_w}{K_aK_b} \quad \text{i.e.} \quad \frac{[H^+]^2}{K_a^2} = \frac{K_w}{K_aK_b} \quad \text{or} \quad [H^+] = \sqrt{\frac{K_wK_a}{K_b}}$$

or $$pH = \tfrac{1}{2}\,(pK_w^o + pK_a^o - pK_b^o)$$

Buffer Solutions A solution which resists the change in its pH value when a small amount of acid or alkali is added to it is known as buffer solution. Such a solution can be prepared by mixing weak acid with the salt of its conjugate base (acidic buffer solution) or mixing weak base with the salt of its conjugate acid (alkaline buffer solution). A solution of salt of a weak acid and a weak base, such as ammonium acetate, also has buffer characteristics.

The pH of a buffer solution containing weak acid and salt of its conjugate base is given by the expression

$$pH = pK_a^o + \log\frac{[\text{salt}]}{[\text{acid}]}$$

For a buffer solution containing a weak base and salt of its conjugate acid, the expression is

$$pOH = pK_b^o + \log\frac{[\text{salt}]}{[\text{base}]}$$

The above expressions of pH and pOH are known as Henderson's equations.

Straight Objective Type

pH of a Solution

1. At 25 °C the pH of a 10^{-8} molar solution of HCl in water is
(a) 8 (b) −8 (c) between 7 and 8 (d) between 6 and 7 (1981)

2. At 90 °C pure water has $[H_3O^+] = 10^{-6}$ mol litre^{-1}. The value of K_w^o at 90 °C is
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8} (1981)

3. Which of the following solutions will have pH close to 1.0?
(a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
(b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH (1992)

4. The pH of pure water is 6.5. Its temperature is
(a) more than 25 °C (b) less than 25 °C (c) equal to 25 °C (d) zero kelvin

5. The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. The pK_a of the acid is about
(a) 4.6 (b) 5.6 (c) 6.0 (d) 6.2

6. The pH of the solution when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) will be about
(a) 9.3 (b) 10.3 (c) 11.3 (d) 11.8

7. The ionic product of water at 100 °C is 49 times that at 25 °C. The pH of pure water at 100 °C is about
(a) 5.15 (b) 5.75 (c) 7.15 (d) 6.15

8. On adding 10^{-3} mol of NaOH to 1.0 dm^3 of water at 25°C, the pH of water
(a) increases about by 2 (b) increases about by 4
(c) decreases about by 2 (d) decreases about by 4

9. The pH of a solution is 3. Its pH is to be raised to 6, then the $[H^+]$ of the original solution has to be
(a) doubled (b) increased 10^3 times (c) halved (d) decreased 10^3 times

10. Water has $pK_w^o = 13.26$ at 50 °C. Its pH will be
(a) 6.0 (b) 7.0 (c) 6.63 (d) 13.26

11. The number of H^+ ions present in 1 mL of a solution having pH = 13 is
(a) 10^{13} (b) 6.023×10^{13} (c) 6.023×10^7 (d) 6.023×10^{10}

12. An aqueous solution has pH = 7.0 at 40 °C. If $pK_w^o = 13.54$ at 40 °C, the solution is
(a) acidic (b) alkaline (c) neutral (d) neither acidic nor alkaline

13. The pH of 0.1 M acetic acid ($K_a = 1.8 \times 10^{-5}$ M) is
(a) 0.1 (b) 1.0 (c) 1.87 (d) 2.87

14. Which of the following expressions is not true?
(a) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution
(b) $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$ for an acidic solution
(c) $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$ for an alkaline solution
(d) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures

15. 10^{-5} M HCl solution at 25 °C is diluted 1000 times. The pH of the solution will
(a) be equal to 8. (b) lie between 7 and 8. (c) lie between 6 and 7. (d) remain unchanged.

16. 10^{-5} M NaOH solution at 25 °C is diluted 1000 times. The pH of the solution will
(a) be equal to 8 (b) lie between 7 and 8 (c) lie between 6 and 7 (d) remain unchanged

17. The concentration of H_3O^+ of pure water at 90 °C is 10^{-6} M. At this temperature, its pK_w will be
(a) 6 (b) 12 (c) – 6 (d) – 12

18. Which of the following statements is correct?
(a) pK_w^o increases with increase of temperature (b) pK_w^o decreases with increase of temperature
(c) $pK_w^o = 14$ at all temperatures (d) $pK_w^o = pH$ at all temperartures

19. For a pure water,
(a) pH increases and pOH decreases with increase in temperature
(b) pH decreases and pOH increases with increase in temperature
(c) both pH and pOH increase with increase in temperature
(d) both pH and pOH decrease with increase in temperature

20. For a pure water, the product of $[H^+]$ and $[OH^-]$
(a) increases with increase in temperature (b) decreases with increase in temperature
(c) remains constant at all temperatures (d) may increase or decrease depending upon the source

21. The pH of 0.1 M H_2SO_4 solution
(a) is equal to one
(b) is more than one
(c) is less than one
(d) may be equal to or greater than or smaller than one depending upon temperature

22. The increasing order of base strength is
(a) $I^- > Cl^- > NO_2^- > CN^-$ (b) $I^- < Cl^- < NO_2^- < CN^-$
(c) $I^- < NO_2^- < Cl^- < CN^-$ (d) $I^- < CN^- < Cl^- < NO_2^-$

23. Mixing of 0.1 mol of NaOH and 0.1 mol of acetic acid in one litre of water results into
(a) an acidic solution (b) an alkaline solution
(c) a neutral solution (d) a solution with no free OH^- ions

24. Which of the following solutions has the maximum pH value?
(a) 0.2 M HNO_3 (b) 0.2 M HCl (c) 0.2 M CH_3COOH (d) 0.2 M CH_3COONa

25. Which of the following shows the lowest percentage dissociation?
(a) 1.0 M HCN ($K_{ioniz}^\circ = 4.0 \times 10^{-10}$) (b) 0.1 M HCN
(c) 1.0 M HNO_2 ($K_{ioniz}^\circ = 4.5 \times 10^{-4}$) (d) 0.1 M HNO_2

26. pK_w° of water at 100 °C will be
(a) more than fourteen (b) less than fourteen (c) equal to fourteen (d) equal to seven

27. The number of H^+ ions present in 1 mL of a solution having pOH = 10 at 25°C is
(a) 10^{13} (b) 6.023×10^{13} (c) 6.023×10^{16} (d) 6.023×10^{10}

28. 200 mL of a strong acid solution of pH = 2.0 is mixed with 800 mL of another acid solution of pH = 3.0. The pH of resultant solution is
(a) 2.10 (b) 2.31 (c) 2.55 (d) 2.89

Weak Acid

29. The pK_a° of acetylsalicyclic acid (aspirin) is 3.5. The pH of gastric juice in the human stomach is about 2 to 3 and the pH in small intestine is about 8. Aspirin will be
(a) unionized in the small intestine and in the stomach
(b) completely ionized in the small intenstine and in the stomach
(c) ionized in the stomach and almost unionized in the small intestine
(d) ionized in the small intenstine and almost unionized in the stomach (1988)

30. The expression of Ostwald dilution law is
(a) $\alpha = \sqrt{K_a c}$ (b) $\alpha = \sqrt{K_a / c}$ (c) $\alpha = \sqrt{c / K_a}$ (d) $\alpha = K_a / c$

31. For a concentrated solution of a weak electrolyte A_xB_y, the degree of dissociation is given as
(a) $\alpha = \sqrt{K_{eq} / c(x+y)}$ (b) $\alpha = \sqrt{K_{eq}\, c / (x\, y)}$
(c) $\alpha = \left(K_{eq} / c^{x+y-1}\, x^x\, y^y\right)^{1/(x+y)}$ (d) $\alpha = \sqrt{K_{eq} / x\, y\, c}$

32. The number of S^{2-} ions present in 1 L of 0.1 M H_2S solution having $[H^+] = 0.1$ M is
(a) 6.625×10^3 (b) 6.625×10^4 (c) 6.625×10^5 (d) 6.625×10^6
(Given: $K_{a1}K_{a2}$ for H_2S is 1.1×10^{-21} M^3.)

33. The addition of sodium acetate to 0.1 M acetic acid will cause
(a) increase in its pH value (b) decrease in its pH value
(c) no change in pH value (d) change in pH which cannot be predicted

34. The addition of ammonium chloride to 0.1 M acetic acid will cause
(a) increase in its pH value (b) decrease in its pH value
(c) no change in pH value (d) change in pH which cannot be predicted

35. 0.1 mol of HCl is added to 1 L of solution containing 0.5 mol of sodium acetate. The pH of the solution will be
(a) 1.0 (b) 4.74 (c) 5.35 (d) 4.15
(*Given* : $K_a(CH_3COOH) = 1.8 \times 10^{-5}$.)

36. 0.1 mol of NaOH is added to 1 L of solution containing 0.5 mol of ammonium chloride. The pH of the solution will be
(a) 1.0 (b) 13.0 (c) 9.85 (d) 8.65
(*Given* : $K_b(NH_4OH) = 1.8 \times 10^{-5}$.)

37. The ratio of acid strength of HOCN and HCN is about
(a) 548 : 1 (b) 1 : 548 (c) 2.86×10^5 : 1 (d) 2.86×10^4 : 1
(*Given* : $K_a(HCN) = 4.2 \times 10^{-10}$ M and $K_a(HOCN) = 1.2 \times 10^{-4}$ M.)

38. If pK_b for fluoride ion at 25 °C is 10.83, the ionization constant of HF in water at this temperature is
(a) 1.74×10^{-5} (b) 3.52×10^{-3} (c) 6.75×10^{-4} (d) 5.38×10^{-2} (1997)

39. An acid solution (0.1 M) has a pH = 4. Its dissociation constant is about
(a) 10^{-5} M (b) 10^{-6} M (c) 10^{-7} M (d) 10^{-8} M

40. Which of the following shows the highest percentage dissociation?
(a) 1.0 M HCN ($K_{diss}^\circ = 4.0 \times 10^{-10}$) (b) 0.1 M HCN
(c) 1.0 M HNO_2 ($K_{diss}^\circ = 4.5 \times 10^{-4}$) (d) 0.1 M HNO_2

41. An aqueous solution of carbonic acid (H_2CO_3) contains
(a) H_2CO_3 only (b) H_2CO_3, H^+, HCO_3^-
(c) H_2CO_3, H^+, HCO_3^-, CO_3^{2-} (d) H_2CO_3, CO_2, H^+, HCO_3^-, CO_3^{2-}

Hydrolysis of Salts

42. The compound whose 0.1 M solution is basic is
(a) ammonium acetate (b) ammonium chloride (c) ammonium sulphate (d) sodium acetate (1986)

43. A solution of $CuSO_4$ is
(a) acidic in nature (b) alkaline in nature (c) neutral in nature (d) amphoteric in nature

44. A solution of NaCN is
(a) acidic in nature (b) alkaline in nature (c) neutral in nature (d) amphoteric in nature

45. A solution of NaCl is
(a) acidic in nature (b) alkaline in nature (c) neutral in nature (d) amphoteric in nature

46. A solution of ammonium cyanide is
(a) acidic in nature (b) alkaline in nature (c) neutral in nature (d) amphoteric in nature

47. The expression to compute pH of NH_4Cl solution is
(a) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ + \frac{1}{2}\mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) + \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$(b) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ + \frac{1}{2}\mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) - \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$
(c) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) - \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$ (d) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) + \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$

48. The expression to compute pH of sodium acetate solution is
(a) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\mathrm{p}K_\mathrm{a}^\circ(\mathrm{CH_3COOH}) - \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$
(b) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ + \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ(\mathrm{CH_3COOH}) - \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$
(c) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ + \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ(\mathrm{CH_3COOH}) + \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$
(d) $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\mathrm{p}K_\mathrm{a}^\circ(\mathrm{CH_3COOH}) + \frac{1}{2}\log\,([\mathrm{salt}]/\mathrm{M})$

49. The pH of 0.1 M solution of the following salts increases in the order
(a) $NaCl < NH_4Cl < NaCN < HCl$ (b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$ (d) $HCl < NaCl < NaCN < NH_4Cl$ (1999)

50. Which of the following salt solutions (0.1 M each) will have the lowest pH values?
(a) $CaCO_3$ (b) $CaCl_2$ (c) $Ca(OH)_2$ (d) CH_3COONa

51. A weak acid HX has $\mathrm{p}K_\mathrm{a}^\circ = 5$. The per cent degree of hydrolysis of 0.1 M solution of salt NaX is
(a) 0.001% (b) 0.01% (c) 0.1% (d) 0.15% (2004)

52. 2.5 mL of (2/5) M weak monoacidic base ($K_\mathrm{b}^\circ = 1 \times 10^{-12}$ at 25°C) is titrated with (2/15) M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_\mathrm{w}^\circ = 1 \times 10^{-14}$ 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 (2008)

53. It is found that 0.1 M solution of three salts NaX, NaY and NaZ have pH's 7.0, 9.0 and 11.0, respectively. Which of the following order regarding acid strength is correct?
(a) HX > HY > HZ (b) HX > HZ > HY (c) HY > HX > HZ (d) HZ > HY > HX

54. The degree of hydrolysis of ammonium acetate is related to its hydrolysis constant by the expression
(a) $\alpha = \dfrac{K_\mathrm{h}}{1+K_\mathrm{h}}$ (b) $\alpha = \dfrac{K_\mathrm{h}}{1+K_\mathrm{h}^2}$ (c) $\alpha = \dfrac{\sqrt{K_\mathrm{h}}}{1+\sqrt{K_\mathrm{h}}}$ (d) $\alpha = \dfrac{\sqrt{K_\mathrm{h}}}{\sqrt{1+K_\mathrm{h}}}$

55. The standard hydrolysis constant of anilinium acetate ($K_\mathrm{a}(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M, $K_\mathrm{b}(\text{aniline}) = 4.6 \times 10^{-10}$ M) at 25 °C is
(a) 1.0 (b) 1.21 (c) 1.35 (d) 2.6×10^{-2}

56. The degree of hydrolysis of anilinium acetate ($K_\mathrm{a}(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M, $K_\mathrm{b}(\text{aniline}) = 4.6 \times 10^{-5}$ M) at 25 °C is
(a) 0.41 (b) 0.46 (c) 0.52 (d) 0.055

57. The expression to compute pH of a solution containing a salt formed from a weak acid and a weak base is
(a) $\mathrm{pH} = \frac{1}{2}\,(\mathrm{p}K_\mathrm{w}^\circ + \mathrm{p}K_\mathrm{b}^\circ - \mathrm{p}K_\mathrm{a}^\circ)$ (b) $\mathrm{pH} = \frac{1}{2}\,(\mathrm{p}K_\mathrm{w}^\circ + \mathrm{p}K_\mathrm{a}^\circ - \mathrm{p}K_\mathrm{b}^\circ)$
(c) $\mathrm{pH} = \frac{1}{2}\,(\mathrm{p}K_\mathrm{a}^\circ - \mathrm{p}K_\mathrm{b}^\circ) + \log\,([\mathrm{salt}]/c^\circ)$ (d) $\mathrm{pH} = \frac{1}{2}\,(\mathrm{p}K_\mathrm{a}^\circ + \mathrm{p}K_\mathrm{b}^\circ) - \log\,([\mathrm{salt}]/c^\circ)$

58. The pH of 0.1 M solution of $NaHCO_3$ (Given: $\mathrm{p}K_\mathrm{a}^\circ(\mathrm{H_2CO_3}) = 6.38$ and $\mathrm{p}K_{\mathrm{a}_2}^\circ(\mathrm{HCO_3^-}) = 10.32$) is
(a) 8.35 (b) 6.5 (c) 4.3 (d) 3.94

Concept of Solubility Product

59. The precipitate of CaF_2 ($K_{sp}^{o} = 1.7 \times 10^{-10}$)is obtained when equal volumes of the following are mixed

(a) 10^{-4} M Ca^{2+} + 10^{-4}M F^- (b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(c) 10^{-5} Ca^{2+} + 10^{-3} M F^- (d) 10^{-3} M Ca^{2+} + 10^{-5} M F^- (1982)

60. The ion that cannot be precipitated by both HCl and H_2S is

(a) Pb^{2+} (b) Cu^{2+} (c) Ag^+ (d) Sn^{2+} (1982)

61. Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid?

(a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+} (c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+} (1986)

62. When equal volumes of the following solutions are mixed precipitation of AgCl ($K_{sp}^{o} = 1.8 \times 10^{-10}$) will occur only with

(a) 10^{-4} M Ag^+ and 10^{-4} M Cl^- (b) 10^{-5} M Ag^+ and 10^{-5} M Cl^-

(c) 10^{-6} M Ag^+ and 10^{-6} M Cl^- (d) 10^{-10} M Ag^+ and 10^{-10} M Cl^- (1988)

63. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperatures (about 25 °C) is

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$ (1990)

64. The reagents, NH_4Cl and aqueous NH_3 will precipitate

(a) Ca^{2+} (b) Al^{3+} (c) Bi^{3+} (d) Mg^{2+}

(e) Zn^{2+} (1991)

65. The solubility product of magnesium phosphate is given as

(a) $K_{sp} = [Mg^{2+}]\,[PO_4^{3-}]$ (b) $K_{sp} = [Mg^{2+}]\,[PO_4^{3-}]^3$

(c) $K_{sp} = [Mg^{2+}]^3\,[PO_4^{3-}]^2$ (d) $K_{sp} = \dfrac{[Mg^{2+}][PO_4^{3-}]}{[Mg_3(PO_4)_2]}$

66. If s_0, s_1, s_2 and s_3 are the solubilities of AgCl in water, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.05 M $AgNO_3$ solutions, respectively, then

(a) $s_0 > s_1 > s_2 > s_3$ (b) $s_0 > s_2 > s_1 > s_3$ (c) $s_0 > s_2 > s_3 > s_1$ (d) $s_0 > s_1 = s_2 > s_3$

67. A solution contains 0.05 M each of NaCl and Na_2CrO_4. Solid $AgNO_3$ is gradually added to it. Which of the following facts is true? Given: $K_{sp}(AgCl) = 1.7 \times 10^{-10}$ M^2 and $K_{sp}(Ag_2CrO_4) = 1.9 \times 10^{-12}$ M^3.

(a) Cl^- ions are precipitated first

(b) CrO_4^{2-} ions are precipitated first

(c) Both Cl^- and CrO_4^{2-} ions are precipitated together

(d) The second ion starts precipitating when half of the first ion is precipitated

68. The pH of $Mg(OH)_2$ is 10.45 at 25 °C. The solubility product of magnesium hydroxide would be

(a) 2.24×10^{-11} M^3 (b) 3.36×10^{-11} M^3 (c) 1.12×10^{-11} M^3 (d) 5.60×10^{-12} M^3

69. The solubility product of A_2X_3 is 1.08×10^{-23}. Its solubility will be

(a) 1.0×10^{-3} M (b) 1.0×10^{-4} M (c) 1.0×10^{-5} M (d) 1.0×10^{-6} M

70. A solution is saturated with respect to $SrCO_3$ and SrF_2. The $[CO_3^{2-}]$ was found to be 1.2×10^{-3} M. The concentration of F^- in the solution would be

(a) 1.3×10^{-3} M (b) 2.6×10^{-2} M (c) 3.7×10^{-2} M (d) 5.8×10^{-7} M

(Given : $K_{sp}(SrCO_3) = 7.0 \times 10^{-10}$ M^2, $K_{sp}(SrF_2) = 7.9 \times 10^{-10}$ M^3.)

71. The maximum pH of a solution which is 0.10 M in Mg^{2+} from which $Mg(OH)_2$ is not precipitated is

(a) 4.96 (b) 6.96 (c) 7.54 (d) 9.04

(Given: $K_{sp}(Mg(OH)_2) = 1.2 \times 10^{-11}$ M^3.)

72. The solubility of sparingly soluble electrolyte M_mA_a in water is given by the expression

(a) $s = \left(\dfrac{K_{sp}}{m^m a^a}\right)^{m+a}$ (b) $s = \left(\dfrac{K_{sp}}{m^m a^a}\right)^{1/(m+a)}$ (c) $s = \left(\dfrac{K_{sp}}{m^a a^m}\right)^{m+a}$ (d) $s = \left(\dfrac{K_{sp}}{m^a a^m}\right)^{1/(m+a)}$

73. In a saturated solution of calcium phosphate, the concentration of PO_4^{3-} ions is 3.3×10^{-7} M. The K_{sp} of $Ca_3(PO_4)_2$ will be

(a) 1.32×10^{-31} (b) 1.32×10^{-32} (c) 1.32×10^{-33} (d) 1.32×10^{-35}

74. The solubility of mercurous chloride in water will be given as

(a) $s = K_{sp}$ (b) $s = K_{sp}/4$ (c) $s = (K_{sp}/4)^{1/2}$ (d) $s = (K_{sp}/4)^{1/3}$

75. The solubility in mol dm^{-3} of A_2X_3 is y. Its solubility product is

(a) $6\ y^4$ (b) $64\ y^4$ (c) $36\ y^5$ (d) $108\ y^5$ (1997)

Solubility

76. A solution is saturated with respect to $MgCO_3$ and Ag_2CO_3. It is found to have $[Mg^{2+}] = 3.2 \times 10^{-5}$ M. If $K_{sp}(MgCO_3) = 1.6 \times 10^{-6}\ M^2$ and $K_{sp}(Ag_2CO_3) = 8.0 \times 10^{-12}\ M^3$, the concentration of Ag^+ in the solution would be about

(a) 1.26×10^{-3} M (b) 1.26×10^{-4} M (c) 1.76×10^{-4} M (d) 1.26×10^{-5} M

77. The solubility of $Pb(OH)_2$ in water is 7×10^{-6} M. The solubility of $Pb(OH)_2$ in a buffer solution of pH = 8 will be about

(a) 1.372×10^{-1} M (b) 1.372×10^{-2} M (c) 1.372×10^{-3} M (d) 1.372×10^{-4} M

78. The concentration of Mg^{2+} ions in the saturated solution of $Mg_3(PO_4)_2$ (its solubility product is $1.08 \times 10^{-13}\ M^5$) is about

(a) 1.0×10^{-2} M (b) 1.0×10^{-3} M (c) 1.0×10^{-4} M (d) 1.0×10^{-6} M

79. The solubility in mol dm^{-3} of A_2X_3 is y. Its solubility product is

(a) $6y^4$ (b) $64y^4$ (c) $36y^5$ (d) $108y^5$

80. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (K_{sp}) with its solubility (s) is

(a) $K_{sp} = s^{p+q} \cdot p^p \cdot q^q$ (b) $K_{sp} = s^{p+q} \cdot p^q \cdot q^p$

(c) $K_{sp} = s^{pq} \cdot p^p \cdot q^q$ (d) $K_{sp} = s^{pq}\ (pq)^{p+q}$ (2001)

81. Identify the correct order of solubility of Na_2S, CuS and ZnS is aqueous medium

(a) CuS > ZnS > Na_2S (b) ZnS > Na_2S > CuS

(c) Na_2S > CuS > ZnS (d) Na_2S > ZnS > CuS (2002)

82. Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are $4.0 \times 10^{-8}\ M^2$, $3.2 \times 10^{-14}\ M^3$ and $2.7 \times 10^{-15}\ M^4$, 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 (2008)

83. Equal volumes of 0.2 M $AgNO_3$ and 0.1 M NaCl solutions are mixed at 25 °C. It $K_{sp}(AgCl) = 1.8 \times 10^{-10}\ M^2$, the concentration of Cl^- ions in the solution will be

(a) 3.6×10^{-8} M (b) 3.6×10^{-9} M (c) 1.34×10^{-5} M (d) 1.34×10^{-6} M

84. The solubility of AgCl ($K_{sp} = 1.7 \times 10^{-10}\ M^2$) in 0.10 M NH_3 (in which $Ag(NH_3)_2^+$ exists with $K_f = 1.8 \times 10^7\ M^{-2}$) is

(a) 5.2×10^{-2} M (b) 5.2×10^{-3} M (c) 5.2×10^{-4} M (d) 5.2×10^{-5} M

Buffer Solution

85. An acidic buffer solution can be prepared by mixing the solutions of

(a) ammonium acetate and acetic acid (b) ammonium chloride and ammonium hydroxide

(c) sulphuric acid and sodium hydroxide (d) sodium chloride and sodium hydroxide (1981)

86. Which of the following can be used as a buffer solution?

(a) A solution containing NaCl and NaOH. (b) A solution containing NaCl and NH_4OH.

(c) A solution containing sodium acetate. (d) A solution containing ammonium acetate.

87. Which of the following solutions containing weak acid and salt of its conjugate base has maximum buffer capacity?

(a) [salt] = [acid] (b) [salt > [acid] (c) [salt] < [acid] (d) [salt] + [acid] is minimum

88. For an acidic buffer solution, pH = pK_a. It implies that

(a) [salt] = [acid] (b) [salt] > [acid] (c) [salt] < [acid] (d) [salt] + acid] is minimum

89. For an acidic buffer solution, which of the following expressions is true?

(a) pH = pK_a^o + [salt]/[acid] (b) pH = pK_a^o + [acid]/[salt]

(c) pH = pK_a^o + ln [salt]/[acid] (d) pH = pK_a^o + log [salt]/[acid]

90. On diluting a buffer solution, its pH
(a) is increased
(b) is decreased
(c) remains constant
(d) changes which cannot be predicted unless dissociation constant of its weak acid (or base) is provided

91. In an acidic buffer solution containing acetic acid and sodium acetate, if some HCl is added, its pH will
(a) increase (b) decrease
(c) remain constant (d) change but cannot be predicted

92. In an acidic buffer solution containing acetic acid and sodium acetate, if some NaOH is added, its pH will
(a) increase a little (b) decrease a little
(c) remain constant (d) change but cannot be predicted

93. In an alkaline buffer solution containing ammonium hydroxide and ammonium chloride, if some HCl is added, its pH will
(a) increase a little (b) decrease a little
(c) remain constant (d) change but cannot be predicted.

94. Which of the following buffer solution containing the indicated ratio of [salt]/[acid] has a maximum buffer capacity?
(a) 1/2 (b) 1 (c) 2/1 (d) 4/1

95. The pH of a solution obtained by mixing 20 mL of 0.2 M sodium acetate and 10 mL of 0.01 M acetic acid ($K_a^\circ = 2.0 \times 10^{-5}$ M) is
(a) 4.7 (b) 4.1 (c) 5.3 (d) 5.1

96. A certain buffer solution contains equal concentrations of HX and X^-. The K_b° for X^- is 10^{-10}. The pH of the buffer is
(a) 4 (b) 7 (c) 10 (d) 14 (1984)

97. 0.1 mol of CH_3NH_2 ($K_b^\circ = 6 \times 10^{-4}$) is added to 0.08 mol of HCl and the solution is diluted to 1 L. The hydrogen-ion concentration in the solution is
(a) 5×10^{-5} M (b) 8×10^{-2} M (c) 1.6×10^{-11} M (d) 6.7×10^{-11} M (2005)

98. A buffer of pH = 8.5 is required. If pK_a° (NH_4^+) = 9.2, the amount of $(NH_4)_2SO_4$ to be added in 500 mL of 0.1 M NH_4OH would be
(a) 0.004 mol (b) 0.005 mol (c) 0.006 mol (d) 0.008 mol

Acid-Base Titrations

99. The best indicator for the detection of end point in a titration of a weak acid and a strong base is
(a) methyl orange (3 to 4) (b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5) (d) phenolphthalein (8 to 9.6)
Note: Figures in the brackets show the pH range of the indicator. (1985)

100. In the titration of HCl versus NaOH, the pH of the solution at equivalence point (when temperature is 25 °C) is
(a) 5 (b) 6 (c) 7 (d) 8

101. In the titration of NH_4OH versus HCl, the pH of the solution at equivalence point (when temperature is 25 °C) is
(a) about 5.5 (b) about 7 (c) about 8.5 (d) about 9.5

102. In the titration of acetic acid versus sodium hydroxide, the pH of the solution at equivalence point (when temperature is 25 °C) is
(a) about 5.5 (b) abount 6.5 (c) about 7 (d) about 8.5

103. Which of the following indicators is best suited in the titration of a weak acid versus a strong base?
(a) Phenolphthalein (8.3 – 10.0) (b) Methyl orange (3.1 – 4.4)
(c) Methyl red (4.2 – 6.3) (d) Litmus (4.5 – 8.3)
(*Note* : The number in the brackets are the indicator ranges.)

104. Which of the following indicators is best suited in the titration of a weak base versus a strong acid?

(a) Phenolphthalein (8.3 – 10.0) (b) Phenol red (6.8 – 8.4)

(c) Methyl organe (3.1 – 4.4) (d) Litmus (4.5 – 8.3)

(*Note* : The numbers in the bracketts are the indicator ranges.)

105. The pink colour of phenolphthalein in alkaline medium is due to

(a) the acidic form of phenolphthalein (b) the anionic form of phenolphthalein

(c) OH^- of the base (d) the non-conjugated structure of phenolphthalein

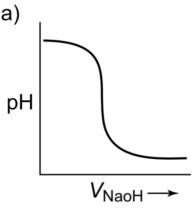
106. An acid-base indicator has $K_a^\circ = 3 \times 10^{-5}$. The acid form of the indicator is red and the base form is blue. The change in $[H^+]$ required to change the indicator from 75% red to 75% blue is

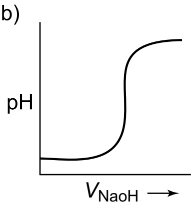
(a) 8×10^{-5} M (b) 9×10^{-5} M (c) 1×10^{-5} M (d) 4×10^{-5} M

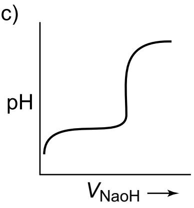
107. A certain weak acid has a dissociation constant of 1.0×10^{-4} M. The equilibrium constant for its reaction with a strong base is

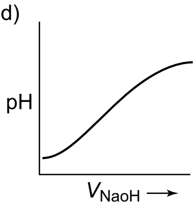
(a) $1.0 \times 10^{-4}\ M^{-1}$ (b) $1.0 \times 10^{-10}\ M^{-1}$ (c) $1.0 \times 10^{10}\ M^{-1}$ (d) $1.0 \times 10^{14}\ M^{-1}$

108. Which of the following plots represents a typical titration between a strong acid and a strong base?

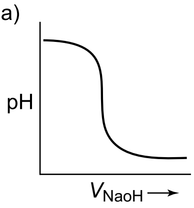
(a)


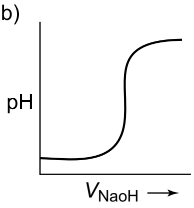
(b)


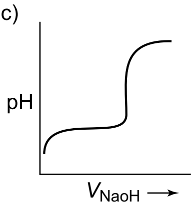
(c)


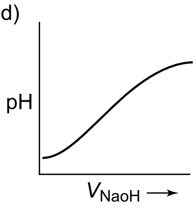
(d)


109. Which of the following plots represents a typical titration of a weak acid against a strong base?

(a)


(b)


(c)


(d)


Concepts of Acids and Bases

110. The conjugate acid of NH_2^- is

(a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4 (1985)

111. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characteristics the conjugate acid-base pair is

(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-) (b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)

(c) $CH_3COOH_2{}^+$, HCl) and (Cl^-, CH_3COOH) (d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH) (1992)

112. Which of the following acts as a Brönsted acid as well as a Brönsted base?

(a) Na_2CO_3 (b) OH^- (c) NH_3 (d) HCO_3^-

113. In the reaction $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$, the conjugate acid-base pair is

(a) HCN, H_2O (b) H_3O^+, CN^- (c) HCN, H_3O^+ (d) HCN, CN^-

114. Which of the following statements is **not** correct?

(a) A substance which supplies OH^- in aqueous medium is a base.

(b) A substance which can accept a proton in aqueous medium is a base.

(c) A substance which can donate a pair of electrons is a base.

(d) A substance which can accept a pair of electrons is a base.

115. Which of the following species is not a Lewis acid?
(a) BF_3 (b) Cu^{2+} (c) NH_3 (d) $AlCl_3$

116. In aqueous solution, which of the following orders regarding acid strength is correct?
(a) $HCN < CH_3COOH < HCl < HClO_4$ (b) $HCN < CH_3COOH < HClO_4 < HCl$
(c) $HCN < HClO_4 < HCl < CH_3COOH$ (d) $HClO_4 < CH_3COOH < HCl < HCN$

117. In aqueous solution, which of the following orders regarding base strength is correct?
(a) $CH_3COO^- < HS^- < NH_3 < CO_3^{2-}$ (b) $CH_3COO^- > HS^- > NH_3 > CO_3^{2-}$
(c) $CH_3COO^- > HS^- > NH_3 < CO_3^{2-}$ (d) $CH_3COO^- > HS^- > CO_3^{2-} > NH_3$

118. The decreasing base strength of OH^-, NH_2^-, $HC{\equiv}C^-$ and $CH_3CH_2^-$ is
(a) $CH_3CH_2^- > NH_2^- > HC{\equiv}C^- > OH^-$ (b) $HC{\equiv}C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC{\equiv}C^- > CH_3CH_2^-$ (d) $NH_2^- > HC{\equiv}C^- > OH^- > CH_3CH_2^-$

119. The compound that is not a Lewis acid is
(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$ (1985)

120. Of the given anions, the strongest Bronsted base is
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^- (1981)

Multiple Correct Choice Type

1. Which of the following statement(s) is (are) correct?
(a) The pH of 1.0×10^{-8} M solution of HCl is 8.
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.
(c) Autoprotolysis constant of water increases with temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = (1/2) pK_a°.

2. For pure water at 25°C
(a) $[H_2O] = 55.56 \text{ mol dm}^{-3}$ if density of water is 1 g cm^{-3}.
(b) $K_w = 1.0 \times 10^{-14} \text{ (mol dm}^{-3})^2$
(c) degree of dissociation, $\alpha = 1.8 \times 10^{-9}$
(d) ionization constant, $K_{\text{ioniz}} = 1.8 \times 10^{-16} \text{ mol dm}^{-3}$.

3. Which of the following statements is/are correct for an aqueous solution having pH = 7 at 298 K?
(a) $[H^+] = 10^{-7} \text{ mol L}^{-1}$
(b) $[OH^-] = 10^{-7} \text{ mol L}^{-1}$
(c) $K_w = 10^{-14} \text{ (mol L}^{-1})^2$
(d) The solution becomes alkaline on diluting the solution.

4. Which of the following expressions is/are **not** correct for a solution of sodium acetate in water?
(a) The pH of the solution is given by the expression $pH = pK_w^\circ + pK_a^\circ + \log (c/c^\circ)$
(b) The degree of hydrolysis of acetate ions is given by $\log \alpha = pK_a^\circ - pK_w^\circ - \log (c/c^\circ)$
(c) The pOH of the solution decreases with increase in the concentration of sodium acetate.
(d) The ionization constant of acetate is given by
$K_b(\text{acetate}) = K_w/K_a$ (acetic acid).

5. For a solution of ammonium acetate, which of the following expressions is/are correct?
(a) The expression of $[H_3O^+]$ is $[H_3O^+] = \left(\dfrac{K_w K_b}{K_a}\right)^{1/2}$
(b) The degree of hydrolysis of salt is given by $\alpha = \dfrac{\sqrt{K_h}}{1+\sqrt{K_h}}$ where $K_h = \dfrac{K_w}{K_a K_b}$
(c) pH of the solution is given by $pH = pK_a^\circ + \dfrac{1}{2} pK_h^\circ$
(d) pOH of the solution increases with increase in the concentration of ammonium acetate.

6. Which of the statements are correct?
   (a) Hydrolysis constant of acetate ion is larger than that of cyanide ion
   (b) The degree of dissociation of water increases with increase in temperature
   (c) $\mathrm{p}K_\mathrm{w}^\circ = \mathrm{pH} + \mathrm{pOH}$ holds good in any aqueous solution at all temperatures
   (d) The solution of NH_4CN is acidic in nature.

7. Which of the following statements is/are **not** correct?
   (a) Pure water at 40 °C has $[\mathrm{H}^+] = 10^{-7}\ \mathrm{mol\ dm^{-3}}$.
   (b) An aqueous solution having pH = 6.9 at 40 °C is acidic in nature.
   (c) $\mathrm{p}K_\mathrm{w}^\circ$ of water at 40 °C is greater than 14.
   (d) For pure water $\mathrm{pH} = (1/2)\ \mathrm{p}K_\mathrm{w}^\circ$.

8. Which of the following expressions is/are valid for ammonium chloride solution?
   (a) The solution is acidic in nature.
   (b) pH of the solution is given by $\mathrm{pH} = \frac{1}{2}\ \mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\ \mathrm{p}K_\mathrm{b}^\circ - \frac{1}{2}\ \log\ (c/c^\circ)$
   (c) The degree of hydrolysis is given by $\alpha = \left(\sqrt{K_\mathrm{b}/K_\mathrm{w}}\right)\ (c)$
   (d) The hydrolytic constant is given by $K_\mathrm{h} = K_\mathrm{w}/K_\mathrm{b}$

9. Which of the following statements are correct?
   (a) Aluminium chloride is a Lewis acid because it can donate electrons.
   (b) Silver fluoride is fairly soluble in water.
   (c) Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water.
   (d) Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia.

10. Which of the following statements are correct?
   (a) The solubility of $Zn(OH)_2$ is greater in an acidic or basic medium than in neutral water.
   (b) All those acids which are stronger than H_3O^+ are completely ionized in aqueous medium.
   (c) The acids $HClO_4$, HNO_3, HCl and HBr appear to have same acid strength in aqueous medium.
   (d) Acids that are weaker than H_3O^+ are levelled in aqueous medium.

11. Which of the following statements are correct?
   (a) The levelling effect is not observed in nonaqueous medium.
   (b) The strength of an acid having general formula $(HO)_mZO_n$ increases with increase in the value of n.
   (c) In a given reaction, the position of equilibrium favours the formation of a weak Brönsted acid and a weak Brönsted base.
   (d) The reaction $HCN + OH^- \rightleftharpoons CN^- + H_2O$ is displaced to the right indicating that the acid strength of HCN is greater than water and the base strength CN^- is greater than that of OH^-.

12. Which of the following statements are correct?
   (a) The acid strength follows the order $HF > H_2O > NH_3$.
   (b) The base strength follows the order $I^- > Br^- > Cl^- > F^-$.
   (c) The amide is strongest base in liquid NH_3.
   (d) Sulphuric acid acts as a base in perchloric acid?

13. Which of the following statements are **not** correct?
   (a) The conjugate base of HSO_4^- in aqueous solution is SO_4^{2-}
   (b) An element that can exist as a positive ion in acidic medium and as a negative ion in basic medium is said to be metalloid.
   (c) The basicity of phosphorous acid is three.
   (d) Ostwald dilution law is valid for strong electrolytes.

14. Which of the following statements are **not** correct?
   (a) A strong acid has weak conjugate base.
   (b) The dissociation constants of two monoprotic weak acids are K_1 and K_2. Their relative acid strength would be given as K_1/K_2.

(c) In a mixture of weak acid and its salt, its ratio of concentrations of salt to acid is increased ten fold. The pH of the solution would decrease by one.
(d) If the solubility of the salt $Li_3Na_3(AlF_6)_2$ is x. Its solubility product would be 2916 x^8.

15. Which of the following statements are **not** correct?
(a) The pH of pure water increases with increase of temperature.
(b) The solubility of $KAl(SO_4)_2$ in terms of its solubility product is $(K_{sp}/2)^{1/4}$.
(c) The pH of a solution obtained by mixing 50 mL of 0.4 M HCl and 50 mL of 0.2 M NaOH would be one.
(d) The standard dissociation constant of NH_4OH is 1.8×10^{-5}. The standard hydrolysis constant of NH_4^+ ions at 25 °C would be 5.56×10^{-10}.

16. Which of the following statements are **not** correct?
(a) The solution of $CuSO_4$ is acidic due to the hydrolysis of Cu^{2+} ions.
(b) The solution at the equivalence point in the titration of weak acid versus strong base would be acidic.
(c) The colour of unionized form of phenolphthalein is colourless whereas that of ionized form is pink.
(d) A buffer has maximum buffer capacity when the ratio of its salt to acid is 1 : 10.

17. Which of the following statements are **not** correct?
(a) The solubility of AgCl in NH_3 is due to the formation of $Ag(NH_3)_2^+$ ions.
(b) The solubility of PbS in water considering hydrolysis of S^{2-} ions would be lesser than that ignoring the hydrolysis.
(c) The compound $Al(OH)_3$ can function both as acid and base. Such a compound is known as amphoteric compound.
(d) In general, in aqueous solution pH + pOH = 14 at all temperatures.

18. Which of the following statements are correct?
(a) The ionization constant of water is related to ionic product by the expression $K_w/[H_2O]$
(b) The pH of pure water is temperature dependent.
(c) The smaller the value of K_a of a weak acid, larger is the hydrolysis constant of its conjugate base.
(d) Larger the value of pK_a^o, stronger the acid.

19. Which of the following statements are correct?
(a) Acetic acid is a stronger acid in liquid NH_3.
(b) The strongest acid in liquid NH_3 is NH_4^+ ions.
(c) The strongest base in liquid NH_3 is NH_2^- ions
(d) For the reaction $N_2O_4 \rightleftharpoons 2NO_2$ (ΔH = 58.04 kJ mol^{-1}), the density of equilibrium mixture decreases with increase of temperature.

20. A buffer solution can be prepared from a mixture of
(a) sodium acetate and acetic acid in water
(b) sodium acetate and hydrochloric acid in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

21. A buffer solution is made by mixing acetic acid (HAc) and sodium acetate (NaAc) in water. Which of the following buffers have identical buffer capacity?
(a) 0.1 M HAc + 0.1 M NaAc (b) 0.1 M HAc + 0.05 M NaAc
(c) 0.05 M HAc + 0.1 M NaAc (d) 0.1 M HAc + 0.6 M NaAc

Linked Comprehension Type

1. Given is 1 dm^3 solution of 1.0 M of a weak acid HA ($K_a = 1.0 \times 10^{-4}$ M).
(i) The volume up to which the solution should be diluted to double pH is
(a) 5×10^2 dm^3 (b) 5×10^3 dm^3 (c) 5×10^4 dm^3 (d) 5×10^5 dm^3
(ii) The volume up to which the solution should be diluted to half the concentration of H^+ is
(a) 3 dm^3 (b) 4 dm^3 (c) 5 dm^3 (d) 6 dm^3
(iii) The amount of NaA needs to be added to reduce to the concentration of H^+ to half is
(a) 0.02 mol (b) 0.03 mol (c) 0.04 mol (d) 0.05 mol

2. 50 mL of 0.1 M Na_2CO_3 solution is titrated with 0.1 M HCl solution. Given:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad K_1^\circ = 2.1 \times 10^{10}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \qquad K_2^\circ = 2.2 \times 10^{6}$$

(i) The pH of solution at the start of titration is about
(a) 6.4 (b) 7.5 (c) 8.3 (d) 11.50

(ii) The pH of solution at the half neutralization point is about
(a) 6.4 (b) 7.5 (c) 8.3 (d) 11.50

(iii) The pH of solution at the complete neutralization point is about
(a) 4.0 (b) 6.0 (c) 7.0 (d) 8.0

3. 50 mL of 0.1 M Na_2CO_3 solution is titrated with 0.1 M HCl solution. Given:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad K_1^\circ = 2.1 \times 10^{10}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \qquad K_2^\circ = 2.2 \times 10^{6}$$

(i) Which of the following statements is correct?
(a) During the titration, CO_3^{2-} is fully converted into HCO_3^- followed by the conversion of HCO_3^- into H_2CO_3.
(b) During the titration, CO_3^{2-} is partially converted into HCO_3^- followed by the conversion of both CO_3^{2-} and HCO_3^- into H_2CO_3
(c) During the titration, CO_3^{2-} is directly converted into H_2CO_3
(d) After the equivalence point, the solution becomes neutral due to expulsion of CO_2 from H_2CO_3.

(ii) Which of the following indicators can be used to detect the half neutralization of Na_2CO_3?
(a) Congo red (3.0–5.0) (b) Methyl red (4.2–6.3)
(c) Phenolphthalein (8.3–10.0) (d) *p*-Nitrophenol (5.0–7.0)
(Numbers within brackets represent indicator range.)

(iii) Which of the following indicators can be used to detect the complete neutralization of Na_2CO_3?
(a) Phenol red (6.8–8.4) (b) Methyl red (4.2–6.3)
(c) Phenolphthalein (8.3–10.0) (d) *m*-Cresol purple (7.4–9.0)
(Numbers within brackets represent indicator range.)

4. A solution is 0.1 M in each of KCl, KBr and K_2CrO_4. To this solution, solid $AgNO_3$ is gradually added. Assume no change in volume of the solution. Given: K_{sp}° (AgCl) = 1.7×10^{-10}, K_{sp}° (AgBr) = 5.0×10^{-13} and K_{sp}° (Ag_2CrO_4) = 1.9×10^{-12}.

(i) The sequence of ions precipitated follows the order
(a) Cl^-, Br^-, CrO_4^{2-} (b) Br^-, Cl^-, CrO_4^{2-}
(c) Cl^-, CrO_4^{2-}, Br^- (d) CrO_4^{2-}, Cl^-, Br^-

(ii) The concentration of the first ion precipitated when the second starts precipitating is about
(a) 0.1 M (b) 0.03 M (c) 0.003 M (d) 0.0003 M

(iii) The concentration of the third ion when the second starts precipitating is about
(a) 0.1 M (b) 0.03 M (c) 0.011 M (d) 0.003 M

5. A solution is 0.1 M in each of Ba^{2+}, Sr^{2+} and Ca^{2+} ions. Solid $(NH_4)_2SO_4$ is gradually added to this solution. Given: K_{sp}° ($BaSO_4$) = 1.5×10^{-9}, K_{sp}° ($CaSO_4$) = 2.5×10^{-5} and K_{sp}° ($SrSO_4$) = 7.5×10^{-7}. Assume no change in volume during the addition of $(NH_4)_2SO_4$.

(i) The correct sequence of ions precipitated is
(a) Ba^{2+}, Ca^{2+}, Sr^{2+} (b) Ba^{2+}, Sr^{2+}, Ca^{2+} (c) Ca^{2+}, Sr^{2+}, Ba^{2+} (d) Ca^{2+}, Ba^{2+}, Sr^{2+}

(ii) The concentration of the first ion precipitated when the second starts precipitating is about
(a) 0.1 M (b) 2.0×10^{-3} M (c) 2.0×10^{-4} M (d) 2.0×10^{-5} M

(iii) The concentration of the second ion precipitated when the third starts precipitating is about
(a) 3×10^{-7} M (b) 3×10^{-8} M (c) 0.1 M (d) 3×10^{-3} M

6. A solution is 0.1 M in each of PO_4^{3-}, SO_4^{2-} and Cl^- ions. Solid $AgNO_3$ is added to this solution which causes no change in volume of the solution. Given: K°_{sp} (AgCl) = 1.8×10^{-10}, K°_{sp} (Ag_2SO_4) = 1.21×10^{-5} and K°_{sp} (Ag_3PO_4) = 2.7×10^{-18}.

(i) The sequence of ions precipitated is
(a) Cl^-, PO_4^{3-}, SO_4^{2-} (b) Cl^-, SO_4^{2-}, PO_4^{3-} (c) PO_4^{3-}, Cl^-, SO_4^{2-} (d) PO_4^{3-}, SO_4^{2-}, Cl^-

(ii) The concentrations of first and third ions when the second ion starts precipitated, respectively, are
(a) 0.1 M, 0.1 M (b) 6×10^{-5} M, 0.1 M
(c) 1.64×10^{-8} M, 0.1 M (d) 2.03×10^{-12} M, 1.64×10^{-8} M

(iii) The concentrations of first and second ions when the third starts precipitated, respectively, are
(a) 0.1 M, 0.01 M (b) 6×10^{-5} M, 0.1 M
(c) 1.64×10^{-8} M, 2.03×10^{-12} M (d) 2.03×10^{-12} M, 1.64×10^{-8} M

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explantation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	**Statement–2**
1.	The solubility of $Zn(OH)_2$ is enhanced in acidic as well as in basic medium as compared to water.	$Zn(OH)_2$ is an amphoteric hydroxide.
2.	pH of water decreases with increasing temperature.	The extent of ionization of water increases with increase in temperature giving more of H^+ ions.
3.	Silver chloride is soluble in ammonium hydroxide.	Silver chloride in NH_4OH exists as Ag^+ and Cl^- ions.
4.	In acid-base titrations, the use of indicator helps locating the end point of the titration.	The pH transition range of the indicator coincides with the steep portion of the titration curve.
5.	The pH of sulphuric acid solution can be computed by considering the ionization $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$.	Sulphuric acid ionizes in stepwise manner.
6.	The hydrolysis of a salt formed from a weak acid and a weak base exhibits extensive hydrolysis.	The hydrolysis of cation drags the hydrolysis of anion and vice versa.
7.	Oxalic acid ($K^\circ_{a_1} = 5.9 \times 10^{-2}$ and $K^\circ_{a_2} = 6.4 \times 10^{-5}$) exhibits stepwise neutralization with NaOH.	A dibasic acid exhibits stepwise dissociation provided $K^\circ_{a1}/K^\circ_{a2} \ge 10^2$
8.	The pH of water decreases with increase in temperature.	The ionization of water is temperature dependent.
9.	A solution of ammonium aceate has characteristics of a buffer solution.	The ions furnished by ammonium acetate are strong conjugate acid and base and have tendencies to react with OH^- and H^+, respectively.
10.	The end point of the titration between weak acid and weak base cannot be determined by using a suitable indicator.	The pH of the solution at the end point does not have a definite value.
11.	Silver chromate is more soluble in water as compared to silver chloride.	The solubility product of silver chromate is larger than that of silver chloride.

Matrix Match Type

1. Column II includes the expressions to compute pH value of some of the salts mentioned in Column I. Match the correct choice from these two columns.

Column I	Column II
(a) Salt formed from strong acid and strong base.	(p) $\text{pH} = \frac{1}{2}(\text{p}K_\text{w}^\circ + \text{p}K_\text{a}^\circ - \text{p}K_\text{b}^\circ)$
(b) Salt formed from strong acid acid and weak base.	(q) $\text{pH} = \frac{1}{2}[\text{p}K_\text{w}^\circ + \text{p}K_\text{a}^\circ + \log(c/c^\circ)]$
(c) Salt formed from weak acid and strong base.	(r) $\text{pH} = \frac{1}{2}\,\text{p}K_\text{w}^\circ$
(d) Salt formed from weak acid and weak base	(s) $\text{pH} = \frac{1}{2}[\text{p}K_\text{w}^\circ - \text{p}K_\text{b}^\circ - \log(c/c^\circ)]$

2. Column I lists a few sparingly soluble salt in water and Column II lists the expressions to compute solubility of the salt. Match the correct choice from these two columns.

Column I	Column II
(a) AB	(p) $(K_\text{sp}/108)^{1/5}$
(b) AB_2	(q) $(K_\text{sp}/27)^{1/4}$
(c) AB_3	(r) $K_\text{sp}^{1/2}$
(d) A_2B_3	(s) $(K_\text{sp}/4)^{1/3}$

3. Column I lists the constituents of a few buffer solution and Column II includes their buffer pH range. Match the correct choice from these two columns.

Column I	Column II
(a) Acetic acid + Sodium acetate	(p) 2.2 – 3.8
(b) Boric acid + Borax	(q) 3.7 – 5.6
(c) Borax + NaOH	(r) 5.0 – 6.3
(d) Phthalic acid + Potassium acid phthalate	(s) 9.2 – 11.0
	(t) 6.8 – 9.2
	(u) 11.0 – 12.0

4. Column I lists some of the acid-base indicators. Their pH transition ranges are given in Column II. Match the correct choices from these columns.

Column I	Column II
(a) Methyl orange	(p) 4.2 – 6.3
(b) Phenolphthalein	(q) 4.5 – 8.3
(c) Methyl red	(r) 8.3 – 10.0
(d) Thymol blue	(s) 3.1 – 4.4
	(t) 8.0 – 9.6
	(u) 5.2 – 6.8

5. Column I lists some of salt solutions, each having molarity of 0.1 M. Column II lists some of pH values. Identify the correct choices. Given are values of ionization constants: $K_\text{a}^\circ(\text{HAc}) = K_\text{b}^\circ(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$, $K_\text{b}^\circ(\text{aniline}) = 4.6 \times 10^{-10}$, $K_\text{a}^\circ(\text{H}_2\text{CO}_3) = 4.7 \times 10^{-11}$ and $K_\text{a}^\circ(\text{HCN}) = 4.9 \times 10^{-10}$ M.

Column I	Column II
(a) Ammonium acetate	(p) 4.71
(b) Ammonium cyanide	(q) 6.4
(c) Anilinium acetate	(r) 9.79
(d) Ammonium carbonate	(s) 9.28
	(t) 3.2
	(u) 7.0

ANSWERS

Straight Objective Type

1. (d) **2.** (b) **3.** (d) **4.** (a) **5.** (b) **6.** (c) **7.** (d)
8. (b) **9.** (d) **10.** (c) **11.** (c) **12.** (b) **13.** (d) **14.** (d)
15. (c) **16.** (b) **17.** (b) **18.** (b) **19.** (d) **20.** (a) **21.** (c)
22. (b) **23.** (b) **24.** (d) **25.** (a) **26.** (b) **27.** (c) **28.** (c)
29. (d) **30.** (b) **31.** (c) **32.** (a) **33.** (a) **34.** (b) **35.** (c)
36. (d) **37.** (a) **38.** (c) **39.** (c) **40.** (d) **41.** (d) **42.** (d)
43. (a) **44.** (b) **45.** (c) **46.** (b) **47.** (c) **48.** (c) **49.** (b)
50. (b) **51.** (b) **52.** (d) **53.** (a) **54.** (c) **55.** (b) **56.** (c)
57. (b) **58.** (a) **59.** (b) **60.** (d) **61.** (a) **62.** (a) **63.** (d)
64. (b) **65.** (c) **66.** (b) **67.** (a) **68.** (c) **69.** (c) **70.** (c)
71. (d) **72.** (b) **73.** (b) **74.** (d) **75.** (d) **76.** (d) **77.** (c)
78. (b) **79.** (d) **80.** (a) **81.** (d) **82.** (d) **83.** (b) **84.** (b)
85. (a) **86.** (d) **87.** (a) **88.** (a) **89.** (d) **90.** (c) **91.** (b)
92. (a) **93.** (b) **94.** (b) **95.** (c) **96.** (a) **97.** (d) **98.** (b)
99. (d) **100.** (c) **101.** (a) **102.** (d) **103.** (a) **104.** (c) **105.** (b)
106. (a) **107.** (c) **108**. (b) **109.** (c) **110.** (a) **111.** (d) **112.** (d)
113. (d) **114.** (d) **115.** (c) **116.** (a) **117.** (a) **118.** (a) **119.** (c)
120. (a)

Multiple Correct Choice Type

1. (b), (c) **2.** (a), (b), (c), (d) **3.** (a), (b), (c) **4.** (a), (b), (c)
5. (b), (c), (d) **6.** (b), (c) **7.** (a), (b), (c) **8.** (a), (b), (d)
9. (b), (c), (d) **10.** (a), (b), (c) **11.** (b), (c) **12.** (a), (c), (d)
13. (c), (d) **14.** (a), (b) **15.** (a), (b) **16.** (b), (d)
17. (b), (d) **18.** (a), (b), (c) **19.** (a), (b), (c), (d) **20.** (a), (c)
21. (b), (c)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (b) **(iii)** (a)
2. **(i)** (d) **(ii)** (c) **(iii)** (a)
3. **(i)** (a) **(ii)** (c) **(iii)** (b)
4. **(i)** (b) **(ii)** (d) **(iii)** (a)
5. **(i)** (b) **(ii)** (c) **(iii)** (d)
6. **(i)** (a) **(ii)** (b) **(iii)** (c)

Assertion and Reason Type

1. (a) **2.** (a) **3.** (d) **4.** (a) **5.** (d) **6.** (a) **7.** (c)
8. (b) **9.** (a) **10.** (c) **11.** (c)

Matrix Match Type

1. (a) – (r); (b) – (s); (c) – (q); (d) – (p) **2.** (a) – (r); (b) – (s); (c) – (q); (d) – (p)
3. (a) – (q); (b) – (t); (c) – (s); (d) – (p) **4.** (a) – (s); (b) – (r); (c) – (p); (d) – (t)
5. (a) – (u); (b) – (s); (c) – (p); (d) – (r)

Hints and Solutions

Straight Objective Type

1. The pH of a 10^{-8} M HCl will be less than 7 as it is an acidic solution.
2. $K_w = [H^+][OH^-]$. For pure water $[H^+] = [OH^-]$. Hence, $K_w = 10^{-12}\ M^2$.
3. Choice b is equivalent to 10 mL M/20 HCl. Its pH will be – log (1/20) = log 20 = 1.3010. Choice d is equivalent to 50 mL of M/10 HCl. Its pH will be – log (1/10) = 1.
4. Increasing temperature causes more ionization of water. Hence $[H^+]$ increases and pH decreases. At 25 °C, pH of water is 7 and pH = 6.5 implies temperature more than 25 °C.
5. Fraction of acid neutralized after the addition of 20.0 mL of NaOH solution = 20/35 = 4/7
   Fraction of acid unneutralized = 1 – 4/7 = 3/7

   Hence $\quad \text{pH} = \text{p}K_a^\circ + \log\{[\text{salt}]/[\text{acid}]\}$ gives

   $$5.75 = \text{p}K_a^\circ + \log\{(4/7)/(3/7)\} \Rightarrow \text{p}K_a^\circ = 5.75 - \log(4/3) = 5.75 - 0.13 = 5.62$$
6. We are given the following solutions.
   200 mL of 10^{-2} M (pH = 2.0) of HCl and 300 mL of 10^{-2} M (pH = 12) of NaOH
   On mixing, 100 mL of 10^{-2} M NaOH will be left unneutralized. Since the total volume of the solution will be 500 mL, the concentration of OH^- in the solution becomes $(1/5)(10^{-2}\ M) = 2 \times 10^{-3}$ M. Hence

   $$\text{pOH} = -\log\{[OH^-]/M\} = -\log(2 \times 10^{-3}) = 2.70$$
   $$\text{pH} = 14 - \text{pOH} = 14 - 2.70 = 11.30$$
7. $[H^+] = \sqrt{K_w} = (49 \times 10^{-14}\ M^2)^{1/2} = 7 \times 10^{-7}$ M

   $\text{pH} = -\log\{[H^+]/M\} = -\log(7 \times 10^{-7}) = 6.15$
8. The solution becomes 10^{-3} M in NaOH. Hence, pOH = 3 and thus pH = 14 – 3 = 11.
9. For pH = 3, $[H^+] = 10^{-3}$ M. For pH = 6, $[H^+] = 10^{-6}$ M. Hence, $[H^+]$ has to be decreased 10^3 times.
10. For water, pH = (1/2) $\text{p}K_w^\circ$ = 6.63.
11. pH = 13 implies $[H^+] = 10^{-13}$ M. One millilitre of this solution will contain 10^{-16} mol of H^+ and number of these species will be equal to 6.023×10^7.
12. pH of water at 40 °C will be (1/2) $\text{p}K_w^\circ$ = 6.77. Since the given solution has pH more than 6.77, the solution will be alkaline in nature.
13. For acetic acid, we have

   $$K_a = \frac{[H^+][Ac^-]}{[HAc]} \simeq \frac{[H^+]^2}{[HAc]_0}$$

   Hence $\quad [H^+] = \sqrt{K_a[HAc]_0} = \sqrt{(1.8 \times 10^{-5}\ M)(0.1\ M)} = 1.33 \times 10^{-3}$ M

   $$\text{pH} = -\log\{[H^+]/M\} = -\log(1.33 \times 10^{-3}) = 2.87$$
14. The value of $[H^+] = [OH^-] = 10^{-7}$ M is true only at 25 °C.
15. The resultant solution is 10^{-8} M HCl. Its pH will lie between 6 and 7 as it is an acidic solution.
16. The resultant solution is 10^{-8} M NaOH. Its pH will lie between 7 and 8 as it is an alkaline solution.
17. $\text{p}K_w^\circ = \text{pH} + \text{pOH} = 2\text{pH} = 2 \times 6 = 12$.
18. K_w increases with increase in temperature and thus $\text{p}K_w^\circ$ decreases with increase in temperature.
19. With increase in temperature, ionization of water increases. Thus, both H^+ and OH^- concentrations increase and pH and pOH decrease.
20. Both H^+ and OH^- concentrations increase with increase in temperature. Thus, product of these two also increases.
21. For H_2SO_4, we have

   $$H_2SO_4 \longrightarrow H^+ + HSO_4^-; \qquad HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

   In solution $[H^+] > 0.1$ M. Hence pH < 1.

22. The corresponding acids are HI, HCl, HNO_2 and HCN. Their acid strength follows the order HI > HCl > HNO_2 > HCN. Hence, their conjugate base follows the reverse order.

23. The resultant solution will be 0.1 molar sodium acetate. The acetate ions undergo hydrolysis reaction: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

24. Sodium acetate solution is alkaline and thus has maximum pH.

25. Smaller ionization constant with larger concentration of acid involves lesser dissociation.

26. At 100 °C, more of water will ionize and $[H^+]$ will be more that 10^{-7} M and K_w will be more that $10^{-14}\ M^2$ and thus pK_w^o will be less than fourteen.

27. pOH 10 $\Rightarrow$ pH = 4 $\Rightarrow$ $[H^+] = 10^{-4}$ M. In 1 mL of solution, $n(H^+) = 10^{-7}$ mol.

$$N = (10^{-7}\ \text{mol})\ (6.023 \times 10^{23}\ \text{mol}^{-1}) = 6.023 \times 10^{16}$$

28. The concentration of H^+ in 200 mL acid solution = 10^{-12} M
The concentration of H^+ in 800 mL acid solution = 10^{-3} M

$$\text{Total amount of } H^+ = \left(\frac{10^{-2}\text{mol}}{1000\ \text{mL}}\right)(200\ \text{mL}) + \left(\frac{10^{-3}\text{mol}}{1000\ \text{mL}}\right)(800\ \text{mL}) = (2 \times 10^{-3}\ \text{mol} + 8 \times 10^{-4}\ \text{mol})$$

$$= 2.8 \times 10^{-3}\ \text{mol}$$

Total volume of solution = 200 mL + 800 mL = 1000 mL = 1 L

$$\text{Concentration of } H^+ \text{ in solution} = \frac{2.8 \times 10^{-3}\ \text{mol}}{1\,\text{L}} = 2.8 \times 10^{-3}\ \text{M}$$

pH of solution = $-\log(2.8 \times 10^{-3}) = 2.55$

29. The pH of stomach is lesser than pK_a^o while that of small intestine is greater than pK_a^o. Hence, aspirin is unionized in stomach while in small intestine it is present in the ionized form.

30. The expression of Ostwald dilution law is $\alpha = \sqrt{K_a/c}$.

31. We have

$$\begin{array}{lcc} A_x\,B_y & \rightleftharpoons & xA^{y+} \quad + \quad yB^{x-} \\ c\,(1-\alpha) & & c\,(x\alpha) \qquad c\,(y\alpha) \end{array}$$

$$K_{eq} = \frac{[A^{y+}]^x\,[B^{x-}]^y}{[A_xB_y]} = \frac{(cx\alpha)^x\,(cy\alpha)^y}{c(1-\alpha)}$$

For a concentrated solution $K_{eq} = c^{x+y-1}\,x^x\,y^y\,\alpha^{x+y}$
Hence $\alpha = [K_{eq}/c^{x+y-1}\,x^x\,y^y]^{1/(x+y)}$

32. We have

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_{a1}\,K_{a2} = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]} \quad \Rightarrow \quad [S^{2-}] = \frac{K_{a1}K_{a2}[H_2S]}{[H^+]^2}$$

$$[S^{2-}] = \frac{(1.1 \times 10^{-21}\ M^3)\,(0.1\ M)}{(0.1\ M)^2} = 1.1 \times 10^{-20}\ M$$

Number of S^{2-} = $(1.1 \times 10^{-20}\ \text{mol})\ (6.023 \times 10^{23}\ \text{mol}^{-1}) = 6.625 \times 10^3$

33. The addition of sodium acetate to acetic acid solution suppresses the ionization of acid. Due to decrease in the concentration of H^+, its pH will increase.

34. The addition of NH_4Cl in water makes the solution acidic. Due to two sources of H^+, the pH of the solution will show a slight decrease.

35. The solution will contain 0.1 M HAc and 0.4 M NaAc. The pH of solution will be

$$pH = pK_a^o + \log\frac{[\text{salt}]}{[\text{acid}]} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.4}{0.1}\right) = 4.75 + 0.60 = 5.35$$

36. The solution will contain 0.1 M NH_4OH and 0.4 M NH_4Cl. Its pH will be 14 – 5.35 = 8.65, where 5.35 is pOH of the solution which can be determined using Henderson's equation. See Q.35.

37. $$\frac{[\mathrm{H}^+]_{\mathrm{HOCN}}}{[\mathrm{H}^+]_{\mathrm{HCN}}} = \left(\frac{K_\mathrm{a}(\mathrm{HOCN})}{K_\mathrm{a}(\mathrm{HCN})}\right)^{1/2} = \left(\frac{1.2\times10^{-4}}{4.2\times10^{-10}}\right)^{1/2} = 535$$

38. In solution $K_\mathrm{w} = K_\mathrm{a}K_\mathrm{b}$ or $\mathrm{p}K_\mathrm{w}^\circ = \mathrm{p}K_\mathrm{a}^\circ + \mathrm{p}K_\mathrm{b}^\circ$. The $\mathrm{p}K_\mathrm{a}^\circ$ of HF will be 14 – 10.83 = 3.17. Its K_a° will be antilog (–3.17) = 6.76×10^{-4}.

39. $\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$; $K_\mathrm{a} = [\mathrm{H}^+]\,[\mathrm{A}^-]/[\mathrm{HA}] \simeq [\mathrm{H}^+]^2/[\mathrm{HA}]_0 = (10^{-4}\ \mathrm{M})^2/0.1\ \mathrm{M} = 10^{-7}\ \mathrm{M}$

40. $\underset{c(1-\alpha)}{\mathrm{HCN}} \rightleftharpoons \underset{c\alpha}{\mathrm{H}^+} + \underset{c\alpha}{\mathrm{CN}^-}$; $K_\mathrm{a} = (c\alpha)^2/c(1-\alpha) = c\alpha^2/(1-\alpha) \simeq c\alpha^2$ or $\alpha = \sqrt{K_\mathrm{a}/c}$.

The values of K_a/c of given choices are:

For HCN, (a) $4 \times 10^{-10}\ \mathrm{M}/1.0\ \mathrm{M} = 4 \times 10^{-10}$, (b) $4 \times 10^{-10}\ \mathrm{M}/0.1\ \mathrm{M} = 4 \times 10^{-9}$

For $\mathrm{HNO_2}$ (c) $4.5 \times 10^{-4}\mathrm{M}/1.0\ \mathrm{M} = 4.5 \times 10^{-4}$, (d) $4.5 \times 10^{-4}\ \mathrm{M}/0.1\ \mathrm{M} = 4.5 \times 10^{-3}$

Larger the value of K_a/c, larger the dissociation.

41. An aqueous soution of carbonic acid involves the following equilibria.

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2O}; \qquad \mathrm{H_2CO_3} \rightleftharpoons \mathrm{H}^+ + \mathrm{HCO_3^-}; \qquad \mathrm{H_2CO_3} \rightleftharpoons \mathrm{H}^+ + \mathrm{CO_3^{2-}}$$

Thus, the solution contains $\mathrm{H_2CO_3}$, $\mathrm{CO_2}$, H^+, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$.

42. 0.1 M solution of sodium acetate is basic due to hydrolysis of acetate ion;

$$\mathrm{CH_3COO^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3COOH} + \mathrm{OH^-}.$$

43. A solution of $\mathrm{CuSO_4}$ is acidic due to the hydrolysis of strong conjugate acid Cu^{2+} ions;

$$\mathrm{Cu}^{2+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cu(OH)}^+ + \mathrm{H}^+.$$

44. A solution of NaCN is alkaline due to the hydrolysis of strong conjugate base CN^- ions;

$$\mathrm{CN}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{HCN} + \mathrm{OH}^-.$$

45. A solution of NaCl is neutral as both Na^+ and Cl^- ions are weak conjugate acid and base, respectively.

46. A solution of $\mathrm{NH_4CN}$ is alkaline because CN^- is more strong (conjugate base) than $\mathrm{NH_4^+}$ (which is conjugate acid). The hydrolysis CN^- proceeds more than that of $\mathrm{NH_4^+}$.

47. For a $\mathrm{NH_4Cl}$ solution, we will have

$$\mathrm{NH_4^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4OH} + \mathrm{H}^+$$

$$K_\mathrm{h} = \frac{K_\mathrm{w}}{K_\mathrm{b}(\mathrm{NH_4OH})} = \frac{[\mathrm{NH_4OH}][\mathrm{H}^+]}{[\mathrm{NH_4^+}]} \simeq \frac{[\mathrm{H}^+]^2}{[\mathrm{NH_4^+}]_0}$$

Hence $\log K_\mathrm{w}^\circ - \log K_\mathrm{b}^\circ(\mathrm{NH_4OH}) = 2\log\{[\mathrm{H}^+]/\mathrm{M}\} - \log\{[\mathrm{NH_4^+}]_0/\mathrm{M}\}$

$$-\,\mathrm{p}K_\mathrm{w}^\circ + \mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) = -2\mathrm{pH} - \log\{[\mathrm{NH_4^+}]_0/\mathrm{M}\}$$

or $\mathrm{pH} = \frac{1}{2}\,\mathrm{p}K_\mathrm{w}^\circ - \frac{1}{2}\,\mathrm{p}K_\mathrm{b}^\circ(\mathrm{NH_4OH}) - \frac{1}{2}\log\{[\mathrm{salt}]/\mathrm{M}\}$

48. For a sodium acetate solution, we will have

$$\mathrm{Ac}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{HAc} + \mathrm{OH}^-$$

$$K_\mathrm{h} = \frac{K_\mathrm{w}}{K_\mathrm{a}(\mathrm{HAc})} = \frac{[\mathrm{HAc}][\mathrm{OH}^-]}{[\mathrm{Ac}^-]} \simeq \frac{[\mathrm{OH}^-]^2}{[\mathrm{Ac}^-]_0}$$

Hence $\log K_\mathrm{w}^\circ - \log K_\mathrm{a}^\circ(\mathrm{HAc}) = 2\log\{[\mathrm{OH}^-/\mathrm{M}]\} - \log\{[\mathrm{Ac}^-]_0/\mathrm{M}\}$

$$-\,\mathrm{p}K_\mathrm{w}^\circ + \mathrm{p}K_\mathrm{a}^\circ(\mathrm{HAc}) = -2\mathrm{pOH} - \log\{[\mathrm{Ac}^-]_0/\mathrm{M}\}$$

or $-\,\mathrm{p}K_\mathrm{w}^\circ + \mathrm{p}K_\mathrm{a}^\circ(\mathrm{HAc}) = -2\mathrm{p}K_\mathrm{w}^\circ + 2\mathrm{pH} - \log\{[\mathrm{Ac}^-]_0/\mathrm{M}\}$

or $\mathrm{pH} = \frac{1}{2}\,\mathrm{p}K_\mathrm{w}^\circ + \frac{1}{2}\,\mathrm{p}K_\mathrm{a}^\circ(\mathrm{HAc}) + \frac{1}{2}\log\{[\mathrm{salt}]/\mathrm{M}\}$

49. The characteristics of the given solutions are:

NaCl	neutral solution
$\mathrm{NH_4Cl}$	slightly acidic due to the reaction $\mathrm{NH_4^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4OH} + \mathrm{H}^+$

NaCN	Slightly alkaline due to the reaction $CN^- + H_2O \rightleftharpoons HCN + OH^-$
HCl	highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline i.e. HCl < NH_4Cl < NaCl < NaCN

50. In $CaCO_3$, both the ions Ca^{2+} and CO_3^{2-} are hydrolysed. In $CaCl_2$, only Ca^{2+} ions are hydrolysed. Both $Ca(OH)_2$ and CH_3COONa are alkaline in nature. Hence, the lowest pH will be that of $CaCl_2$ solution. The hydrolysis constant of

$$\begin{array}{llll} X^- + & H_2O & \rightleftharpoons HX + & OH^- \\ c(1-\alpha) & & c\alpha & c\alpha \end{array}$$

is
$$K_b = \frac{[HX][OH^-]}{[X^-]} = \frac{[H^+][OH^-]}{[H^+][X^-]/[HX]} = \frac{K_w}{K_a} = \frac{10^{-14}\ M^2}{10^{-5}\ M} = 10^{-9}\ M$$

Also
$$K_b = \frac{[HX][OH^-]}{[X^-]} = \frac{[c\alpha][\alpha]}{c(1-\alpha)} \simeq c\alpha^2$$

Hence,
$$\alpha = \sqrt{K_b/c} = \sqrt{10^{-9}\ M/0.1\ M} = 10^{-4}$$

The percent degree of hydrolysis if $10^{-4} \times 100$, i.e $10^{-2}\%$

51. Volume of (2/15) M HCl to neutralize the given 2.5 mL of (2/5)M weak monoacidic base is

$$V_{acid} = \frac{V_{base}\,M_{base}}{M_{acid}} = \frac{(2.5\ mL)\{(2/5)\ M\}}{\{(2/15)\ M\}} = 7.5\ mL$$

Total volume of solution at the equilibrium point is 2.5 mL + 7.5 mL = 10.0 mL
Molarity of the salt (B^+Cl^-) at the equivalence point is

$$M_{salt} = \frac{V_{base}\,M_{base}}{V_{total}} = \frac{(2.5\ mL)\{(2/5)\ M\}}{(10\ mL)} = 0.1\ M$$

The cation of the salt formed undergoes hydrolysis $B^+ + H_2O \rightleftharpoons BOH + H^+$, the hydrolysis constant of this reaction is

$$K_h = \frac{[BOH]}{[B^+][OH^-]}$$

Multiplying and dividing by $[OH^-]$ in the solution, we get

$$K_h = \frac{[BOH]}{[B^+][OH^-]}[H^+][OH^-] = \frac{K_w}{K_b} = \frac{10^{-14} M^2}{10^{-12} M} = 10^{-2}\ M$$

52. In the solution, [BOH} = $[H^+]$ and $[B^+] = [B^+]_0 - [H^+]$. Hence,

$$K_h = \frac{[H^+]^2}{[B^+]_0 - [H^+]} \quad \text{i.e. } [H^+]^2 + K_h\,[H^+] - K_h\,[B^+]_0 = 0$$

Substituting the values of K_h and $[B^+]_0$, we get

$$[H^+]^2 + (0.01\ M)\,[H^+] - 0.001\ M^2 = 0$$

Solving for $[H^+]$, we get

$$[H^+] = \frac{-(0.01\,M) + \sqrt{(0.01\,M)^2 + 4(0.001\,M^2)}}{2} = \frac{-(0.01\,M) + \sqrt{(0.0041\,M^2)}}{2} = \frac{(-0.01 + 0.064)\ M}{2} = 0.027\ M$$

53. The pH of NaX is 7, thus the acid HX must be a strong acid.
The ions Y^- and Z^- undergo hydrolysis

$$Y^- + H_2O \rightleftharpoons HY + OH^- \quad \text{and} \quad Z^- + H_2O \rightleftharpoons HY + OH^-$$

The stronger the base, larger the OH^- concentration and thus larger the pH of the solution. Thus, Z^- is more strong base then Y^- and thus the conjugate acid HZ will be weaker than HY. Hence, the correct order is HX > HY > HZ.

55. $K_h = \dfrac{K_w}{K_a K_b} = \dfrac{1.0 \times 10^{-14}\,\mathrm{M}^2}{(1.8 \times 10^{-5}\,\mathrm{M})(4.6 \times 10^{-10}\,\mathrm{M})} = 1.21$

56. We have

$$\underset{c(1-\alpha)}{NH_4^+} + \underset{c(1-\alpha)}{Ac^-} + H_2O = \underset{c\alpha}{NH_4OH} + \underset{c\alpha}{HAc}$$

$$K_h = \frac{[NH_4OH][HAc]}{[NH_4^+][Ac^-]} = \frac{(c\alpha)\,(c\alpha)}{\{c(1-\alpha)\}\{c(1-\alpha)\}} = \frac{\alpha^2}{(1-\alpha)^2}$$

or $\dfrac{\alpha}{1-\alpha} = \sqrt{K_h}$ or $\alpha = \dfrac{\sqrt{K_h}}{1+\sqrt{K_h}}$

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}\,\mathrm{M}^2}{(1.8 \times 10^{-5}\,\mathrm{M})(4.6 \times 10^{-5}\,\mathrm{M})} = 1.208$$

$$\alpha = \frac{\sqrt{K_h}}{1+\sqrt{K_h}} = \frac{\sqrt{1.208}}{1+\sqrt{1.208}} = \frac{1.099}{1+1.099} = 0.52$$

58. $\mathrm{pH} = \dfrac{1}{2}(\mathrm{p}K_a^\circ + \mathrm{p}K_b^\circ) = \dfrac{1}{2}(6.38 + 10.32) = 8.35$

59. Only for choice b, ionic-product exceeds solubility product; $[Ca^{2+}]\ [F^-]^2 = (10^{-2}\ \mathrm{M})\ (10^{-3}\ \mathrm{M})^2 = 10^{-8}\ \mathrm{M}^3$.

60. Sn^{2+} is not precipitated by hydrochloric acid.

61. Both Bi^{3+} and Sn^{4+} are precipitated.

62. For choice a, the ionic-product exceeds solubility product; $[Ag^+]\ [Cl^-] = (10^{-4}\ \mathrm{M})\ (10^{-4}\ \mathrm{M}) = 10^{-8}\ \mathrm{M}^2$.

63. The solubility of hydroxides of alkaline-earth metals decreases down the group. Hence, the solubility product of $Ba(OH)_2$ will be minimum.

64. Al^{3+} is precipited in the medium containing NH_4Cl and NH_4OH.

65. We have

$$Mg_3(PO_4)_2 \rightleftharpoons 3Mg^{2+} + 2PO_4^{3-}$$

$$K_{sp} = [Mg^{2+}]^3\ [PO_4^{3-}]^2$$

66. $s_0 = \sqrt{K_{sp}(AgCl)}$; $s_1 = K_{sp}(AgCl)/0.02$ M; $s_2 = K_{sp}(AgCl)/0.01$ M; $s_3 = K_{sp}(AgCl)/0.05$ M

Hence $s_0 > s_2 > s_1 > s_3$

67. Ag^+ ions required to precipitate $Cl^- = \dfrac{K_{sp}(AgCl)}{0.05\,\mathrm{M}}$

Ag^+ ions required to precipitate $CrO_4^{2-} = \left(\dfrac{K_{sp}(Ag_2CrO_4)}{0.05\,\mathrm{M}}\right)^{1/2}$. Because of square root in the second expression, the $[Ag^+]$ comes to be larger than the $[Ag^+]$ in the first expression. Hence, Cl^- ions are precipitated first.

68. pH = 10.45 implies $[H^+] = 10^{-10.45}$ M or $[OH^-] = 10^{-3.55}$ M

$$K_{sp}(Mg(OH_2)) = [Mg^{2+}]\ [OH^-]^2 = \left(\frac{1}{2} \times 10^{-3.55}\ \mathrm{M}\right)(10^{-3.55}\mathrm{M})^2 = 0.5 \times 10^{-10.65}\ \mathrm{M}^3$$

$$= (0.5 \times 10^{0.35})\ (10^{-11})\ \mathrm{M}^3 = (0.5 \times 2.24)\ (10^{-11}\ \mathrm{M}^3) = 1.12 \times 10^{-11}\ \mathrm{M}^3$$

69. We have

$$K_{\mathrm{sp}} = [\mathrm{A}^{3+}]^2\,[\mathrm{X}^{2-}]^3 = (2x)^2\,(3x)^3 = 108\,x^5$$

$$x = \left(\frac{K_{\mathrm{sp}}}{108}\right)^{1/5} = \left(\frac{1.08\times10^{-23}\ \mathrm{M}^5}{108}\right)^{1/5} = 1\times10^{-5}\ \mathrm{M}$$

70. We have

$$[\mathrm{Sr}^{2+}] = \frac{K_{\mathrm{sp}}(\mathrm{SrCO_3})}{[\mathrm{CO}_3^{2-}]} = \frac{7.0\times10^{-10}\ \mathrm{M}^2}{1.2\times10^{-3}\ \mathrm{M}} = 5.8\times10^{-7}\ \mathrm{M}$$

$$[\mathrm{F}^-] = \left[\frac{K_{\mathrm{sp}}(\mathrm{SrF_2})}{\mathrm{Sr}^{2+}}\right]^{1/2} = \left(\frac{7.9\times10^{-10}\ \mathrm{M}^3}{5.8\times10^{-7}\ \mathrm{M}}\right)^{1/2} = (1.36\times10^{-3}\ \mathrm{M}^2)^{1/2} = 3.7\times10^{-2}\ \mathrm{M}$$

71. The concentration of OH^- required to precipitate $\mathrm{Mg(OH)_2}$ is

$$[\mathrm{OH}^-] = \left(\frac{K_{\mathrm{sp}}}{[\mathrm{Mg}^{2+}]}\right)^{1/2} = \left(\frac{1.2\times10^{-11}\ \mathrm{M}^3}{0.10\ \mathrm{M}}\right)^{1/2} = 1.1\times10^{-5}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log\,(1.1\times10^{-5}) = 4.96 \quad \text{and} \quad \mathrm{pH} = 14 - 4.96 = 9.04$$

72. We have

$$\underset{}{\mathrm{M}_m\mathrm{A}_a} \rightleftharpoons \underset{(ms)}{m\mathrm{M}^{a+}} + \underset{(as)}{a\mathrm{A}^{m-}}$$

$$K_{\mathrm{sp}} = (ms)^m\,(as)^a; \qquad s = \left(\frac{K_{\mathrm{sp}}}{m^m a^a}\right)^{1/(m+a)}$$

73. We have

$$\mathrm{Ca_3(PO_4)_2} \rightleftharpoons \underset{3s}{3\mathrm{Ca}^{2+}} + \underset{2s}{2\mathrm{PO}_4^{3-}}$$

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^3\,[\mathrm{PO}_4^{3-}]^2 = \left(\frac{3}{2}\times3.3\times10^{-7}\ \mathrm{M}\right)^3 (3.3\times10^{-7}\ \mathrm{M})^2 = 1.32\times10^{-32}\ \mathrm{M}^5$$

74. We have

$$\mathrm{Hg_2Cl_2} \rightleftharpoons \underset{s}{\mathrm{Hg}_2^{2+}} + \underset{2s}{2\mathrm{Cl}}$$

$$K_{\mathrm{sp}} = [\mathrm{Hg}_2^{2+}]\,[\mathrm{Cl}^-]^2 = (s)\,(2s)^2 = 4s^3; \qquad s = (K_{\mathrm{sp}}/4)^{1/3}$$

75. We have

$$\mathrm{A_2X_3} \rightleftharpoons \underset{2y}{2\mathrm{A}^{3+}} + \underset{3y}{3\mathrm{X}^{2-}}$$

$$K_{\mathrm{sp}} = [\mathrm{A}^{3+}]^2\,[\mathrm{X}^{2-}]^3 = (2y)^2\,(3y)^3 = 108\,y^5$$

76. From the solubility expression of $\mathrm{MgCO_3}$, we find that

$$[\mathrm{CO}_3^{2-}] = \left(\frac{K_{\mathrm{sp}}(\mathrm{MgCO_3})}{[\mathrm{Mg}^{2+}]}\right)^{1/2} = \frac{1.6\times10^{-6}\ \mathrm{M}^2}{3.2\times10^{-5}\ \mathrm{M}} = 0.05\ \mathrm{M}$$

Hence $$[\mathrm{Ag}^+] = \left(\frac{K_{\mathrm{sp}}(\mathrm{Ag_2CO_3})}{[\mathrm{CO}_3^{2+}]}\right)^{1/2} = \left(\frac{8.2\times10^{-12}\ \mathrm{M}^3}{0.05\ \mathrm{M}}\right)^{1/2} = 1.28\times10^{-5}\ \mathrm{M}$$

77. If x is the solubility of $\mathrm{Pb(OH)_2}$ in water, we will have

$$\mathrm{Pb(OH)_2\ (s)} \rightleftharpoons \underset{x}{\mathrm{Pb}^{2+}}\mathrm{(aq} + \underset{2x}{2\mathrm{OH}^-}\mathrm{(aq)}; \quad K_{\mathrm{sp}} = x\,(2x)^2 = 4x^3$$

It is given that $x = 7.0 \times 10^{-6}$ M. Hence $K_{\text{sp}} = 4\ (7.0 \times 10^{-6}\ \text{M})^3 = 1.372 \times 10^{-15}\ \text{M}^3$

Solubility in a solution of pH = 8 (i.e. pOH = 6 or $[\text{OH}^-] = 10^{-6}$ M) is

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{1.372\times10^{-15}\ \text{M}^3}{(10^{-6}\ \text{M})^2} = 1.372 \times 10^{-3}\ \text{M}$$

78. $\text{Mg}_3(\text{PO}_4)_2 \rightleftharpoons \underset{3x}{3\text{Mg}^{2+}} + \underset{2x}{2\text{PO}_4^{3-}}$; $K_{\text{sp}} = (3x)^3\ (2x)^2 = 108\ x^5$

$$x = (K_{\text{sp}}/108)^{1/5} = (1.08 \times 10^{-13}\ \text{M}^5/108)^{1/5} = 10^{-3}\ \text{M}$$

79. $\text{A}_2\text{X}_3(\text{s}) \rightleftharpoons \underset{2y}{2\text{A}^{3+}(\text{aq})} + \underset{3y}{3\text{X}^{2-}(\text{aq})}$

$$K_{\text{sp}} = [\text{A}^{3+}]^2\ [\text{X}^{2-}]^3 = (2y)^2\ (3y)^3 = 108y^5$$

80. $\text{A}_p\text{B}_q \rightleftharpoons p\text{A}^{q+} + q\text{B}^{p-}$. If s is the solubility of A_pB_q, then $[\text{A}^{q+}] = ps$ and $[\text{B}^{p-}] = qs$

Hence $K_{\text{sp}} = [\text{A}^{q+}]^p\ [\text{B}^{p-}]^q = (ps)^p\ (qs)^q = p^p q^q\ s^{(p\,+\,q)}$

81. Sodium sulphide is soluble in water. The solubility product (and hence solubility) of ZnS is larger than that of CuS.

82. For MX, we have $\text{MX} \rightleftharpoons \text{M}^+ + \text{X}^-$; $K_{\text{sp}} = [\text{M}^+]\ [\text{X}^-] = (s)\ (s) = s^2$

Hence $s = K_{\text{sp}}^{1/2} = (4.0 \times 10^{-8}\ \text{M}^2)^{1/2} = 2 \times 10^{-4}$ M

For MX_2, we have $\text{MX}_2 \rightleftharpoons \text{M}^{2+} + 2\text{X}^-$; $K_{\text{sp}} = [\text{M}^{2+}]\ [\text{X}^-]^2 = (s)\ (2s)^2 = 4s^3$

Hence $s = (K_{\text{sp}}/4)^{1/3} = (3.2 \times 10^{-14}\ \text{M}^3/4)^{1/3} = 2 \times 10^{-5}$ M

For M_3X, we have $\text{M}_3\text{X} \rightleftharpoons 3\text{M}^+ + \text{X}^{3-}$; $K_{\text{sp}} = [\text{M}^+]^3\ [\text{X}^{3-}] = (3s)^3\ (s) = 27s^4$

Hence $s = (K_{\text{sp}}/27)^{1/4} = (2.7 \times 10^{-15}\ \text{M}^4/27)^{1/4} = 1.0 \times 10^{-4}$ M

Hence, the solubility follows the order $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

83. On mixing the two solutions, 0.1 M of AgNO_3 which is left in excess becomes 0.05 M due to doubling of the volume. Hence

$$[\text{Cl}^-] = \frac{K_{\text{sp}}(\text{AgCl})}{[\text{Ag}^+]} = \frac{1.8\times10^{-10}\text{M}^2}{0.05\ \text{M}} = 3.6 \times 10^{-9}\ \text{M}$$

84. We have

$$\begin{array}{ll} \text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}); & K_{\text{sp}} = 1.8 \times 10^{-10}\ \text{M}^2 \\ \text{Ag}^+(\text{aq}) + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+; & K_1 = 1.8 \times 10^{7}\ \text{M}^{-2} \\ \hline \text{AgCl(s)} + 2\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2^+] + \text{Cl}^- & K = K_{\text{sp}}\ K_1 = 3.24 \times 10^{-3} \end{array}$$

Let x be the amount of AgCl(s) dissolve in 0.1 M NH_3. We will have

$$K = \frac{[\text{Ag(NH}_3)_2^+]\ [\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{(x)\,(x)}{(0.1\,\text{M} - 2x)^2} = 3.24 \times 10^{-3}$$

$$\frac{x}{0.1\,\text{M} - 2x} = 0.057 \quad \text{or} \quad x = \frac{0.1\times 0.057}{1 + 2\times 0.057}\ \text{M} = 0.0052\ \text{M}$$

85. An acidic buffer is prepared by mixing weak acid and salt of its conjugate base, e.g., acetic acid and ammonium acetate.

86. Ammonium acetate contains strong conjugate cation and strong conjugate anion. Hence, its solution can be used as a buffer solution.

87. A buffer has a maximum buffer capacity if [salt] = [acid].

88. For an acidic buffer solution, pH = $\text{p}K_{\text{a}}^{\text{o}}$ when [salt] = [acid].

89. For an acidic buffer solution, pH = $\text{p}K_{\text{a}}^{\text{o}}$ + log ([salt]/[acid]).

90. On diluting a buffer solution, the ratio of salt to acid (or base) does not change. Hence, its pH remains constant.

91. The addition of HCl causes the replacement of salt(NaAc) with acid(HAc).

92. The addition of NaOH causes the replacement of acid(HAc) with salt(NaAc). The ratio of salt to acid increases. Hence, the pH of buffer solution will also increase.

93. The addition of HCl causes the replacement of base (NH_4OH) with salt (NH_4Cl). The ratio of salt to base increases. Hence, the pOH of buffer solution will increase and its pH will decrease.

94. The buffer capacity is maximum when the ratio of concentrations of acid is one. It decreases on either sides of this ratio.

95. [salt] = (0.02 M) (20/30) and [acid] = (0.01 M) (10/30)

[salt]/[acid] = 4. pH = $\mathrm{p}K_a^\circ$ + log [salt]/[acid] = – log (2.0×10^{-5}) + log 4 = 4.7 + 0.60 = 5.3

96. $K_a^\circ(HX) = K_w^\circ/K_b^\circ\,(X^-) = 10^{-14}/10^{-10} = 10^{-4}$

$$\mathrm{pH} = \mathrm{p}K_a^\circ + \log([\text{salt}]/[\text{acid}]) = 4$$

97. We have

$$\begin{array}{lcccc} & CH_3NH_2 \; + & HCl \;\rightarrow & C\,H_3\,\overset{+}{N}H_3 \; + & Cl^- \\ \text{Initially} & 0.1\ \text{mol} & 0.08\ \text{mol} & 0 & 0 \\ \text{Finally} & 0.02\ \text{mol} & - & 0.08\ \text{mol} & 0.08\ \text{mol} \end{array}$$

The expression of K_b of CH_3NH_2 is

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Hence,
$$K_b = \frac{\left[CH_3NH_3^+\right]\left[OH^-\right]}{[CH_3NH_2]} = \frac{(0.08\ \text{mol})\left[OH^-\right]}{0.02\ \text{mol}}$$

$$[OH^-] = \frac{K_b}{4} = \frac{6 \times 10^{-4}\,\text{M}}{4} = 1.5 \times 10^{-4}\ \text{M}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-4}\,\text{M}^2}{1.5 \times 10^{-4}\,\text{M}} = 6.7 \times 10^{-11}\,\text{M}$$

98. We have

$$\mathrm{pH} = \mathrm{p}K_a^\circ + \log\left[\frac{\text{salt}}{\text{acid}}\right] = \mathrm{p}K_a^\circ + \log\left[\frac{n_\text{salt}}{n_\text{acid}}\right]$$

$$8.5 = 9.2 + \log\left(\frac{n_\text{salt}}{0.05\ \text{mol}}\right) = 9.2 + \log(n_\text{salt}/\text{mol}) - \log(0.05)$$

$$-\,0.7 = \log(n_\text{salt}/\text{mol}) - (\bar{2}.6990)$$

$$\log(n_\text{salt}/\text{mol}) = -\,2.0 \quad \text{or} \quad n_\text{salt} = 10^{-2}\ \text{mol}$$

Since $(NH_4)_2SO_4$ includes $2NH_4^+$ ions, the amount of $(NH_4)_2SO_4$ required will be 0.005 mol.

99. The pH of the solution at the equivalence point lies in the alkaline range. Hence, phenolphthalein is the best indicator.

100. At the equivalence point, the solution will contain NaCl. Its pH would be 7.

101. At the equivalence point, the solution will contain NH_4Cl. Due to the hydrolysis of NH_4^+, its pH will be lesser than seven.

102. At the equivalence point, the solution will contain sodium acetate. Due to the hydrolysis of Ac^-, its pH will be greater than seven.

103. The pH of the solution at the equivalence point is about 8. Phenolphthalein is best to use as indicator.

104. The pH of the solution at the equivalence point is about 5. Methyl orange is best to use as indicator.

105. The pink colour of phenolphthalein is due to its anionic form.

106. For 75% red, we have

$$\text{pH} = \text{p}K_a^\circ + \log\,[\text{salt}/[\text{acid}] = -\log\,(3 \times 10^{-5}) + \log\,(25/75)$$
$$= 4.52 - 0.48 = 4.04 \quad \Rightarrow \quad [\text{H}^+] = 9.12 \times 10^{-5}\ \text{M}$$

For 75% blue, we have

$$\text{pH} = -\log\,(3 \times 10^{-5}) + \log\,(75/25) = 4.52 + 0.48 = 5.00 \quad \Rightarrow \quad [\text{H}^+] = 10^{-5}\ \text{M}$$

Hence $\Delta[\text{H}^+] = 9.2 \times 10^{-5}\ \text{M} - 1.0 \times 10^{-5}\ \text{M} = 8.12 \times 10^{-5}\ \text{M}$

107. The reaction is $\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$. Its equilibrium constant is

$$K_\text{eq} = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}\,\frac{1}{[\text{H}^+][\text{OH}^-]} = \frac{K_a}{K_w} = \frac{10^{-4}\text{M}}{10^{-14}\text{M}^2} = 10^{10}\ \text{M}^{-1}$$

110. The conjugate acid of NH_2^- is NH_3.

111. The conjugate acid-base pairs are (HCl, Cl^-) and ($\text{CH}_3\text{COOH}_2^+$, CH_3COOH).

112. HCO_3^- can be converted into CO_3^{2-} as well as to H_2CO_3.

113. In the reaction $\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$, the conjugate acid pair is (HCN, CN^-).

114. A substance which can donate a pair of electrons is a base. Thus, choice d is incorrect.

115. NH_3 donate pair of electrons while BF_3, Cu^{2+} and AlCl_3 accept lone pair of electrons.

117. The conjugate acids are CH_3COOH, H_2S, NH_4^+ and HCO_3^-. Their order of acid strength is $\text{CH}_3\text{COOH} > \text{H}_2\text{S} > \text{NH}_4^+ > \text{HCO}_3^-$. The base strength of their conjugate base follows the reverse order.

118. The conjugate acids are H_2O, NH_3, $\text{HC} \equiv \text{CH}$ and CH_3CH_3. Their order of acid strength is $\text{CH}_3\text{CH}_3 < \text{NH}_3 < \text{HC} \equiv \text{CH} < \text{H}_2\text{O}$. Their conjugate base follows the reverse order.

Multiple Correct Choice Type

1. (a) pH will be less than 7.

(d) $\text{pH} = \text{p}K_a$.

2. (a) $c = \dfrac{n}{V} = \dfrac{(m/M)}{V} = \dfrac{(1000\ \text{g}/18\ \text{g mol}^{-1})}{1\ \text{dm}^3} = 55.56\ \text{mol dm}^{-3}$

(c) $$\underset{c(1-\alpha)}{\text{H}_2\text{O}} \rightleftharpoons \underset{c\alpha}{\text{H}^+} + \underset{c\alpha}{\text{OH}^-}; \qquad K_w = [\text{H}^+]\,[\text{OH}^-] = (c\alpha)^2$$

$$\alpha = \frac{\sqrt{K_w}}{c} = \frac{\sqrt{1.0 \times 10^{-14}\text{M}^2}}{55.56\ \text{M}} = 1.8 \times 10^{-9}$$

(d) $$K_\text{ioniz} = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{1.0 \times 10^{-14}\text{M}^2}{55.56\ \text{M}} = 1.8 \times 10^{-16}\ \text{M}$$

4. (b) $$\underset{c(1-\alpha)}{\text{CH}_3\text{COO}^-} + \text{H}_2\text{O} \rightleftharpoons \underset{c\alpha}{\text{CH}_3\text{COOH}} + \underset{c\alpha}{\text{OH}^-}; \qquad K_h = K_w/K_a$$

$$K_h = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \simeq c\alpha^2 \quad \text{i.e.} \quad \alpha = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a c}}$$

$$\log \alpha = \frac{1}{2}\,(\log K_w^\circ - \log K_a^\circ - \log c/c^\circ) = \frac{1}{2}\,(-\,\text{p}K_w^\circ + \text{p}K_a^\circ - \log c/c^\circ)$$

(c) Larger the concentration, lesser the degree of hydrolysis and thus lesser is $[\text{OH}^-]$ and hence larger is the pOH.

(a) $[\text{OH}^-] = c\alpha = \sqrt{K_h c} = \sqrt{K_w c/K_a}\,;\qquad [\text{H}^+] = K_w/[\text{OH}^-] = \sqrt{K_w K_a/c}$

$$\log\{H^+/c^\circ\} = \frac{1}{2}\,[\log K^\circ_w + \log K^\circ_a - \log(c/c^\circ)]$$

$$pH = \frac{1}{2}\,[pK^\circ_w + pK^\circ_a + \log(c/c^\circ)]$$

5. (a) The correct expression is $[H^+] = \sqrt{K_w K_a / K_b}$

(b) See Q.56 of straight objective questions

(c) $pH = pK^\circ_a + \frac{1}{2}\,pK^\circ_h = pK_a + \frac{1}{2}\,(pK^\circ_w - pK^\circ_a - pK^\circ_b) = \frac{1}{2}\,(pK^\circ_w + pK^\circ_a - pK^\circ_b)$

(d) See Q. 4.(c)

6. (a) $K_a(HCN) < K_a(CH_3COOH)$. Since $K_h = K_w/K_a$, K_h for CN^- ions is larger than CH_3COO^- ions.

(d) The solution of NH_4CN is alkaline and CN^- undergoes more hydrolysis than NH_4OH.

7. Larger the temperature, larger the ionization of water yielding $[H^+] > 10^{-7}$ mol dm^{-3} and thus pH < 7.

8. (c) $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$c(1-\alpha) \qquad c\alpha \qquad c\alpha$

$$K_h = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \simeq c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b c}}$$

9. (a) Lewis acid accepts pair of electrons and does not donate them.

(b) This is due to formation of $Na^+AgCl_2^-$.

10. (a) $Zn(OH)_2$ is an amphoteric species. In acidic medium, it exists as Zn^{2+} while in alkaline solution as $Zn(OH)_4^{2-}$.

(b) This is known as levelling effect.

(c) Since all are stronger than H_3O^+.

(d) Only acids stronger than H_3O^+ are levelled in water.

11. (d) Reaction proceeds in a direction favouring weak acids and bases. So, CN^- is also a weaker base than OH^-.

12. (b) The base strength of conjugate bases follows the reverse order of the acid strength. Since HI > HBr > HCl > HF, the correct sequence of base strength would be $I^- < Br^- < Cl^- < F^-$.

(c) The self-ionization of NH_3 is $NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

In NH_3, NH_4^+ is the strongest acid and NH_2^- is the strongest base.

(d) Perchloric acid is stronger acid than sulphuric acid.

Linked Comprehension Type

1. **(i)** $HA \rightleftharpoons H^+ + A^-;\ K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{x^2}{1.0\,M - x}$

$1.0\,M - x \qquad x \qquad x$

Assuming $x < 1.0$ M, we get

$$\frac{x^2}{1.0\,M} = 1.0 \times 10^{-4}\,M \;\Rightarrow\; x = 1.0 \times 10^{-2}\,M \;\Rightarrow\; pH = -\log x/M = 2$$

If the pH is doubled, then $[H^+] = 1.0 \times 10^{-4}$ M. Hence

$$\frac{(1.0 \times 10^{-4}\,M)^2}{c - 1.0 \times 10^{-4}\,M} = 1.0 \times 10^{-4}\,M \quad \text{i.e.} \quad 1.0 \times 10^{-8}\,M^2 = c(1.0 \times 10^{-4}\,M) - 1.0 \times 10^{-8}\,M^2$$

or $$c = \frac{2.0 \times 10^{-8}\,M}{1.0 \times 10^{-4}\,M} = 2.0 \times 10^{-4}\,M$$

If V is the final volume of the solution, we will have $V\,(2.0 \times 10^{-4}\ \text{M}) = (1\ \text{dm}^3)\,(1.0\ \text{M})$

or $\quad V = 5.0 \times 10^3\ \text{dm}^3$

(ii) Here, $[\text{H}^+] = 0.005$ M. Hence

$$\frac{(0.005\ \text{M})^2}{c - (0.005\ \text{M})} = 1.0 \times 10^{-4}\ \text{M}$$

Assuming $0.005\ \text{M} < c$, we have

$$c = \frac{(0.005\ \text{M})^2}{1.0 \times 10^{-4}\ \text{M}} = 2.5 \times 10^{-1}\ \text{M}$$

Hence $\quad V\,(0.25\ \text{M}) = (1\ \text{dm}^3)\,(1.0\ \text{M})$. Thus $V = 4\ \text{dm}^3$

(iii) $\text{pH} = \text{p}K_\text{a}^\text{o} + \log\{[\text{salt}]/[\text{acid}]\}$

$$-\log(0.005) = -\log(1.0 \times 10^{-4}) + \log\frac{[\text{salt}]}{(0.1\ \text{M})}$$

$$2.30 = 4 + \log\frac{[\text{salt}]}{(0.1\ \text{M})} \quad \text{or} \quad \log\left\{\frac{[\text{salt}]}{(0.1\ \text{M})}\right\} = -1.70$$

or $$\frac{[\text{salt}]}{(0.1\ \text{M})} = 0.02 \quad \text{or} \quad [\text{salt}] = 0.02\ \text{M}$$

2. **(i)** $\underset{0.1\ \text{M}-x}{\text{CO}_3^{2-}} + \text{H}_2\text{O} \rightleftharpoons \underset{x}{\text{HCO}_3^-} + \underset{x}{\text{OH}^-}$; $K_\text{h} = \dfrac{K_\text{w}}{K_\text{a}(\text{HCO}_3^-)} = \dfrac{10^{-14}}{1/(2.1 \times 10^{10})} = 2.1 \times 10^{-4}\ \text{M}$

$$K_\text{h} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.1\ \text{M} - x}$$

Assuming $x < 0.1$ M, we get

$$x = \sqrt{(0.1\ \text{M})\,K_\text{h}} = \sqrt{2.1 \times 10^{-5}\ \text{M}^2} = 4.58 \times 10^{-3}\ \text{M}$$

$\text{pOH} = -\log(4.58 \times 10^{-3}\ \text{M}) = 2.34$; $\quad \text{pH} = 14 - 2.34 = 11.66$

(ii) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \qquad K_3^\circ = 1/(2.2 \times 10^6) = 0.45 \times 10^{-6}$

$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \qquad K_4^\circ = 1/(2.1 \times 10^{10}) = 0.48 \times 10^{-10}$

$\text{p}K_3^\circ = -\log(0.45 \times 10^{-6}) = 6.34$ and $\text{p}K_4^\circ = -\log(0.48 \times 10^{-10}) = 10.32$

$$\text{pH} = \frac{1}{2}(\text{p}K_3^\circ + \text{p}K_4^\circ) = \frac{1}{2}(6.34 + 10.32) = 8.33$$

(iii) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \qquad K_3^\circ = 1/(2.2 \times 10^6) = 0.45 \times 10^{-6}$

Total volume of the solution will become 150 mL. Hence, the molarity of H_2CO_3 will become one third of the original molarity of CO_3^{2-}. Hence

$$\text{Molarity of H}_2\text{CO}_3 = \frac{0.1\ \text{M}}{3} = 0.033\ \text{M}$$

If the molarity x of H_2CO_3 is present in the ionized form, we will have

$$\underset{0.033\ \text{M}-x}{\text{H}_2\text{CO}_3} \rightleftharpoons \underset{x}{\text{H}^+} + \underset{x}{\text{HCO}_3^-}$$

Hence $$K_3^\circ = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)\,(x)}{0.033\ \text{M} - x} = 0.45 \times 10^{-6}\ \text{M}$$

Assuming $x < 0.033$ M, we will have

$$x = \sqrt{(0.03\,\mathrm{M})(0.45\times10^{-6}\mathrm{M})} = 1.22 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pH} = -\log\left(\frac{x}{\mathrm{M}}\right) = -\log(1.22 \times 10^{-4}) = 3.91$$

3. **(i)** Since $(K_1^\circ/K_2^\circ) > 10^3$, CO_3^{2-} is first converted into HCO_3^-

(ii) Since pH at the mid of titration is 8.3 (see Q. 2 (ii)), the suitable indicator will be methyl red.

(iii) Since pH at the end of titration is about 4 (see. Q.2(iii)), the suitable indicator will be methyl red.

4. **(i)** $[Ag^+]$ to start the precipitation of Cl^- ion

$$= \frac{K_{sp}(AgCl)}{[Cl^-]} = \frac{1.7\times10^{-10}\mathrm{M}^2}{0.1\,\mathrm{M}} = 1.7 \times 10^{-9}\ \mathrm{M}$$

$[Ag^+]$ to start the precipitation of Br^- ion

$$= \frac{K_{sp}(AgBr)}{[Br^-]} = \frac{5.0\times10^{-13}\mathrm{M}^2}{0.1\,\mathrm{M}} = 5.0 \times 10^{-12}\ \mathrm{M}$$

$[Ag^+]$ to start the precipitation of CrO_4^{2-} ion

$$= \left[\frac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{2-}]}\right]^{1/2} = \left[\frac{1.9\times10^{-12}\mathrm{M}^2}{0.1\,\mathrm{M}}\right]^{1/2} = 4.36 \times 10^{-6}\ \mathrm{M}$$

When $AgNO_3$ is added, the concentration will gradually increase, the order of precipitation will be Br^-, Cl^- and CrO_4^{2-}

(ii) When Cl^- starts precipitating, Br^- ion concentration in the solution will be

$$\frac{K_{sp}(AgBr)}{[Ag^+]_{Cl^-}} = \frac{5.0\times10^{-13}\ \mathrm{M}^2}{1.7\times10^{-9}\ \mathrm{M}} \simeq 3 \times 10^{-4}\ \mathrm{M}$$

(iii) When Cl^- starts precipitating, the ionic product of Ag_2CrO_4 is

$$[Ag^+]^2_{Cl^-}[CrO_4^{2-}] = (1.7 \times 10^{-9}\ \mathrm{M})^2\ (0.1\ \mathrm{M}) = 2.89 \times 10^{-19}\ \mathrm{M}^3$$

Since the value $2.89 \times 10^{-19}\ \mathrm{M}^3$ is less than $K_{sp}(Ag_2CrO_4)$, the solution will contain all the CrO_4^{2-} ions, i.e. 0.1 M

5. **(i)** The concentrations of SO_4^{2-} ions to initiate precipitations are as follows.

Ba^{2+} ion $$[SO_4^{2-}]_{Ba^{2+}} = \frac{K_{sp}(BaSO_4)}{[Ba^{2+}]} = \frac{1.5\times10^{-9}\ \mathrm{M}^2}{0.1\,\mathrm{M}} = 1.5 \times 10^{-8}\ \mathrm{M}$$

Sr^{2+} ion $$[SO_4^{2-}]_{Sr^{2+}} = \frac{K_{sp}(SrSO_4)}{[Sr^{2+}]} = \frac{7.5\times10^{-7}\ \mathrm{M}^2}{0.1\,\mathrm{M}} = 7.5 \times 10^{-6}\ \mathrm{M}$$

Ca^{2+} ion $$[SO_4^{2-}]_{Ca^{2+}} = \frac{K_{sp}(CaSO_4)}{[Ca^{2+}]} = \frac{2.5\times10^{-5}\ \mathrm{M}^2}{0.1\,\mathrm{M}} = 2.5 \times 10^{-4}\ \mathrm{M}$$

Since the concentration of $[SO_4^{2-}]$ will be gradually increased, the order of precipitation is Ba^{2+}, Sr^{2+} and Ca^{2+}.

(ii) When Sr^{2+} ions start precipitating, the concentration of SO_4^{2-} in the solution will be 7.5×10^{-6} M. At this concentration

$$[Ba^{2+}] = \frac{K_{sp}(BaSO_4)}{[SO_4^{2-}]_{Sr^{2+}}} = \frac{1.5\times10^{-9}\ \mathrm{M}^2}{7.5\times10^{-6}\ \mathrm{M}^2} = 2.0 \times 10^{-4}\ \mathrm{M}$$

(iii) When Ca^{2+} ions start precipitating, we will have

$$[Sr^{2+}] = \frac{K_{sp}(SrSO_4)}{[SO_4^{2-}]_{Ca^{2+}}} = \frac{7.5\times10^{-7}\ M^2}{2.5\times10^{-4}\ M} = 3 \times 10^{-3}\ M$$

6. (i) The concentrations of Ag^+ ions to start precipitation are as follows.

PO_4^{3-} ion
$$\left[Ag^+\right]_{PO_4^{3-}} = \left[\frac{K_{sp}(Ag_3PO_4)}{\left[PO_4^{3-}\right]}\right]^{1/3} = \left[\frac{2.7\times10^{-18}\ M^4}{0.1\,M}\right]^{1/3} = 3 \times 10^{-6}\ M$$

SO_4^{2-} ion
$$\left[Ag^+\right]_{SO_4^{2-}} = \left[\frac{K_{sp}(Ag_2SO_4)}{\left[SO_4^{2-}\right]}\right]^{1/2} = \left[\frac{1.21\times10^{-5}\ M^3}{0.1\,M}\right]^{1/2} = 11 \times 10^{-3}\ M$$

Cl^- ion
$$\left[Ag^+\right]_{Cl^-} = \left(\frac{K_{sp}(AgCl)}{\left[Cl^-\right]}\right) = \frac{1.8\times10^{-10}\ M^2}{0.1\,M} = 1.8 \times 10^{-9}\ M$$

Since Ag^+ ions concentration will gradually increase in the solution, the order of ions precipitation is Cl^-, PO_4^{3-} and SO_4^{2-}.

(ii) When PO_4^{3-} starts precipitating, the concentration of Ag^+ ions in the solution will be 3×10^{-6} M. At this concentration, we will have

$$[Cl^-] = \frac{K_{sp}(AgCl)}{\left[Ag^+\right]_{PO_4^{3-}}} = \frac{1.8\times10^{-10}\ M^2}{3\times10^{-6}\ M} = 6 \times 10^{-5}\ M$$

Ionic product of Ag_2SO_4 in the solution will be

$$[Ag^+]^2\ [SO_4^{2-}] = (3 \times 10^{-6}\ M)^2\ (0.1\ M) = 3 \times 10^{-13}\ M^3$$

Since this product is smaller than $K_{sp}(Ag_2SO_4)$, the concentration of SO_4^{2-} ions in the solution will be 0.1 M

(iii) When the third starts precipitating, the concentration of Ag^+ in the solution will be 11×10^{-3} M. At this concentration, we will have

$$[PO_4^{3-}] = \frac{K_{sp}(Ag_3PO_4)}{11\times10^{-3}M} = \frac{2.7\times10^{-18}\ M^4}{(11\times10^{-3}\ M)^3} = 2.02 \times 10^{-12}\ M$$

$$[Cl^-] = \frac{K_{sp}(AgCl_4)}{\left[Ag^+\right]^2_{SO_4^{2-}}} = \frac{1.80\times10^{-10}\ M^3}{(11\times10^{-3}\ M)^2} = 1.64 \times 10^{-8}\ M$$

ANNEXURE II

Subjective Problems for Practice

SOLVED PROBLEMS

1. What amount of sodium propanate should be added to one litre of an aqueous solution containing 0.02 mol of propanoic acid to obtain a buffer solution of pH 4.75? What will be the pH if 0.01 mol of hydrogen chloride is dissolved in the above buffer solution? Compare the last pH value with the pH of 0.01 molar HCl solution. Dissociation constant of propanoic acid at 25 °C is 1.34×10^{-5}M. (1981)

Solution Using the expression

$$\text{pH} = \text{p}K_\text{a}^\circ + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get $$4.75 = -\log(1.34 \times 10^{-5}) + \log \frac{[\text{salt}]}{0.02\,\text{M}} \quad \text{which gives} \quad 4.75 = 4.87 + \log \frac{[\text{salt}]}{0.02\,\text{M}}$$

or $$\frac{[\text{salt}]}{0.02\,\text{M}} = 0.76 \quad \text{or} \quad [\text{salt}] = 1.52 \times 10^{-2}\ \text{M}$$

Hence, Amount of sodium propanoate to be added $= 1.52 \times 10^{-2}$ mol

The addition of 0.01 mol of hydrogen chloride convert the equivalent amount of sodium propanoate into propanoic acid. Hence, we will have

$$\text{pH} = 4.87 + \log \frac{(0.0152 - 0.01)\ \text{mol L}^{-1}}{(0.02 + 0.01)\ \text{mol L}^{-1}} = 4.87 + \log(0.173) = 4.87 - 0.76 = 4.11$$

The pH of 0.01 molar HCl solution would be

$$\text{pH} = -\log(0.01) = 2.$$

2. Twenty mL of 0.2 M NaOH is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5}M. (1982)

Solution The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence,

$$\text{Concentration of acetic acid after the addition of sodium hydroxide} = \frac{30}{70} \times 0.2\ \text{M}$$

$$\text{Concentration of sodium acetate after the addition of sodium hydroxide} = \frac{20}{70} \times 0.2\ \text{M}$$

Hence, using the expression $\text{pH} = \text{p}K_\text{a}^\circ + \log \dfrac{[\text{salt}]}{[\text{acid}]}$, we get (1)

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{20}{30}\right) = 4.745 - 0.177 = 4.568$$

Let V be the additional volume of 0.2 M NaOH that need to be added to make pH of the solution equal to 4.74. Substituting this value in Eq. (1), we would get

$$4.74 = 4.745 + \log\left(\frac{20\ \text{mL} + V}{30\ \text{mL} - V}\right)$$

or $$\log \frac{20\ \text{mL} + V}{30\ \text{mL} - V} = -0.005 \quad \text{or} \quad \frac{20\ \text{mL} + V}{30\ \text{mL} - V} = 0.9866$$

or $$V = \frac{30\ \text{mL} \times 0.9866 - 20\ \text{mL}}{1.9866} = 4.83\ \text{mL}.$$

3. The dissociation constant of a weak acid HA is 4.9×10^{-8}M. After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7. (1983)

Solution (i) If α is the degree of dissociation of the weak acid HA, we will have

$$\underset{(0.1\ \text{M})(1-\alpha)}{\text{HA}} \rightleftharpoons \underset{(0.1\ \text{M})\alpha}{\text{H}^+} + \underset{(0.1\ \text{M})\alpha}{\text{A}^-}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.1\text{M})\,\alpha^2}{1-\alpha}$$

Assuming $\alpha << 1$, we will have

$$K_a = (0.1\ \text{M})\ \alpha^2$$

or $$\alpha = \sqrt{\frac{K_a}{0.1\ \text{M}}} = \sqrt{\frac{4.9\times10^{-8}\ \text{M}}{0.1\ \text{M}}} = 7 \times 10^{-4}$$

Hence, $$\text{Percentage ionization} = \frac{7\times10^{-4}}{1} \times 100 = 7 \times 10^{-2}$$

(ii) We have

$$[\text{H}^+] = (0.1\ \text{M})\alpha = 7 \times 10^{-5}\ \text{M}$$
$$\text{pH} = -\log\{[\text{H}^+]/\text{M}\} = -\log(7 \times 10^{-5}) = 4.15$$

(iii) Since water has a pH = 7, we will have

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7}\ \text{M} \quad \text{or} \quad [\text{H}^+]\ [\text{OH}^-] = 10^{-14}\ \text{M}^2$$

Thus, $[OH^-]$ in 0.1 M solution of acid would be

$$[\text{OH}^-] = \frac{10^{-4}\ \text{M}^2}{[\text{H}^+]} = \frac{10^{-14}\ \text{M}^2}{7\times10^{-5}\ \text{M}} = 1.43 \times 10^{-10}\ \text{M}.$$

4. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.1 M) which are separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What precentage of that metal ion is precipitated. Given: $K^\circ_{sp}(AgI) = 8.5 \times 10^{-17}$ and $K_{sp}^{o}(Hg_2I_2) = 2.5 \times 10^{-26}$. (1984)

Solution We have

$$\text{AgI(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{I}^-\text{(aq)} \qquad K_{sp}(\text{AgI}) = [\text{Ag}^+]\ [\text{I}^-]$$
$$\text{Hg}_2\text{I}_2\text{(s)} \rightleftharpoons \text{Hg}_2^{2+}\text{(aq)} + 2\text{I}^-\text{(aq)} \qquad K_{sp}(\text{Hg}_2\text{I}_2) = [\text{Hg}_2^{2+}]\ [\text{I}^-]^2$$

Hence,

Concentration of I^- required to precipitate Ag^+ ions

$$= \frac{K_{sp}(\text{AgI})}{[\text{Ag}^+]} = \frac{8.5\times10^{-17}\ (\text{mol L}^{-1})^2}{(0.10\ \text{mol L}^{-1})} = 8.5 \times 10^{-16}\ \text{mol L}^{-1}$$

Concentration of I^- required to precipitate Hg_2^{2+} ions

$$= \left(\frac{K_{sp}(\text{Hg}_2\text{I}_2)}{[\text{Hg}_2^{2+}]}\right)^{1/2} = \left(\frac{2.5\times10^{-26}\ (\text{mol L}^{-1})^3}{0.1\ \text{mol L}^{-1}}\right)^{1/2} = 5 \times 10^{-13}\ \text{mol L}^{-1}$$

Since $[I^-]$ required to precipitate Ag^+ ions is lesser than that required for Hg_2^{2+}, it is Ag^+ ions that are precipitated first. The precipitation of Ag^+ will continue till $[I^-]$ in solution becomes 5×10^{-13} mol L^{-1} at which the second ion (i.e. Hg_2^{2+}) will also start precipitating. At this stage, the concentration of Ag^+ ions remaining in the solution is given as

$$[\text{Ag}^+]_{\text{left}} = \frac{8.5\times10^{-17}\ (\text{mol L}^{-1})^2}{(5\times10^{-13}\ \text{mol L}^{-1})} = 1.7 \times 10^{-4}\ \text{mol L}^{-1}$$

Hence, $$\text{Percentage of Ag}^+\ \text{ions precipitated} = \frac{(0.1\text{M} - 1.7\times10^{-4}\ \text{M})}{0.1\ \text{M}} \times 100 = 99.83.$$

5. The concentration of hydrogen ion in a 0.2 molar solution of formic acid is 6.4×10^{-3} mol L^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution. The dissociation constant of formic acid is 2.4×10^{-4}M and the degree of dissociation of sodium formate is 0.75. (1985)

Solution Assuming that the addition of sodium formate suppresses the ionization of formic acid, we can use the expression

$$\mathrm{pH} = \mathrm{p}K_a^\circ + \log \frac{[\text{salt}]}{[\text{acid}]}$$

to compute pH of the solution. Since salt is 75 per cent dissociated, we will get

$$\mathrm{pH} = -\log(2.4 \times 10^{-4}) + \log \frac{0.75}{0.2} = 3.62 + 0.57 = 4.19.$$

6. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g L^{-1}. Calculate its solubility (g L^{-1}) in 0.02 M $Mg(NO_3)_2$ solution. (1986)

Solution We have

Molar mass of $Mg(OH)_2$ = 58 g mol^{-1}

Concentration of $Mg(OH)_2$ in pure water $= \dfrac{9.57 \times 10^{-3}\ \text{g L}^{-1}}{58\ \text{g mol}^{-1}} = 1.65 \times 10^{-4}\ \text{mol L}^{-1}$

It follows that

$$\underset{}{Mg(OH)_2(s)} \rightleftharpoons \underset{1.65 \times 10^{-4}\ \text{mol L}^{-1}}{Mg^{2+}(aq)} + \underset{2 \times 1.65 \times 10^{-4}\ \text{mol L}^{-1}}{2OH^-(aq)}$$

Hence, $K_{sp}(Mg(OH)_2) = [Mg^{2+}][OH^-]^2 = (1.65 \times 10^{-4})(2 \times 1.65 \times 10^{-4})^2\ (\text{mol L}^{-1})^3$

$$= 1.80 \times 10^{-11}\ (\text{mol L}^{-1})^3$$

Now in 0.02 M $Mg(NO_3)_2$ solution, concentration of Mg^{2+} ions = 0.02 M

The concentration of OH^- that can exist in 0.02 M $Mg(NO_3)_2$ solution is

$$[OH^-] = \left(\frac{K_{sp}}{[Mg^{2+}]}\right)^{1/2} = \left(\frac{1.80 \times 10^{-11}\ (\text{mol L}^{-1})^3}{0.02\ \text{mol L}^{-1}}\right)^{1/2} = 3 \times 10^{-5}\ \text{mol L}^{-1}$$

Concentration of $Mg(OH)_2$ in 0.02 M $Mg(NO_3)_2$ solution $= \dfrac{1}{2} \times 3 \times 10^{-5}\ \text{mol L}^{-1}$

Solubility of $Mg(OH)_2$ in 0.02 M $Mg(NO_3)_2$ solution $= \left(\dfrac{1}{2} \times 3 \times 10^{-5}\ \text{mol L}^{-1}\right)\left(58\ \text{g mol}^{-1}\right) = 8.7 \times 10^{-4}\ \text{g L}^{-1}$.

7. What is the pH of the solution when 0.2 mol of hydrochloric acid is added to one litre of a solution containing (i) 1 M each of acetic acid and acetate ion and (ii) 0.1 M each of acetic acid and acetate ion? Assume that the total volume is one litre. K_a for acetic acid = 1.8×10^{-5}M. (1987)

Solution (i) The addition of 0.2 mol of HCl would convert equivalent amount of acetate ions into acetic acid. Hence, after the addition of HCl, we will have

Concentration of acetic acid = 1.2 M

Concentration of acetate ions = 0.8 M

Hence, using the expression

$$\mathrm{pH} = \mathrm{p}K_a^\circ + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get $\mathrm{pH} = -\log(1.8 \times 10^{-5}) + \log \dfrac{0.8}{1.2} = 4.745 - 0.176 = 4.569 \simeq 4.57$

(ii) The solution will now contain 0.2 M acetic acid and 0.1 M HCl. Assuming no ionization of acetic acid due to the common ion H^+ from HCl, we find that

$[H^+] \simeq 0.1$ M

Hence, $\mathrm{pH} = -\log\{[H^+]/M\} = -\log(0.1) = 1.$

8. What amount of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 mol of NaCN. Given: $K^{\circ}_{\text{ioniz}}(\text{HCN}) = 4.1 \times 10^{-10}$. (1988)

Solution The addition of HCl converts NaCN into HCN. Let x be the amount of HCl added. We will have

$$[\text{NaCN}] = 0.01\ \text{M} - x \qquad \text{and} \qquad [\text{HCN}] = x$$

Substituting these values along with pH and K_a in the expression,

$$\text{pH} = -\log K_a^{\circ} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get $$8.5 = -\log (4.1 \times 10^{-10}) + \log \frac{0.01\,\text{M} - x}{x}$$

or $$8.5 = 9.387 + \log \frac{0.01\,\text{M} - x}{x} \quad \text{or} \quad \log \frac{0.01\,\text{M} - x}{x} = -0.887 \quad \text{or} \quad \frac{0.01\,\text{M} - x}{x} = 0.13$$

or $$x = \frac{0.01\,\text{M}}{0.13} = 8.85 \times 10^{-3}\ \text{M}$$

Hence, Amount of HCl to be added = 8.85×10^{-3} mol.

9. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of ammonium chloride and 0.05 mol/L of ammonium hydroxide. Calculate the concentrations of aluminium and magnesium ions in solution. Given: $K_b^{\circ}(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$, $K_{sp}^{\circ}(\text{Mg(OH)}_2) = 8.9 \times 10^{-12}$ and $K_{sp}^{\circ}(\text{Al(OH)}_3) = 6 \times 10^{-32}$. (1989)

Solution To start with we have a buffer solution containing 0.25 mol L^{-1} of NH_4Cl and 0.05 mol L^{-1} of NH_4OH. In the equilibrium reaction

$$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

we will have $$[\text{NH}_4\text{OH}] = 0.05\ \text{mol L}^{-1} \qquad \text{and} \qquad [\text{NH}_4^+] = 0.25\ \text{mol L}^{-1}$$

The dissolution of Mg(OH)_2 and Al(OH)_3 create extra OH^- ions and thus cause the above equilibrium reaction to shift more towards left. If z is the concentration of OH^- ions in the resultant solution, we will have

$$\text{Mg(OH)}_2 \rightleftharpoons \underset{x}{\text{Mg}^{2+}} + \underset{z}{2\text{OH}^-}; \qquad \text{Al(OH)}_3 \rightleftharpoons \underset{y}{\text{Al}^{3+}} + \underset{z}{3\text{OH}^-}$$

$$\underset{0.05\ \text{mol L}^{-1} + \alpha}{\text{NH}_4\text{OH}} \rightleftharpoons \underset{0.25\ \text{mol L}^{-1} - \alpha}{\text{NH}_4^+} + \underset{z}{\text{OH}^-}$$

where x and y are the solubilities of Mg(OH)_2 and Al(OH)_3, respectively, and α is the concentration of NH_4^+ ions that is replaced by NH_4OH. We will have

$$K_{sp}(\text{Mg(OH)}_2) = [\text{Mg}^{2+}]\,[\text{OH}^-]^2 = xz^2 = 8.9 \times 10^{-12}\ \text{M}^3 \qquad (1)$$

$$K_{sp}(\text{Al(OH)}_3) = [\text{Al}^{3+}]\,[\text{OH}^-]^3 = yz^3 = 6 \times 10^{-32}\ \text{M}^4 \qquad (2)$$

$$K_b(\text{NH}_4\text{OH}) = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{(0.25\,\text{M} - \alpha)\,(z)}{0.05\,\text{M} + \alpha} = 1.8 \times 10^{-5}\ \text{M} \qquad (3)$$

Since the solution is electrically neutral, we will also have

$$2\,[\text{Mg}^{2+}] + 3[\text{Al}^{3+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{Cl}^-]$$

i.e. $$2x + 3y + (0.25\ \text{M} - \alpha) = z + 0.25\ \text{M}$$

or $$2x + 3y - \alpha = z \qquad (4)$$

From the values of solubility product constants, we may conclude that

$$y << x \quad \text{or} \quad 3y << 2x$$

With this, Eq. (4) becomes

$$2x - \alpha = z \quad \text{or} \quad \alpha = 2x - z \qquad (5)$$

Moreover, due to the consumption of OH^- ions in Eq. (3), we may also expect that

$$z << 2x$$

(This may be verified from the final computed values of x and z.)

With this, Eq. (5) is simplified to

$$\alpha = 2x \tag{6}$$

Substituting this in Eq. (3), we get

$$\frac{(0.25\ \text{M} - 2x)(z)}{0.05\ M + 2x} = 1.8 \times 10^{-5}\ \text{M}$$

Replacing x in terms of z from Eq. (1), we get

$$\frac{\left(0.25\ \text{M} - \dfrac{2 \times 8.9 \times 10^{-12}\ \text{M}^3}{z^2}\right)(z)}{0.05\ M + 2\left(\dfrac{8.9 \times 10^{-12}\ \text{M}^3}{z^2}\right)} = 1.8 \times 10^{-5}\ \text{M}$$

$$(0.25\ \text{M})\, z^3 - (0.05\ \text{M})\,(1.8 \times 10^{-5}\ \text{M})\, z^2 - (2)\,(8.9 \times 10^{-12}\ \text{M}^3)\, z - 2\,(8.9 \times 10^{-12}\ \text{M}^3)\,(1.8 \times 10^{-5}\ \text{M}) = 0$$

or $$z^3 = (3.6 \times 10^{-6}\ \text{M})z^2 + (7.12 \times 10^{-11}\ \text{M}^2)\, z + 1.28 \times 10^{-15}\ \text{M}^3$$

The above expression may be solved by the method of successive approximation. We may start with $z = 10^{-5}$ M and substitute this in the right hand side of the above expression and then take cube root of this to get new refined value of z. This refined value is again substituted in the right hand side and get the second refined value. This is continued till the two successive values of z agree within the allowed accuracy, say up to two decimals. Carrying out the above approximation, we get

Cycle No.	$[\text{OH}^-]$/M
1	1.0×10^{-5}
2	1.33×10^{-5}
3	1.42×10^{-5}
4	1.45×10^{-5}
5	1.45×10^{-5}

Thus, taking $[\text{OH}^-] = 1.45 \times 10^{-5}$ M, we get

From Eq. (1) $$[\text{Mg}^{2+}] = \frac{8.9 \times 10^{-12}\ \text{M}^3}{(1.45 \times 10^{-5}\ \text{M})^2} = 0.042\,3\ \text{M}$$

From Eq. (2) $$[\text{Al}^{3+}] = \frac{6 \times 10^{-32}\ \text{M}^4}{(1.45 \times 10^{-5}\ \text{M})^3} = 1.97 \times 10^{-17}\ \text{M}$$

From the above results, the approximations made in solving the above problem is justified as

$$[\text{Al}^{3+}] \ll [\text{Mg}^{2+}] \qquad \text{and} \qquad [\text{OH}^-] \ll 2\,[\text{Mg}^{2+}]$$

10. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resultant solution will be twice the original value. Given : K_a°(acetic acid) = 1.8×10^{-5}. (1990)

Solution We have

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$$

$$K_\text{a} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]_0 - [\text{H}^+]} \simeq \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]_0}$$

Hence, $$[\text{H}^+] = (K_\text{a}\ [\text{CH}_3\text{COOH}]_0)^{1/2} = (1.8 \times 10^{-5})^{1/2}\ \text{mol L}^{-1} = 4.30 \times 10^{-3}\ \text{mol L}^{-1}$$

$$\text{pH} = -\log\{[\text{H}^+]/\text{mol L}^{-1}\} = -\log(4.3 \times 10^{-3}) = 2.37$$

Now the pH of the diluted solution would be pH = 2 × 2.37

which gives $$-\log\{[\text{H}^+]/\text{mol L}^{-1}\} = 2 \times 2.37$$

or $$\left(\frac{[\mathrm{H}^+]}{\mathrm{mol\ L^{-1}}}\right)^{1/2} = 4.30 \times 10^{-3} \quad \text{or} \quad [\mathrm{H}^+] = 1.8 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

Substituting this in the expression

$$K_a = \frac{[\mathrm{H}^+]^2}{[\mathrm{CH_3COOH}]_0 - [\mathrm{H}^+]} \quad \text{we get} \quad 1.8 \times 10^{-5}\ \mathrm{mol\ L^{-1}} = \frac{(1.8\times10^{-5}\ \mathrm{mol\ L^{-1}})^2}{[\mathrm{CH_3COOH}]_0 - (1.8\times10^{-5}\ \mathrm{mol\ L^{-1}})}$$

This gives $[\mathrm{CH_3COOH}]_0 = 3.6 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$

Volume of dilute acetic acid containing 1 mol of acid would be $V = \dfrac{1\ \mathrm{mol}}{3.65\times10^{-5}\ \mathrm{mol\ L^{-1}}} = 2.7 \times 10^4$ L.

11. A 40.0 mL solution of a weak base, BOH is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid, respectively. Find the dissociation constant of the base. (1991)

Solution Let N_{base} be the normality of the base BOH. Substituting the given data in the expression

$$\mathrm{pOH} = \mathrm{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

we get

(i) $$14 - 10.04 = \mathrm{p}K_b + \log\left(\frac{5.0\times0.1}{40.0\times N_{\text{base}} - 5.0\times0.1}\right) \qquad (1)$$

(ii) $$14 - 9.14 = \mathrm{p}K_b + \log\left(\frac{20.0\times0.1}{40.0\times N_{\text{base}} - 20.0\times0.1}\right)$$

Equating the values of pK_b from these two expressions, we get

$$3.96 - \log\left(\frac{0.5}{40.0\times N_{\text{base}} - 0.5}\right) = 4.86 - \log\left(\frac{2.0}{40.0\times N_{\text{base}} - 2.0}\right)$$

or $$\log\left(\frac{2.0}{40.0\times N_{\text{base}} - 2.0}\times\frac{40.0\times N_{\text{base}} - 0.5}{0.5}\right) = 0.9 \quad \text{or} \quad \left(\frac{4(40.0\times N_{\text{base}} - 0.5)}{40.0\times N_{\text{base}} - 2.0}\right) = 7.943$$

Solving for N_{base}, we get $N_{\text{base}} = \dfrac{2.0\,(7.943/4) - 0.5}{40.0(7.943/4) - 40.0} = \dfrac{3.472}{39.44} = 0.088$

Substituting the above value in Eq. (1), we get

$$3.96 = \mathrm{p}K_b^\circ + \log\left(\frac{0.5}{40.0\times0.088 - 0.5}\right) \quad \text{or} \quad \mathrm{p}K_b^\circ = 3.96 - \log(0.166) = 3.96 - (-0.78) = 4.74$$

This gives $K_b^\circ = 1.83 \times 10^{-5}$.

12. The solubility product of $\mathrm{Ca(OH)_2}$ at 25 °C is $4.42 \times 10^{-5}\mathrm{M}^3$. A 500 mL of saturated solution of $\mathrm{Ca(OH)_2}$ is mixed with equal volume of 0.4 M NaOH. How much $\mathrm{Ca(OH)_2}$ in milligrams is precipitated? (1992)

Solution The total volume of the solution would become 1 L. Hence, the concentration of NaOH would become half, i.e. 0.2 M. Hence,

$$[\mathrm{Ca}^{2+}] = \frac{K_{sp}(\mathrm{Ca(OH)_2})}{[\mathrm{OH}^-]^2} = \frac{4.42\times10^{-5}\ \mathrm{M}^3}{(0.2\,\mathrm{M})^2} = 1.105 \times 10^{-3}\ \mathrm{M}$$

To start with, the concentration of Ca^{2+} were

$$[\mathrm{Ca}^{2+}] = \left(\frac{K_{sp}(\mathrm{Ca(OH)_2})}{4}\right)^{1/3} = \left(\frac{4.42\times10^{-5}\ \mathrm{M}^3}{4}\right)^{1/3} = 0.0223\ \mathrm{M}$$

In 500 mL of the solution,

Amount of Ca^{2+} was $\frac{1}{2} \times 0.022\,3$ mol, i.e. 0.011 15 mol.

Of this, the remaining Ca^{2+} ions after the addition of NaOH is 0.001 105 mol. Hence,

Amount of Ca^{2+} ions precipitated = (0.011 15 − 0.001 105) mol = 0.010 045 mol

Mass of $Ca(OH)_2$ precipitated = 0.010 045 × 74 g = 0.743 33 g = 743.33 mg.

13. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volumes of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.4? K_a^o for H_2CO_3 in blood is 7.8×10^{-7}. (1993)

Solution Let V be the required volume of 5 M $NaHCO_3$ solution. Total volume of the system becomes V + 10 mL. Now in the solution

$$[HCO_3^-] = (5\ \text{M}) \left(\frac{V}{V + 10\ \text{mL}}\right); \qquad [H_2CO_3] = (2\ \text{M}) \left(\frac{10\ \text{mL}}{V + 10\ \text{mL}}\right)$$

Using the expression $\text{pH} = \text{p}K_a^o + \log \dfrac{[HCO_3^-]}{[H_2CO_3]}$,

we get $$7.4 = -\log(7.8 \times 10^{-7}) + \log \frac{(5\ \text{M})\,V}{(2\ \text{M})\,(10\ \text{mL})} = 6.108 + \log\left(\frac{1}{4}\right) + \log(V/\text{mL})$$

or $$\log(V/\text{mL}) = 7.4 - 6.108 + 0.062 = 1.894$$

Hence, $$V = 78.34\ \text{mL}.$$

14. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? K_{sp} for MS = $6.0 \times 10^{-21}\text{M}^2$, concentration of saturated H_2S = 0.1 M, $K_1^o = 10^{-7}$ and $K_2^o = 1.3 \times 10^{-13}$ for H_2S. (1993)

Solution The concentration of S^{2-} ions needed to precipitate MS is

$$[S^{2-}] = \frac{K_{sp}}{[M^{2+}]} = \frac{6.0 \times 10^{-21}\ \text{M}^2}{0.05\ \text{M}} = 1.2 \times 10^{-19}\ \text{M}$$

In the solution, H_2S ionizes as

$$H_2S \rightleftharpoons H^+ + HS^- \qquad K_1 = 10^{-7}\text{M}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_2 = 1.3 \times 10^{-13}\ \text{M}$$

Hence, $$K_1 K_2 = \left(\frac{[H^+]^2\,[S^{2-}]}{[H_2S]}\right)$$

This gives $$[H^+] = \left(\frac{K_1 K_2 [H_2S]}{[S^{2-}]}\right)^{1/2} = \left(\frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{1.2 \times 10^{-19}}\right)^{1/2} \text{M} = 0.104\ \text{M}$$

Hence, the minimum pH at which MS will precipitate is

$$\text{pH} = -\log(0.104) = 0.98$$

15. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.) (1995)

Solution Ammonium formate undergoes hydrolysis as

$$NH_4^+ + HCOO^- + H_2O \rightleftharpoons NH_4OH + HCOOH$$

$$K_h = \frac{[NH_4OH]\,[HCOOH]}{[NH_4^+]\,[HCOO^-]} \qquad (1)$$

Using the expressions

Formic acid, $$K_a = \frac{[\mathrm{HCOO^-}][\mathrm{H^+}]}{[\mathrm{HCOOH}]} \qquad (2)$$

Ammonium hydroxide, $$K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_4OH}]} \qquad (3)$$

we get $$K_h = \frac{[\mathrm{OH^-}]}{K_b}\,\frac{[\mathrm{H^+}]}{K_a} = \frac{K_w}{K_a\,K_b} \qquad (4)$$

where K_w is ionic product of water. Moreover, in the solution, we will have

$$[\mathrm{NH_4OH}] = [\mathrm{HCOOH}] \qquad \text{and} \qquad [\mathrm{NH_4^+}] = [\mathrm{HCOO^-}]$$

With these Eq. (1) becomes

$$K_h = \frac{[\mathrm{HCOOH}]^2}{[\mathrm{HCOO^-}]^2}$$

Using Eqs. (2) and (4), we get

$$\frac{K_w}{K_a\,K_b} = \frac{[\mathrm{H^+}]^2}{K_a^2} \qquad \text{or} \qquad [\mathrm{H^+}]^2 = \frac{K_w\,K_a}{K_b}$$

Taking logarithm and multiplying by − 1 throughout, we get

$$2(-\log\,[\mathrm{H^+}]/\mathrm{M}) = (-\log\,K_w^{\circ}) + (-\log\,K_a^{\circ}) - (-\log\,K_b^{\circ})$$

i.e. $$2\mathrm{pH} = \mathrm{p}K_w^{\circ} + \mathrm{p}K_a^{\circ} - \mathrm{p}K_b^{\circ}$$

or $$\mathrm{pH} = \frac{1}{2}\,[\mathrm{p}K_w^{\circ} + \mathrm{p}K_a^{\circ} - \mathrm{p}K_b^{\circ}] = \frac{1}{2}\,[14 + 3.8 - 4.8] = 6.5.$$

16. What is the pH of 10^{-7} mol L^{-1} HCl solution at 25 °C?

Solution For 10^{-7} M HCl, the concentration of $\mathrm{H^+}$ due to the dissociation of water will not be negligible in comparison to the concentration $\mathrm{H^+}$ from the acid. Hence, we have

$$[\mathrm{H^+}]_{\mathrm{total}} = [\mathrm{H^+}]_{\mathrm{acid}} + [\mathrm{H^-}]_{\mathrm{water}}$$

Since water furnishes equal amounts of $\mathrm{H^+}$ and $\mathrm{OH^-}$, we can express the above equilibrium as

$$[\mathrm{H^+}]_{\mathrm{total}} = [\mathrm{H^+}]_{\mathrm{acid}} + [\mathrm{OH^-}]_{\mathrm{water}}$$

Since, in aqueous solution, $\mathrm{H^+}$ and $\mathrm{OH^-}$ are related through the expression

$$K_w = [\mathrm{H^+}]\,[\mathrm{OH^-}]$$

we can express the above equation as

$$[\mathrm{H^+}]_{\mathrm{total}} = [\mathrm{H^+}]_{\mathrm{acid}} + \frac{K_w}{[\mathrm{H^+}]_{\mathrm{total}}}$$

or $$[\mathrm{H^+}]^2_{\mathrm{total}} - [\mathrm{H^+}]_{\mathrm{acid}}\,[\mathrm{H^+}]_{\mathrm{total}} - K_w = 0$$

Solving for $[\mathrm{H^+}]_{\mathrm{total}}$, we get

$$[\mathrm{H^+}]_{\mathrm{total}} = \frac{[\mathrm{H^+}]_{\mathrm{acid}} + \sqrt{[\mathrm{H^+}]^2_{\mathrm{acid}} + 4\,K_w}}{2}$$

Substituting $[\mathrm{H^+}]_{\mathrm{acid}} = 10^{-7}$ M and $K_w = 10^{-14}$ M^2, we get

$$[\mathrm{H^+}]_{\mathrm{total}} = \frac{10^{-7}\ \mathrm{M} + \sqrt{(10^{-7}\ \mathrm{M})^2 + 4\,(10^{-14}\ \mathrm{M}^2)}}{2} = \frac{10^{-7}\ \mathrm{M} + 2.24 \times 10^{-7}\ \mathrm{M}}{2} = 1.62 \times 10^{-7}\ \mathrm{M}$$

$$\mathrm{pH} = -\log\,\{[\mathrm{H^+}]/\mathrm{mol\ L^{-1}}\} = -\log\,(1.62 \times 10^{-7}) = 6.79.$$

17. Given a solution that is 0.5 mol L^{-1} in acetic acid. To what volume must one litre of this solution be diluted in order to (a) double the pH and (b) double the hydroxide ion concentration? Given: $K_a(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M.

Solution We have

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]_0 - [H^+]} \simeq \frac{[H^+]^2}{[HA]_0}$$

or $[H^+] = \sqrt{K_a [HA]_0} = [(1.8 \times 10^{-5}\ M)\ (0.5\ M)]^{1/2} = 3.0 \times 10^{-3}\ M$

$pH = -\log (3.0 \times 10^{-3}) = 2.523$

(a) Now to double the pH, we will have

$[H^+] = \text{antilog}\ (-2 \times 2.523) = 9.0 \times 10^{-6}\ M$

Now from the expression $K_a = \dfrac{[H^+]^2}{[HA]_0 - [H^+]}$ we get $1.8 \times 10^{-5}\ M = \dfrac{(9.0 \times 10^{-6}\ M)^2}{[HA]_0 - (9.0 \times 10^{-6}\ M)}$

This gives $[HA]_0 = \dfrac{(9.0 \times 10^{-6}\ M)^2 + (1.8 \times 10^{-5}\ M)(9.0 \times 10^{-6}\ M)}{(1.8 \times 10^{-5}\ M)} = \dfrac{8.0 \times 10^{-11}\ M^2 + 1.62 \times 10^{-10}\ M^2}{1.8 \times 10^{-5}\ M}$

$$= \frac{2.42 \times 10^{-10}\ M^2}{1.8 \times 10^{-5}\ M} = 1.344 \times 10^{-5}\ M$$

$$\text{Dilution factor} = \frac{0.5\ M}{1.344 \times 10^{-5}\ M} = 3.72 \times 10^4$$

(b) To double the $[OH^-]$, we have

$$[H^+] = \frac{1}{2} \times 3.0 \times 10^{-3}\ M$$

Hence, $[HA]_0 = \dfrac{[H^+]^2}{K_a} = \dfrac{(1.5 \times 10^{-3}\ M)^2}{(1.8 \times 10^{-5}\ M)} = 0.125\ M$

$$\text{Dilution factor} = \frac{0.5\ M}{0.125\ M} = 4.$$

18. Consider a 0.5 M NH_4Cl solution. What is its pH? To what volume must 1 L of this solution be diluted to get a solution of pH = 6.0? Given: $K_b(NH_4OH) = 1.8 \times 10^{-5}$ M.

Solution We have

$$\underset{0.5\ M - x}{NH_4^+} + H_2O \rightleftharpoons \underset{x}{NH_4OH} + \underset{x}{H^+}$$

$$K_h = \frac{K_w}{K_b} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{(x)(x)}{0.5\ M - x}$$

Now $\dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}\ M^2}{1.8 \times 10^{-5}\ M} = 5.56 \times 10^{-10}\ M$

Hence, $\dfrac{x^2}{0.5\ M - x} = 5.56 \times 10^{-10}\ M$

Ignoring x in comparison to 0.5 M, we get

$x^2 = 0.5 \times 5.56 \times 10^{-10}\ M$ or $x = 1.67 \times 10^{-5}\ M$

Now $pH = -\log \{[H^+]/\text{mol L}^{-1}\} = -\log (1.67 \times 10^{-5}) = 4.78$

To have pH = 6, we must have

$[H^+] = 10^{-6}\ M$

Hence, $[NH_4^+] = \dfrac{[H^+]^2}{K_h} = \dfrac{1.0 \times 10^{-12}\ M^2}{5.56 \times 10^{-10}\ M} = 1.80 \times 10^{-3}\ M$

$$\text{Dilution factor} = \frac{0.5\ \text{M}}{1.80\times10^{-3}\ \text{M}} = 277.8.$$

19. Will a precipitate at 298 K of $Mg(OH)_2$ form in a 10^{-4} M solution of $Mg(NO_3)_2$ if pH of the solution is adjusted to 9.0? Given: $K_{sp}(Mg(OH)_2) = 8.5 \times 10^{-12}\ \text{M}^3$. At what minimum value of pH will precipitation start?

Solution For pH = 9.0, we have $[H^+] = 1.0 \times 10^{-9}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}\ \text{M}}{1.0\times10^{-9}\ \text{M}} = 1.0 \times 10^{-5}\ \text{M}$$

Hence, Ionic product of $Mg(OH)_2 = [Mg^{2+}]\,[OH^-]^2 = (10^{-4}\ \text{M})\,(10^{-5}\ \text{M})^2 = 10^{-14}\ \text{M}^3$

Since ionic product is smaller than solubility product, $Mg(OH)_2$ will not be precipitated at pH = 9.0. The minimum concentration of OH^- ions at which Mg^{2+} ions start precipitating is

$$[OH^-] = \left(\frac{K_{sp}(Mg(OH)_2)}{[Mg^{2+}]}\right)^{1/2} = \left(\frac{8.5\times10^{-12}\ \text{M}^3}{10^{-4}\ \text{M}}\right)^{1/2} = 2.915 \times 10^{-4}\ \text{M}$$

The corresponding H^+ of the solution will be

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}\ \text{M}^2}{2.915\times10^{-4}\ \text{M}} = 3.43 \times 10^{-11}\ \text{M}$$

Hence, $\text{pH} = -\log\{[H^+]/\text{M}\} = -\log(3.43 \times 10^{-11}) = 10.46.$

20. At what concentration of OH^- (pH or pOH), is the solubility of $Zn(OH)_2$ minimum? What is the minimum solubility?

Given : $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2\ OH^-(aq);$ $K_{sp} = [Zn^{2+}]\,[OH^-]^2 = 1.2 \times 10^{-17}\ \text{M}^3$

$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq);$ $K_f = \dfrac{[Zn(OH)_4^{2-}]}{[OH^-]^2} = 0.13\ \text{M}^{-1}$

Solution The solubility of $Zn(OH)_2$ will be given as

$$S = [Zn^{2+}] + [Zn(OH)_4^{2-}] = \frac{K_{sp}}{[OH^-]^2} + K_f\,[OH^-]^2 \qquad (1)$$

The minimum solubility will be obtained by setting $dS/d[OH^-] = 0$. Hence,

$$-\frac{2K_{sp}}{[OH^-]^3} + 2\,K_f\,[OH^-] = 0$$

or

$$[OH^-] = \left(\frac{2K_{sp}}{2K_f}\right)^{1/4} = \left(\frac{1.2\times10^{-17}\ \text{M}^3}{0.13\ \text{M}^{-1}}\right)^{1/4} = 9.8 \times 10^{-5}\ \text{M} \qquad (2)$$

$\text{pOH} = -\log\{[OH^-]/\text{mol L}^{-1}\} = 4.01$

and $\text{pH} = 14 - 4.01 = 9.99$

Now the minimum solubility will be obtained by substituting Eq. (2) in Eq. (1). Thus, we get

$$S_{min} = \frac{1.2\times10^{-17}\ \text{M}^3}{(9.8\times10^{-5}\ \text{M})^2} + (0.13\ \text{M}^{-1})\,(9.8 \times 10^{-5}\ \text{M})^2 = 2.5 \times 10^{-9}\ \text{M}.$$

21. A solution is saturated with respect to $MgCO_3$ and Ag_2CO_3. It is found to have $[Mg^{2+}] = 2.2 \times 10^{-5}$ M. Find $[Ag^+]$. Given: $K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}\ \text{M}^3$ and $K_{sp}(MgCO_3) = 1.6 \times 10^{-6}\ \text{M}^2$.

Solution We have

$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Mg^{2+}]\,[CO_3^{2-}]$

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$

From the $K_{sp}(MgCO_3)$, we find that

$$[CO_3^{2-}] = \frac{K_{sp}(MgCO_3)}{[Mg^{2+}]} = \frac{1.6\times10^{-6}\ \text{M}^2}{2.2\times10^{-5}\ \text{M}} = 7.27 \times 10^{-2}\ \text{M}$$

Hence $$[Ag^+] = \left(\frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2-}]}\right)^{1/2} = \left(\frac{8.2\times10^{-12}\ M^3}{7.27\times10^{-2}\ M}\right)^{1/2} = 1.06 \times 10^{-5}\ M.$$

22. The solubility of calcium arsenate $Ca_3(AsO_4)_2$ in water is 9.0×10^{-13} mol L^{-1}. Determine its solubility product?

Solution We have

Concentration of $Ca_3(AsO_4)_2$ in solution = 9.0×10^{-3} M

Concentration of Ca^{2+} in the solution = $3 \times 9.0 \times 10^{-3}$ M

Concentration of AsO_4^{3-} in the solution = $2 \times 9.0 \times 10^{-3}$ M

Hence, $$K_{sp} = [Ca^{2+}]^3\,[AsO_4^{3-}]^2 = (3 \times 9.0 \times 10^{-3}\ M)^3\,(2 \times 9.0 \times 10^{-3}\ M)^2 = 6.38 \times 10^{-9}\ M^5.$$

23. A solution has 0.01 M Ag^+ and 0.01 M Ba^{2+}. Solid K_2CrO_4 is added slowly. Assuming no volume change, (a) Calculate the $[CrO_4^{2-}]$ when Ag_2CrO_4 and $BaCrO_4$ start precipitating. (b) Which ion is precipitated first? (c) What is the concentration of first ion when the second starts precipitating? (d) Would the addition of CrO_4^{2-} be a practical method of separating Ag^+ and Ba^{2+}? Given: $K_{sp}(Ag_2CrO_4) = 1.1 \times 10^{-12}\ M^3$ and $K_{sp}(BaCrO_4) = 2.2 \times 10^{-10}\ M^2$.

Solution We have

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$

$$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = [Ba^{2+}]\,[CrO_4^{2-}]$$

Concentration of CrO_4^{2-} when Ag^+ ions start precipitating $= \dfrac{K_{sp}(Ag_2CrO_4)}{[Ag^+]^2} = \dfrac{1.1\times10^{-12}\ M^3}{(0.01\ M)^2} = 1.1 \times 10^{-8}$ M

Concentration of CrO_4^{2-} when Ba^{2+} ions start precipitating $= \dfrac{K_{sp}(BaCrO_4)}{[Ba^{2+}]} + = \dfrac{2.2\times10^{-10}\ M^2}{0.01\ M} = 2.2 \times 10^{-8}$ M

Since in solution, 1.1×10^{-8} M CrO_4^{2-} is reached first. It is Ag^+ ions which, starts precipitating first. It continues to precipitate till $[CrO_4^{2-}]$ in solution is reached to 2.2×10^{-8} M where the second ion also starts precipitating. At this point, the concentration of Ag^+ ions remaining in the solution is

$$[Ag^+] = \left(\frac{K_{sp}(AgCrO_4)}{[CrO_4^{2-}]}\right)^{1/2} = \left(\frac{1.1\times10^{-12}\ M^2}{2.2\times10^{-8}\ M}\right)^{1/2} = 7.07 \times 10^{-3}\ M$$

Percentage of Ag^+ ions remaining in the solution $= \dfrac{7.07\times10^{-3}\ M}{0.01\ M} \times 100 = 70.7$

Since only 29.3 per cent of Ag^+ is precipitated out, the addition of CrO_4^{2-} is not a practical method to separate Ag^+ from Ba^{2+}.

24. What are the concentrations of H^+, HSO_4^-, SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given: $H_2SO_4 \rightarrow H^+ + HSO_4^-$ strong

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $\quad K_2 = 1.3 \times 10^{-2}$

Solution Since the first dissociation is complete, the concentration of H^+ due to this dissociation is 0.20 M. Let x be the amount of H^+ produced in the second dissociation. Hence,

$$[H^+]_{total} = 0.20\ M + x$$

$$\underset{0.20\ M - x}{HSO_4^-} \rightleftharpoons \underset{0.20\ M + x}{H^+} + \underset{x}{SO_4^{2-}}$$

$$K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.20\ M + x)(x)}{(0.20\ M - x)} = 1.3 \times 10^{-2}\ M$$

or $$(0.20\ M + x)(x) = (1.3 \times 10^{-2}\ M)(0.20\ M - x)$$

or $$x^2 + (0.20\ M + 1.3 \times 10^{-2}\ M)\,x - 1.3 \times 10^{-2} \times 0.2\ M^2 = 0$$

or $$x = \frac{-0.213\,\text{M} + \sqrt{(0.213\,\text{M})^2 + 4\,(1.3\times10^{-2})\,(0.2)\text{M}^2}}{2} = \frac{-0.213 + 0.2362}{2}\ \text{M} = 0.0116\ \text{M}.$$

Hence, $[\text{H}^+]_{\text{total}} = (0.2\ \text{M} + x) = 0.2116\ \text{M}$; $[\text{HSO}_4^-] = (0.2\ \text{M} - x) = 0.1884\ \text{M}$

$[\text{SO}_4^{2-}] = x = 0.0116\ \text{M}$; $[\text{H}_2\text{SO}_4] = 0$.

25. In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX?

Solution: Let M_1 and M_2 be the molarities of acid HX and the base NaOH, respectively, and let V be the volume of acid. Substituting the given data in Henderson's equation

$$\text{pH} = \text{p}K_\text{a}^\circ + \log\frac{[\text{salt}]}{[\text{acid}]}$$

we get
$$5.8 = \text{p}K_\text{a}^\circ + \log\left[\frac{(10\ \text{mL})M_2}{VM_1 - (10\ \text{mL})M_2}\right] \tag{1}$$

$$6.402 = \text{p}K_\text{a}^\circ + \log\left[\frac{(20\ \text{mL})M_2}{VM_1 - (20\ \text{mL})M_2}\right] \tag{2}$$

Substracting Eq. (1) from Eq. (2), we get

$$0.602 = \log\left[\frac{(20\ \text{mL})M_2}{VM_1 - (20\ \text{mL})M_2}\ \frac{VM_1 - (10\ \text{mL})M_2}{(10\ \text{mL})M_2}\right]$$

or $$\frac{2[VM_1 - (10\ \text{mL})M_2]}{VM_1 - (20\ \text{mL})M_2} = 4 \quad \text{or} \quad \frac{VM_1}{M_2} = \frac{60\ \text{mL}}{2} = 30\ \text{mL}$$

Substituting this in either Eq. (1) or Eq. (2), we get

$$\text{p}K_\text{a}^\circ = 5.8 - \log\left(\frac{10}{30-10}\right) = 5.8 + 0.30 = 6.1.$$

26. The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid?

Solution Fraction of acid neutralized after the addition of 20.0 mL of NaOH solution $= \frac{20}{35} = \frac{4}{7}$

Fraction of acid remaining unneutralized $= 1 - \frac{4}{7} = \frac{3}{7}$

Now using the expression $\text{pH} = \text{p}K_\text{a}^\circ + \log\frac{[\text{salt}]}{[\text{acid}]}$, we get

$$5.75 = \text{p}K_\text{a}^\circ + \log\frac{4/7}{3/7} \quad \text{or} \quad \text{p}K_\text{a}^\circ = 5.75 - \log\frac{4}{3} = 5.75 - 0.13 = 5.62$$

or $K_\text{a}^\circ = 2.4 \times 10^{-6}$.

27. At what minimum pH will 10^{-3} mol of Al(OH)_3 go into solution ($V = 1$ L) as Al(OH)_4^- and at what maximum pH it will dissolved as Al^{3+}?

Given: $\text{Al(OH)}_4^- \rightleftharpoons \text{Al}^{3+} + 4\text{OH}^-$ $\quad K_\text{eq} = 1.3 \times 10^{-34}\text{M}^4$

$\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$ $\quad K_\text{sp} = 5.0 \times 10^{-33}\text{M}^4$

Solution In the solution, the following two equilibrium conditions are simultaneously satisfied.

$$K_\text{eq} = \frac{[\text{Al}^{3+}][\text{OH}^-]^4}{[\text{Al(OH)}_4^-]} = 1.3 \times 10^{-34}\text{M}^4 \tag{1}$$

$$K_\text{sp} = [\text{Al}^{3+}]\,[\text{OH}^-]^3 = 5.0 \times 10^{-33}\text{M}^4 \tag{2}$$

Now when Al(OH)_3 goes into solution as Al(OH)_4^-, then $[\text{Al(OH)}_4^-] = 10^{-3}\ \text{mol L}^{-1}$

Substituting Eq. (2) in Eq. (1), we get

$$\frac{(5.0\times10^{-33}\text{M}^4)\,[\text{OH}^-]}{[\text{Al(OH)}_4^-]} = 1.3 \times 10^{-34}\text{M}^4$$

Hence, for the present problem we get

$$[\text{OH}^-] = \frac{1.3\times10^{-34}}{5.0\times10^{-33}}\,(10^{-3}\text{ mol L}^{-1}) = 2.6 \times 10^{-5}\text{ mol L}^{-1}$$

$$\text{p(OH)} = -\log\{[\text{OH}^-]/\text{M}\} = -\log(2.6\times10^{-5}) = 4.6$$

Thus, $\text{pH} = 14.0 - 4.6 = 9.4$

When Al(OH)_3 dissolves as Al^{3+}, we will have $[\text{Al}^{3+}] = 10^{-3}\text{ mol L}^{-1}$

Substituting this in Eq. (2), we get

$$[\text{OH}^-] = \left(\frac{K_\text{sp}}{[\text{Al}^{3+}]}\right)^{1/3} = \left(\frac{5.0\times10^{-33}}{10^{-3}}\text{M}^3\right)^{1/3} = 1.71\times10^{-10}\text{ mol L}^{-1}$$

$$\text{p(OH)} = -\log(1.71\times10^{-10}) = 9.78$$

$$\text{pH} = 14 - \text{p(OH)} = 4.22.$$

28. What is the pH of a 0.50 M aqueous NaCN solution? $\text{p}K_\text{b}$ of CN^- is 4.70. (1996)

Solution The CN^- ions undergo hydrolysis as

$$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$$

Hence, $$K_\text{b} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \simeq \frac{[\text{OH}^-]^2}{[\text{CN}]_0}$$

or $$-\log K_\text{b}^\text{o} = -2\log([\text{OH}^-]/\text{M}) + \log([\text{CN}^-]_0/\text{M})$$

$$4.70 = 2\,\text{pOH} + \log(0.50)$$

or $$\text{pOH} = \frac{4.70 + 0.30}{2} = 2.5$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.5 = 11.5$$

29. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl. Given: ($K_\text{sp}(\text{Ag}_2\text{CO}_3) = 8.2\times10^{-12}\text{M}^3$.) (1997)

Solution The involved reaction is

$$\underset{}{2\text{AgCl}} + \underset{1.5\text{ M}}{\text{CO}_3^{2-}(\text{aq})} \rightleftharpoons \text{Ag}_2\text{CO}_3(\text{s}) + \underset{0.0026\text{ g L}^{-1} = 7.324\times10^{-5}\text{ M}}{2\text{Cl}^-(\text{aq})}$$

Assuming $[\text{CO}_3^{2-}] \simeq 1.5$ M as very small quantity ($= 3.662\times10^{-5}$ M) of CO_3^{2-} combines, we get

$$[\text{Ag}^+] = \left(\frac{K_\text{sp}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]}\right)^{1/2} = \left(\frac{8.2\times10^{-12}\text{ M}^3}{1.5\text{ M}}\right)^{1/2} = 2.338\times10^{-6}\text{ M}$$

Hence, $$K_\text{sp}(\text{AgCl}) = [\text{Ag}^+]\,[\text{Cl}^-] = (2.338\times10^{-6}\text{ M})\,(7.324\times10^{-5}\text{ M}) = 1.71\times10^{-10}\text{ M}^2$$

30. An acid indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[\text{In}^-]/[\text{HIn}]$ is greater than 10 or smalles than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_\text{a}^\circ = 1.0\times10^{-5}$)? (1997)

Solution Using the Henderson's equation $\text{pH} = \text{p}K_\text{a}^\circ + \log\{[\text{In}^-]/[\text{HIn}]\}$, we get

$$\text{pH}_1 = -\log(1.0\times10^{-5}) + \log(1/10) = 5 - 1 = 4$$

$$\text{pH}_2 = -\log(1.0\times10^{-5}) + \log(10/1) = 5 + 1 = 6$$

The pH of the solution should change from 4 to 6.

31. Given: $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$, $K_c = 6.2 \times 10^{-8} M^2$ and K_{sp} of AgCl = $1.8 \times 10^{-10} M^2$ at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of complex in 1.0 M aqueous ammonia. (1998)

Solution We have

$$K_{sp}(AgCl) = [Ag^+]\,[Cl^-] = 1.8 \times 10^{-10}\ M^2 \qquad (1)$$

$$K_c = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.2 \times 10^{-8}\ M^2 \qquad (2)$$

The charge-balance expression in the solution is

$$[Ag^+] + [Ag(NH_3)_2^+] = [Cl^-]$$

Making use of Eqs (1) and (2), we get

$$\frac{(6.2 \times 10^{-8}\ M^2)[Ag(NH_3)_2^+]}{[NH_3]^2} + [Ag(NH_3)_2^+] = \frac{1.8 \times 10^{-10}\ M^2}{[Ag^+]} = \frac{(1.8 \times 10^{-10}\ M^2)[NH_3]^2}{(6.2 \times 10^{-8}\ M^2)[Ag(NH_3)_2^+]}$$

For 1.0 M ammonia solution, we get

$$(6.2 \times 10^{-8})\,[Ag(NH_3)_2^+] + [Ag(NH_3)_2^+] = \frac{(1.8 \times 10^{-10}\ M^2)}{(6.2 \times 10^{-8})[Ag(NH_3)_2^+]}$$

or $$[Ag(NH_3)_2^+] = \frac{1.8 \times 10^{-10}\ M^2}{(6.2 \times 10^{-8})[Ag(NH_3)_2^+]}$$

or $$[Ag(NH_3)_2^+] = \left(\frac{1.8 \times 10^{-10}\ M^2}{6.2 \times 10^{-8}}\right)^{1/2} = 0.054\ M$$

32. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)? (1998)

Solution We are given the following solutions.

200 mL of 10^{-2} M (pH = 2.0) of HCl and 300 mL of 10^{-2} M (pH = 12.0) of NaOH

On mixing, 100 mL of 10^{-2} M NaOH will be left unneutralised. Since the total volume of the solution would be 500 mL, the concentration of OH^- in the solution would be (1/5) (10^{-2} M) = 2.0×10^{-3} M

Hence, $$pOH = -\log([OH^-]/M) = -\log(2.0 \times 10^{-3}) = 2.70$$

$$pH = 14 - pOH = 14 - 2.70 = 11.30$$

33. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. (1999)

Solution If x is the solubility of $Pb(OH)_2$ in water, we will have

$$\underset{}{Pb(OH)_2(s)} \rightleftharpoons \underset{x}{Pb^{2+}(aq)} + \underset{2x}{2OH^-(aq)} \qquad K_{sp} = [Pb^{2+}]\,[OH^-]^2 = x(2x)^2 = 4x^3$$

It is given that $x = 6.7 \times 10^{-6}$ M. Hence

$$K_{sp} = 4(6.7 \times 10^{-6}\ M)^3 = 1.20 \times 10^{-15}\ M^3$$

The solubility of $Pb(OH)_2$ in a buffer solution of pH = 8 (i.e. $[H^+] = 10^{-8}$ M or $[OH^-] = 10^{-6}$ M) will be

$$[Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.20 \times 10^{-15}\ M^3}{(10^{-6}\ M)^2} = 1.20 \times 10^{-3}\ M$$

34. 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 mol in 500 mL water is shaken at 25 °C with excess 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 mol of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. (1996)

Solution We have

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

Initial amount	0.152 mol	0
Final amount	(0.152 – 0.0358) mol = 0.1162 mol	0.0358 mol
Concentrations	2 × 0.1162 M	2 × 0.0358 M

In the solution, the concentration of Ag^+ as dictated by solubility product is

$$\left\{\frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2-}]}\right\}^{1/2} = \left\{\frac{K_{sp}(Ag_2C_2O_4)}{[C_2O_4^{2-}]}\right\}^{1/2}$$

This gives $K_{sp}(Ag_2CO_3) = K_{sp}(Ag_2C_2O_4)\left(\dfrac{[CO_3^{2-}]}{[C_2O_4^{2-}]}\right)$

Since, the degrees of dissociation of $K_2C_2O_4$ and K_2CO_3 are equal, we will have

$$\begin{aligned} K_{sp}(Ag_2CO_3) &= K_{sp}(Ag_2C_2O_4)\left(\frac{[K_2CO_3]}{[K_2C_2O_4]}\right) = (1.29 \times 10^{-11}\ M^3)\left(\frac{2\times 0.0358\ M}{2\times 0.1162\ M}\right) \\ &= 3.97 \times 10^{-12}\ M^3 \end{aligned}$$

35. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles $litre^{-1}$ and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. (2000)

Solution For 10 ppm of SO_2 in the atmosphere, the partial molar volume of SO_2 in a total volume of 10^6 dm^3 of the atmospheric air will be equal to 10 dm^3. Its molar concentration in air would be

$$\begin{aligned} c &= \frac{(10\ dm^3)/\{(22.414\ dm^3\ mol^{-1})(298\ K)/(273\ K)\}}{10^6\ dm^3} \\ &= 4.087 \times 10^{-7}\ mol\ dm^{-3}. \end{aligned}$$

This concentration is very much less than the given solubility of SO_2 in water. Hence, it may be assumed that the entire SO_2 in air will dissolve in rain water.

If the concentration x of dissolved SO_2 is present in the ionized form, we will have

$$\underset{c-x}{H_2SO_3} \rightleftharpoons \underset{x}{H^+} + \underset{x}{HSO_3^-}$$

Hence $\quad K_a = \dfrac{[H^+][HSO_3^-]}{[H_2SO_3]} = \dfrac{x^2}{c-x} \quad$ or $\quad x^2 + K_a x - K_a c = 0 \quad$ i.e. $\quad x = \dfrac{-K_a \pm \sqrt{K_a^2 + 4\,K_a c}}{2}$

It is given that $K_a^\circ = 10^{-1.92} = 0.012$

Substituting K_a and c in Eq. (1), we get

$$x = \frac{(-0.012\ M) + \sqrt{(0.012\ M)^2 + 4(0.012\ M)(4.087 \times 10^{-7}\ M)}}{2} = 4.08 \times 10^{-7}\ M$$

that is, almost whole of dissolved SO_2 is present in the ionized form H^+ and HSO_3^-. This is to be expected since the concentration of dissolved SO_2 is very small (Ostwald dilution law).

For this small concentration of H^+ from the dissolved SO_2, the contribution coming from the dissociation of water may not be negligible. Hence, in solution we will have

$$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water} = [H^+]_{acid} + [OH^-]_{water} = [H^+]_{acid} + \frac{K_w}{[H^+]_{total}}$$

or $$[H^+]^2_{total} - [H^+]_{acid}\,[H^+]_{total} - K_w = 0$$

Solving for $[H^+]_{total}$, we get

$$[H^+]_{total} = \frac{[H^+]_{acid} + \sqrt{[H^+]^2_{acid} + 4\,K_w}}{2} = \frac{(4.08\times10^{-7}\,M) + \sqrt{(4.08\times10^{-7}\,M)^2 + 4(1\times10^{-14}\,M^2)}}{2}$$

$$= 4.31 \times 10^{-7}\ M$$

Hence, $$pH = -\log\{[H^+]/M\} = -\log(4.31\times10^{-7}) = 6.37$$

36. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}.] (2002)

Solution On mixing 500 mL of 0.2 M acetic acid with 500 mL of 0.2 M HCl, the volume of solution becomes 1000 mL and thus the molarity of each acid becomes half, i.e.

Molarity of acetic acid, $c = 0.1$ M; Molarity of HCl, $c' = 0.1$ M

Since HCl is completely ionized, we will have $[H^+]_{HCl} = c' = 0.1$ M

If α is the degree of dissociation of HC_3COOH, then

$$\underset{c(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{c\alpha}{CH_3COO^-} + \underset{c\alpha + c'}{H^+}$$

and $$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(c\alpha)(c\alpha + c')}{c(1-\alpha)}$$

Assuming $\alpha << 1$, we get

$$K_a = \frac{\alpha(c\alpha + c')}{1}$$

Substituting the values of c, c' and K_a, we get

$$1.75\times10^{-5}\ M = \alpha\{(0.1\ M)\,\alpha + (0.1\ M)\} \quad \text{or} \quad \alpha^2 + \alpha - 1.75\times10^{-4} = 0$$

Solving for α, we get

$$\alpha = \frac{-1 + \sqrt{1 + 4\times1.75\times10^{-4}}}{2} = 1.75\times10^{-4}$$

The concentration of H^+ in the solution is

$$[H^+] = c\alpha + c' = (0.1\ M)(1.75\times10^{-4} + 1) \simeq 0.1\ M$$

Hence, $$pH = -\log\{[H^+]/M\} = -\log(0.1) = 1$$

(ii) Amount of NaOH added = 6 g/40 g mol^{-1} = 0.15 mol

Molarity of NaOH in solution = 0.15 mol/1 L = 0.15 M

The added NaOH will combine firstly with strong acid and then with weak acid. Hence, whole of HCl (0.1 M) and 0.05 M of acetic acid will be neutralized. The resultant solution will contain 0.05 M of acetic acid and 0.05 M CH_3COONa. In solution, we will have

$$\underset{c(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{c\alpha + 0.05\,M}{CH_3COO^-} + \underset{c\alpha}{H^+} \qquad (\text{where } c = 0.05\ M)$$

$$K_a = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]} = \frac{(c\alpha + 0.05\,\mathrm{M})(c\alpha)}{c(1-\alpha)} = \frac{c(\alpha+1)\alpha}{1-\alpha}$$

Assuming $\alpha << 1$, we get

$$\alpha = \sqrt{\frac{K_a}{c}} = \left(\frac{1.75 \times 10^{-5}\,\mathrm{M}}{0.05\,\mathrm{M}}\right)^{1/2} = 3.5 \times 10^{-4}$$

$$[\mathrm{H^+}] = c\alpha = (0.05\ \mathrm{M})\ (3.5 \times 10^{-4}) = 1.75 \times 10^{-5}\ \mathrm{M}$$

$$\mathrm{pH} = -\log\{[\mathrm{H^+}]/\mathrm{M}\} = -\log(1.75 \times 10^{-5}) = 4.76$$

(alternatively, one can use the expression

$$\mathrm{pH} = \mathrm{p}K_a^{\circ} + \log\{[\mathrm{salt}]/[\mathrm{acid}]\}$$

since [salt] = [acid], we get $\mathrm{pH} = \mathrm{p}K_a^{\circ}$.

UNSOLVED PROBLEMS

1. The degree of dissociation of water was found to be 1.8×10^{-9} at 25 °C. Calculate its ionization constant and ionic product at 25 °C.
2. The ionic product of water at 100 °C is 55 times that at 25 °C. Calculate the pH of pure water at 100 °C. A given solution at 100 °C has a pH value of 7.0. Indicate whether this solution is acidic, alkaline or neutral.
3. Calculate K_a for an acid whose 0.1 M solution has a pH of 4.50.
4. Calculate the pH of 10^{-8} M HCl solution.
5. What is the pH of a 0.1 M solution of acetic acid? To what volume must one litre of this solution be diluted so as to have pH twice as that of original solution? Given: K_a(acetic acid) = 1.8×10^{-5} M.
6. Calculate the pH of each of the following solutions at 25 °C.
   (a) 0.25 M NaCN : $K_a(\mathrm{HCN}) = 4.8 \times 10^{-15}$ M
   (b) 0.015 M $\mathrm{NH_4Cl}$: $K_b(\mathrm{NH_4OH}) = 1.8 \times 10^{-5}$ M.
   (c) 0.015 M $\mathrm{CH_3COONa}$: $K_a(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M
7. Calculate $[\mathrm{H^+}]$, $[\mathrm{HS^-}]$ and $[\mathrm{S^{2-}}]$ in 0.1 M solution of $\mathrm{H_2S}$. Given: $K_{a1}^{\circ} = 1.1 \times 10^{-7}$ and $K_{a2}^{\circ} = 1.0 \times 10^{-14}$.
8. Calculate the degree of hydrolysis and pH of (a) 0.1 M ammonium acetate solution. Given : $K_b(\mathrm{NH_4OH}) = K_a(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M, and (b) 0.1 M anilinium acetate; Given; K_a(acetic acid) = 1.8×10^{-5} M and K_b(aniline) = 4.6×10^{-10} M.
9. Calculate the pH change when 100 mL of (a) 0.05 M NaOH and (b) 0.05 M HCl are added to 400 mL of a buffer solution that is 0.2 M in $\mathrm{NH_3}$ and 0.3 M in $\mathrm{NH_4Cl}$.
10. What volumes of 0.5 M acetic acid ($K_a^{\circ} = 1.75 \times 10^{-5}$) and 0.426 M sodium hydroxides should be mixed to get 100 mL of a buffer solution having pH = 5.0?
11. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.
12. A weak acid (50.0 mL) is titrated aginst 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point.
13. Determine the pH of a solution obtained by mixing 1.0 mol of sodium acetate and 1.0 mol of HCl in water to make one litre solution. $K_a(\mathrm{CH_3COOH}) = 1.8 \times 10^{-5}$ M.
14. Calculate the solubility of magnesium phosphate in 500 mL of saturated solution. Given: $K_{sp}(\mathrm{Mg_3(PO_4)_2}) = 1.0 \times 10^{-13}\ \mathrm{M^5}$, $M(\mathrm{Mg}) = 24.3\ \mathrm{g\ mol^{-1}}$ and $M(\mathrm{P}) = 31.0\ \mathrm{g\ mol^{-1}}$.
15. A solution is saturated with respect to $\mathrm{SrCO_3}$ and $\mathrm{SrF_2}$. the $\mathrm{CO_3^{2-}}$ was found to be $1.2 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$. Determine $[\mathrm{F^-}]$.Given: $K_{sp}(\mathrm{SrCO_3}) = 7.0 \times 10^{-10}\ \mathrm{M^2}$ and $K_{sp}(\mathrm{SrF_2}) = 7.9 \times 10^{-10}\ \mathrm{M^3}$.
16. What is the maximum pH of 0.10 M solution in $\mathrm{Mg^{2+}}$ from which $\mathrm{Mg(OH)_2}$ will not precipitate. Given: $K_{sp}(\mathrm{Mg(OH)_2}) = 1.2 \times 10^{-11}\ \mathrm{M^3}$.

17. (a) A solution is 0.1 M in Cl^- and 0.001 M in CrO_4^{2-}. If solid $AgNO_3$ is gradually added to this solution, which will precipitate first, AgCl or Ag_2CrO_4? Assume that the addition causes no change in volume. Given: $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$ and $K_{sp}(Ag_2CrO_4) = 1.79 \times 10^{-12}\ M^3$.

(b) What per cent of Cl^- remains in the solution when CrO_4^{2-} starts precipitating?

18. At what pH, aluminium hydroxide will have minimum solubility. What is its value? Given:

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^- \qquad K_{sp} = 2 \times 10^{-32}\ M^4$$

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^- \qquad K_f = 6 \times 10^9.$$

19. A solution is 0.1 M in each of Cl^-, Br^- and I^- ions. Solid $AgNO_3$ is gradually added to this solution. Assuming that the addition of $AgNO_3$ does not change the volume, answer the following:

(a) How much of Ag^+ ions are required to start precipitation of the three ions?

(b) Which ion will precipitate first?

(c) What will be the concentration of this ion when the second ion starts precipitating?

(d) What will be the concentrations of both the ions when the third ion starts precipitating?

20. At what mamimum concentration of OH^- will 10^{-3} mol of $Zn(OH)_2$ goes into the solution (V = 1 L) as $Zn(OH)_4^{2-}$ and as Zn^{2+}? Given;

$$Zn(OH)_4^{2-} \rightleftharpoons Zn^{2+} + 4OH^- \qquad K^\circ_{eq} = 10^{-15}$$

$$Zn(OH)^2 \rightleftharpoons Zn^{2+} + 2OH^- \qquad K^\circ_{sp} = 4.5 \times 10^{-17}$$

21. Calculate the solubility of AgCN in a buffer solution of pH = 5.0. Given: $K_{sp}(AgCN) = 2.1 \times 10^{-16}\ M^2$ and $K_a(HCN) = 6.2 \times 10^{-10}$ M.

ANSWERS

1. 1.8×10^{-16} M, $1.0 \times 10^{-14}\ M^2$

2. 6.13, alkaline

3. 1.296×10^{-8} M

4. 6.98

5. 2.37, 2.567×10^4 L

6. (a) 11.36, (b) 5.54, (c) 8.46

7. $[H^+] = [HS^-] = 1.0 \times 10^{-4}$ M,
$[S^{2-}] = 1.0 \times 10^{-14}$ M

8. (a) 5.53×10^{-3}, 7 (b) 0.775, 9.79

9. (a) From 9.07 to 9.11, (b) From 9.07 to 9.02

10. 42.8 mL of sodium hydroxide and 57.2 mL of acetic acid

11. 1.75×10^{-5} M, 5.27

12. 1.75×10^{-5} M, 8.73

13. 2.38

14. 0.1295 g

15. 3.7×10^{-2} M

16. 9.04

17. AgCl, 3.9×10^{-3} %

18. 13.75, 0.45 M

19. (a) for chloride, $[Ag^+] = 1.7 \times 10^{-9}$ M
Bromide, $[Ag^+] = 5.0 \times 10^{-12}$ M
Iodide, $[Ag^+] = 8.5 \times 10^{-16}$ M
(b) AgI,
(c) $[I^-] = 1.7 \times 10^{-5}$ M
(d) $[I^-] = 5.0 \times 10^{-8}$ M, $[Br^-] = 3.0 \times 10^{-4}$ M

20. 0.149 M, 2.12×10^{-7} M.

21. 1.883×10^{-6} M

CHAPTER 8

ELECTROCHEMISTRY

SECTION I ELECTROLYSIS

The phenomenon of electrolysis involves the breaking of electrolytes when an electric current is passed through them. The apparatus used to carry out electrolysis is known as electrolytic cell. The main characteristics of an electrolytic cell are described in Table 8.1.

Table 8.1 Main Characteristics of an Electrolytic Cell

	Cathode	*Anode*
Sign	Negative as it is attached to the negative end of the external battery	Positive as it is attached to the positive end of the external battery
Direction of electron movement	Into the cell	Out of the cell
Ions attracted within the cell	Cations	Anions
Half-reaction	Reduction	Oxidation

Thus, electrons are received from the negative end of the external battery by the negative electrode of the cell. These are used up in the reduction reaction at this electrode. The number of electrons received at the negative end are given back to the positive end of the external battery from the positive electrode of the cell where electrons are released as a result of oxidation reaction. Within the cell, current is carried by the movement of ions; cation towards the negative electrode (called the cathode) and anion towards the positive electrode (called the anode).

The electrolysis of molten salts produces substances which are characteristic of the salt. When certain aqueous salt solutions are electrolyzed, however, water is involved in the electrode reactions rather than ions derived from the solute. Hence, current carrying ions are not necessarily discharged at the electrodes. The reaction involving the electrolysis of water are as follows.

$$\text{Oxidation}: \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{Reduction}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

The following rules are helpful, while predicting the electrode reaction during the electrolysis of aqueous salt solutions.

1. The species having a large reduction potential is preferentially reduced at the cathode.
2. The reduction potential of water is -0.828 V. Water is reduced in preference to the cations having more negative potential than -0.828 V. Examples are Li^+, K^+, Na^+, Mg^{2+} and Al^{3+} ions.
3. Cations having less negative potential than -0.828 V are reduced in preference to water. Examples are Fe^{2+}, Sn^{2+}, Pb^{2+}, Ag^+ and Cu^{2+} ions.
4. In acidic medium with larger concentrations of H^+ ions, the cathodic reaction involves the reduction of H^+ ions, i.e. $2H^+ + 2e^- \rightarrow H_2$.
5. At the anode, the species having maximum reduction potential is formed from the oxidation of corresponding oxidizable species.
6. If the anion is not oxidized readily, water is oxidized liberating O_2. Examples are SO_4^{2-} and NO_3^- ions.
7. If the solution is highly alkaline, the anode process is $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
8. Chloride liberates Cl_2 but O_2 is also liberated as the solution is diluted. This is due to the phenomenon of over voltage.
9. Metallic anodes more reactive than platinum tend to pass into solution instead of O_2 being produced.
10. Soluble iodides always liberate iodine at the anode.

FARADAY'S LAWS OF ELECTROLYSIS

The quantitative relationships between electricity and chemical change were established by Michael Faraday. These are:

1. The mass of a chemical substance involved at an electrode is directly proportional to the quantity of electricity (expressed in coulombs, which is product of current in amperes and time in seconds) passed through the cell.

2. The masses of different substances produced by a given quantity of electricity are proportional to the equivalent mass (i.e. mass corresponding to a total of unit charge on each ion of the substance) of the substance.

Mathematically, the above two laws are expressed as

$$m = \frac{Q}{F}\frac{M}{|\nu_e|} = \frac{It}{F}\frac{M}{|\nu_e|}$$

where the various symbols have their usual meanings.

Straight Objective Tpe

Electrolytic Cell and Electrolysis

1. Molten sodium chloride conducts electricity due to the presence of
(a) free electrons (b) free ions
(c) free molecules (d) atoms of sodium and chlorine (1981)

2. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode respectively are
(A) H_2, O_2 (b) O_2, H_2 (c) O_2, Na (d) O_2, SO_2 (1987)

3. When a lead storage battery is discharged
(a) SO_2 is evolved (b) lead sulphate is consumed
(c) lead is formed (d) sulphuric acid is consumed (1987)

4. In an electrolytic cell, which of the facts is **not** true?
(a) Cathode is negative terminal
(b) Cathode is positive terminal
(c) Reduction occurs at cathode
(d) Electrons enter into cathode from the external cell

5. When a lead storage cell is charged
(a) sulphuric acid is consumed (b) sulphuric acid is formed
(c) lead sulphate is formed (d) lead is consumed

6. The reaction occurring at anode when the electrolysis of $CuSO_4$ is done using Pt electrode, is
(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (b) $2SO_4^{2-} + 2H_2O \rightarrow H_2SO_4 + O_2 + 4e^-$
(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (d) $2Cu \rightarrow Cu_2^{2+} + 2e^-$

7. The reaction occurring at anode when the electrolysis of an aqueous solution containing Na_2SO_4 and $CuSO_4$ is done using Pt electrodes, is
(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (b) $2SO_4^{2-} + 2H_2O \rightarrow 2H_2SO_4 + O_2 + 4e^-$
(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (d) $2Cl^- \rightarrow Cl_2(g) + 2e^-$

8. Which of the following does not evolve oxygen at anode when the electrolysis is carried out of
(a) dilute H_2SO_4 with Pt electrodes (b) fused sodium hydroxide with Pt electrodes
(c) acidic water with Pt electrodes (d) dilute sulphuric acid using Cu electrodes

9. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode respectively are
(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na (c) O_2, Na (d) $S_2O_8^{2-}$, H_2 (1996)

10. Which of the following reactions occurs at anode when the electrolysis of $CuCl_2$ solution is carried out by using platinum electrodes?
(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (b) $2Cl^- \rightarrow Cl_2(g) + 2e^-$
(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (d) $2Cu \rightarrow Cu_2^{2+} + 2e^-$

11. Which of the following reactions occurs at anode when the electrolysis of $CuSO_4$ solution is carried out by using copper electrodes?
(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (b) $2SO_4^{2-} + 2H_2O \rightarrow 2H_2SO_4 + O_2 + 4e^-$
(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (d) $2Cu \rightarrow Cu_2^{2+} + 2e^-$

12. In an electrolytic cell, which of the following is **not** true?
(a) Anode is positive terminal (b) Anode is negative terminal
(c) Oxidation occurs at cathode (d) Reduction occurs at cathode

13. Which of the following statements is **not** correct?
(a) Electrons enter through cathode in an electrolytic cell
(b) Electrons leave through anode in an electrolytic cell
(c) Cations in the electrolytic cell move toward cathode and anions toward anode
(d) Cations are reduced at anode and anions are oxidized at cathode in an electrolytic cell

14. Which of the following statements is correct for an electrolytic cells?
(a) Electrons flow from cathode to anode through the external battery.
(b) Electrons flow from cathode to anode within the electrolytic solution.
(c) Migration of ions along with oxidation reaction at cathode and reduction reaction at anode.
(d) Migration of ions along with reduction reaction at cathode and oxidation reaction at anode. (2003)

15. The number of electrons carrying a total charge equivalent to one K^+ ion is equal to
(a) 6.02×10^{23} (b) 6.02×10^{21} (c) 6.20×10^{18} (d) 6.20×10^{16}

16. Which of the following statements regarding the variations of resistance with temperature occur during electrolytic and metallic conductions?
(a) increase in electrolytic, decrease in metallic (b) decrease in electrolytic, increase in metallic
(c) increase in both (d) decrease in both

17. Which of the following metals form a protective layer of oxide to prevent corrosion?
(a) Cu (b) Ag (c) Au (d) Al

Faraday Laws of Electrolysis

18. Faraday's law of electrolysis are related to the
(a) atomic number of the cation (b) atomic number of the anion
(c) equivalent mass of the electrolyte (d) speed of the cation (1983)

19. Which of the following expression is written correctly?
(a) $I = Qt$ (b) $I = Q/t$ (c) $I = 1/Qt$ (d) $I = t/Q$

20. Which of the following expressions regarding the electrolysis of an electrolytic solution is represented correctly?
(a) $m = \dfrac{ItF}{M|\nu_e|}$ (b) $m = \dfrac{It|\nu_e|}{MF}$ (c) $m = \dfrac{QF}{M|\nu_e|}$ (d) $m = \dfrac{QM}{F|\nu_e|}$

21. The density of Cu is 8.94 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ solution is
(a) 13 586 C (b) 27 172 C (c) 40 758 C (d) 20 348 C

22. A current of 9.65 A is passed for 3 h between nickel electrodes in 0.5 L of a 2 M solution of $Ni(NO_3)_2$. The molarity of solution after electrolysis would be
(a) 0.46 M (b) 0.625 M (c) 0.92 M (d) 1.25 M

23. The time required to coat a metal surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 10.5 g cm^{-3}) with the passage of 3A current through a silver nitrate solution is
(a) 1150 s (b) 1250 s (c) 1350 s (d) 1450 s

24. In an electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP liberated at cathode would be
(a) 1.2 L (b) 2.4 L (c) 2.6 L (d) 4.8 L

25. In the electrolysis of $CuCl_2$ solution using copper electrode, if 2.5 g of Cu is deposited at cathode, then at anode
(a) 890 mL of Cl_2 at STP is liberated (b) 445 mL of O_2 at STP is liberated
(c) 2.5 g of copper is deposited (d) a decrease of 2.5 g of mass takes place

26. On passing an electric current, the quantity of deposition of a metal on cathode depends on the
(a) shape of cathode (b) size of cathode
(c) concentration of electrolytic solution (d) quantity of charge and charge number of metal ion

27. In the electrolysis of alkaline water, a total of 1 mol of gases is evolved. The amount of water decomposed would be
(a) 1 mol (b) 2 mol (c) (1/3) mol (d) (2/3) mol

28. In an electrolysis of a metallic chloride 3.283 g of the metal (molar mass 197 g mol^{-1}) was deposited on the cathode by the passage of 4 825 C of electric charge. The charge number of metal ion is
(a) 0.5 (b) 1 (c) 2 (d) 3

29. In acidic medium, MnO_4^- is converted to Mn^{2+} when acts as an oxidizing agent. The quantity of electricity required to reduce 0.05 mol of MnO_4^- would be
(a) 0.01 F (b) 0.05 F (c) 0.25 F (d) 0.15 F

30. Twenty grams of molten $SnCl_2$ (Molar mass: 190.0 g mol^{-1}) is electrolysed using inert electrodes until 0.119 g of Sn (Molar mass: 119 g mol^{-1}) is deposited at the cathode. The ratio of masses of $SnCl_2$ and $SnCl_4$ after electrolysis would be about
(a) 75.2 : 1 (b) 65.2 : 1 (c) 55.2 : 1 (d) 45.2 : 1

31. In an electrolysis experiment, current was passed into two cells in series. The first cell contains a soltuion of auric chloride and the second contains copper sulphate solution. If 9.85 g of gold (molar mass: 197 g mol^{-1}) is deposited in the first cell, the mass of copper (molar mass: 108 g mol^{-1}) deposited would be about
(a) 4.26 g (b) 4.76 g (c) 5.26 g (d) 5.76 g

32. A current of 4 A is passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 mm thick layers of silver. If the density of silver (molar mass: 108 g mol^{-1}) is 10.8 g cm^{-3}, the time for which the current is passed is about
(a) 84.5 g (b) 90.5 s (c) 96.5 s (d) 100.5 s

33. The quantity of electricity that would be required to reduce 12.3 g of nitrobenzene (molar mass: 123 g mol^{-1}) to aniline is about
(a) 42900 C (b) 47900 C (c) 52900 C (d) 57900 C

34. The time taken to decompose electrolytically 18 g water by 2 A current is about
(A) 24.8 h (b) 26.8 h (c) 28.8 h (d) 30.8 h

35. A current was passed in series through a solution of XCl and a solution of $ZnSO_4$ using zinc electrodes. If 0.348 g of X and 1.264 g on Zn (molar mss: 65.4 g mol^{-1}) are deposited, the molar mass of X would be about
(a) 9 g mol^{-1} (b) 12 g mol^{-1} (c) 16 g mol^{-1} (d) 20 g mol^{-1}

36. A current of 13.4 A is passed through 1.0 L of 1.0 M HCl solution for 1.0 h. The pH of the solution after the experiment is over will be about
(a) 0.20 (b) 0.30 (c) 0.40 (d) 0.50

37. A current of 13.4 A is passed through 1.0 L of 1.0 M HCl solution for 1.0 h. The volume of gases envolved would be about
(a) 11200 mL (b) 14900 mL (c) 18600 mL (d) 22400 mL

38. A sample of gadolinium metal (atomic mass: 157 u) is dessolved in hydrochloric acid and the resultant solution is electrolysed. If 0.87 g of gadolinium is deposited on passing 1608 C of charge, the charge number of gadolinium ion is
(a) 1 (b) 2 (c) 3 (d) 4

39. The mass of silver (molar mass: 108 g mol^{-1}) deposited on passing 10 A of current for 10 h in the solution of silver nitrate is about
(a) 253 g (b) 303 g (c) 353 g (d) 403 g

40. Which of the following gives the charge of an electron?
(a) $1\ F/1\ N_A$ (b) $1\ F$ (c) $1\ F \times 1\ N_A$ (d) $1\ N_A/1\ F$

41. The amount or mass of Cl_2 produced when 1 A current is passed through NaCl solution for 30 min is
(a) 0.33 g (b) 0.66 g (c) 0.33 mol (d) 0.66 mol

42. In an electrolysis of an aqueous solution of NaOH, 2.8 L of oxygen gas at STP was liverated at anode. The volume of hydrogen gas at STP liberated at cathode would be
(a) 2.8 L (b) 5.6 L (c) 11.2 L (d) 22.4 L

43. In the electrolysis of copper(II) chloride solution, the mass of cathode is increased by 3.15 g. At copper anode, we will have
(a) the liberation of 1120 mL of Cl_2 at STP (b) the liberation of 560 mL of O_2 at STP
(c) the loss of 3.15 g of Cu (d) the gain of 3.15 g of Cu

44. The electric charge for electrode deposition of one equivalent of the substance is
(a) one ampere per second (b) 96500 C per second
(c) one ampere per hour (d) charge on 1 mol of electrons (1984)

45. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday constant = 96500 C mol^{-1})
(a) 9.65×10^4 s (b) 19.3×10^4 s (c) 28.95×10^4 s (d) 38.6×10^4 s (2008)

46. In an electrolysis of MCl_3, 0.15 g of metal was deposited on the cathode by the passage of 1 A current for 6 min. The atomic mass of M is
(a) 60.3 g mol^{-1} (b) 90.4 g mol^{-1} (c) 120.6 g mol^{-1} (d) 241.2 g mol^{-1}

47. A certain quantity of electricity is passed through an aqueous solution of $AgNO_3$ and $CuSO_4$ solution in series. If the mass of Ag deposited is 1.08 g, the mass of copper deposited will be
(a) 0.635 g (b) 6.35 g (c) 0.3175 g (d) 1.270 g

Multiple Correct Choice Type

1. In an electrolytic cell, which of the following statements is/are correct?
(a) Cathode is the negative terminal. (b) Reduction occurs at cathode.
(c) Anode is the negative terminal. (d) Reduction occurs at anode.

2. Which of the following statements regarding an electrolytic cell are correct?
(a) The electrode connected to negative terminal of the external battery acts as a anode.
(b) The electrode connected to positive terminal of the external battery acts as a anode.
(c) Oxidation occurs at anode.
(d) Oxidation occurs at the negative terminal

3. Which of the following statements are **not** correct?
(a) Sodium can be obtained by the electrolysis of aqueous solution of NaCl using Pt electrodes.
(b) The current carrying ions in an electrolytic cell are not necessarily discharged at the electrodes.
(c) The mass of a substance deposited on the cathode or anode during electrolysis is given as $m = QM/F|\nu_e|$.
(d) In the purification of a metal by electrolytic method, the impure metal is made cathode.

4. Which of the following statements are **not** correct?
(a) Dilute sulphuric acid on electrolysis liberates oxygen at the anode.
(b) The electrical conductivity of a solution of acetic acid will decrease if a solution of sodium hydroxide is added.
(c) The electrolysis of molten sodium hydride liberates H_2 gas at the anode.
(d) In an electrolytic cell, cathode serves as the negative terminal and reduction reaction occurs at this electrode.

5. Which of the following statements are correct?
(a) In an electrolytic cell, anode serves as the positive terminal and oxidation reaction occurs at this electrode.
(b) One faraday constant has a value of 96 487 C mol^{-1}
(c) 96 487 C of electric change is carried by one mol of positron.
(d) One coulomb of charge is carried by 1×10^{10} electrons.

6. Which of the following statements are correct?
(a) In an electrolytic cell, electrons enter through cathode and leave through anode.
(b) An electrolytic cell, reduction occurs at anode.
(c) An electrolytic cell gives out electrons from anode to the cathode of the external cell.
(d) The reaction involving oxidation of water is $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

7. Which of the following statements are **not** correct?
(a) The reaction involving reduction of water is $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
(b) The species having a lesser reduction potential is preferentially reduced at the cathode.
(c) Water is reduced in preference to the cations having more positive potential than – 0.828 V.
(d) In the electrolysis of a solution containing SO_4^{2-} anions only, the anodic reaction is $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

8. Which of the following statements are **not** correct?

(a) The electrolysis of a solution containing Cl^- anions produces Cl_2 at anode but O_2 is also liberated as the solution is diluted.
(b) The quantitative relationship between electricity and chemical change were established by Faraday.
(c) When an aqueous solution of sodium fluoride is electrolysed, the gas liberated at the anode is F_2.
(d) In an electrolytic refining of an impure metal, the pure metal is obtained at anode.

9. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are

(a) Ag (b) Mg
(c) Cu (d) Al (e) Cr (1990)

Linked Comprehension Type

1. A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (relative atomic mass: Na = 23, Hg = 200; 1 F = 96500 C mol^{-1}).

(i) The amount of chlorine gas evolved is
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0

(ii) If the cathode is a Hg electrode, the maximum mass of amalgam formed from this solution is
(a) 200 g (b) 225 g (c) 400 g (d) 446 g

(iii) The total charge required for complete electrolysis is
(a) 24125 C (b) 48250 C (c) 96500 C (d) 193000 C

Matrix Match Type

1. Column I lists some physical quantities and their units are mentioned in Column II. Match each entry in Column I with its correct unit from Column II.

Column I	**Column II**
(a) Conductance	(p) $cm^2\ V^{-1}\ s^{-1}$
(b) Conductivity	(q) $S\ cm^2\ mol^{-1}$
(c) Molar conductivity	(r) $S\ cm^{-1}$
(d) Ionic mobility	(s) Ω^{-1}

2. Column I lists four cations and Columns II lists ionic molar conductivities. Match the correct entries from these two columns.

Column I	**Column II**
(a) OH^-	(p) 38.66 $S\ cm^2\ mol^{-1}$
(b) Li^+	(q) 50.11 $S\ cm^2\ mol^{-1}$
(c) Na^+	(r) 73.52 $S\ cm^2\ mol^{-1}$
(d) K^+	(s) 197.6 $S\ cm^2\ mol^{-1}$

3. Column I lists four physical quantities and the Column II includes their defining equations. Match each entry in Column I with its correct defining equation from Column II.

Column I	**Column II**
(a) Λ_m	(p) Gl/A
(b) t_+	(q) $\lambda_+/z_+\ F$
(c) u_+	(r) κ/c
(d) κ	(s) $\nu_+\lambda_+/\Lambda$
	(t) $1/\rho c$

ANSWERS

Straight Objective Type

1. (b) **2.** (a) **3.** (d) **4.** (b) **5.** (b) **6.** (c) **7.** (c)
8. (d) **9.** (a) **10.** (b) **11.** (a) **12.** (b) **13.** (d) **14.** (d)

15. (c) **16.** (b) **17.** (d) **18.** (c) **19.** (b) **20.** (d) **21.** (b)
22. (c) **23.** (b) **24.** (d) **25.** (d) **26.** (d) **27.** (d) **28.** (d)
29. (c) **30.** (a) **31.** (b) **32.** (c) **33.** (d) **34.** (b) **35.** (a)
36. (b) **37.** (a) **38.** (c) **39.** (d) **40.** (a) **41.** (b) **42.** (b)
43. (c) **44.** (d) **45.** (b) **46.** (c) **47.** (c)

Multiple Correct Choice Type

1. (a), (b) **2.** (b), (c) **3.** (a), (d) **4.** (b), (c)
5. (a), (b), (c) **6.** (a), (c), (d) **7.** (b), (c), (d) **8.** (c), (d)
9. (b), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (d) **(iii)** (d)

Matrix Match Type

1. (a) – (s); (b) – (r); (c) – (q); (d) – (p)
2. (a) – (s); (b) – (p); (c) – (q); (d) – (r)
3. (a) – (r), (t); (b) – (s); (c) – (q); (d) – (p)

Hints and Solutions

Straight Objective Type

1. Molten sodium chloride conducts electricity due to the presence of free ions.
2. Electrolysis of a solution of sodium sulphate yields H_2 and O_2.
3. During the discharge of a lead storage battery, sulphuric acid is consumed.
4. Cathode is negative terminal.
5. While charging lead storage cell, sulphuric acid is formed.
6. Anodic reaction is $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$.
7. Same as Q.6.
8. In the electrolysis of dilute H_2SO_4 using Cu electrodes, the reaction occurring at anode is $Cu \longrightarrow Cu^{2+} + 2e^-$.
9. The products are O_2 and H_2.
10. Cl^- is oxidized in preference to H_2O

18. Faraday's law of electrolysis are related to the equivalent mass of the electrolyte.
19. By defination, $Q = It$.
20. Faraday's laws of electrolysis follow the expression $m = (Q/F)\,(M/|\nu_e|)$.
21. Amount of Cu deposited = mass of Cu deposited/molar mass of Cu

$$= \text{(density} \times \text{volume) of Cu deposited/molar mass of Cu}$$
$$= (8.94\ \text{g cm}^{-3})\,(10 \times 10 \times 10^{-2}\ \text{cm}^3)/(63\ \text{g mol}^{-1}) = 0.142\ \text{mol}$$

Since 2 electrons are required to convert Cu^{2+} to Cu, the quantity of electricity needed is

$$(2 \times 96500\ \text{C mol}^{-1})\,(0.142\ \text{mol}) = 27388\ \text{C}.$$

22. We have $Q = It = (9.65\ \text{A})\,(3 \times 60 \times 60\ \text{s}) = 104\ 220\ \text{C}$

$$\text{Amount of Ni deposited} = \frac{104\,220\ \text{C}}{2 \times 96\,500\ \text{C mol}^{-1}} = 0.54\ \text{mol}$$

Amount of Ni^{2+} left behind = 1 mol – 0.54 mol = 0.46 mol
Molarity of solution = 0.46 mol/0.5 L = 0.92 mol L^{-1}

23. Using the expression $m = (Q/F)\,(M/|\nu_e|)$, we get

$$(80 \times 5 \times 10^{-3}\ \text{cm}^3)\ (10.5\ \text{g cm}^{-3}) = \frac{(3\ \text{A})t}{(96500\,\text{C mol}^{-1})}\left(\frac{108\ g\ \text{mol}^{-1}}{1}\right)$$

This gives $t = \dfrac{(80 \times 5 \times 10^{-3})\,(10.5)\,(96\,500)}{3\,(108)}\ \text{s} = 1251\ \text{s}$

24. The reactions are $2H^+ + 2e^- \longrightarrow H_2$ and $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$
The volume of H_2 liberated will be twice that of O_2.

25. The reaction occurring at anode is $Cu \longrightarrow Cu^{2+} + 2e^-$. Thus, 2.5 g of Cu will be lost at anode.

26. The quantity of deposition of a metal on cathode depends on the quantity of charge and charge number of metal ion.

27. The overall decomposition reaction is $2H_2O \longrightarrow 2H_2O + O_2$

The amount of water decomposed is (2/3) mol.

28. Using the expression $m = (Q/F)\ (M/|\nu_e|)$, we get

$$|\nu_e| = \frac{Q}{F}\frac{M}{m} = \left(\frac{4825\ \text{C}}{96\,500\ \text{C mol}^{-1}}\right)\left(\frac{197\ \text{g mol}^{-1}}{3.283}\right) = 3$$

29. The reaction is $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
The quantity of electricity needed = $(1\ \text{F mol}^{-1})(5 \times 0.05\ \text{mol}) = 0.25\ \text{F}$

30. The reactions occurring at the electrodes are *Cathode* $Sn^{2+} + 2e^- \rightarrow Sn$ *Anode* $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
If 0.119 g of Sn is deposited at the cathode, then 0.119 g of Sn^{4+} will be formed at the anode. Thus, a total of 2×0.119 g of Sn^{2+} is lost from the solution. Hence mass of the remaining $SnCl_2$

$$= 20\ \text{g} - \frac{M_{SnCl_2}}{M_{Sn}} \times m_{Sn} = 20\ \text{g} - \frac{189.6}{119} \times 2 \times 0.119\ \text{g} = (20 - 0.38)\text{g} = 19.62\ \text{g}.$$

Mass of $SnCl_4$ formed $= \dfrac{M_{SnCl_4}}{M_{Sn}} \times m_{Sn} = \dfrac{260.2}{119} \times 0.119\ \text{g} = 0.26\ \text{g}.$ $\quad \dfrac{m(SnCl_2)}{m(SnCl_4)} = \dfrac{19.62}{0.26} = 75.5$

31. Amount of gold deposited $= \dfrac{9.85\ \text{g}}{197\text{g mol}^{-1}} = 0.05\ \text{mol}$

Based on the reaction $Au^{3+} + 3e^- \rightarrow Au$, it follows that the amount of electrons passed is 3×0.05 mol. For the reaction $Cu^{2+} + 2e^- \rightarrow Cu$, we can write

Amount of Cu deposited $= \dfrac{3 \times 0.05\ \text{mol}}{2} = 0.0075\ \text{mol}$

Mass of Cu deposited = $(0.0075\ \text{mol})\ (63.5\ \text{g mol}^{-1}) = 4.76$ g.

32. Volume of metal deposited = $(80\ \text{cm}^2)\ (5 \times 10^{-4}\ \text{cm}) = 0.04\ \text{cm}^3$
Mass of metal deposity = $\rho V = (10.8\ \text{g cm}^{-3})\ (0.04\ \text{cm}^3) = 0.432\ \text{g}$

Amount of metal deposited $= \dfrac{0.432\ \text{g}}{108\ \text{g mol}^{-1}} = 0.004\ \text{mol}$

Quantity of electricity passed = $(0.004\ \text{mol})\ (96500\ \text{C mol}^{-1}) = 386\ \text{C}$

Time for which 4A current is passed $= \dfrac{386\ \text{C}}{4\text{A}} = 96.5\ \text{s}$

33. The reaction is $C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O$.

Amount of nitrobenzene to be reduced $= \dfrac{12.3\ \text{g}}{123\ \text{g mol}^{-1}} = 0.1\ \text{mol}$

Amount of electricity required = $(6 \times 0.1\ \text{mol})\ (96500\ \text{C mol}^{-1}) = 57900\ \text{C}$

34. The reactions are $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
For the passage of 4 mol of electrons, the net reaction occurring is

$$6H_2O \rightarrow O_2 + 2H_2 + 4H^+ + 4OH^- \quad \text{or} \quad 2H_2O \rightarrow 2H_2 + O_2$$

that is, 2 mol of water (i.e. 36 g) is deposited by the passage of 4 mol of electrons. Thus

Time required to decompose water = $\left(\dfrac{4\text{ mol electrons}}{36\text{ g H}_2\text{O}}\right)$ (18 g H_2O) (96500 C / 2A) = 96500 s ≡ 26.8 h

35. Amount of Zn deposited = $\dfrac{1.264\text{ g}}{65.4\text{ g mol}^{-1}}$ = 0.01933 mol

Amount of electrons required = 2 × 0.01933 mol = 0.03866 mol

Since the metal X is monovalent, we have

Amount of X deposited = 0.03866 mol

If M is the molar mass of X, then $M = \dfrac{0.348\text{ g}}{0.03866\text{ mol}} = 9\text{ g mol}^{-1}$

36. The reactions occuring are $2H^+ + 2e^- \rightarrow H_2(g)$ and $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Quantity of electricity passed = (13.4 A) (60 × 60 s) = 48240 C

Amount of electrons passed = $\dfrac{48240\text{ C}}{96480\text{ C mol}^{-1}}$ = 0.5 mol

Decrease in amount of H^+ = 0.5 mol

Amount of remaining H^+ = 1 mol – 0.5 mol = 0.5 mol

pH of the solution = – log 0.5 = 0.30

37. From Q.36, we conclude that on passing 2 mol of electrons 2 mol of gases (1 mol H_2 and 1 mol Cl_2) are evolved. Hence, on passing 0.5 mol of electrons, 0.5 mol of gases will be evolved. Thus, volume of total gas evolved = (0.5 mol) (22400 mL mol $^{-1}$) = 11200 mL.

38. Since $m = (Q / F)(M / |\nu_e|)$, we get

$$|\nu_e| = \frac{Q}{F}\frac{M}{m} = \left(\frac{1608\text{ C}}{96500\text{ C mol}^{-1}}\right)\left(\frac{157\text{ g mol}^{-1}}{0.87\text{g}}\right) = 3.0$$

39. $m = \dfrac{Q}{F}\dfrac{M}{|\nu_e|} = \dfrac{(10\text{ A})(10\times60\times60\text{s})}{(96500\text{ C mol}^{-1})}\dfrac{(108\text{ g mol}^{-1})}{1} = 403\text{ g.}$

41. Amount = $\dfrac{1}{2}\left(\dfrac{1\text{ mol}}{96500\text{ C}}\right)(1\times30\times60\text{ C}) = \dfrac{1}{2}\times0.0187\text{ mol}$

Mass = $\dfrac{1}{2}\times0.0187\times71\text{ g} = 0.664\text{ g}$

42. The reactions are $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ and $H_2O \rightarrow \dfrac{1}{2}O_2 + 2H^+ + 2e^-$

Volume of H_2 will be double than that of O_2.

43. Since anode is copper, the reaction occurring here is $Cu \rightarrow Cu^{2+} + 2e^-$. Thus, there will occur a loss of Cu at anode which will also equal to 3.15 g

45. We have

$$m = \frac{Q}{F}\frac{M}{|\nu_e|} = \frac{I\,t\,M}{F|\nu_e|} \Rightarrow t = \frac{(m/M)\,F\,\nu_e}{I} = \frac{(0.01\text{ mol})(96500\text{ C mol}^{-1})(2)}{(10\times10^{-3}\text{A})} = 193\,000\text{s}$$

46. $M = \dfrac{mF|\nu_e|}{It} = \dfrac{(0.15\text{g})(96500\text{ C mol}^{-1})(3)}{(1\text{A})(6\times60\text{ s})} = 120.6\text{ g mol}^{-1}$

47. $m_{Ag} = \dfrac{Q}{F}\dfrac{M_{Ag}}{1}$ and $m_{Cu} = \dfrac{Q}{F}\dfrac{M_{Cu}}{2}$

$$m_{Cu} = \frac{1}{2}\left(\frac{M_{cu}}{M_{Ag}}\right)m_{Ag} = \frac{1}{2}\left(\frac{63.5}{108}\right)(1.08\text{ g}) = 0.3175\text{ g}$$

Multiple Correct Choice Type

1. Cations in the cell move toward negatively charged electrode (known as cathode) where these are reduced.
2. Anions in the cell move towards positively charged electrode (known as anode) where these are oxidized.
3. In aqueous solution, it is H_2O which is reduced. $2H_2O + 2e^- \rightarrow 2H_2 + 2OH^-$. The impure metal is made anode and undergoes oxidation.
4. H_2O is oxidized at anode liberating O_2. The addition of NaOH to start with decreases conductivity due to neutralization of H^+ and also it suppresses the ionization of acetic acid due to common-ion effect.
Hydride is H^- which moves towards anode and is oxidized liberating H_2.
7. SO_4^{2-} is difficult to oxidize and water is oxidized instead.
Larger the reduction potential, larger the tendency for reduction.
8. It is oxygen liberated instead of F_2.
Pure metal is made cathode where metallic ions in solution get reduced to pure metal.

Linked Comprehension Type

1. (i) Amount of Na^+ or Cl^- ion in solution undergoing electrolysis = $(4.0\ \text{mol L}^{-1})\ (0.5\ \text{L}) = 2.0$ mol
Chlorine is formed due to the reaction

$$\underset{(2\ \text{mol})}{2Cl^-} \rightarrow \underset{(1\ \text{mol})}{Cl_2} + 2e^-$$

Hence, from 2 mol of Cl^- ions, 1 mol of Cl_2 is formed.

(ii) At cathode, the reaction occurring is $Na^+ + e^- \rightarrow Na$
For 2 mol of Na^+ ions, 2 mol of Na is formed and the amalgam, Na(Hg), formed will also be 2 mol. Hence the total mass of amalgam will be 2 (23 g + 200 g) = 446 g

(iii) For complete electrolysis, 2 mol of electrons are required. Total charge carried by these electrons is (2 mol) $(96500\ \text{C mol}^{-1})$ = 193 000 C.

ANNEXURE I

Subjective Problems for Practice

SOLVED PROBLEMS

1. Ninteen grams of molten $SnCl_2$ is electrolysed for some time using inert electrodes until 0.119 g of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the masses of $SnCl_2$ and $SnCl_4$ after electrolysis. (1980)

Solution The reactions occurring at the electrodes are

Cathode $Sn^{2+} + 2e^- \rightarrow Sn$ *Anode* $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

If 0.119 g of Sn is deposited at cathode, then 0.119 g of Sn^{4+} will be formed at the anode. Thus, a total of 2 × 0.119 g of Sn^{2+} is lost from the solution. Hence,

$$\text{Mass of remaining } SnCl_2 = 19\ \text{g} - \frac{M_{SnCl_2}}{M_{Sn}} \times m_{Sn} = 19\ \text{g} - \frac{189.6}{119} \times 2 \times 0.119\ \text{g} = (19 - 0.379)\text{g} = 18.621\ \text{g}$$

$$\text{Mass of } SnCl_4 \text{ formed} = \frac{M_{SnCl_4}}{M_{Sn}} \times m_{Sn} = \frac{260.2}{119} \times 0.119\ \text{g} = 0.26\ \text{g}$$

$$\text{Now} \quad \frac{m(SnCl_2)}{m(SnCl_4)} = \frac{18.621}{0.260} = \frac{71.62}{1}$$

2. In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the mass of copper deposited on the cathode of the second cell. Also calculate the current passed through the experiment. (1983)

Solution We have

$$\text{Amount of gold deposited} = \frac{9.85\ \text{g}}{197\ \text{g mol}^{-1}} = 0.05\ \text{mol}$$

Based on the reaction $Au^{3+} + 3e^- \rightarrow Au$, it may be concluded that

$$\text{Amount of electrons passed} = 3 \times 0.05\ \text{mol} = 0.15\ \text{mol}$$

Now, the same quantity of electricity is passed through $CuSO_4$ solution causing the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ at cathode. We will have

$$\text{Amount of Cu deposited} = \frac{0.15\ \text{mol}}{2} = 0.075\ \text{mol}$$

$$\text{Mass of Cu deposited} = (0.075\ \text{mol})\ (63.5\ \text{g mol}^{-1}) = 4.762\,5\ \text{g}$$

$$\text{Quantity of electricity passed} = (0.15\ \text{mol})\ (96\,500\ \text{C mol}^{-1}) = 14\,475\ \text{C}$$

$$\text{Quantity of current passed} = \frac{Q}{t} = \frac{14\,475\ \text{C}}{5 \times 60 \times 60\ \text{s}} = 0.804\,2\ \text{A}.$$

3. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of silver is 10.5 g cm^{-3}. (1985)

Solution We have

$$\text{Volume of metal deposited} = (80\ \text{cm}^2)\ (0.000\,5\ \text{cm}) = 0.04\ \text{cm}^3$$

$$\text{Mass of metal deposited} = \rho V = (10.5\ \text{g cm}^{-3})\ (0.04\ \text{cm}^3) = 0.42\ \text{g}$$

$$\text{Amount of silver deposited} = \frac{0.42\ \text{g}}{108\ \text{g mol}^{-1}} = 3.889 \times 10^{-3}\ \text{mol}$$

$$\text{Quantity of electricity passed} = (3.889 \times 10^{-3}\ \text{mol})\ (96\,500\ \text{C mol}^{-1}) = 375.27\ \text{C}$$

$$\text{Time for which 3A current is passed} = \frac{375.27\ \text{C}}{3\ \text{A}} = 125.09\ \text{s}$$

4. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g mL^{-1}. Sulphuric acid of density 1.294 g mL^{-1} is 39% H_2SO_4 by mass and that of density 1.139 g mL^{-1} is 20% H_2SO_4 by mass. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge. Calculate the number of ampere-hour for which the battery must have been used. The charging and discharging reactions are

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \quad \text{(charging)}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \quad \text{(discharging)}$$

(1986)

Solution We have

$$\text{Mass of } H_2SO_4 \text{ solution to start with, } \rho V = (1.294\ \text{g mL}^{-1})\ (3.5 \times 10^3\ \text{mL}) = 4\,529\ \text{g}$$

$$\text{Actual mass of } H_2SO_4 \text{ in this solution} = \left(\frac{39}{100}\right)(4\,529\ \text{g}) = 1766.3\ \text{g}$$

$$\text{Mass of } H_2SO_4 \text{ solution at the end} = (1.139\ \text{g mL}^{-1})\ (3.5 \times 10^3\ \text{mL}) = 3986.5\ \text{g}$$

$$\text{Actual mass of } H_2SO_4 \text{ in this solution} = \left(\frac{20}{1000}\right)(3\,986.5\ \text{g}) = 797.3\ \text{g}$$

$$\text{Mass of } H_2SO_4 \text{ consumed} = (1\,766.3 - 91.3)\ \text{g} = 969.0\ \text{g}$$

$$\text{Amount of } H_2SO_4 \text{ consumed} = \frac{969.0\ \text{g}}{98\ \text{g mol}^{-1}} = 9.888\ \text{mol}$$

$$\text{Amount of } H^+ \text{ consumed} = 2 \times 9.888\ \text{mol}$$

Since 4 mol of H^+ are consumed per 2 mol of electrons during discharge, we have

$$\text{Amount of electrons discharged} = \left(\frac{2\ \text{mol}}{4\ \text{mol}}\right)(2 \times 9.888\ \text{mol}) = 9.888\ \text{mol}$$

$$\text{Quantity of electricity discharged} = (9.888\ \text{mol})(96\,500\ \text{C mol}^{-1}) = 954\,192\ \text{C}$$

$$\text{Number of ampere-hour for which the battery has been used} = \frac{954192}{60 \times 60} = 265.05.$$

5. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours? (1987)

Solution Since $W = VI$, we have

$$I = \frac{100\text{ W}}{110\text{ V}} = \frac{10}{11}\text{ A};\quad Q = It = \left(\frac{10}{11}\text{ A}\right)(10 \times 60 \times 60\text{ s}) = 32\,727.3\text{ C}$$

$$\text{Mass of Cd deposited } (\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}) = \frac{M_{\text{Cd}}}{2F} \times Q = \left(\frac{112.4\text{ g mol}^{-1}}{2 \times 96500\text{ C mol}^{-1}}\right)(32727.3\text{ C}) = 19.06\text{ g.}$$

6. In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen gas is oxidized at the anode and oxygen is reduced at the cathode. If 67.2 L of H_2 at STP reacts in 15 minutes, what is the average current produced? If the entire current is used for electrodeposition of copper from copper(II) solution, what mass of copper will be deposited?

Anode reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (1988)

Solution Amount of hydrogen oxidized $= \dfrac{67.2\text{ L}}{22.4\text{ L mol}^{-1}} = 3\text{ mol}$

Amount of electrons produced $= 2 \times 3$ mol

Quantity of electricity produced $= 2 \times 3 \times 96\,500$ C

Current produced $= \dfrac{2 \times 3 \times 96500\text{ C}}{15 \times 60\text{ s}} = 643.33$ A

Since 1 mol of Cu is deposited by the absorption of 2 mol electrons, we will have

Amount of Cu deposited = 3 mol Mass of Cu deposited = (3 mol) (63.5 mol^{-1}) = 190.5 g.

7. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 amperes. Calculate the volume of gases evolved at STP during the entire electrolysis. (1989)

Solution Assuming Cu^{2+} salt to be $CuSO_4$, the reactions occurring at the electrodes would be

Anode $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ *Cathode* $Cu^{2+} + 2e^- \rightarrow Cu$

After the complete deposition of copper, the reactions would be

Anode $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ *Cathode* $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Now Amount of Cu deposited $= \dfrac{0.4\text{ g}}{63.6\text{ g mol}^{-1}} = 0.00629$ mol

Amount of oxygen liberated $= \frac{1}{2} \times 0.00629$ mol $= 0.003\,145$ mol

Quantity of electricity passed in seven minutes after the deposition of the entire copper
$= (1.2\text{ A})(7 \times 60\text{ s}) = 504\text{ C}$

Amount of electrons carrying this much of electricity $= \dfrac{504\text{ C}}{96\,500\text{ C mol}^{-1}} = 0.00522$ mol

From the electrode reactions which occur after the deposition of copper, we conclude

Amount of oxygen liberated $= \frac{1}{4} \times 0.00522$ mol $= 0.001\,305$ mol

Amount of hydrogen liberated $= \frac{1}{2} \times 0.00522$ mol $= 0.00261$ mol

Total amount of gases liberated in the entire electrolysis $= (0.003\,145 + 0.001\,305 + 0.00261)$ mol
$= 0.00706$ mol

Volume of the gases evolved at STP during the entire electrolysis
$= (0.00706\text{ mol})(22414\text{ mL mol}^{-1}) = 158.2$ mL

If the salt of Cu^{2+} ions is $CuCl_2$, then the anodic reaction during the deposition of copper would be
$2Cl^- \rightarrow Cl_2 + 2e^-$

In this case, Total amount of gases liberated would be $= (0.00629 + 0.001\,305 + 0.00261)$ mol $= 0.010205$ mol
Volume of the gases evolved would be $= (0.010\,205\text{ mol})(22\,414\text{ mL mol}^{-1}) = 228.7$ mL.

8. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? (1990)

Solution The reduction reaction is $C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O$

Mass of $C_6H_5NO_2$ to be reduced = 12.3 g

$$\text{Amount of } C_6H_5NO_2 \text{ to be reduced} = \frac{12.3\,\text{g}}{M(C_6H_5NO_2)} = \frac{12.3\,\text{g}}{123\,\text{g mol}^{-1}} = 0.1 \text{ mol}$$

To reduce 0.1 mol $C_6H_5NO_2$, 0.6 mol of electrons would be required. But the current efficiency is 50%. Hence, the amount of electrons required would be 1.2 mol. Now

Electricity carried by 1.2 mol electrons = (1.2 mol) (96500 C mol^{-1}) = 115800 C

Energy consumed = (115800 C) (3.0 V) = 347400 J = 347.4 kJ.

9. A current of 1.70 A is passed through 300.0 mL of 0.160 M solution of $ZnSO_4$ for 230 s with a current efficiency of 90 per cent. Find out the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. (1991)

Solution

$$\text{Amount of electrons passed} = \frac{It}{F} = \frac{(1.70\,\text{A})(230\,\text{s})}{(96500\,\text{C mol}^{-1})} = 0.00405 \text{ mol}$$

$$\text{Amount of electrons actually used in the reduction of } Zn^{2+} = (0.00405)\left(\frac{90}{100}\right) = 0.00365 \text{ mol}$$

$$\text{Amount of } Zn^{2+} \text{ ions reduced} = \tfrac{1}{2} \times 0.00365 \text{ mol} = 0.001825 \text{ mol}$$

$$\text{Molarity of } Zn^{2+} \text{ after the deposition of Zn} = 0.160\text{ M} - \left(0.001825 \times \frac{1000}{300}\right)\text{ M} = 0.154 \text{ M}$$

10. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to the reaction

$$2Cl^-(aq) + 2H_2O \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

A direct current of 25 amperes with current efficiency of 62% is passed through 20 litres of NaCl solution (20% by mass). Write down the reactions taking place at the anode and cathode. How long will it take place to produce 1 kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? Assume there is no loss due to evaporation. (1992)

Solution The reactions occurring at the electrodes are

Anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

$$\text{Amount of } Cl_2 \text{ to be produced} = \frac{10^3\,\text{g}}{71\,\text{g mol}^{-1}} = 14.08 \text{ mol}$$

Amount of electrons needed to carry out electrolysis = 2 × 14.08 mol

Quantity of electricity carried by the these electrons = 2 × 14.08 × 96500 C

$$\text{Time required to carry out electrolysis } t = \frac{Q}{I} = \frac{2 \times 14.08 \times 96500\,\text{C}}{(25\,\text{A})(62/100)} = 175300 \text{ s}$$

$$= (175300/60 \times 60) \text{ h} = 48.69 \text{ h}$$

Amount of OH^- ions released in the electrolysis = 2 × 14.08 mol

$$\text{Molarity of } OH^- \text{ ions} = \frac{2 \times 14.08\,\text{mol}}{20\,\text{L}} = 1.408 \text{ mol L}^{-1}.$$

11. How much time in hours is required for a current of 2 A to decompose electrolytically 18 g water?

Solution The electrode reactions occurring are

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{and} \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

For the passage of 4 mol of electrons, the net reaction occurring would be

$$6H_2O \rightarrow O_2 + 2H_2 + 4H^+ + 4OH^- \quad \text{or} \quad 2H_2O \rightarrow O_2 + 2H_2$$

that is, 2 mol of water (= 36 g) is decompsed by the passage of 4 mol of electrons. Thus,

Amount of electrons required to decompose 18 g of water = 2 mol

Quantity of electricity required = 2 × 96500 C

$$\text{Time required} = \frac{2 \times 96500\,\text{C}}{2\,\text{A}} = 96500 \text{ s} = \frac{96500}{60 \times 60} \text{ h} = 26.806 \text{ h}.$$

12. A current of 20.0 A is used to plate Ni from a $NiSO_4$ solution. Both Ni and H_2 are liberated at cathode. The current efficiency with respect to liberation of Ni is 50%. (a) What mass of Ni is plated on cathode per hour? (b) What is the thickness of plating ion on both the sides of the square cathode of edge length 4 cm? Given: Atomic mass of Ni = 58.79 amu and its density = 8.9 g cm^{-3}.

Solution Since the current efficiency with respect to liberation of Ni is 50%, 10.0 A out of 20.0 A current will be used for the liberation of Ni. Hence,

$$\text{Quantity of electricity available in 1 h to deposit Ni} = (10.0\ \text{A})\ (60 \times 60\ \text{s}) = 36000\ \text{C}$$

$$\text{Amount of electrons used in plating out Ni} = \left(\frac{36000\,\text{C}}{96500\,\text{C mol}^{-1}}\right) = 0.373\ \text{mol}$$

$$\text{Amount of Ni plated out} = \tfrac{1}{2} \times 0.373\ \text{mol} = 0.1865\ \text{mol}$$

$$\text{Mass of Ni plated out} = (0.1865\ \text{mol})\ (58.79\ \text{g mol}^{-1}) = 10.964\ \text{g}$$

$$\text{Mass of Ni plated out on either side of square cathode} = \tfrac{1}{2} \times 10.964\ \text{g} = 5.482\ \text{g}$$

$$\text{Volume of Ni plated out on either side of square cathode} = \frac{5.482\,\text{g}}{8.9\,\text{g cm}^{-3}} = 0.616\ \text{cm}^3$$

$$\text{Thickness of Ni plated out on either side of square cathode} = \frac{0.616\,\text{cm}^3}{(4\,\text{cm})(4\,\text{cm})} = 0.0385\ \text{cm}$$

13. A current was passed in series through a solution of salt of a metal X and solution of $ZnSO_4$ using zinc electrodes. After a certain time, 0.348 g of X and 1.264 g of Zn had been deposited. Calculate the molar mass of X if the salt is represented as XCl.

Solution

$$\text{Amount of Zn deposited} = \frac{1.264\ \text{g}}{65.4\,\text{g mol}^{-1}} = 0.01933\ \text{mol}$$

$$\text{Amount of electrons consumed} = 2 \times 0.01933\ \text{mol} = 0.03866\ \text{mol}$$

Since the metal X is monovalent, we have

$$\text{Amount of X deposited} = 0.03866\ \text{mol}$$

If M is the molar mass of X, we will have

$$\frac{0.348\,\text{g}}{M} = 0.03866\ \text{mol} \qquad \text{or} \qquad M = \frac{0.348\,\text{g}}{0.03866\,\text{mol}} = 9\ \text{g mol}^{-1}$$

14. A current of 10.0 A is passed through 1.0 L of 1.0 M HCl solution for 1.0 h. Calculate the pH of the solution at the end of the experiment. What is the volume of total gas evolved at STP?

Solution The reactions occurring are

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad \text{and} \qquad 2Cl^- \rightarrow Cl_2(g) + 2e^-$$

$$\text{Quantity of electricity passed} = (10.0\ \text{A})\ (60 \times 60\ \text{s}) = 36000\ \text{C}$$

$$\text{Amount of electrons passed} = \frac{36000\,\text{C}}{96500\,\text{C mol}^{-1}} = 0.373\ \text{mol}$$

$$\text{Decrease in the amount of } H^+ = 0.373\ \text{mol}$$

$$\text{Amount of remaining } H^+ \text{ in the solution} = 1.0\ \text{mol} - 0.373\ \text{mol} = 0.627\ \text{mol}$$

$$\text{pH of the solution} = -\log(0.627) = 0.20$$

On passing 2 mol electrons, 2 mol of gases (1 mol H_2 and 1 mol Cl_2) are evolved. Hence, on passing 0.373 mol electrons, 0.373 mol of gases will be evolved. Thus

$$\text{Volume of total gas evolved} = (0.373\ \text{mol})\ (22414\ \text{mL mol}^{-1}) = 8360.4\ \text{mL}.$$

15. A sample of gadolinium metal (atomic mass = 157 amu) is dissolved in hydrochloric acid and the resulting solution is electrolysed. When 1608 C has passed through the cell 0.87 g of gadolinium is found to be deposited at the cathode. Calculate the charge number on the gadolinium ion.

Solution Let z be the charge number on the gadolinium ion. Substituting the given data in the expression

$$m = \frac{Q}{F}\frac{M}{z}$$

we get

$$0.87\ \text{g} = \frac{1608\,\text{C}}{(96500\,\text{C mol}^{-1})}\frac{(157\,\text{g mol}^{-1})}{z} \qquad \text{which gives} \qquad z = \frac{1608 \times 157}{96500 \times 0.87} = 3.0.$$

16. In the electrolysis of a $CuSO_4$ solution, there are two possible reactions at the anode

(i) $Cu \rightarrow Cu^{2+} + 2e^-$ and (ii) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

A current of 1.0 A is passed for 2.0 h. The loss in mass of the Cu anode was 1.50 g. How much volume of oxygen at STP was liberated? What fraction of current is used in the production of Cu^{2+} ions?

Solution Amount of Cu converted to Cu^{2+} ions $= \dfrac{1.50\,\text{g}}{63.5\,\text{g mol}^{-1}} = 0.023\,62$ mol

Amount of electrons involved $= 2 \times 0.023\,62$ mol $= 0.047\,24$ mol

Amount of electrons actually passed through solution $= \dfrac{It}{F} = \dfrac{(1.0\,\text{A})(2\times60\times60\,\text{s})}{(96\,500\,\text{C mol}^{-1})} = 0.074\,61$ mol

Amount of electrons involved in converting H_2O to O_2 = (0.074 61 – 0.047 24) mol = 0.027 37 mol

Amount of oxygen liberated $= \frac{1}{4} \times 0.027\,37$ mol $= 0.006\,843$ mol

Volume of oxygen liberated at STP = (0.006 843 mol) (22 414 mL mol^{-1}) = 153.4 mL

Fraction of current used in the production of Cu^{2+} ions $= \dfrac{0.047\,24}{0.074\,61} = 0.633.$

17. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction $Mn^{2+}(aq) + 2H_2O \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. (1997)

Solution The electrode reactions are

Anode $Mn^{2+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + 2e^-$

Cathode $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall reaction $Mn^{2+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$

The actual current needed to deposit 1 kg MnO_2 is given by the expression

$$I = m\left(\frac{F}{t}\right)\left(\frac{z}{M}\right) = (1000\ \text{g})\left(\frac{96500\ \text{C mol}^{-1}}{24\times60\times60\ \text{s}}\right)\left[\frac{2}{(54.9+2\times16)\,\text{g mol}^{-1}}\right] = 25.70\ \text{A}$$

$$\text{The current efficiency} = \left(\frac{25.70\ \text{A}}{27\ \text{A}}\right)(100) = 95.185\%$$

18. What mass of silver could be plated out on a serving tray by electrolysis of a solution containing silver in + 1 oxidation state for a period of 8 hours at a current of 8.46 amperes? What is the area of tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3. (1997)

Solution Using the expression $m = \dfrac{It}{F}\dfrac{M}{|\nu_e|}$

we get $m = \dfrac{(8.46\ \text{A})(8\times60\times60\ \text{s})(107.8\ \text{g mol}^{-1})}{(96500\ \text{C mol}^{-1})\ (1)} = 272.18$ g (1)

Volume of silver plated out, $V = \dfrac{m}{\rho} = \dfrac{272.18\ \text{g}}{10.5\ \text{g cm}^{-3}} = 25.92\ \text{cm}^3$

Area of the tray plated $= \dfrac{25.92\ \text{cm}^3}{0.00254\ \text{cm}} = 10204.7\ \text{cm}^2$

19. Copper sulphate (250 mL) was electrolysed using a platinum anode and copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. (2000)

Solution The reaction occurring at the electrodes are

Cathode $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ *Anode* $H_2O(l) \rightarrow 2H^+(aq) + \frac{1}{2}O_2(g) + 2e^-$

The concentration of Cu^{2+} ions decreases during the electrolysis of copper sulphate solution. The amount of Cu^{2+} deposited when a current of 2 mA is passed for 16 min, will be

$$\Delta n = \frac{\Delta m}{M_{Cu}} = \frac{It}{F}\frac{1}{|\nu_e|} = \frac{(2 \times 10^{-3}\,A)(16 \times 60\,s)}{(96500\,C\,mol^{-1})}\frac{1}{2} = 9.948 \times 10^{-6}\ mol$$

Since the absorbance (which is directly proportional to the Cu^{2+} concentration in the solution) after the electrolysis is half of its value in the original solution, the amount of Cu^{2+} ions in the original solution will be

$$n_i = 2 \times 9.948 \times 10^{-6}\ mol$$

Since the volume of solution is 250 mL (the volume of water decomposed during electrolysis is negligible), the concentration of $CuSO_4 \cdot 5H_2O$ in the original solution would be

$$c_i = \frac{n_i}{V} = \frac{2 \times 9.948 \times 10^{-6}\,mol}{0.250\,L} = 7.96 \times 10^{-5}\ mol\ L^{-1}$$

20. A current of 3.7 amperes is passed for 6 hours between nickel electrodes in 0.5 L of a 2 M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of electrolysis?

Solution Amount of electricity passed $= \frac{It}{F} = \frac{(3.7\,A)(6 \times 60 \times 60\,s)}{(96500\,C\,mol^{-1})} = 0.828\ mol$

Amount of Ni deposited based on the reaction $Ni^{2+} + 2e^- \rightarrow Ni$ is given by

$$n_1 = \frac{0.828}{2}\ mol = 0.414\ mol$$

Amount of Ni^{2+} ions to start with $n_2 = VM = (0.5\ L)\ (2\ mol\ L^{-1}) = 1.0\ mol$

Amount of Ni^{2+} ions remaining in the solution after electrolysis

$$n_3 = n_2 - n_1 = (1.0 - 0.414)\ mol = 0.586\ mol$$

Molarity of solution after electrolysis is $M = \frac{n_3}{V} = \frac{0.586\,mol}{0.5\,L} = 1.172\ mol\ L^{-1}$

21. Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.20 ampere for 3 hours. Calculate the thickness of silver deposited, given its density as 10.47 g cm^{-3}.

Solution Amount of electricity passed $\frac{It}{F} = \frac{(0.2\,A)(3 \times 60 \times 60\,s)}{(96500\,C\ mol^{-1})} = 0.0224\ mol$

Amount of silver deposited as per the reaction $Ag^+ + e^- \rightarrow Ag$ is $n = 0.0224$ mol

Mass of silver deposited $m = nM = (0.0224\ mol)\ (107.9\ g\ mol^{-1}) = 2.415\ g$

If x is the thickness of silver deposited, then the mass of silver deposited is also given by

$$m = (Ax)\,\rho = (800\ cm^2)\ (x)\ (10.47\ g\ cm^{-3})$$

Equating the two masses and solving for x, we get $x = \frac{2.415}{800 \times 10.47}\ cm = 2.88 \times 10^{-4}\ cm$

22. The density of copper is 8.94 g/mL. Find out the number of coulombs needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte.

Solution Area to be plated = (10 cm) (10 cm) (10^{-2} cm) = 1 cm^3

Mass of Cu to be plated $= \rho V = (8.94\ g\ cm^{-3})\ (1\ cm^3) = 8.94\ g$

Amount of Cu to be plated $= \frac{m}{M} = \frac{8.94\,g}{63.5\,g\,mol^{-1}} = 0.1408\ mol$

Amount of electricity required as per equation $Cu^{2+} + 2e^- \rightarrow Cu$ is

$$n_Q = 2 \times 0.1408\ mol = 0.2816\ mol$$

Since $n_Q = It/F = Q/F$, we have $Q = n_Q F = (0.2816\ mol)\ (96\,500\ C\ mol^{-1}) = 27\,172\ C$

23. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation $CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$
Calculate (a) the mass of chromium plated out by 24,000 C and (b) how long will it take to plate out 1.5 g of chromium by using 12.5 A current? (1993)

Solution The given equation is $CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$

(a) Using the expression $m = \frac{Q}{F}\frac{M}{z}$ we get (1)

$$m = \left(\frac{24\,000\ \mathrm{C}}{96\,500\ \mathrm{C\,mol^{-1}}}\right)\left(\frac{52\ \mathrm{mol^{-1}}}{6}\right) = 2.155\ \mathrm{g}$$

(b) Since $Q = It$, Eq. (1) gives

$$t = m\left(\frac{F}{I}\right)\left(\frac{z}{M}\right) = (1.5\ \mathrm{g})\left(\frac{96\,500\ \mathrm{C\ mol^{-1}}}{12.5\ \mathrm{A}}\right)\left(\frac{6}{52\ \mathrm{g\ mol^{-1}}}\right) = 1336.15\ \mathrm{s} \equiv 22.27\ \mathrm{min}$$

UNSOLVED PROBLEMS (ELECTROLYSIS)

1. Predict the products of electrolysis in each of the following.
   (a) An aqueous solution of Na_2SO_4. (b) An aqueous solution of KI.
   (c) An aqueous solution of KCl. (d) An aqueous solution of $CuSO_4$ involving Cu electrodes
2. Calculate the time required to plate a spoon 14.0 cm^2 in area to a depth of 0.01 cm with silver using $Ag(CN)_2^-$ in a plating bath with a current of 0.0120 A. Given: $\rho(Ag) = 10.5\ g\ cm^{-3}$.
3. A current of 0.5 A is passed through sodium sulphate solution for one hour. What is the volume of gases evolved at electrodes at 17 °C and 750 mmHg?
4. What is the concentration of Ni^{2+} remaining in a solution after the electrolysis of 100 mL of 0.5 M $NiSO_4$ solution when one uses 1.5 A for one hour? Assume no volume change during electrolysis.
5. What is the current efficiency of an electrodeposition of copper metal in which 9.80 g of Cu is deposited by the passage of 3.0 A current for 10^4 s?
6. A current of 0.01 A is passed through a solution of iridium bromide. The only reaction at the cathode is the deposition of Ir. After 3.0 h, 0.072 g of Ir is deposited. What is the charge number of iridium ion?
   Given: $M(Ir) = 192.22\ g\ mol^{-1}$ and $M(Br) = 79.9\ g\ mol^{-1}$
7. Calculate the quantity of charge necessary to produce 10 L of $H_2(g)$ measured at STP from the electrolysis of water. What amount of water will undergo electrolysis and what will be the amount of $O_2(g)$ liberated?
8. A metal forms the fluoride MF_3. Electrolysis of molten fluoride by a current of 3.86 A for 16.2 min deposits 1.25 g of the metal. Calculate the molar mass of the metal.
9. Find the number of electrons passed through an electrolytic cell in which the concentration of aqueous $CuSO_4$ is changed from 1.0 M to 0.8 M. The volume of $CuSO_4$ solution taken in the cell is 500 cm^3. How much electricity flows through the cell? If the time taken to cause the above change is 1 h, how much current has been used?

ANSWERS

1. (a) Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ Anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
(b) Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ Anode $2I^- \rightarrow I_2 + 2e^-$
(c) Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ Anode $2Cl^- \rightarrow Cl_2 + 2e^-$
If the solution is dilute, O_2 is also liberated $2H_2O \rightarrow O_2 + 4H^+ + e^-$
(d) Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

2. 1.095×10^5 s
3. 0.225 L H_2 and 0.1125 LO_2
4. 0.22 M
5. 99.29%
6. 3
7. 86100 C
8. 96.45 g mol^{-1}
9. 1.205×10^{23}, 19300 C, 5.36 A

SECTION II ELECTROLYTIC CONDUCTION

Introduction The flow of electric current through an electrolytic solution is known as electrolytic conduction. This conduction is due to the movement of ions in the solution. This may be compared to the metallic conduction which is due to the flow of valence electrons in metals.

Ohm's Law Both electrolytic and metallic conductions follow Ohm's law: $I = E/R$
where I is the current (unit: ampere), E is the electric potential difference (unit: volt) across the two electrodes and R is the resistance (unit: ohm) offered by the metallic wire or the electrolytic solution between the two electrodes of a conductivity cell dipped in the solution.

The resistance offered by an electrolytic solution decreases while that of a metallic wire increases with increase in temperature.

Resistance and Conductance of a Solution The resistance (R) offered by an electrolytic solution enclosed within the two electrodes is directly proportional to distance (l) between the electrodes and inversely to the cross-sectional area (A) of the electrodes, i.e. $R \propto l$ and $R \propto 1/A$
Taking together, we have $R \propto l/A$ or $R = \rho\,(l/A)$

where ρ is known as *resistivity* (unit: Ω m). The reciprocal of resistance is known as conductance (symbol: G) and that of resistivity is known as conductivity (unit: $\Omega^{-1}\,m^{-1}$ or S Ω^{-1}, where S = Ω^{-1} and is known as siemen).

The quantity l/A is known as cell constant (symbol: K). Hence $R = \rho K$ and $\rho = K/R$

Equivalent and Molar Conductivities The equivalent conductivity of a solution gives the conducting power of the ions produced by 1 equivalent mass (i.e. the mass corresponding to one mole of unit charge on each type of ion) of an electrolyte at any particular concentration. it is defined as follows.

The equivalent conductivity of an electrolyte may be defined as the conductance of a volume of solution containing one equivalent mass of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution.
Mathematically, we have

$$G = \frac{1}{R} = \frac{1}{\rho}\frac{A}{l} = \kappa\frac{A}{l}$$

where l is the distance between the two electrodes and A is the area of electrodes covered by the solution containing one equivalent mass of the substance. Multiplying and dividing by the distance l, we get

$$G = \kappa\frac{A_{\text{eq}} \times l}{l^2} = \kappa\frac{V_{\text{eq}}}{l^2}$$

By definition, $\Lambda_{\text{eq}} = Gl^2/\text{eq} = \kappa V_{\text{eq}}$. If l = unit length, then $\Lambda_{\text{eq}}/\text{m}^2\ \text{eq}^{-1} = G$.

Unit of Equivalent Conductivity We have

$$\Lambda_{\text{eq}} = \kappa V_{\text{eq}}$$

Unit of Λ_{eq} = (unit of κ) (unit of V containing one quivalent of electrolyte)

$$= (\Omega^{-1}\ \text{m}^{-1})\ (\text{m}^3\ \text{eq}^{-1}) = \Omega^{-1}\ \text{m}^2\ \text{eq}^{-1}$$

Alternative Defining Expression of Equivalent Conductivity If c is the concentration of the solution in equivalent per unit volume, then one equivalent mass of the electrolyte will be contained in the volume $1/c$. Hence

$$\Lambda_{\text{eq}} = \kappa V_{\text{eq}} = \kappa/c$$

The molar conductivity of a solution gives the conducting power of ions produced by one molar mass of an electrolyte at any particular concentration. It is defined as

$$\Lambda_{\text{m}} = \kappa/c \qquad ;\ (c \text{ is the molar concentration})$$

The unit of molar conductivity is $\Omega^{-1}\ \text{m}^2\ \text{mol}^{-1}$.

If $\nu_+ z_+$ (or $\nu_- |z_-|$) is the total charge number of the cations (or anions) of a single molecule of an electrolyte, then

$$1 \text{ mole} = (\nu_+ z_+)\ (1 \text{ equivalent})$$

It follows that $$\Lambda_{\text{eq}} = \frac{\kappa}{c_{\text{eq}}} = \frac{\kappa}{(\nu_+ z_+\ \text{eq}\,\text{mol}^{-1})c}\ ; = \frac{\Lambda_{\text{m}}}{(\nu_+ z_+\ \text{eq}\,\text{mol}^{-1})} \qquad (c \text{ is the molar concentration})$$

Variation of Molar Conductivity with Concentration Both the conductivity and molar conductivity of a solution vary with concentration. The conductivity increases with increase in concentration, whereas the molar conductivity increases on dilution, i.e. decrease in concentration.

The conductivity of solution increases with increase in concentration because more ions are available for conduction.

The molar conductivity of a solution gives the conducting ability of all the ions produced by 1 mol of an electrolyte at any particular concentration. The increase in molar conductivity of a strong electrolyte on dilution is due to the increase in the number of ions caused by weakening of ion-ion interactions. The variation in molar conductivity for a strong electrolyte is almost linear in dilute solutions and is given by the expression

$$\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\infty - b\sqrt{c}$$

where $\Lambda_\mathrm{m}^\infty$ is molar conductivity at infinite dilution and b is constant.

The increase in molar conductivity of a weak electrolyte is due to increase in the degree of dissociation on dilution which causes increase in the number of ions. This fact is known as *Ostwald dilution law*.

The degree of dissociation of a weak electrolyte in a solution of known concentration can be computed by using Arrhenius equation:

$$\Lambda = \Lambda_c / \Lambda^\infty$$

where Λ_c is the molar conductivity of the solution at the given concentration.

Kohlrausch's Law of Independent Migration of Ions The molar conductivity at infinite dilution for a strong electrolyte can be determined by extrapolating the plot of Λ_c versus $\sqrt{c}$ to a value of $\sqrt{c} = 0$. This procedure cannot be adopted for a weak electrolyte as the variation of Λ_c with dilution is not linear. However, the value of $\Lambda_\mathrm{m}^\infty$ can be determined by the application of Kohlrausch's law of independent migration of ions. This law states that at infinite dilution, where dissociation of all electrolytes is complete (including weak electrolytes since degree of dissociation approaches one as the concentration approaches zero) and where all interionic effects disappear (because of larger distance between ions), each ion migrate independent of its co-ion and contributes to the total molar conductivity of an electrolyte a definite share which depends only on its own nature and not at all on the ion with which it is associated. Thus, we can write

$$\Lambda_\mathrm{m}^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

where ν_+ and ν_- are the respective stoichiometric numbers of cation and anion in one molecule of the electrolyte.

Exceptionally High Values of λ^∞(H$^+$) and λ^∞(OH$^-$) In aqueous solutions, the molar conductivities at infinite dilution for H$^+$ and OH$^-$ are exceptionally larger than those of other ions. This was explained by von Grotthus and is known as Grotthus conduction. It was explained on the basis of transfer of a proton from one water molecule to another. The process of proton transfer results in a more rapid transfer of positive charge from one region of the solution to another, than would be possible if H_3O^+ ion has to push its way through the solution as other ions do.

Variation of $\Lambda_\mathrm{m}^\infty$ of Alkali Ions in Solution It is expected that the molar conductivity value should decrease with increase in the size of ion. However, the reverse is observed in alkali metal ions. This is due to decrease in extent of hydration of alkali metal ions with increasing size of ions. Thus, the effective size of hydrated ions in solution is $Na^+ > K^+ > Rb^+$ and hence the molar conductivities of these ions follow the trend $Rb^+ > K^+ > Na^+$

Transference Number The fraction of the total current carried by each ion in solution is known as the transference number of the ion. This may be computed by using the expression

$$t = \frac{\text{Conductivity of the ion in solution}}{\text{Total conductivity of the solution}}$$

Since $\lambda = \kappa/c$, we will have $t = \dfrac{c\,\lambda}{\Sigma_i\, c_i\, \lambda_i}$

Ionic Mobility The velocity of an ion in a solution is directly proportional to the potential gradient across the electrodes of a conductivity cell, i.e.

$$v \propto (\mathrm{d}\phi/\mathrm{d}l) \qquad \text{or} \qquad v = u\,(\mathrm{d}\phi/\mathrm{d}l)$$

where u, the proportionality constant, is known as ionic mobility. Its unit is

$$\frac{\text{unit of } v}{\text{unit of } \mathrm{d}\phi/\mathrm{d}l} = \frac{\mathrm{m\ s^{-1}}}{\mathrm{V\ m^{-1}}} = \mathrm{m^2\ V^{-1}\ s^{-1}}$$

The ionic mobility of an ion is given by the expression $u_+ = \dfrac{\lambda_m^+}{z_+ F} = \dfrac{\lambda_{\mathrm{eq}}^+}{F}$

where λ_{m}^+ is the molar conductivity, z_+ is the charge number of the ion and F is faraday constant (96500 C $\mathrm{mol^{-1}}$).

Straight Objective Type

Conductivity

1. Which of the following is **not** correct?
- (a) The metallic conduction is due to the movement of electrons in the metal.
- (b) The electrolytic conduction is due to the movement of ions in the solution.
- (c) The current carrying ions are not necessarily discharged at the electrodes.
- (d) The metallic conduction increases with increase in temperature, whereas that of electrolytic conduction decreases with temperature.

2. Which of the following is correct?
- (a) Conductivity of a solution decreases with dilution, whereas molar conductivity increases with dilution
- (b) Conductivity of a solution increases with dilution, whereas molar conductivity decreases with dilution
- (c) Both conductivity and molar conductivity decrease with dilution
- (d) Both conductivity and molar conductivity increase with dilution.

3. According to Ohm's law,

(a) $I = E/R$ (b) $I = ER$ (c) $I = R/E$ (d) $I = 1/ER$

where the various symbols have their usual meanings.

4. The unit of resistivity is

(a) Ω (b) Ω m (c) Ω/m (d) $\Omega\ \mathrm{m^2}$

5. The cell constant of a conductivity cell is defined as

(a) $K = l/A$ (b) $K = lA$ (c) $K = A/l$ (d) $K = 1/lA$

where l is the distance between two electrodes and A is the area of cross section of each of the two electrodes

6. The unit of conductance is

(a) Ω (b) Ω^{-1} (c) $\Omega^{-1}\ \mathrm{cm^{-1}}$ (d) $\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$

7. The unit of conductivity is

(a) Ω^{-1} (b) $\Omega^{-1}\ \mathrm{cm^{-1}}$ (c) $\Omega^{-1}\ \mathrm{cm^2\ eq^{-1}}$ (d) $\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$

8. A conductance cell when filled with 0.5 M KCl solution (conductivity = $6.67 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm^{-1}}$) registers a resistance of 243 Ω. Its cell constant is

(a) 1.62 cm (b) 1.62 $\mathrm{cm^{-1}}$ (c) 1.62 $\mathrm{dm^{-1}}$ (d) 1.62 $\mathrm{m^{-1}}$

Equivalent and Molar Conductivities

9. If one molecule of an electrolyte dissociates to produce ν_+ number of cations A^{z+} and ν_- number of anions B^{z-}, then the relation between molar conductivity (Λ_{m}) and equivalent conductivity (Λ_{eq}) is

(a) $\Lambda_{\mathrm{m}} = (\nu_+\ z_+)\ \Lambda_{\mathrm{eq}}$ (b) $\Lambda_{\mathrm{m}} = \Lambda_{\mathrm{eq}}/(\nu_+\ z_+)$ (c) $\Lambda_{\mathrm{m}} = \nu_+\ \Lambda_{\mathrm{eq}}/z_+$ (d) $\Lambda_{\mathrm{m}} = z_+\ \Lambda_{\mathrm{eq}}/\nu_+$

10. The unit of molar conductivity is

(a) Ω^{-1} (b) $\Omega^{-1}\ \mathrm{cm^{-1}}$ (c) $\Omega^{-1}\ \mathrm{cm^{-1}\ mol^{-1}}$ (d) $\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$

11. Molar conductivity is defined as

(a) κ/V_{m} (b) κV_{m} (c) Gl (d) κl^2

where κ is the conductivity, G is conductance, l is the distance between two electrodes of conductivity cell and V is the volume of solution containing 1 mol of electrolyte.

12. Molar conductivity is defined as

(a) Gl (b) κl (c) Gl^2/mol (d) κl^2

where κ is the conductivity, G is conductance and l is the distance between two electrodes of conductivity cell.

13. Molar conductivity is defined as

(a) κc (b) κc^2 (c) κ / c^2 (d) κ / c

where κ is the conductivity and c is the molar concentration of electrolyte.

14. For a dilute solution of a strong electrolyte, the variation of molar conductivity with concentration is given by

(a) $\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\infty + bc$ (b) $\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\infty - bc$ (c) $\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\infty + b\sqrt{c}$ (d) $\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^\infty - b\sqrt{c}$

15. Which of the following ion is expected to have highest value of molar conductivity at infinite dilution in an aqueous solution?

(a) Na^+ (b) K^+ (v) H^+ (d) $\frac{1}{2}Ca^{2+}$

16. Which of the following ion is expected have least value of molar conductivity at infinite dilution in an aqueous solution?

(a) Na^+ (b) K^+ (c) Rb^+ (d) Cs^+

17. Which of the following ion is expected to have highest value of molar conductivity at infinite dilution in an aqueous solution?

(a) F^- (b) Cl^- (c) Br^- (d) OH^-

18. The degree of dissociation of a weak electrolyte is given by

(a) $\alpha = \Lambda_c / \Lambda^\infty$ (b) $\alpha = \Lambda^\infty / \Lambda_c$ (c) $\alpha = \Lambda_c^2 / \Lambda^\infty$ (d) $\alpha = \Lambda_c\, \Lambda^\infty$

19. The equilibrium constant of acetic acid in an aqueous solution of concentration c is given by

(a) $K = \dfrac{c\Lambda_c^2}{\Lambda^\infty - \Lambda_c}$ (b) $K = \dfrac{c\Lambda_c^2}{\Lambda^\infty(\Lambda^{\infty`} - \Lambda_c)}$ (c) $K = \dfrac{c\Lambda_c^2}{\Lambda^\infty + \Lambda_c}$ (d) $K = \dfrac{c\, \Lambda_c^2}{\Lambda^\infty(\Lambda^\infty - \Lambda_c)}$

20. Equivalent conductivity of $Fe_2(SO_4)_3$ is given by

(a) $\Lambda_\mathrm{eq}^\infty = \lambda_\mathrm{eq}^\infty(\mathrm{Fe}^{3+}) + \lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$ (b) $\Lambda_\mathrm{eq}^\infty = 2\lambda_\mathrm{m}^\infty(\mathrm{Fe}^{3+}) + \lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$

(c) $\Lambda_\mathrm{eq}^\infty = \lambda_\mathrm{eq}^\infty(\mathrm{Fe}^{3+}) + 3\lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$ (d) $\Lambda_\mathrm{eq}^\infty = 2\lambda_\mathrm{eq}^\infty(\mathrm{Fe}^{3+}) + 3\lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$

21. Molar conductivity of $Fe_2(SO_4)_3$ is given by

(a) $\Lambda_\mathrm{m}^\infty = \lambda_\mathrm{eq}^\infty(\mathrm{Fe}^{3+}) + \lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$ (b) $\Lambda_\mathrm{m}^\infty = \lambda_\mathrm{m}^\infty(\mathrm{Fe}^{3+}) + \lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$

(c) $\Lambda_\mathrm{m}^\infty = \lambda_\mathrm{eq}^\infty(\mathrm{Fe}^{3+}) + 3\lambda_\mathrm{eq}^\infty(\mathrm{SO}_4^{2-})$ (d) $\Lambda_\mathrm{m}^\infty = 2\lambda_\mathrm{m}^\infty(\mathrm{Fe}^{3+}) + 3\lambda_\mathrm{m}^\infty(\mathrm{SO}_4^{2-})$

22. Which of the following expressions is correct?

(a) $\Lambda_\mathrm{m}^\infty(\mathrm{NH_4OH}) = \Lambda_\mathrm{m}^\infty(\mathrm{NH_4Cl}) + \Lambda_\mathrm{m}^\infty(\mathrm{NaOH}) - \Lambda_\mathrm{m}^\infty(\mathrm{NaCl})$

(b) $\Lambda_\mathrm{m}^\infty(\mathrm{NH_4OH}) = \Lambda_\mathrm{m}^\infty(\mathrm{NH_4Cl}) - \Lambda_\mathrm{m}^\infty(\mathrm{NaOH}) + \Lambda_\mathrm{m}^\infty(\mathrm{NaCl})$

(c) $\Lambda_\mathrm{m}^\infty(\mathrm{NH_4OH}) = \Lambda_\mathrm{m}^\infty(\mathrm{NH_4Cl}) - \Lambda_\mathrm{m}^\infty(\mathrm{NaOH}) - \Lambda_\mathrm{m}^\infty(\mathrm{NaCl})$

(d) $\Lambda_\mathrm{m}^\infty(\mathrm{NH_4OH}) = \Lambda_\mathrm{m}^\infty(\mathrm{NH_4Cl}) + \Lambda_\mathrm{m}^\infty(\mathrm{NaOH}) + \Lambda_\mathrm{m}^\infty(\mathrm{NaCl})$

23. Equivalent conductivity of $Fe_2(SO4)_3$ is related to molar conductivity by the expression

(a) $\Lambda_\mathrm{eq} = \Lambda_\mathrm{m}$ (b) $\Lambda_\mathrm{eq} = \Lambda_\mathrm{m}/3$ (c) $\Lambda_\mathrm{eq} = 3\ \Lambda_\mathrm{m}$ (d) $\Lambda_\mathrm{eq} = \Lambda_\mathrm{m}/6$

24. The equivalent conductivity of a solution containing 2.54 g of $CuSO_4$ per litre is 91.0 Ω^{-1} cm^2 eq^{-1}. Its conductivity would be

(a) $1.45 \times 10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$ (b) $2.17 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (c) $2.90 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^2$ (d) $2.9 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$

25. A conductivity cell whose cell constant is 3.0 cm^{-1} is filled with 0.1 M solution of a weak acids. Its resistance is found to be 3000 Ω. If $\Lambda_\mathrm{m}^\infty$ = 400 Ω^{-1} cm^2 mol^{-1}, the degree of dissociation of the weak acid is about

(a) 0.015 (b) 0.025 (c) 0.035 (d) 0.055

26. The molar conductivity of 0.05 M of solution of an electrolyte is 200 Ω^{-1} cm^2 mol^{-1}. The resistance offered by a conductivity cell with cell constant (1/3) cm^{-1} would be about

(a) 11.11 Ω (b) 22.22 Ω (c) 33.33 Ω (d) 44.44 Ω

27. If $\lambda_\mathrm{m}^\infty(\mathrm{K}^+)$ = 73.5 Ω^{-1} cm^2 mol^{-1}, $\lambda_\mathrm{m}^\infty(\mathrm{Al}^{3+})$ = 189 Ω^{-1} cm^2 mol^{-1} and $\lambda_\mathrm{m}^\infty(\mathrm{SO}_4^{2-})$ = 160 Ω^{-1} cm^2 mol^{-1}, the molar conductivity of potash alum will be about

(a) 1165 Ω^{-1} cm^2 mol^{-1} (b) 422.5 Ω^{-1} cm^2 mol^{-1} (c) 582.5 Ω^{-1} cm^2 mol^{-1} (d) 145.6 Ω^{-1} cm^2 mol^{-1}

28. If $\lambda^{\infty}_{\rm m}(K^+)$ = 73.5 Ω^{-1} cm^2 mol^{-1}, $\lambda^{\infty}_{\rm m}(Al^{3+})$ = 189 Ω^{-1} cm^2 mol^{-1} and $\lambda^{\infty}_{\rm m}(SO_4^{2-})$ = 160 Ω^{-1} cm^2 mol^{-1}, the equivalent conductivity of potash alum will be about

(a) 1165 Ω^{-1} cm^2 eq^{-1} (b) 582.5 Ω^{-1} cm^2 eq^{-1} (c) 291.3 Ω^{-1} cm^2 eq^{-1} (d) 145.6 Ω^{-1} cm^2 eq^{-1}

29. The conductivity of a saturated solution of a sparingly soluble salt MX_2 is found to be 4.0 × 10^{-5} Ω^{-1} cm^{-1}. If $\lambda^{\infty}_{\rm m}\left(\frac{1}{2}M^{2+}\right)$ = 50.0 Ω^{-1} cm^2 mol^{-1} and $\lambda^{\infty}_{\rm m}(X^-)$ = 50 Ω^{-1} cm^2 mol^{-1}, the solubility product of the salt is about

(a) 2 × 10^{-10} M^3 (b) 2 × 10^{-12} M (c) 32 × 10^{-12} M (d) 8 × 10^{-14} M

30. The conductivity of a saturated solution of silver oxalate is 4.5 × 10^{-5} Ω^{-1} cm^{-1}. If its $K_{\rm sp}$= 1.35 × 10^{-11} M^3, the molar conductivity of the saturated solution would be

(a) 250 Ω^{-1} cm^2 mol^{-1} (b) 300 Ω^{-1} cm^2 mol^{-1} (c) 350 Ω^{-1} cm^2 mol^{-1} (d) 400 Ω^{-1} cm^2 mol^{-1}

31. If $\Lambda^{\infty}_{\rm m}$(NaOH) = 221 Ω^{-1} cm^2 mol^{-1}, $\Lambda^{\infty}_{\rm m}$(HCl) = 403 Ω^{-1} cm^2 mol^{-1} and $\Lambda^{\infty}_{\rm m}$(NaCl) = 112 Ω^{-1} cm^2 mol^{-1}, the value of $\Lambda^{\infty}_{\rm m}(H^+, OH^-)$ would be about

(a) 70 Ω^{-1} cm^2 mol^{-1} (b) 294 Ω^{-1} cm^2 mol^{-1} (c) 736 Ω^{-1} cm^2 mol^{-1} (d) 512 Ω^{-1} cm^2 mol^{-1}

32. Which of the following solutions will show the minimum value of transference number of Cl^- ions?

(a) 0.1 M NaCl solution (b) 0.1 M KCl solution (c) 0.1 M HCl solution (d) 0.1 M $MgCl_2$ solution

33. Which of the following anions will have largest value of molar conductivity in liquor ammonia?

(a) NH_2^- (b) OH^- (c) F^- (d) CH_3COO^-

34. If $\Lambda^{\infty}_{\rm eq}$(NaCl), $\Lambda^{\infty}_{\rm eq}$(KCl) and $\Lambda^{\infty}_{\rm eq}(K_2SO_4)$ are 123.7, 147.0 and 152.1 Ω^{-1} cm^2 eq^{-1}, then the $\Lambda^{\infty}_{\rm eq}(Na_2SO_4)$ would be

(a) 128.8 Ω^{-1} cm^2 eq^{-1} (b) 257.6 Ω^{-1} cm^2 eq^{-1} (c) 105.5 Ω^{-1} cm^2 eq^{-1} (d) 118.6 Ω^{-1} cm^2 eq^{-1}

35. If Λ_c of NH_4OH is 11.5 Ω^{-1} cm^2 mol^{-1}, its degree of dissociation would be

(a) 0.157 (b) 0.058 (c) 0.0424 (d) 0.0848

(Given: $\lambda^{\infty}_{NH_4^+}$ = 73.4 Ω^{-1} cm^2 mol^{-1} and $\lambda^{\infty}_{OH^-}$ = 197.6 Ω^{-1} cm^2 mol^{-1}.)

36. Given: $\lambda^{\infty}\left(\frac{1}{3}Al^{3+}\right)$ = 63 Ω^{-1} cm^2 mol^{-1} and $\lambda^{\infty}(\frac{1}{2}SO_4^{2-})$ = 80 Ω^{-1} cm^2 mol^{-1}. The value $\Lambda^{\infty}_{\rm m}(Al_2(SO_4)_3)$ would be

(a) 143 Ω^{-1} cm^2 mol^{-1} (b) 858 Ω^{-1} cm^2 mol^{-1} (c) 206 Ω^{-1} cm^2 mol^{-1} (d) 286 Ω^{-1} cm^2 mol^{-1}

37. For a dilute solution of a strong electrolyte, which of the following facts is correct?

(a) The graph between $\Lambda_{\rm m}$ and c is linear (b) The graph between log $\Lambda_{\rm m}$ and c is linear

(c) The graph between $\Lambda_{\rm m}$ and $\sqrt{c}$ is linear (d) The graph between log $\Lambda_{\rm m}$ and log c is linear

38. Which of the following expressions is correct?

(a) $\Lambda_{\rm eq}(Al_2(SO_4)_3) = \{2\lambda_{\rm m}(Al^{3+}) + 3\lambda_{\rm m}(SO_4^{2-})\}/6$ (b) $\Lambda_{\rm eq}(Al_2(SO_4)_3) = 6\{\lambda_{\rm m}(Al^{3+}) + \lambda_{\rm m}(SO_4^{2-})\}$

(c) $\Lambda_{\rm eq}(Al_2(SO_4)_3) = \lambda_{\rm m}(Al^{3+}) + \lambda_{\rm m}(SO_4^{2-})$ (d) $\Lambda_{\rm eq}(Al_2(SO_4)_3) = 2\lambda_{\rm m}(Al^{3+}) + 3\lambda_{\rm m}(SO_4^{2-})$

39. Which of the following expressions can be used to determine conductivity at infinity dilution for oxialic acid (OxH_2)?

(a) $\Lambda^{\infty}_{\rm m}(OxH_2) = \Lambda^{\infty}_{\rm m}(Na_2Ox) + \Lambda^{\infty}_{\rm m}(H_2SO_4) + \Lambda^{\infty}_{\rm m}(Na_2SO_4)$

(b) $\Lambda^{\infty}_{\rm m}(OxH_2) = \Lambda^{\infty}_{\rm m}(Na_2Ox) + \Lambda^{\infty}_{\rm m}(H_2SO_4) - \Lambda^{\infty}_{\rm m}(Na_2SO_4)$

(c) $\Lambda^{\infty}_{\rm m}(OxH_2) = \Lambda^{\infty}_{\rm m}(Na_2Ox) - \Lambda^{\infty}_{\rm m}(H_2SO_4) - \Lambda^{\infty}_{\rm m}(Na_2SO_4)$

(d) $\Lambda^{\infty}_{\rm m}(OxH_2) = \Lambda^{\infty}_{\rm m}(Na_2Ox) - \Lambda^{\infty}_{\rm m}(H_2SO_4) + \Lambda^{\infty}_{\rm m}(Na_2SO_4)$

40. The correct order of equivalent conductivity at infinite dilution of LiCl, NaCl and KCl is

(a) LiCl > NaCl > KCl (b) LiCl > KCl > NaCl (c) KCl > NaCl > LiCl (d) NaCl > KCl > LiCl

41. Which of the following facts is correct when a solution of an electrolyte is diluted?

(a) Conductivity increases, molar conductivity increases

(b) Conductivity increases, molar conductivity decreases

(c) Conductivity decreases, molar conductivity increases

(d) Conductivity decreases, molar conductivity decreases

42. The conductivity of a saturated solution of CaF_2 is found to be 4.0 × 10^{-5} S cm^{-1}. If $\lambda^{\infty}_{\rm m}$ = 104.0 S cm^2 mol^{-1} and $\lambda^{\infty}_{\rm m}(F^-)$ = 48.0 S cm^2 mol^{-1}, the solubility product of CaF_2 will be

(a) 3.2 × 10^{-10} M^3 (b) 3.2 × 10^{-11} M^3 (c) 3.2 × 10^{-12} M^3 (d) 3.2 × 10^{-13} M^3

43. The molar conductivity of a weak electrolyte HA at infinite dilution can be determined by
(a) extrapolating Λ_m versus c plot to $c \rightarrow 0$.
(b) extrapolating Λ_m versus $\sqrt{c}$ plot to $c \rightarrow \infty$.
(c) using Kohlrausch law with the data on Λ_m^∞(HCl), Λ_m^∞(NaA) and Λ_m^∞(NaCl)
(d) Using Kohlrausch law with the data on Λ_m^∞(HA) and Λ_m^∞(NaA)

44. The conductivity of a saturated solution is 1.65×10^{-6} S cm^{-1}. If Λ_m^∞ (Co^{2+}) = 86 S cm^2 mol^{-1} and Λ_m^∞ ($Fe(CN)_6^{3-}$) = 444 S cm^2 mol^{-1}, the solubility of $Co_2[Fe(CN)_6]$ in water will be
(a) 2.7×10^{-4} mol dm^{-3} (b) 2.7×10^{-5} mol dm^{-3} (c) 2.7×10^{-6} mol dm^{-3} (d) 2.7×10^{-7} mol dm^{-3}

45. The conductivity of water at 298 K is 0.55×10^{-7} S cm^{-1}. If $\lambda_m(H^+)$ = 350 S cm^2 mol^{-1} and $\lambda(OH^-)$ = 200 S cm^2 mol^{-1}, the degree of dissociation of water will be
(a) 1.82×10^{-6} (b) 1.82×10^{-7} (c) 1.82×10^{-8} (d) 1.82×10^{-9}

46. If λ_m (Na^+) = 50 S m^2 mol^{-1} and λ_m (SO_4^{2-}) = 160 S cm^2 mol^{-1}, then the transference number of Na^+ in 0.1 M Na_2SO_4 will be
(a) 5/21 (b) 10/26 (c) 5/8 (d) 2.5/16

47. If $\lambda_m(M^+)$ = 48 S cm^2 mol^{-1}, the ionic mobility of NH_4^+ ion will be
(a) 4.97×10^{-2} cm^2 V^{-1} s^{-1} (b) 4.8×10^{-3} cm^2 V^{-1} s^{-1}
(c) 4.97×10^{-4} cm^2 V^{-1} s^{-1} (d) 4.8×10^{-6} cm^2 V^{-1} s^{-1}

Linked Comprehension Type

1. Given are the following ionic molar conductivities.

$\lambda_m^\infty(Na^+)$ = 50.1 S cm^2 mol^{-1} and $\lambda_m^\infty\left(\frac{1}{2}\text{ Oxalate }^{2-}\right)$ = 74.1 S cm^2 mol^{-1}

Based on this information, answer the following three questions or for 0.1 M sodium oxalate.
(i) The molar ionic conductivity at infinite dilution for Na_2OX is
(a) 124.1 S cm^2 mol^{-1} (b) 174.3 S cm^2 mol^{-1} (c) 248.4 S cm^2 mol^{-1} (d) 62.1 S cm^2 mol^{-1}
(ii) The conductivity of 0.1 M solution of Na_2 OX is
(a) 0.0124 S cm^{-1} (b) 0.0174 S cm^{-1} (c) 0.0248 S cm^{-1} (d) 6.21 S cm^2 mol^{-1}
(iii) The transference number of Na^+ ion in 0.1 M Na_2SO_4 solution is
(a) 0.7 (b) 0.6 (c) 0.5 (d) 0.4

2. Given are the following data.
Conductivity of a saturated solution of silver oxalate = 3.8×10^{-5} S cm^{-1}
K_{sp}° (silver oxalate) = 1.1×10^{-11} and $\lambda_m^\infty(Ag^+)$ = 62 S cm^2 mol^{-1}
Based on this information, answer the following three questions
(i) The solubility of silver oxalate in water is
(a) 3.31×10^{-6} M (b) 2.52×10^{-3} M (c) 1.4×10^{-4} M (d) 4.44×10^{-4} M
(ii) Molar conductivity at infinite dilution for silver oxalate is
(a) 284.6 S cm^2 mol^{-1} (b) 310.2 S cm^2 mol^{-1} (c) 271.4 S cm^2 mol^{-1} (d) 185.6 S cm^2 mol^{-1}
(iii) Equivalent conductivity of oxalate ion at infinite dilution is
(a) 160 S cm^2 mol^{-1} v(b) 92.5 S cm^2 mol^{-1} (c) 60 S cm^2 mol^{-1} (d) 73.2 S cm^2 mol^{-1}

ANSWERS

Straight Objective Type

1. (d) **2.** (a) **3.** (a) **4.** (b) **5.** (a) **6.** (b) **7.** (b)
8. (b) **9.** (a) **10.** (d) **11.** (b) **12.** (c) **13.** (d) **14.** (d)
15. (c) **16.** (a) **17.** (d) **18.** (a) **19.** (b) **20.** (a) **21.** (d)
22. (a) **23.** (d) **24.** (d) **25.** (b) **26.** (c) **27.** (a) **28.** (d)
29. (c) **30.** (b) **31.** (d) **32.** (c) **33.** (a) **34.** (a) **35.** (c)
36. (b) **37.** (c) **38.** (a) **39.** (b) **40.** (c) **41.** (c) **42.** (b)
43. (c) **44.** (c) **45.** (d) **46.** (b) **47.** (c)

Linked Comprehension Type

1. **(i)** (c) **(ii)** (c) **(iii)** (d)
2. **(i)** (c) **(ii)** (c) **(iii)** (d)

Hints and Solutions

Straight Objective Type

1. The metallic conduction decreases with increase in temperature while that of electrolytic conduction increases.

2. Conductivity of a solution decreases with dilution due to decrease in concentration of the electrolyte. On the other hand, molar conductivity increases due to (i) the more dissociation of a weak electrolyte, and (ii) decrease the interactions between ions of a strong electrolyte.

3. According to Ohm's law, $I = E/R$

4. The unit of resistivity is Ω m.

5. The cell constant of a conductivity cell is defined as $K = l/A$, where l is the distance between the electrodes and A is their area of cross-section.

8. $K = \kappa R = (6.67 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1})\ (243\ \Omega) = 1.62\ \text{cm}^{-1}$

Amount of electricity passed = (108 g)/(108 g mol^{-1}) = 0.01

Mass of copper deposited = (63.5 g mol^{-1}/2) (0.01 mol) = 0.3175 g

The sizes of hydrated ions in solution follow the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The equivalent conductivity of these ions follow the reverse order.

9. The relation connecting molar and equivalent conductivities is $\Lambda_\text{m} = (\nu_+ z_+)\ \Lambda_\text{eq}$

10. The unit of molar conductivity is $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

11. Molar conductivity is defined as $\Lambda_\text{m} = \kappa V_\text{m}$

12. Molar conductivity is defined as $\Lambda_\text{m} = Gl^2/\text{mol}$

13. Molar conductivity is defined as $\Lambda_\text{m} = \kappa/c$

14. For a dilute solution, the variation of molar conductivity with concentration is given by $\Lambda_\text{m} = \Lambda_\text{m}^\infty - b\sqrt{c}$

15. H^+ ions will have the maximum molar conductivity amongst the given cations.

16. Na^+ ions will have least value of molar conductivity due to extensive hydration of ions.

17. OH^- ions will have highest molar conductivity amongst the given anions.

18. The degree of dissociation of a weak electrolyte is given by $\alpha = \Lambda_c/\Lambda^\infty$.

19. We have

$$\underset{c(1-\alpha)}{\text{CH}_3\text{COOH}} \rightleftharpoons \underset{c\alpha}{\text{CH}_3\text{COO}^-} + \underset{c\alpha}{\text{H}^+} \qquad K = \frac{[\text{CH}_3\text{COO}][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha^2}{(1-\alpha)}$$

Since $\alpha = \Lambda_c/\Lambda^\infty$, we get $K = \dfrac{c(\Lambda_c/\Lambda^\infty)^2}{1-(\Lambda_c/\Lambda_\infty)} = \dfrac{c\Lambda_c^2}{\Lambda^\infty(\Lambda^\infty - \Lambda_c)}$

20. Equivalent conductivity of $\text{Fe}_2(\text{SO}_4)_3$ is given by $\Lambda_\text{eq}^\infty = \lambda_\text{eq}^\infty(\text{Fe}^{3+}) + \lambda_\text{eq}^\infty(\text{SO}_4^{2-})$

21. Molar conductivity of $\text{Fe}_2(\text{SO}_4)_3$ is given by $\Lambda_\text{m}^\infty = 2\,\lambda_\text{m}^\infty(\text{Fe}^{3+}) + 3\,\lambda_\text{m}^\infty(\text{SO}_4^{2-})$

22.
$$\begin{aligned}\Lambda_\text{m}^\infty(\text{NH}_4\text{OH}) &= \lambda_\text{m}^\infty(\text{NH}_4^+) + \lambda_\text{m}^\infty(\text{OH}^-)\\ &= \lambda_\text{m}^\infty(\text{NH}_4^+) + \lambda_\text{m}^\infty(\text{Cl}^-) + \lambda_\text{m}^\infty(\text{Na}^+) + \lambda_\text{m}^\infty(\text{OH}^-) - \lambda_\text{m}^\infty(\text{Na}^+) - \lambda_\text{m}^\infty(\text{Cl}^-)\\ &= \Lambda_\text{m}^\infty(\text{NH}_4\text{Cl}) + \Lambda_\text{m}^\infty(\text{NaOH}) - \Lambda_\text{m}^\infty(\text{NaCl})\end{aligned}$$

23. Since total charge of cations is 6+ in $\text{Fe}_2(\text{SO}_4)_3$, we have $\Lambda_\text{eq}(\text{Fe}_2(\text{SO}_4)_3) = (1/6)\ \Lambda_\text{m}(\text{Fe}_2(\text{SO}_4)_3)$

24. $\kappa = \Lambda_\text{eq} c = (91.0\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}) \left[\dfrac{2.54}{(159/2)\times 1000}\ \text{eq cm}^{-3}\right] = 2.9 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$

25. We have

$$\kappa = \frac{K}{R} = \frac{3.0\ \text{cm}^{-1}}{3000\ \Omega} = 0.001\ \text{S cm}^{-1} \quad \text{and} \quad \Lambda_\text{m} = \frac{\kappa}{c} = \frac{0.001\ \text{S cm}^{-1}}{0.1 \times 10^{-3}\ \text{mol cm}^{-3}} = 10\ \text{S cm}^2\ \text{mol}^{-1}$$

Degree of dissociation, $\alpha = \dfrac{\Lambda_\text{m}}{\Lambda_\text{m}^\infty} = \dfrac{10}{400} = 0.025$

26. $\kappa = \Lambda c = (200\ \text{S cm}^2\ \text{mol}^{-1})\ (0.05 \times 10^{-3}\ \text{mol cm}^{-1}) = 0.01\ \text{S cm}^{-1}$

$$R = \frac{1}{\kappa}\left(\frac{l}{A}\right) = \frac{1}{(0.01\ \text{S cm}^{-1})}\left(\frac{1}{3}\ \text{cm}^{-1}\right) = 33.33\ \Omega$$

27. $\Lambda_\text{m}^\infty(\text{potash alum}) = 2\Lambda_\text{m}^\infty(\text{K}^+) + 2\Lambda_\text{m}^\infty(\text{Al}^{3+}) + 4\Lambda_\text{m}^\infty(\text{SO}_4^{2-})$

$= (2 \times 73.5 + 2 \times 189 + 4 \times 160)\ \text{S cm}^2\ \text{mol}^{-1} = 1165\ \text{S cm}^2\ \text{mol}^{-1}$

28. From Q.27, $\Lambda_\text{m}^\infty = 1165\ \text{S cm}^2\ \text{mol}^{-1}$

$$\Lambda_\text{eq}^\infty = \frac{\Lambda_\text{m}^\infty}{8\ \text{eq mol}^{-1}} = \frac{1165\ \text{S cm}^2\ \text{mol}^{-1}}{8\ \text{eq mol}^{-1}} = 145.6\ \text{S cm}^2\ \text{eq}^{-1}$$

29. $\Lambda_\text{m}^\infty(\text{MX}_2) = \Lambda_\text{m}^\infty(\text{M}^{2+}) + 2\Lambda_\text{m}^\infty(\text{X}^-) = 2\Lambda_\text{m}^\infty(\tfrac{1}{2}\ \text{Ca}^{2+}) + 2\Lambda_\text{m}^\infty(\text{X}^-)$

$= (2 \times 50 + 2 \times 50)\ \text{S cm}^2\ \text{mol}^{-1} = 200\ \text{S cm}^2\ \text{mol}^{-1}$

$$c = \frac{\kappa}{\Lambda_\text{m}^\infty} = \frac{4.0 \times 10^{-5}\ \text{S cm}^{-1}}{200\ \text{S cm}^2\ \text{mol}^{-1}} = 2 \times 10^{-7}\ \text{mol cm}^{-3} = 2 \times 10^{-4}\ \text{mol dm}^{-3}$$

$K_\text{sp} = [\text{M}^{2+}]\ \{2\ [\text{X}^-]\}^2 = (2 \times 10^{-4}\ \text{mol dm}^{-3})\ (4 \times 10^{-4}\ \text{mol dm}^{-3})^2 = 32 \times 10^{-12}\ \text{M}^3$

30. $\text{Ag}_2\text{C}_2\text{O}_4 \rightleftharpoons \underset{2s}{2\text{Ag}^+} + \underset{s}{\text{C}_2\text{O}_4^{2-}}\ ;\ K_\text{sp} = [\text{Ag}^+]^2\ [\text{C}_2\text{O}_4^{2-}] = 4s^3$

$$s = \left(\frac{K_\text{sp}}{4}\right)^{1/3} = \left(\frac{1.35 \times 10^{-11}\ \text{M}^3}{4}\right)^{1/3} = 1.5 \times 10^{-4}\ \text{M};\quad \Lambda_\text{m} = \frac{\kappa}{s} = \frac{4.5 \times 10^{-5}\ \text{S cm}^{-1}}{1.5 \times 10^{-7}\ \text{mol cm}^3} = 300\ \text{S cm}^2\ \text{mol}^{-1}$$

31. $\Lambda_\text{m}^\infty(\text{H}^+, \text{OH}^-) = \Lambda_\text{m}^\infty(\text{NaOH}) + \Lambda_\text{m}^\infty(\text{HCl}) - \Lambda_\text{m}^\infty(\text{NaCl}) = (221 + 403 - 112)\ \text{S cm}^2\ \text{mol}^{-1} = 512\ \text{S cm}^2\ \text{mol}^{-1}$

32. t_{H^+} has a maximum value as compared to the transference number of other cations. Hence, t_{Cl^-} will be minimum in 0.1 M HCl solution.

34. $\Lambda_\text{eq}^\infty(\text{Na}_2\text{SO}_4) = \Lambda_\text{eq}^\infty(\text{NaCl}) + \Lambda_\text{eq}^\infty(\text{K}_2\text{SO}_4) - \Lambda_\text{eq}^\infty(\text{KCl}) = (123.7 + 152.1 - 147.0)\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

$= 128.8\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

35. $\alpha = \dfrac{\Lambda}{\Lambda^\infty} = \dfrac{11.5}{(73.4 + 197.6)} = \dfrac{11.5}{271.0} = 0.0424$

36. $\Lambda^\infty(\text{Al}^{3+}) = 3\Lambda^\infty\left(\tfrac{1}{3}\ \text{Al}^{3+}\right) = 3 \times 63\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 189\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

$\Lambda^\infty(\text{SO}_4^{2-}) = 2\Lambda^\infty\left(\tfrac{1}{2}\ \text{SO}_4^{2-}\right) = 2 \times 80\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 160\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

$\Lambda^\infty(\text{Al}_2(\text{SO}_4)_3) = 2\ \Lambda^\infty(\text{Al}^{3+}) + 3\ \Lambda^\infty(\text{SO}_4^{2-}) = (2 \times 189 + 3 \times 160)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 858\ \Omega\ \text{cm}^2\ \text{mol}^{-1}$

37. For a dilute solution of a strong electrolyte, the molar conductivity varies as $\Lambda_\text{m} = \Lambda_\text{m}^\infty - \text{b}\sqrt{c}$.

38. $\Lambda_\text{eq}(\text{Al}_2(\text{SO}_4)_3) = \dfrac{1}{6}\ \Lambda_\text{m}(\text{Al}_2(\text{SO}_4)_3) = \dfrac{1}{6}\ [2\lambda_\text{m}(\text{Al}^{3+}) + 3\lambda_\text{m}(\text{SO}_4{}^{2-})]$

39. $\Lambda_\text{m}^\infty(\text{OxH}_2) = \Lambda_\text{m}^\infty(\text{Na}_2\text{Ox}) + \Lambda_\text{m}^\infty(\text{H}_2\text{SO}_4) - \Lambda_\text{m}^\infty(\text{Na}_2\text{SO}_4)$

$= [2\lambda_\text{m}^\infty(\text{Na}^+) + \lambda_\text{m}^\infty(\text{Ox}^{2-})] + [2\lambda_\text{m}^\infty(\text{H}^+) + \lambda_\text{m}^\infty(\text{SO}_4{}^{2-}) - [2\lambda_\text{m}^\infty(\text{Na}^+) + 2\ \lambda_\text{m}^\infty(\text{SO}_4^{2-})$

40. The sizes of hydrated ions in solution follow the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The equivalent conductivity of these ions follow the reverse order.

42. $c = \dfrac{\kappa}{\Lambda_\text{m}} = \dfrac{4.0 \times 10^{-5}\ \text{S cm}^{-1}}{(104 + 2 \times 48)\ \text{S cm}^{-1}\ \text{mol}^{-1}} = 2.0 \times 10^{-7}\ \text{mol cm}^{-3} = 2.0 \times 10^{-4}\ \text{mol dm}^{-3}$

$K_\text{sp} = [\text{Ca}^{2+}]\ [\text{F}^-]^2 = (2.0 \times 10^{-4}\ \text{M})\ (4.0 \times 10^{-4}\ \text{M})^2 = 3.2 \times 10^{-11}\ \text{M}^3$

44. $\Lambda_{\mathrm{m}}^{\infty} = 2\ \lambda_{\mathrm{m}}^{\infty}(\mathrm{Co}^{2+}) + \lambda_{\mathrm{m}}^{\infty}(\mathrm{Fe(CN)_6}^{4-}) = 2\ (86 + 444)\ \mathrm{S\ cm^2\ mol^{-1}} = 616\ \mathrm{S\ cm^2\ mol^{-1}}$

$$c = \frac{\kappa}{\Lambda_{\mathrm{m}}^{\infty}} = \frac{\left(1.65 \times 10^{-6}\mathrm{S\ cm^{-1}}\right)}{\left(616\,\mathrm{S\,cm^2\ \ mol^{-1}}\right)} = 2.7 \times 10^{-9}\ \mathrm{mol\ cm^{-3}} = 2.7 \times 10^{-6}\ \mathrm{mol\ dm^3}$$

45. $\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$

$c(1 - \alpha)\quad c\alpha \qquad c\alpha$

$$\kappa = [\mathrm{H^+}]\ \lambda_{\mathrm{m}}(\mathrm{H^+}) + [\mathrm{OH^-}]\ \lambda_{\mathrm{m}}(\mathrm{OH^-}) = c\alpha\ [\lambda_{\mathrm{m}}(\mathrm{H}) + \lambda_{\mathrm{m}}(\mathrm{OH^-})]$$

$$= \left[\frac{(1000/18)\,\mathrm{mol}}{1\,\mathrm{dm^3}}\right]\ \alpha\ [(350 + 200)\ \mathrm{S\ cm^2\ mol^{-1}}]$$

$$\alpha = \frac{0.55 \times 10^{-7}\ \mathrm{S\,cm^{-1}}}{\left(55.56\,\mathrm{mol\,dm^{-3}}\right)\left(550\,\mathrm{S\,cm^2 mol^{-3}}\right)} = 1.80 \times 10^{-9}$$

46. Concentration of $\mathrm{Na^+}$ ions in solution = 2 × 0.1 M
Concentration of $\mathrm{SO_4^{2-}}$ ions in solution = 0.1 M

$$t_+ = \frac{c_+\,\lambda_+}{c_+\,\lambda_+ + c_-\,\lambda_-} = \frac{(0.2\,\mathrm{M})\,(50\,\mathrm{S\,cm^2\ mol^{-1}})}{(0.2\,\mathrm{M})\left(50\,\mathrm{S\,cm^2\ mol^{-1}}\right) + (0.1\,\mathrm{M})\,(160\,\mathrm{S\,cm^2\ mol^{-1}})} = \frac{0.2 \times 50}{0.2 \times 50 + 0.1 \times 160} = \frac{10}{26}$$

47. Ionic mobility $= \dfrac{\lambda_+}{F} = \dfrac{48.0\,\mathrm{S\,cm^2\ mol^{-1}}}{96500\,\mathrm{C\,mol^{-1}}} = 4.97 \times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$

Linked Comprehension Type

1. (i) $\Lambda_{\mathrm{m}}^{\infty}(\mathrm{Na_2OX}) = 2\ \lambda_{\mathrm{m}}^{\infty}(\mathrm{Na^+}) + \lambda_{\mathrm{m}}(\mathrm{Ox^{2-}}) = 2\ \lambda_{\mathrm{m}}^{\infty}(\mathrm{Na^+}) + 2\ \lambda_{\mathrm{m}}(\tfrac{1}{2}\,\mathrm{Ox^{2-}})$

$= 2\ (50.1 + 74.1)\ \mathrm{S\ cm^2\ mol^{-1}} = 248.4\ \mathrm{S\ cm^2\ mol^{-1}}$

(ii) $\kappa = \Lambda_{\mathrm{m}}^{\infty}c = (248.4\ \mathrm{S\ cm^2\ mol^{-1}})\ (0.1\ \mathrm{mol\ dm^{-3}}) = (248.4\ \mathrm{S\ cm^2\ mol^{-1}})\ (10^{-4}\ \mathrm{mol\ cm^{-3}}) = 0.02485\ \mathrm{cm^{-1}}$

(iii) $t_+ = \dfrac{c_+\,\lambda_+^{\infty}}{c_+\,\lambda_+^{\infty} + c_-\,\lambda_-^{\infty}} = \dfrac{(0.2\,\mathrm{M})(50.1\,\mathrm{S\,cm^2\ mol^{-1}})}{(0.2\mathrm{M})(50.1\,\mathrm{S\,cm^2\ mol^{-1}}) + (0.1\,\mathrm{M})(142.2\,\mathrm{S\,cm^2\ mol^{-1}})} = \dfrac{50.1}{50.1 + 74.1} = 0.4$

2. (i) $\mathrm{Ag_2Ox} \rightleftharpoons \underset{(2s)}{2\mathrm{Ag^+}} + \underset{s}{\mathrm{Ox^{2-}}}$; $K_{\mathrm{sp}} = [\mathrm{Ag^+}]^2\ [\mathrm{Ox^{2-}}] = 4s^3$

$$s = \left(\frac{K_{\mathrm{sp}}}{4}\right)^{1/3} = \left(\frac{1.1 \times 10^{-11}\mathrm{M^3}}{4}\right)^{1/3} = 1.4 \times 10^{-4}\ \mathrm{M}$$

(ii) $\Lambda_{\mathrm{m}}^{\infty}\ (\mathrm{Ag_2Ox}) = \dfrac{\kappa}{c} = \dfrac{3.8 \times 10^{-5}\,\mathrm{S\,cm^{-1}}}{2.2 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}} = \dfrac{3.8 \times 10^{-5}\ \mathrm{S\,cm^{-1}}}{1.4 \times 10^{-7}\ \mathrm{mol\ \ cm^{-3}}} = 271.4\ \mathrm{S\ cm^2\ mol^{-1}}$

$$\lambda_{\mathrm{Ox^{2-}}}^{\infty} = \Lambda_{\mathrm{m}}^{\infty}\ (\mathrm{Ag_2Ox}) - 2\ \lambda_{\mathrm{Ag+}}^{\infty} = (271.4 - 2 \times 62.5)\ \mathrm{S\ cm^2\ mol^{-1}} = 146.4\ \mathrm{S\ cm^2\ mol^{-1}}$$

(iii) $\lambda_{\mathrm{eq}}^{\infty}(\mathrm{Ox^{2-}}) = (146.4/2)\ \mathrm{S\ cm^2\ mol^{-1}} = 73.2\ \mathrm{S\ cm^2\ mol^{-1}}$

ANNEXURE II

Subjective Problems for Practice

SOLVED PROBLEMS

1. A conductivity cell whose cell constant is 2.0 $\mathrm{cm^{-1}}$ is filled with 0.1 M acetic acid solution. Its resistance is found to be 3765 Ω. Calculate the degree of dissociation and equilibrium constant of acetic acid. Given: $\lambda_{\mathrm{m}}^{\infty}(\mathrm{H}) = 349.8\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ and $\lambda_{\mathrm{m}}^{\infty}(\mathrm{Ac^-}) = 40.9\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$.

Solution Conductivity of acetic acid solution is $\kappa = \dfrac{K}{R} = \dfrac{2.0\ \text{cm}^{-1}}{3765\ \Omega} = 5.3\times10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$

Molar conductivity of 0.1 M acetic acid solution is

$$\Lambda_\text{m} = \frac{\kappa}{c} = \frac{5.3\times10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}}{0.1\ \text{mol dm}^{-3}} = 5.3\times10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}\text{dm}^3\ \text{mol}^{-1} = 5.3\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Degree of dissociation of 0.1 M acetic acid is $\alpha = \dfrac{\Lambda_\text{m}}{\lambda_\text{m}(\text{H}^+) + \lambda_\text{m}^\infty(\text{Ac}^-)} = \dfrac{5.3}{(349.8+40.9)} = 0.0136$

The equilibrium constant of

$$\underset{c(1-\alpha)}{\text{CH}_3\text{COOH}} \rightleftharpoons \underset{c\alpha}{\text{CH}_3\text{COO}^-} + \underset{c\alpha}{\text{H}^+}$$

is

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \cong c\alpha^2$$

Substituting the values, we get $K = (0.1\ \text{M})\ (0.0136)^2 = 1.84\times10^{-5}\ \text{M}$

2. The molar conductivity of 0.05 M solution of MgCl_2 is 194.2 $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ at 25 °C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.05 M MgCl_2 solution. How much current will flow when the potential difference between the two electrodes is 2.00 V?

Solution Conductivity of 0.05 M solution is

$$\kappa = \Lambda c = (194.2\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1})\ (0.05\ \text{mol dm}^{-3}) = 9.71\ \Omega^{-1}\ (\text{cm}^2\ \text{dm}^{-3}) = 9.71\times10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$$

Conductance of 0.05 M solution is $G = \kappa\left(\dfrac{A}{l}\right) = \left(9.71\times10^{-3}\,\Omega^{-1}\text{cm}^{-1}\right)\left(\dfrac{1.50\ \text{cm}^2}{0.50\ \text{cm}}\right) = 2.91\times10^{-2}\ \Omega^{-1}$

Resistance offered by the solution is $R = \dfrac{1}{G} = \dfrac{1}{2.91\times10^{-2}\,\Omega^{-1}} = 34.34\ \Omega$

Current flowing through the electrodes is $I = \dfrac{E}{R} = \dfrac{2.00\ \text{V}}{34.34\ \Omega} = 0.058\ \text{A}$

3. The conductivity of 0.1 M NaOH solution is 0.0221 $\Omega^{-1}\ \text{cm}^{-1}$. When an equal volume of 0.1 M HCl solution is added, the conductivity decreases to 0.0056 $\Omega^{-1}\ \text{cm}^{-1}$. A further addition of HCl solution, the volume of which is equal to that of the first portion added, the conductivity increases to 0.017 $\Omega^{-1}\ \text{cm}^{-1}$. Calculate (a) Λ_m(NaOH), (b) Λ_m(NaCl), (c) Λ_m(HCl), and $\Lambda_\text{m}(\text{H}^+, \text{OH}^-)$.

Solution Molar conductivity of 0.1 M NaOH is

$$\Lambda_\text{m}(\text{NaOH}) = \frac{\kappa}{c} = \frac{0.0221\,\Omega^{-1}\text{cm}^{-1}}{0.1\ \text{mol dm}^{-3}} = 0.221\,\Omega^{-1}(\text{cm}^{-1}\text{dm}^3)\ \text{mol}^{-1} = 221\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

On adding equal volume of 0.1 M HCl solution, the total volume becomes double and the concentration of the salt formed will be 0.05 M. Hence, molar conductivity of 0.05 M NaCl solution is

$$\Lambda_\text{m}(\text{NaCl}) = \frac{\kappa}{c} = \frac{0.0056\ \Omega^{-1}\ \text{cm}^{-1}}{0.05\ \text{mol dm}^{-3}} = 0.112\,\Omega^{-1}(\text{cm}^{-1}\text{dm}^3)\ \text{mol}^{-1} = 112\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

On further addition of equal volume of the acid, the solution will become 0.033 M in NaCl and 0.033 M in HCl. The conductivity of this solution will be given by the expression

$$\kappa = c(\text{NaCl})\ \Lambda_\text{m}(\text{NaCl}) + c(\text{HCl})\ \Lambda_\text{m}(\text{HCl})$$

From this expression, we get

$$0.017\ \Omega^{-1}\ \text{cm}^{-1} = (0.033 \times 10^{-3}\ \text{mol cm}^{-3})\ (112\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}) + (0.033 \times 10^{-3}\ \text{mol cm}^{-3})\ \Lambda_\text{m}(\text{HCl})$$

This gives $\Lambda_\text{m}(\text{HCl}) = 403.15\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

Molar conductivity $\Lambda_\text{m}(\text{H}^+, \text{OH}^-)$ will be given by the expression

$$\Lambda_\text{m}(\text{H}^+, \text{OH}^-) = \Lambda_\text{m}(\text{NaOH}) + \Lambda_\text{m}(\text{HCl}) - \Lambda_\text{m}(\text{NaCl})$$

$$= (221 + 403.15 - 112)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 512.15\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

4. Calculate the molar and equivalent conductivities at infinite dilution of potash alum. Given: $\Lambda_\text{m}(\text{K}^+) = 73.5\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$, $\Lambda_\text{m}(\text{Al}^{3+}) = 189\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ and $\Lambda_\text{m}(\text{SO}_4^{2-}) = 160\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

Solution The formula of potash alum is $\text{K}_2\text{SO}_4{\cdot}\text{Al}_2\,(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. Thus, at infinite dilution of 1 mol of potash alum will produce 2 mol of K^+, 2 mol of Al^{3+} and 4 mol of SO_4^{2-}. Hence,

$$\Lambda_\text{m}^\infty(\text{potash alum}) = 2\ \lambda_\text{m}^\infty(\text{K}^+) + 2\ \lambda_\text{m}^\infty(\text{Al}^{3+}) + 4\ \lambda_\text{m}^\infty(\text{SO}_4^{2-})$$

$$= (2 \times 73.5 + 2 \times 189 + 4 \times 160)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 1165\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Since total positive (or negative) charge carried by 1 molecule of potash alum is 8, we will have

$$\Lambda_\text{eq}^\infty(\text{potash alum}) = \frac{\Lambda_\text{m}^\infty(\text{potash alum})}{8\ \text{eq mol}^{-1}} = \frac{1165\,\Omega^{-1}\text{cm}^2\ \text{mol}^{-1}}{8\ \text{eq mol}^{-1}} = 145.6\,\Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

5. A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. Five hundred grams of sodium chloride were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool. Given: $\Lambda_c(\text{NaCl}) = 126.5\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ and $\Lambda_\text{m}(\text{KCl})$ at 0.02 M $= 138.3\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

Solution Conductivity of 0.02 M KCl solution is

$$\kappa = \Lambda_\text{m}c = (138.3\ \Omega^{-1}\text{cm}^2\ \text{mol}^{-1})(0.02{\times}10^{-3}\text{mol cm}^{-3}) = 0.002766\ \Omega^{-1}\ \text{cm}^{-1}$$

Cell constant is $K = \kappa R = (0.002766\ \Omega^{-1}\ \text{cm}^{-1})(85\ \Omega) = 0.2351\ \text{cm}^{-1}$

Conductance of water is $G_1 = 1/R_1 = 1/9200\ \Omega$

Conductance of water after NaCl has been added is $G_2 = \dfrac{1}{R_2} = 1/7600\ \Omega$

Conductance due to NaCl is $G = G_2 - G_1 = \dfrac{1}{7600\ \Omega} - \dfrac{1}{9200\ \Omega} = 2.288 \times 10^{-5}\,\Omega^{-1}$

Conductivity due to NaCl is $\kappa = GK = (2.288{\times}10^{-5}\ \Omega^{-1})\ (0.2351\ \text{cm}^{-1}) = 5.379 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$

Concentration of NaCl in the swimming pool is

$$c = \frac{\kappa}{\Lambda_\text{m}} = \frac{5.379 \times 10^{-6}\,\Omega^{-1}\ \text{cm}^{-1}}{(126.5\,\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1})} = 4.253 \times 10^{-8}\ \text{mol cm}^{-3} = 4.253 \times 10^{-5}\ \text{mol dm}^{-3}$$

Mass of NaCl in 1 dm^3 solution is $m = cM = (4.253 \times 10^{-5}\ \text{mol dm}^{-3})\ (58.5\ \text{g mol}^{-1}) = 0.002488\ \text{g mol}^{-1}$

Volume of water in swimming pool is $V = \left(\dfrac{1\ \text{dm}^3}{0.002488\ \text{g}}\right)(500\ \text{g}) = 2.0 \times 10^5\ \text{dm}^3$

6. The conductivity of a saturated solution of CaF2 is 18°C was found to be $4.2 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$. The conductivity of water used is $2.8 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$. Given: $\lambda^\infty\left(\frac{1}{2}\,\text{Ca}^{2+}\right) = 52.0$ and $\Lambda^\infty(\text{F}^-) = 48.0\ \Omega^{-1}\ \text{cm}^{2\prime}\text{mol}^{-1}$, calculate the solubility product and solubility in g dm^{-3} of CaF2.

Solution Conductivity due to CaF_2 is

$$\kappa = \kappa(\text{CaF}_2\text{ soln.}) - \kappa(\text{water}) = (4.2 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1} - 2.8 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}) = 3.92 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$$

Molar conductivity at infinite dilution of CaF_2 is

$$\Lambda_\text{m}^\infty(\text{CaF}_2) = \lambda_\text{m}^\infty(\text{Ca}^{2+}) + 2\,\lambda_\text{m}^\infty(\text{F}^-) = 2\,\lambda_\text{m}^\infty(\tfrac{1}{2}\text{Ca}^{2+}) + 2\,\lambda_\text{m}^\infty(\text{F}^-)$$

$$= (2 \times 52.0 + 2 \times 48.0)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 200.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Concentration of CaF_2 in water is

$$c = \frac{\kappa}{\Lambda} = \frac{3.92 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}}{200.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}} = 1.96 \times 10^{-7}\ \text{mol cm}^{-3} = 1.96 \times 10^{-4}\ \text{mol dm}^{-3}$$

Mass of CaF_2 in 1 dm^3 solution is $m = cM = (1.96 \times 10^{-4}\ \text{mol dm}^{-3})\ (78\ \text{g mol}^{-1}) = 0.0153\ \text{g dm}^{-3}$

Solubility product of CaF_2 is $K_\text{sp} = [\text{Ca}^{2+}]\ [\text{F}^-]^2 = (1.96 \times 10^{-4}\ \text{M})\ (2 \times 1.96 \times 10^{-4}\ \text{M})^2 = 3.01 \times 10^{-11}\ \text{M}^3$

7. The conductivity of a saturated aqueous solution of silver oxalate is $3.8 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$ at 25°C. Calculate the molar conductivity of oxalate ion. Given at 25°C, conductivity of water is $6.2 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$, $\lambda_\text{m}^\infty(\text{Ag}^+) = 62\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ and solubility product of silver oxalate = $1.1 \times 10^{-11}\ \text{M}^3$.

Solution Silver oxalate ionizes as $Ag_2C_2O_4 \rightleftharpoons 2Ag^+ + C_2O_4^{2-}$

If s is the solubility of $Ag_2C_2O_4$, then $K_\text{sp} = [\text{Ag}^+]^2\ [\text{C}_2\text{O}_4^{2-}] = (2s)^2(s) = 4s^3$

or $$s = \left(\frac{K_\text{sp}}{4}\right)^{1/3} = \left(\frac{1.1 \times 10^{-11}\ M^3}{4}\right)^{1/3} = 1.40 \times 10^{-4}\ \text{M}$$

Conductivity due to $Ag_2C_2O_4$ is $\kappa = 3.8 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1} - 6.2 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1} \simeq 3.8 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$

Molar conductivity of $Ag_2C_2O_4$ is $$\Lambda_\text{m} = \frac{\kappa}{c} = \frac{3.8 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}}{1.4 \times 10^{-7}\ \text{mol cm}^{-3}} = 271.4\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Molar conductivity of oxalate ion is $\lambda_\text{m}(\text{C}_2\text{O}_4^{2-}) = \Lambda_\text{m}(\text{Ag}_2\text{C}_2\text{O}_4) - 2\,\lambda_\text{m}(\text{Ag}^+) = (271.4 - 2 \times 62)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 147.4\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

8. At 25 °C, the resistance of a cell filled with 0.01 M KCl solution is 525 ohms. The resistance of the same cell filled with 0.1 M NH_4OH is 2030 ohms. Calculate the degree of dissociation and equilibrium constant of NH_4OH. Given: $\lambda^\infty(\text{K}^+) = 73.52$, $\lambda^\infty(\text{Cl}^-) = 76.34$, $\lambda^\infty(\text{NH}_4^+) = 73.4$ and $\lambda^\infty(\text{OH}^-) = 197.6\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

Solution Molar conductivity at infinite dilution of KCl is

$$\Lambda_\text{m}^\infty(\text{KCl}) = \lambda_\text{m}^\infty(\text{K}^+) + \lambda_\text{m}^\infty(\text{Cl}^-) = (73.52 + 76.34)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 149.86\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Conductivity of 0.01 M KCl is

$$\kappa_1 = \Lambda_\text{m}^\infty\ c = (149.86\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1})\ (0.01 \times 10^{-3}\ \text{mol cm}^{-3}) = 1.4986 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$$

Cell constant is $K = \kappa_1 R = (1.4986 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1})\ (525\ \Omega) = 0.7868\ \text{cm}^{-1}$

Conductivity of 0.1 M NH_4OH is $$\kappa_2 = \frac{K}{R} = \frac{0.7868\ \text{cm}^{-1}}{2030\ \Omega} = 3.876 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$$

Molar conductivity of 0.1 M NH_4OH is $$\Lambda_c(\text{NH}_4\text{OH}) = \frac{\kappa_2}{c} = \frac{3.876 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}}{0.1 \times 10^{-3}\ \text{mol cm}^{-3}} = 3.876\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Molar conductivity of NH_4OH at infinite dilution is

$$\Lambda_\text{m}^\infty(\text{NH}_4\text{OH}) = \lambda_\text{m}^\infty(\text{NH}_4^+) + \lambda_\text{m}^\infty(\text{OH}^-) = (73.4 + 197.6)\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} = 271.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Degree of dissociation of NH_4OH is $$\alpha = \frac{\Lambda_c}{\Lambda_\text{m}^\infty} = \frac{3.876\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}}{271.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}} = 0.0143$$

Equilibrium constant of NH_4OH is $$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{(c\alpha)\,(c\alpha)}{c(1-\alpha)} \simeq c\alpha^2 = (0.1\ \text{M})\ (0.0143)^2 = 2.05 \times 10^{-5}\ \text{M}$$

9. A saturated solution of silver bromide is made 10^{-7} M in silver nitrate. Calculate the conductivity of the solution. Given:

$$K^{\circ}_{sp}(\text{AgBr}) = 3.0 \times 10^{-13}, \qquad \lambda^{\infty}_{m}(\text{Ag}^{+}) = 6 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1},$$

$$\lambda^{\infty}_{m}(\text{NO}_3^{-}) = 7 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1}, \qquad \lambda^{\infty}_{m}(\text{Br}^{-}) = 8 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1},$$

and $\kappa(\text{water}) = 7.5 \times 10^{-6}\ \text{S m}^{-1}$. (2006)

Solution Let x be the solubility of AgBr in 10^{-7} M $AgNO_3$ solution. We will have

$$\underset{}{\text{AgBr(s)}} \rightarrow \underset{10^{-7}\text{M} + x}{\text{Ag}^{+}(\text{aq})} + \underset{x}{\text{Br}^{-}(\text{aq})}$$

Since $K_{sp} = [\text{Ag}^{+}]\,[\text{Br}^{-}]$, we have

$$(10^{-7}\ \text{M} + x)\,(x) = 3.0 \times 10^{-13}\ \text{M}^2 \quad \text{or} \quad x^2 + (10^{-7}\ \text{M})x - 30 \times 10^{-14}\ \text{M}^2 = 0$$

This gives $x = 5 \times 10^{-7}$ M

$$\lambda^{\infty}_{m}(\text{AgNO}_3) = \lambda^{\infty}_{m}(\text{Ag}^{+}) + \lambda^{\infty}_{m}(\text{NO}_3^{-}) = (6 + 7) \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1} = 13 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1}$$

$$\Lambda^{\infty}_{m}(\text{AgBr}) = \lambda^{\infty}_{m}(\text{Ag}^{+}) + \lambda^{\infty}_{m}(\text{Br}^{-}) = (6 + 8) \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1} = 14 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1}$$

$$\kappa(\text{AgNO}_3) = [\Lambda^{\infty}_{m}(\text{AgNO}_3)\}c = (13 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1})\,(10^{-7}\ \text{M}) = (13 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1})\,(10^{-4}\ \text{mol m}^{-3})$$
$$= 13 \times 10^{-7}\ \text{S m}^{-1}$$

$$\kappa(\text{AgBr}) = \{\Lambda^{\infty}_{m}(\text{AgBr})\}c = (14 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1})\,(5 \times 10^{-7}\ \text{M})$$
$$= (14 \times 10^{-3}\ \text{S m}^2\ \text{mol}^{-1})\,(5 \times 10^{-4}\ \text{mol m}^{-3}) = 70 \times 10^{-7}\ \text{S m}^2\ \text{mol}^{-1}$$

$$\kappa(\text{soln}) = \kappa(\text{AgNO}_3) + \kappa(\text{AgBr}) + \kappa(\text{water}) = (13 \times 10^{-7} + 70 \times 10^{-7} + 75 \times 10^{-7})\ \text{S m}^{-1}$$
$$= 158 \times 10^{-7}\ \text{S m}^{-1}$$

SECTION III GALVANIC CELLS

In galvanic cells, current is generated as a result of a spontaneous chemical reaction that occurs in the cell. The main characteristics of galvanic cells are given in Table 8.2.

Table 8.2 Main Characteristics of Galvanic Cells

	Cathode	*Anode*
Sign	Positive as the electrons are consumed at this electrode	Negative as the electrons are released at this electrode
Half-reaction	Reduction	Oxidation
Direction of electron movement	Into the cell	Out of cell

Thus, electrons are generated at the anode because of the oxidation reaction. As the electrons are negatively charged species, the anode becomes the negative end of the cell. The generated electrons move through the external wire to the other electrode (cathode) where these are consumed due to the reduction reaction. This electrode is deficient in electrons and is, therefore, the positive terminal of the cell.

Cell Reaction A cell can be briefly represented by a cell diagram following the rules given below.

1. The separation of two phases is shown by a vertical line.
2. The various materials present in the same phase are shown together with the help of commas.
3. The two half-cells are joined with the help of double vertical lines.
4. The significant features of the substances such as pressure of the gas, concentration of ions, etc. are indicated in brackets, drawn immediately after writing the substance.

According to the recommended convention, if a cell is written in brief, known as cell diagram, the left half-cell (LHC) is considered as the negative terminal and the right half- cell (RHC) as the positive terminal. Thus, the oxidation reaction occurs at the left electrode and the reduction reaction at the right electrode.

A few examples of illustrating the above convention are described below.

1. $Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$

LHC: Oxidation $Zn \rightarrow Zn^{2+}(aq) + 2e^-$

RHC: Reducion $Cu^{2+}(aq) + 2e^- \rightarrow Cu$

Overall reaction $Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$

2. $Pt \mid H_2(g) \mid H^+(aq) \parallel Zn^{2+}(aq) \mid Zn$

LHC: Oxidation $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

RHC: Reduction $Zn^{2+}(aq) + 2e^- \rightarrow Zn$

Overall reaction $H_2(g) + Zn^{2+}(aq) \rightarrow 2H^+(aq) + Zn$

A galvanic cell is made up of two half-cells. The electrodes used in a half-cell can be broadly classified into the following categories.

Gas-Ion Half-Cell In the gas-ion half-cell, an inert collector of electrons (platinum or graphite) is in contact with gas and a solution containing specified ion. A few examples of this type of half-cell are given below.

Half-Cell	*Half-Cell Reaction*
$H^+(aq) \mid H_2(g) \mid Pt$	$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$
$OH^-(aq) \mid H_2(g) \mid Pt$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
$OH^-(aq) \mid O_2(g) \mid Pt$	$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
$H^+(aq) \mid O_2(g) \mid Pt$	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
$Cl^-(aq) \mid Cl_2(g) \mid Pt$	$\frac{1}{2} Cl_2(g) + e^- \rightarrow Cl^-(aq)$

Metal-Metal Ions Half-Cell In this half-cell, a metal acting as electrode is in contact with the metal ions. Examples are

$Cu^{2+}(aq) \mid Cu$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu$
$Zn^{2+}(aq) \mid Zn$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn$
$Sn^{2+}(aq) \mid Sn$	$Sn^{2+}(aq) + 2e^- \rightarrow Sn$

Metal-Insoluble Salt-Anion Half-Cell In this half-cell, a metal coated with its insoluble salt is in contact with a solution containing anion of the insoluble salt. Examples are:

$Cl^-(aq) \mid AgCl(s) \mid Ag$	$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$
$Br^-(aq) \mid AgBr(s) \mid Ag$	$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$
$Cl^-(aq) \mid Hg_2Cl_2(s) \mid Hg(Pt)$	$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$
$OH^-(aq) \mid Cu(OH)_2(s) \mid Cu$	$Cu(OH)_2(s) + 2e^- \rightarrow Cu(s) + 2OH^-(aq)$

Oxidation-Reduction Half-Cells In this half-cell, an inert metal collector is in contact with two ions of the same metal in different states of oxidation. Examples are

$Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
$MnO_4^-(aq), Mn^{2+}(aq), H^+(aq) \mid Pt$	$MnO_4^-(aq) + 8\,H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$Cr_2O_7^{2-}(aq), Cr^{3+}(aq), H^+(aq) \mid Pt$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$Co^{3+}(aq), Co^{2+}(aq) \mid Pt$	$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$

Standard Potentials The electronic movement is due to the different tendencies of the appropriate species to accept the electrons at the two electrodes of a galvanic cell. This tendency is measured relative to the standard hydrogen electrode whose potential is assigned a zero value at 25 °C. In the standard hydrogen electrode, pressure of H_2 is 1 bar and the concentration of H^+ ions is 1 M. To determine the reduction potential of a half-cell, a cell is constructed in which the left half-cell is the standard hydrogen-hydrogen ions half-cell and the right hand cell is the standard half-cell containing the species whose reduction potential is to be determined. By definition, the emf of such a cell is the reduction potential of the right-half cell. A table of half-cell reduction potentials is constructed which describes the relative tendencies of different reduction species with respect to the reduction of H^+ to H_2. A positive potential implies that the species under study has a larger reduction tendency than that of $H^+(aq)$ into $H_2(g)$ and the negative potential implies that the species has a lower reduction tendency.

Cell Reaction and EMF of a Cell The cell reaction is obtained by adding the oxidation reaction at the left half-cell and the reduction reaction at the right half-cell. Alternatively, it can be obtained by subtracting the reduction reaction at the left half-cell from that occurring at the right half-cell. The emf of the cell is obtained by subtracting the half-cell potential of the left half-cell from that of the right half-cell, i.e.

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

when $E_{\text{R}} > E_{\text{L}}$, then E_{cell} is positive and the cell reaction is spontaneous. On the other hand, if $E_{\text{R}} < E_{\text{L}}$, then E_{cell} is negative and the cell reaction is nonspontaneous.

Since the standard hydrogen-hydrogen ions half-cell is very inconvenient to use, it is replaced by a reference half-cell whose potential has been accurately determined with respect to hydrogen-hydrogen ions half-cell. The most common type of reference electrons are as follows.

1. Calomel electrode $KCl(aq) \mid Hg_2Cl_2(s) \mid Hg$
2. Silver-silver chloride electrode $KCl(aq) \mid AgCl(s) \mid Ag$
3. Mercury-mercurous sulphate electrode $K_2SO_4(Ag) \mid Hg_2SO_4(s) \mid Hg$

The most commonly used electrode is calomel electrode for 0.1 M, 1 M and saturated KCl solution, the potential are 0.336 V, 0.283 V and 0.244 V, respectively, at 298 K.

Nernst Equation The cell potential of a half-cell (and also that of a complete cell) depends upon the concentrations of involved ions and also on the pressure of the gaseous species. The cell potential also varies with temperature. The relation connecting cell potential with these factors is given by the Nernst equation. It is expressed as

$$E = E^\circ - \frac{RT}{nF}\ \ln Q^\circ$$

where Q° is the standard reaction quotient, defined as

$$Q^\circ = \frac{\text{Product of concentration (or pressure) of products each raised to the corresponding stoichiometric number}}{\text{Product of concentration (or pressure) of reactants each raised to the corresponding stoichiometric number}}$$

and n is the number of electrons involved in the half-cell reaction. Each concentration or pressure term is divided by the corresponding standard unit ($c^\circ = 1\ \text{mol dm}^{-3}$ or 1 bar as the case may be).

For example for the cell $\quad \text{Zn(s)} \mid \text{Zn}^{2+}(c_1) \parallel \text{Cu}^{2+}(c_2) \mid \text{Cu}$ we have

Cell	*Reduction reaction*	*Reduction potential*
(i) RHC	$Cu^{2+} + 2e^- \rightarrow Cu$	$E_{Cu^{2+} \mid Cu} = E^\circ_{Cu^{2+} \mid Cu} - \frac{RT}{2F}\ \ln \frac{c^\circ}{[Cu^{2+}]}$
(ii) LHC	$Zn^{2+} + 2e^- \rightarrow Zn$	$E^\circ_{Zn^{2+} \mid Zn} = E^\circ_{Zn^{2+} \mid Zn} - \frac{RT}{2F}\ \ln \frac{c^\circ}{[Zn^{2+}]}$

Substracting Eq. (ii) from Eq. (i), we get

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \tag{1}$$

with $\quad E_{cell} = E_{Cu^{2+} \mid Cu} - E_{Zn^{2+} \mid Zn}$

$$= \left(E^\circ_{Cu^{2+}|Cu} - \frac{RT}{2F} \ln \frac{c^\circ}{[Cu^{2+}]}\right) - \left(E^\circ_{Zn^{2+}|Zn} - \frac{RT}{2F} \ln \frac{c^\circ}{[Zn^{2+}]}\right) = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{2}$$

with $\quad E^\circ_{cell} = E^\circ_{Cu^{2+} \mid Cu} - E^\circ_{Zn^{2+} \mid Zn}$

Equation (2) can be directly obtained from Eq. (1).

Relation Between Standard Potentials of Metal-Metal Ion and the corresponding Metal-Insoluble Salt-Anion Half-Cells Considering the examples of $Ag^+ \mid Ag$ and $Cl^- \mid AgCl \mid Ag$ half-cells, we can write

$$E_{Ag^+ \mid Ag} = E^\circ_{Ag^+ \mid Ag} - \frac{RT}{F}\ \ln \frac{c^\circ}{[Ag^+]} \tag{3}$$

and

$$E_{Cl^- \mid AgCl \mid Ag} = E^\circ_{Cl^- \mid AgCl \mid Ag} - \frac{RT}{F}\ \ln \frac{[Cl^-]}{c^\circ} \tag{4}$$

Consider a silver electrode dipped into a solution of silver nitrate. If to this half-cell, excess of NaCl (more than to precipitate whole of silver nitrate) is added, the following equilibrium is established:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

with its solubility product as $\quad K_{sp} = [Ag^+]\,[Cl^-]$

Replacing $[Ag^+]$ in Eq. (3) by $K_{sp}/[Cl^-]$, we get

$$E_{Ag^+ \mid Ag} = E^\circ_{Ag^+ \mid Ag} - \frac{RT}{F}\ \ln \frac{[Cl^-]}{K^\circ_{sp}} = \left(E^\circ_{Ag^+|Ag} + \frac{RT}{F} \ln K^\circ_{sp}\right) - \frac{RT}{F} \ln \{[Cl^-]/c^\circ\} \tag{5}$$

The present half-cell may be treated as $Cl^- \mid AgCl \mid Ag$ half-cell. Thus $E_{Cl^- \mid AgCl \mid Ag}$ in Eq. (4) will be identical with $E_{Ag^+ \mid Ag}$ in Eq. (5). Equating these two equations, we get

$$E^\circ_{Cl^- \mid AgCl \mid Ag} = E^\circ_{Ag^+ \mid Ag} + \frac{RT}{F}\ \ln K^\circ_{sp}$$

Relation Between Standard Potentials of Half-Cells Containing a Metal in Different Oxidation States

From the following three half-cells

$$Fe^{3+} + 3e^- = Fe \qquad E^\circ_{Fe^{3+} \mid Fe} \tag{6}$$

$$Fe^{2+} + 2e^- = Fe \qquad E^\circ_{Fe^{2+} \mid Fe} \tag{7}$$

$$Fe^{3+} + e^- = Fe^{2+} \qquad E^\circ_{Fe^{3+},\, Fe^{2+} \mid Pt} \tag{8}$$

Equation (8) can be obtained by subtracting Eq. (7) from Eq. (6). Thus, we can write

$$\Delta G^{\circ}_{(3)} = \Delta G^{\circ}_{(1)} - \Delta G^{\circ}_{(2)}$$

Hence, $$-F\,E^{\circ}_{\mathrm{Fe^{3+}, Fe^{2+} | Pt}} = -3FE^{\circ}_{\mathrm{Fe^{3+}| Fe}} + 2FE^{\circ}_{\mathrm{Fe^{2+}| Fe}} \quad \text{or} \quad E^{\circ}_{\mathrm{Fe3+, Fe2+ | Pt}} = 3E^{\circ}_{\mathrm{Fe3+ | Fe}} - 2\,E^{\circ}_{\mathrm{Fe2+ | Fe}}$$

Potentiometric Titrations Acid-base, redox and precipitation titrations can be carried out by measuring potential of a cell made from indicator electrode (involving titrating solution) and a suitable reference electrode. For acid-base titrations, quinhydrone (a mixture of quinone and hydroquinone) electrode or glass electrodes is used as a reference electrode.

Quinhydrone electrode $Q + 2H^+ + 2e^- \rightleftharpoons H_2Q$

$$E = E^{\circ} - \frac{RT}{2F}\ln\frac{1}{\left\{\left[\mathrm{H^+}\right]/\mathrm{mol\ dm^{-3}}\right\}^2} = E^{\circ} - \frac{2.303\,RT}{F}\ \mathrm{pH}$$

Glass electrode Ag | AgCl(s) | 0.1 M HCl | glass | unknown pH solution

$$E_{\mathrm{glass}} = E^{\circ}_{\mathrm{glass}} + \frac{2.303\,RT}{F}\ \mathrm{pH}$$

A typical titration curve and its first derivative curve are as follows.

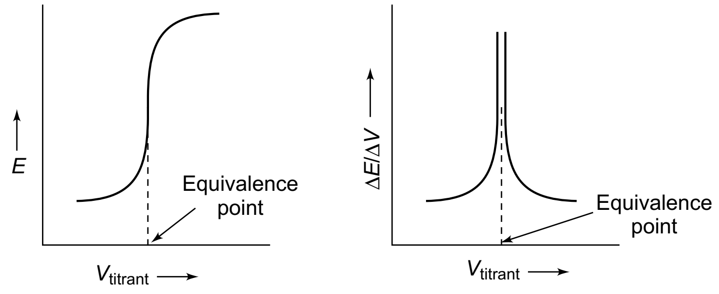


Fig. 8.1

Straight Objective Type

Characteristics of Galvanic Cell

1. When a galvanic cell is written in a cell diagram then
   (a) left electrode serves as cathode (b) left electrode serves as anode
   (c) reduction reaction occurs at anode (d) left electrode constitutes the positive terminal
2. Which of the following statements is correct?
   (a) Cathode is positive terminal in an electrolytic cell
   (b) Cathode is negative terminal in a galvanic cell
   (c) Reduction occurs at cathode in either of cells
   (d) Oxidation occurs at cathode in either of cells
3. Which of the following statements is correct for a galvanic cell, written in a cell diagram?
   (a) Left electrode is cathode (b) Right electrode is anode
   (c) Left electrode is positive terminal (d) Right electrode is positive terminal
4. Which of the following statements is correct?
   (a) Cathode is negative terminal both in galvanic and electrolytic cells
   (b) Anode is positive terminal both in galvanic and electrolytic cells
   (c) Cathode is negative terminal in an electrolytic cell whereas anode is negative terminal in a galvanic cell
   (d) Anode is negative terminal in an electrolytic cell whereas cathode is positive terminal in a galvanic cell

5. Which of the following statements is correct?
(a) Oxidation occurs at anode in both galvanic and electrolytic cells
(b) Reduction occurs at anode in both galvanic and electrolytic cells
(c) Reduction occurs at anode in electrolytic cell whereas oxidation occurs at cathode in a galvanic cell
(d) Oxidation occurs at anode in electrolytic cell whereas reduction occurs at anode in a galvanic cell.

6. Which of the following facts regarding the movements of cations in the solution is correct?
(a) Towards cathode in an electrolytic cell and towards anode in a galvanic cell
(b) Towards anode in an electrolytic cell and towards cathode in a galvanic cell
(c) Towards cathode in both types of cells
(d) Towards anode in both types of cells

7. Which of the following facts regarding the movement of anions in the solution is correct
(a) Towards cathode in an electrolytic cell and towards anode in a galvanic cell
(b) Towards anode in an electrolytic cell and towards cathode in a galvanic cell
(c) Towards cathode in both types of cells
(d) Towards anode in both types of cells

8. Two half cells have potentials – 0.76 V and – 0.13 V respectively. A galvanic cell is made from these two half-cells. Which of the following statements is correct?
(a) Electrode of half-cell potential –0.76 V serves as cathode
(b) Electrode of half-cell potential –0.76 V serves as anode
(c) Electrode of half-cell potential –0.13 V serves as anode
(d) Electrode of half-cell –0.76 V serves as positive electrode and – 0.13 V as negative electrode

9. Which of the following is **not** correct for a galvanic cell when written in an abbreviated form?
(a) Left half electrode is a negative terminal
(b) Left half electrode is an anode
(c) Electrons are given out in the external circuit from the anode
(d) Electrons are given out in the external circuit from the cathode

10. Two half-cells have potentials – 0.44 V and 0.799 V, respectively. These two are coupled to make a galvanic cell. Which of the following statements is true?
(a) Electrode of half-cell potential – 0.44 V acts as anode
(b) Electrode of half-cell potential – 0.44 V acts as cathode
(c) Electrode of half-cell potential 0.799 V acts as anode
(d) Electrode of half-cell potential – 0.44 V acts as a positive terminal

11. Two half-cells have potentials – 0.76 V and – 0.13 V, respectively. A galvanic cell is made from these two half-cells. Which of the following statements is correct?
(a) Electrode of half-cell potential – 0.76 V serves as cathode
(b) Electrode of half-cell potential – 0.76 V serves as anode
(c) Electrode of half-cell potential – 0.13 serves as anode
(d) The nature of electrodes cannot be determined.

12. In a galvanic cell,
(a) Cations move towards cathode and anions move towards anode
(b) Cations move towards anode and anions towards cathode
(c) Both Cations move towards cathode
(d) Both cations move towards anode

13. When a lead storage cell is discharged, there occurs
(a) consumption of H_2SO_4
(b) formation of PbO_2(s)
(c) increase in the cell potential
(d) consumption of $PbSO_4$(s)

14. In a lead-storage cell, the emf
(a) increases with increase in the percentage of H_2SO_4
(b) decreases with increase in the percentage of H_2SO_4
(c) does not change with increase in the percentage of H_2SO_4
(d) is not affected by the change in temperature of the cell

15. Which of the following statements regarding the movement of ions in a cell is/are correct?
(a) Cations move towards cathode and anions towards anode in both galvanic and electroyytic cells.
(b) Cations move towards cathode and anions towards anode in an electrolytic cell and the reverse is true for a galvanic cell.
(c) Cations move towards cathode and anions towards anode in a galvanic cell and the reverse is true for an electrolytic cell.
(d) Cations move towards anode and anions towards cathode in a galvanic cell and the reverse is true for an electrolytic cell.

16. Saturated solution of KNO_3 is used to make 'salt-bridge' because
(a) velocity of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocities of both K^+ and NO_3^- are nearly the same
(d) KNO_3 is highly soluble in water (2001)

17. A current of 9.65 A is drawn from a Daniell cell for exactly one hour. If molar masses of Cu and Zn are 63.5 g mol^{-1} and 65.4 g mol^{-1}, respectively, the loss in mass at anode and gain in mass at cathode respectively are
(a) 11.43 g, 11.77 g (b) 11.77 g, 11.43 g (c) 22.86 g, 23.54 g (d) 23.54 g, 22.86 g

Oxidation and Reduction Abilities

18. The standard potential at 298 K for the following half reactions are given against each:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ -0.762 V $2H^+(aq) + 2e^- \rightleftharpoons Cr(s)$ 0.000

$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$ -0.740 V $Fe^{3+}(aq) + 2e^- \rightleftharpoons Fe^{2+}(aq)$ 0.770 V

Which is the strongest reducing agent?
(a) Zn(s) (b) Cr(s) (c) $H_2(g)$ (d) $Fe^{2+}(aq)$ (1981)

19. Given: $E°(Cu^{2+} | Cu) = 0.337$ V and $E°(Sn^{2+} | Sn) = -0.136$ V. Which of the following statements is correct?
(a) Cu^{2+} ions can be reduced by $H_2(g)$ (b) Cu can be oxidized by H^+
(c) Sn^{2+} ions can be reduced by $H_2(g)$ (d) Cu can reduce Sn^{2+}

20. Given that $E°$ values of $Ag^+ | Ag$, $K^+ | K$, $Mg^{2+} | Mg$ and $Cr^{3+} | Cr$ are 0.80 V, -2.93 V, -2.37 V, and -0.74 V, respectively. Which of the following orders regarding the reducing power of metals is correct?
(a) Ag > Cr > Mg > K (b) Ag < Cr < Mg < K (c) Ag > Cr > K > Mg (d) Cr > Ag > Mg > K

21. The following facts are available.

$$2X^- + Y_2 \rightarrow 2Y^- + X_2; \quad 2W^- + Y_2 \rightarrow \text{No reaction}; \quad 2Z^- + X_2 \rightarrow 2X^- + Z_2$$

Which of the following statements is correct?
(a) $E^\circ_{W^-|W_2} > E^\circ_{Y^-|Y_2} > E^\circ_{X^-|X_2} > E^\circ_{Z^-|Z_2}$ (b) $E^\circ_{W^-|W_2} < E^\circ_{Y^-|Y_2} < E^\circ_{X^-|X_2} < E^\circ_{Z^-|Z_2}$
(c) $E^\circ_{W^-|W_2} < E^\circ_{Y^-|Y_2} > E^\circ_{X^-|X_2} > E^\circ_{Z^-|Z_2}$ (d) $E^\circ_{W^-|W_2} > E^\circ_{Y^-|Y_2} < E^\circ_{X^-|X_2} < E^\circ_{Z^-|Z_2}$

22. Which of the following facts is not true?
(a) If $E°(M^{n+} | M)$ is negative, H^+ will be reduced to H_2 by the metal M
(b) If $E°(M^{n+} | M)$ is positive, M^{n+} will be reduced to M by H_2
(c) In a cell, $M^{n+} | M$ assembly is attached to hydrogen-half cell. To produce spontaneous cell reaction, metal M will act as negative electrode if the potential $M^{n+} | M$ is negative. It will serve as positive electrode, if $M^{n+} | M$ has a positive cell potential.
(d) Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.

23. Consider the cell potentials $E^\circ_{Mg^{2+}|Mg} = -2.37$ V and $E^\circ_{Fe^{3+}|Fe} = -0.04$ V. The best reducing agent would be
(a) Mg^{2+} (b) Fe^{3+} (c) Mg (d) Fe

24. Adding powdered Pb and Fe to a solution containing 1.0 M in each of Pb^{2+} and Fe^{2+} ions would result into the formation of
(a) more of Pb and Fe^{2+} ions (b) more of Fe and Pb^{2+} ions
(c) more of Fe and Pb (d) more of Fe^{2+} and Pb^{2+} ions
(Given: $E^\circ_{Fe^{2+}|Fe} = -0.44$ V and $E^\circ_{Pb^{2+}|Pb} = -0.13$ V.)

25. A solution containing one mole per litre each of $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$, $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard potentials are

$E^\circ_{\mathrm{Ag^+ \mid Ag}} = 0.80$ V, $E^\circ_{\mathrm{Hg_2^{2+} \mid Hg}} = 0.79$ V, $E^\circ_{\mathrm{Cu^{2+} \mid Cu}} = 0.34$ V, $E^\circ_{\mathrm{Mg^{2+} \mid Mg}} = -2.3$ V

With increasing voltage, the sequence of deposition of metals on the cathode will be

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag (c) Ag, Hg, Cu (d) Cu, Hg, Ag

26. A standard hydrogen electrode has zero electrode potential because

(a) hydrogen is easiest to oxidise (b) this electrode potential is assumed to be zero

(c) hydrogen atom has only one electron (d) hydrogen is the lightest element (1997)

27. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, – 3.03 and – 1.18 V, respectively. The order of reducing power of the corresponding metals is

(a) Y > Z > X (b) X > Y > Z (c) Z > Y > X (d) Z > X > Y (1998)

28. 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 reduction potential of Z > Y > X, then

(a) Y will oxidise X and not Z (b) Y will oxidise Z and not X

(c) Y will oxidise both X and Z (d) Y will reduce both X and Z (1999)

29. For the electrochemical cell, $\mathrm{M\,|M^+|\,|X^-|\,X}$, $E^\circ(\mathrm{M^+|M}) = 0.44$ V and $E^\circ(\mathrm{X|X^-}) = 0.33$ V. From this data one can deduce that

(a) $\mathrm{M + X \rightarrow M^+ + X^-}$ is the spontaneous reaction (b) $\mathrm{M^+ + X^- \rightarrow M + X}$ is the spontaneous reaction

(c) $E_{\mathrm{cell}} = 0.77$ V (d) $E_{\mathrm{cell}} = -0.77$ V (2000)

30. Given: E° $(\mathrm{Ag^+|Ag}) = 0.799$ V and E° $(\mathrm{Zn^{2+} \mid Zn}) = -0.673$ V, which of the following statements is correct?

(a) $\mathrm{Ag^+}$ can be reduced by $\mathrm{H_2(g)}$ (b) Ag can be oxidized by $\mathrm{H^+}$

(c) $\mathrm{Zn^{2+}}$ can be reduced by $\mathrm{H_2(g)}$ (d) Ag can reduced $\mathrm{Zn^{2+}}$

31. A large quantity of cobalt metal was dropped into a solution containing $\mathrm{Ag^+}$, $\mathrm{Fe^{3+}}$ and $\mathrm{Cu^{2+}}$, all at unit concentration. If $E^\circ(\mathrm{Ag^+|Ag}) = 0.799$ V, $E^\circ(\mathrm{Fe^{3+}, Fe^{2+}|Pt}) = 0.77$ V, $E^\circ(\mathrm{Cu^{2+}|Cu}) = 0.34$ V, $E^\circ(\mathrm{Fe^{3+}|Fe}) = -0.04$ V, $E^\circ(\mathrm{Cu^{2+}, Cu^+|Pt}) = 0.153$ V and $E^\circ(\mathrm{Co^{2+}|Co}) = 0.28$ V, then the solution would contain

(a) Ag, Fe and Cu (b) Ag, Fe, and $\mathrm{Cu^+}$ (c) $\mathrm{Fe^{2+}}$, Cu and $\mathrm{Co^{2+}}$ (d) $\mathrm{Fe^{2+}}$, Cu, Ag and $\mathrm{Co^{2+}}$

32. The standard potentials at 298 K are $E^\circ(\mathrm{Zn^{2+} \mid Zn}) = -0.6762$ V, $E^\circ(\mathrm{Cr^{3+} \mid Cr}) = -0.740$ V, $E^\circ(\mathrm{H^+ \mid H_2 \mid Pt}) = 0.00$ V and $E^\circ(\mathrm{Fe^{3+}, Fe^{2+} \mid Pt}) = 0.770$ V. Which one of the following species is the strongest reducing agent?

(a) Zn(s) (b) Cr(s) (c) $\mathrm{H_2(g)}$ (d) $\mathrm{Fe^{2+}(aq)}$

33. Given $E^\circ(\mathrm{Cu^{2+} \mid Cu}) = 0.337$ V and $E^\circ(\mathrm{Sn^{2+} \mid Sn}) = -0.136$ V. Which of the statements is correct?

(a) $\mathrm{Cu^{2+}}$ ions can be reduced by $\mathrm{H_2(g)}$ (b) Cu can be oxidized by $\mathrm{H^+}$

(c) $\mathrm{Sn^{2+}}$ can reduced by $\mathrm{H_2(g)}$ (d) Cu can reduce $\mathrm{Sn^{2+}}$

34. A solution containing 1 mol $\mathrm{L^{-1}}$ of each of $\mathrm{Cu(NO_3)_2}$, $\mathrm{AgNO_3}$ and $\mathrm{Mg(NO_3)_2}$ is being electrolysed by using inert electrodes. If $E^\circ(\mathrm{Ag^+|Ag}) = 0.80$ V, $E^\circ(\mathrm{Cu^{2+}|Cu}) = 0.34$ V and $E^\circ(\mathrm{Mg^{2+}|Mg}) = -2.37$ V, the sequence of deposition of metals on the cathode with increasing voltage would be

(a) Cu, Ag, Mg (b) Mg, Cu, Ag (c) Cu, Mg, Ag (d) Mg, Ag, Cu

35. The reaction occurring at the cathode of miniature electrochemical cell during the rusting of iron is

(a) $\mathrm{Fe \longrightarrow Fe^{2+} + 2e^-}$ (b) $\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + e^-}$

(c) $\mathrm{O_2 + H_2O + 2e^- \longrightarrow 2OH^-}$ (d) $\mathrm{H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-}$

36. If a strip of Cu is placed in a solution of ferrous sulphate, which one of the following alternatives is observed?

(a) copper will precipitate out (b) iron will precipitate out

(c) Cu dissolves as $\mathrm{Cu^{2+}}$, $\mathrm{Fe^{2+}}$ is deposited as Fe (d) no reaction

37. Given: $E^\circ(\mathrm{Sn^{2+}, Sn^{4+}|Pt}) = 0.15$ V, $E^\circ(\mathrm{Hg_2^{2+}, Hg^{2+}|Pt}) = 0.92$ V and $E^\circ(\mathrm{Pb^{2+}, H^+|PbO_2}) = 1.45$ V. Based on this data, which of the following statements is correct?

(a) $\mathrm{Sn^{4+}}$ is a stronger oxidizing agent than $\mathrm{Pb^{4+}}$ (b) $\mathrm{Sn^{2+}}$ is a stronger reducing agent than $\mathrm{Hg_2^{2+}}$

(c) $\mathrm{Hg^{2+}}$ is a stronger oxidizing agent than $\mathrm{Pb^{4+}}$ (d) $\mathrm{Pb^{2+}}$ is a stronger reducing agent than $\mathrm{Sn^{2+}}$

38. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below.

$$\mathrm{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)} \qquad E^\circ = 1.51\ \mathrm{V}$$

$$\mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} \qquad E^\circ = 1.38\ \mathrm{V}$$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^\circ = 0.77$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\circ = 1.40$ V

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$.
(a) MnO_4^- can be used in aqueous HCl (b) CrO_7^{2-} can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4 (d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4 (2002)

39. Given below are some standard reduction potentials.

$Sn^{2+} + 2e^- = Sn$; $E^\circ = -0.14$ V $Hg_2^{2+} + 2e^- = 2Hg$ $E^\circ = 0.79$ V

Which of the following statements is correct?
(a) Hg can reduce Sn^{2+} to Sn
(b) Sn^{2+} can oxidize Hg to Hg_2^{2+}
(c) Hg_2^{2+} can oxidize Sn to Sn^{2+}
(d) Between Hg_2^{2+} and Sn^{2+}, Sn^{2+} is stronger oxidising agent than Hg_2^{2+}.

40. Given that E° values of $Ag^+|Ag$, $K^+|K$, $Mg^{2+}|Mg$ and $Cr^{3+}|Cr$ are 0.80 V, – 2.93 V, –2.37 V, and – 0.74 V, respectively. Which of the following orders regarding the reducing power of metals is correct?
(a) Ag > Cr > Mg > K (b) Ag < Cr < Mg < K (c) Ag > Cr > K > Mg (d) Cr > Ag > Mg > K

Cell Representation, Cell Reaction and Cell Potential

41. The reaction $\frac{1}{2}H_2(g) + AgCl(s) = H^+(aq) + Cl^-(aq) + Ag(s)$ occurs in the galvanic cell
(a) $Ag | AgCl(s) | KCl(aq) || AgNO_3(aq) | Ag$ (b) $Pt | H_2(g) | HCl(aq) || AgNO_3(aq) | Ag$
(c) $Pt | H_2(g) | HCl(aq) | AgCl(s) | Ag$ (d) $Pt | H_2(g) | KCl(aq) | AgCl(s) | Ag$ (1981)

42. The standard reduction potentials, E°, for the half reactions are

$Zn^{2+} + 2e^- = Zn$ $E^\circ = -0.76$ V and $Fe^{2+} + 2e^- = Fe$ $E^\circ = -0.41$ V

The standard emf of the cell involving the reaction $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is
(a) – 0.35 V (b) +1.17 V (c) +0.35 V (d) – 1.17 V (1988)

43. The reaction $Ag(s) + \frac{1}{2}Br(l) = AgBr(s)$ occurs in the galvanic cell
(a) $Ag | AgNO_3(s) || KBr(aq) | Br_2(l) | Pt$ (b) $Ag | AgBr(s) | KBr(aq) | Br_2(l) | Pt$
(c) $Pt | Br_2(l) | KBr(aq) | AgBr(s) | Ag$ (d) $Pt | Br_2(l) | KBr(aq) || AgNO_3(aq) | Ag$

44. The standard cell potential for the cell $Pt | Hg(l) | Hg_2Cl_2(s) | KCl\ (0.1\ M) || ZnCl_2(0.1\ M) | Zn(s)$ (Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V and $E^\circ_{Cl^-|Hg_2Cl_2|Hg} = 0.34$ V) is
(a) – 1.10 V (b) 1.10 V (c) – 0.99 V (d) 0.99 V

Nernst Equation

45. The reduction potential of hydrogen half-cell will be negative if
(a) $p(H_2) = 1$ bar and $[H^+] = 1$ M (b) $p(H_2) = 1$ bar and $[H^+] = 2$ M
(c) $p(H_2) = 2$ bar and $[H^+] = 1$ M (d) $p(H_2) = 2$ bar and $[H^+] = 2$ M

46. By how much will the potential of half-cell $Cu^{2+}|Cu$ change if the solution is diluted to 100 times at 298 K?
(a) Increases by 59 mV (b) Decreases by 59 mV
(c) Increases by 29.5 mV (d) Decreases by 29.5 mV

47. Given that $E_{H_2O|H_2|Pt} = 0$ at 298 K. The pressure of H_2 gas would be
(a) 10^{-7} bar (b) 10^{-10} bar (c) 10^{-12} bar (d) 10^{-14} bar

48. The value of $E_{H_2O|H_2(1\ bar)|Pt}$ at 298 K would be
(a) – 0.207 V (b) – 0.414 V (c) 0.207 V (d) 0.414 V

49. The reduction potential $H^+|H_2|Pt$ in 1 M NaOH solution at 25 °C will be about
(a) 0.412 V (b) 0.828 V (c) – 0.414 V (d) – 0.828 V

50. The pressure of H_2 required to make the potential of the hydrogen electrode in water equal to zero at 298 K is
(a) 10^{-7} atm (b) 10^{-14} atm (c) 10^{-5} atm (d) 10^{-10} atm

51. The reduction potential of hydrogen electrode in pure water at 298 K would be
(a) 0.414 V (b) – 0.414 V (c) 0.828 V (d) – 0.828 V

52. The reduction potential of hydrogen electrode will be positive if
(a) $p(H_2) = 1$ atm, $[H^+] = 1$ M (b) $p(H_2) = 1$ atm, $[H^+] = 2$ M
(c) $p(H_2) = 2$ atm, $[H^+] = 1$ M (d) $p(H_2) = 2.5$ atm, $[H^+] = 1.5$ M

53. By how much will the potential of a copper electrode change if the solution of $CuSO_4$ in which it is immersed is diluted 10 times at 298 K?
(a) Increases by 30 mV (b) Decreases by 30 mV (c) Increases by 60 mV (d) Decreases by 60 mV

54. Nernst equation at 25 °C involving the reaction $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ is
(a) $E = E° + (RT/nF)\ \ln\ ([Fe^{2+}]/[Fe^{3+}])$ (b) $E = E° - (RT/nF)\ \log\ ([Fe^{2+}]/[Fe^{3+}])$
(c) $E = E° - (0.0595\ V)\ \ln\ ([Fe^{2+}]/[Fe^{3+}])$ (d) $E = E° - (0.0595\ V)\ \log\ ([Fe^{2+}]/[Fe^{3+}])$

55. On diluting the concentration of mecurous chloride ten times, the change in potential of mercuric to mercurous at 298 K is
(a) increased by 0.059 V (b) decreased by 0.059 V
(c) increased by 0.02915 V (d) decreased by 0.02915 V

56. On diluting the concentration of Cl^- ions by ten times in a calomel cell, its potential at 298 K is
(a) increased by 0.059 V (b) decreased by 0.059 V
(c) increased by 0.02915 V (d) decreased by 0.02915 V

57. The cell potential of Ag | AgBr(s) | HBr (0.02 M) | H_2(0.5 atm) | Pt (Given $E°_{Br^- | AgBr | Ag} = 0.071$ V) is
(a) 0.26 V (b) – 0.26 V (c) 0.16 V (d) – 0.16 V

Half-Cell Potentials

58. Given that $E°_{Fe^{3+}|Fe}$ and $E°_{Fe^{2+}|Fe}$ are – 0.036 V and – 0.439 V, respectively. The value of $E°_{Fe^{3+}, Fe^{2+}|Pt}$ would be
(a) (– 0.036 – 0.439) V (b) (– 0.036 + 0.439) V
(c) [3(– 0.036) + 2(– 0.439)] V (d) [3(– 0.036) – 2(– 0.439)] V

59. The standard reduction potentials of Cu^{2+} | Cu and Cu^{2+} | Cu^+ are 0.337 V and 0.153 V, respectively. The standard electrode potential of Cu^+|Cu half cell is
(a) 0.184 V (b) 0.827 V (c) 0.521 V (d) 0.490 V (1997)

60. Given is Latimer diagram in acidic medium (H^+ = 1 M):

$$\begin{tikzcd}HNO_2 \arrow[r, "0.996\ V"] \arrow[rr, bend right, "E°"'] & NO \arrow[r, "1.59\ V"] & N_2O\end{tikzcd}$$

The value of $E°$ would be
(a) 2.586 V (b) 0.594 V (c) 1.293 V (d) – 1.293 V

61. In acid medium, the standard reduction potential of NO converted to N_2O is 1.59 V. Its standard potential in alkaline medium would be
(a) – 1.59 V (b) 0.764 V (c) – 0.764 V (d) 0.062 V

62. Given is the Latimer diagram in acidic medium (H^+ = 1M):

$$\begin{tikzcd}O_2 \arrow[r, "E°"] \arrow[rr, bend right, "1.229\ V"'] & H_2O_2 \arrow[r, "1.763\ V"] & H_2O\end{tikzcd}$$

The value of $E°$ would be
(a) 2.992 V (b) 0.401 V (c) 0.695 V (d) – 0.401 V

63. Given is the Latimer diagram in acidic medium (H^+ = 1M):

$$\begin{tikzcd}HClO_2 \arrow[r, "1.674\ V"] \arrow[rr, bend right, "E°"'] & HClO \arrow[r, "1.630\ V"] & Cl_2\end{tikzcd}$$

The value of $E°$ would be
(a) 3.304 V (b) 0.044 V (c) 1.718 V (d) 1.659 V

64. Given is the Latimer diagram in acidic medium (H^+ = 1M):

$$\begin{tikzcd}MnO_4^- \arrow[r, "E°"] \arrow[rr, bend right, "1.51\ V"'] & MnO_2 \arrow[r, "1.23\ V"] & Mn^{2+}\end{tikzcd}$$

The value $E°$ would be
(a) 1.696 V (b) 0.28 V (c) 2.74 V (d) 0.91 V

65. Given is the Latimer diagram in acidic medium ($H^+ = 1M$)

$$\begin{tikzcd} Hg^{2+} \arrow[r, "0.911\text{ V}"] \arrow[rr, bend right, "0.854\text{ V}"'] & Hg_2^{2+} \arrow[r, "E°"] & Hg \end{tikzcd}$$

The value of $E°$ is
(a) 0.057 V (b) 0.114 V (c) 0.794 V (d) 0.882

66. If $E°(HNO_2, NO, H^+|Pt) = 0.996$ V and $K°_{eq}$ for $HNO_2 \rightleftharpoons H^+ + NO_2^-$ is 4.5×10^{-4}, then the value of $E°(NO_2^-, NO, OH^-)$ would be
(a) 0.46 V (b) – 0.17 V (c) 0.17 V (d) – 0.46 V

67. Given that $E°_{Fe^{3+}|Fe}$ and $E°_{Fe^{2+}|Fe}$ are –0.036 V and –0.439 V, respectively. The value of $E°_{Fe^{3+}, Fe^{2+}|Pt}$ would be
(a) (– 0.036 – 0.439) V (b) (– 0.036 + 0.439) V
(c) [3(– 0.036) + 2(– 0.439)] V (d) [3(– 0.036) – 2(– 0.439)] V

Applications of Galvanic Cell

68. Given: $E°(Ag^+|Ag) = 0.80$ V and $E°(I^-|AgI|Ag) = -0.15$ V. The value of standard solubility product of AgI would be about
(a) 7.9×10^{-17} (b) 8.9×10^{-15} (c) 8.9×10^{-13} (d) 8.9×10^{-11}

69. The expression connecting $E°_{cell}$ and $K°_{eq}$ of the reaction occurring in a galvanic cell is
(a) $\log K°_{eq} = nFE°/RT$ (b) $\log K°_{eq} = -nFE°/RT$ (c) $\ln K°_{eq} = nFE°/RT$ (d) $\ln K°_{eq} = -nFE°/RT$

70. For the cell, $Zn|Zn^{2+}(1\text{ M})||Sn^{2+}(1\text{ M})|Sn$, $E°_{cell} = 0.6264$ V. The value of $K°_{eq}$ for the reaction $Sn + Zn^{2+} \rightleftharpoons Zn + Sn^{2+}$ will be given by the expression
(a) $\log K°_{eq} = 21.23$ (b) $\log K°_{eq} = -21.23$ (c) $\ln K°_{eq} = 21.23$ (d) $\ln K°_{eq} = -21.23$

71. At 25 °C, $E°$ for the reaction $Cu^{2+} + Sn(s) \longrightarrow Cu(s) + Sn^{2+}$ is 0.48 V, the standard equilibrium constant for the reaction is
(a) 1.3×10^8 (b) 6.8×10^4 (c) 4.9×10^{20} (d) 1.8×10^{16}

72. The standard free energy change of the reaction $Cu^{2+} + Sn(s) \longrightarrow Cu(s) + Sn^{2+}$ (Given: $E° = 0.48$ V) is
(a) – 31.8 kJ mol^{-1} (b) – 62.1 kJ mol^{-1} (c) – 79.2 kJ mol^{-1} (d) – 92.64 kJ mol^{-1}

73. Hydrogen-oxygen fuel cells are used in spacecrafts to supply
(a) oxygen (b) hydrogen (c) water (d) illumination

74. In the titration of Fe^{2+} ions versus $Cr_2O_7^{2-}$ ions using diphenylamine as the internal indicator, phosphoric acid is added in the solution containing Fe^{2+} ions. The role of phosphoric acid is to
(a) lower the value of $E°(Fe^{3+}, Fe^{2+}|Pt)$
(b) raise the value of $E°(Fe^{3+}, Fe^{2+}|Pt)$
(c) form complex with ferrous ions
(d) to change the reduction potential involving the indicator

75. The emf of the cell $Zn | Zn^{2+}$ (0.001 M) $||$ Fe^{2+} (0.01 M) $|$ Fe at 298 K is 0.3495 V. The value of equilibrium constant for the cell reaction is
(a) exp (0.32/0.0295) (b) exp (0.3495/0.0295) (c) $10^{(0.32/0.0295)}$ (d) $10^{(-0.32/0.0295)}$

76. From the following data

$$2H^+(aq) + \tfrac{1}{2}O_2(g) + 2e^- \rightarrow H_2O(l); \qquad E° = 1.23\text{ V}$$
$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s); \qquad E° = -0.44\text{ V}$$

Show that $\Delta G°$ for $2Fe(s) + 4H^+(aq) + O_2(g) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$ is
(a) – 322.3 kJ mol^{-1} (b) – 483.5 kJ mol^{-1} (c) – 644.6 kJ mol^{-1} (d) 644.6 kJ mol^{-1} (2005)

77. Iron powder is added to 1.0 M solution of $CdCl_2$ at 298 K. The reaction occurring is $Cd^{2+}(aq) + Fe(s) \rightarrow Cd(s) + Fe^{2+}(aq)$. If the standard potential of a cell producing this reaction is 0.037 V, the concentrations of Cd^{2+} and Fe^{2+} ions in the above reaction at equilibrium respectively will be
(a) 0.05 M, 0.95 M (b) 0.95 M, 0.05 M (c) 0.40 M, 0.60 M (d) 0.60 M, 0.40 M

78. The ionic product of water at 298 K is 10^{-14} M^2. The standard emf of the cell producing the reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ will be

(a) 0.723 V (b) – 0.723 V (c) 0.82 V (d) – 0.82 V

79. Which of the following order regarding the standard potentials E_1°, E_2°, E_3° of half-cells Cl^- | AgCl | Ag, Br^- | Ag Br | Ag and I^- | AgI | Ag, respectively, is correct?

(a) $E_1^\circ > E_2^\circ > E_3^\circ$ (b) $E_1^\circ > E_3^\circ > E_2^\circ$ (c) $E_2^\circ > E_1^\circ > E_3^\circ$ (d) $E_2^\circ > E_3^\circ > E_1^\circ$

80. Which of the following order regarding the standard potentials E_1°, E_2° and E_3° of half-cells H^+ | H_2 | Pt, H^+, H_2O | O_2 | Pt and OH^-, H_2O | O_2 | Pt, respectively, is correct? Given: $E^\circ{}_2 > 0.826$ V.

(a) $E_1^\circ > E_2^\circ > E_3^\circ$ (b) $E_3^\circ > E_2^\circ > E_1^\circ$ (c) $E_2^\circ > E_1^\circ > E_3^\circ$ (d) $E_2^\circ > E_3^\circ > E_1^\circ$

Multiple Correct Choice Type

1. Which of the following statements are correct?
(a) Copper metal can reduce Fe^{2+} in acidic medium.
(b) The absolute value of standard electrode potential can be determined experimentally.
(c) In a Daniell cell, electrons flow from zinc electrode to copper electrode outside the cell.
(d) Cell voltage is an intensive quantity.

2. Which of the following statements are **not** correct?
(a) The standard potential of Cl^- | AgCl | Ag half-cell is related to that of Ag^+ | Ag through the expression

$$E^{o}_{Ag^+|Ag} = E^{o}_{Cl^-|AgCl|Ag} + \frac{RT}{F}\ln K^\circ_{sp}(AgCl)$$

(b) Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.
(c) The standard potential of hydrogen half-cell is zero at all conditions of temperature and pressure.
(d) The conventional value of zero of the standard hydrogen half-cell holds good at all temperatures.

3. Which of the following statements are correct?
(a) The cell potential is given as $E_{cell} = E_R - E_L$, where R and L are for right and left half-cells, respectively.
(b) In a galvanic cell, the half-cell with higher potential provides a reducing agent.
(c) In a galvanic cell, the half-cell with higher potential provides an oxidizing agent
(d) Once the cell is written, the electrode of left half-cell acts as the negative terminal.

4. Which of the following statements are correct?
(a) A positive half-cell potential implies that the element can lose its electrons more readily than hydrogen.
(b) The external cell in the electrolysis experiment acts as a galvanic cell.
(c) Silver is a noble metal but in the presence of I^-, S^{2-} or CN^-, it may behave as an active metal.
(d) A half-cell reaction is $A^{(x+n)+} + ne^- = A^{x+}$. It is possible to determine the value of n from the measurement of cell potentials.

5. Which of the following statements are **not** correct?
(a) The cell potential becomes half if the cell reaction is divided by 2 throughout.
(b) The dependence of electrode potential for the electrode M^{n+} | M with concentration under STP conditions is given by the expression:

$$E = E^\circ + \frac{(0.0519\ \mathrm{V})}{n}\log\left\{\left[M^{n+}\right]/\mathrm{mol\ L^{-1}}\right\}$$

(c) The cell potentials follow the order Cl^- | Cl_2 | Pt > Br^- | Br_2 | Pt > I^- | I_2 | Pt
(d) The cell potential $Na^+ + e^- \rightarrow Na$ is negative.

6. For a galvanic cell,
(a) anode is a negative terminal and cathode is a positive terminal.
(b) oxidation takes place at anode and reduction at cathode.
(c) electrons in the external wire move from anode to cathode.
(d) $E_{cell} = E_R - E_L$

7. The emf of the cell Pt | H_2(g) | HCl(c_1) | | HCl(c_2) | H_2(g) | Pt can be increased by

(a) decreasing c_2 (b) decreasing c_1 (c) increasing c_1 (d) increasing c_2

8. Which of the following statements is/are correct for a cell diagram?
(a) Left half-cell acts as anode. (b) Reduction reaction occurs at left half-cell.
(c) Anion in the solution moves towards left half-cell (d) Left half-cell acts as a negative terminal.

9. (a) Cations having more negative potential than – 0.828 V are reduced in preference to water.
(b) At the anode, the species having minimum reduction potential is formed from the oxidation of corresponding oxidizable species.
(c) In highly alkaline medium, the anodic process during the electrolytic process is

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

(d) Metallic anode more reactive than platinum tend to pass into the solution instead of O_2 being produced.

10. The half-cell reactions occurring in the cell

$$Pt \mid H_2(g) \mid NaOH \text{ saturated with } HgO \mid HgO(s) \mid Hg(l) \mid Pt$$

are
(a) $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$ (b) $Hg(l) + 2OH^- \rightarrow HgO(s) + H_2O(l) + 2e^-$
(c) $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ (d) $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Linked Comprehension Type

1. For the reaction $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$, it is given that $E°(MnO_4^-, H^+, Mn^{2+}|Pt) = 1.51$ V and $E°(Fe^{3+}, Fe^{2+}|Pt) = 0.77$ V.

(i) The contribution made to the standard emf of the cell by the oxidation half cell is
(a) 0.77 V (b) – 0.77 V (c) 1.51 V (d) – 1.51 V

(ii) The contribution made to the standard emf of the cell by the reduction half cell is
(a) 0.77 V (b) – 0.77 V (c) 1.51 V (d) – 1.51 V

(iii) Increasing pH of the solution causes
(a) increase in cell potential
(b) decrease in cell potential
(c) no change in cell potential
(d) change in cell potential which cannot be predicted.

2. For the reaction $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$, it is given that $E°(MnO_4^-, Mn^{2+}, H^+|Pt) = 1.51$ V and $E°(Fe^{3+}, Fe^{2+}|Pt) = 0.77$ V.

(i) The cell emf could be increased above the standard emf by
(a) increasing $[Mn^{2+}]$ (b) increasing $[Fe^{3+}]$
(c) decreasing $[MnO_4^-]$ (d) decreasing pH of the solution

(ii) Reducing $[Fe^{3+}]$ to 0.50 M keeping all other concentrations at unity, the emf of the cell will be changed by
(a) – 0.059 V (b) – 0.0178 V (c) 0.059 V (d) 0.0178 V

(iii) Reducing $[MnO_4^-]$ to 0.50 M keeping all other concentrations at unity, the emf of the cell will be changed by
(a) – 0.018 V (b) 0.0036 V (c) 0.018 V (d) – 0.0036 V

3. Given: $O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l)$: $E° = 1.229$ V

(i) The standard half-cell potential for the reaction $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- = H_2O$ will be
(a) (1.229 V)/2 (b) 2(1.229 V) (c) 1.229 V (d) cannot be predicted

(ii) The standard half-cell potential for $O_2(g) + 2H_2O(l) + 4e^- = 4OH^-(aq)$ will be
(a) 1.229 V (b) 0.401 V (c) – 0.401 V (d) 0.802 V

(iii) If $O_2(g)$ at 1 atm is passed through water, the cell potential for $O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l)$ would be
(a) 0.413 V (b) – 0.413 V (c) 0.816 V (d) – 0.816 V

4. For the reaction $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$, the following data are available.

$AgCl + e^- = Ag + Cl^-$; $E° = 0.222$ V

$Ag(NH_3)_2^+ + e^- = Ag + 2NH_3$; $E° = 0.373$ V

(i) The standard cell potential producing the given reaction is about
(a) 0.151 V (b) – 0.151 V (c) 0.595 V (d) – 0.595 V

(ii) The value of $\Delta_rG°$ for the given reaction is about
(a) 14.57 kJ mol^{-1} (b) 29.14 kJ mol^{-1} (c) – 14.57 kJ mol^{-1} (d) 57.42 kJ mol^{-1}

(iii) The equilibrium constant for the given reaction at 298 K is about
(a) 23.18 (b) 3.58×10^2 (c) 9.88×10^{-1} (d) 2.79×10^{-3}

5. It is given that

$$AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-: \qquad \Delta_rG° = 14.57 \text{ kJ mol}^{-1}$$

$$NH_4OH \rightarrow NH_3 = H_2O; \qquad \Delta_rG° = 10.04 \text{ kJ mol}^{-1}$$

(i) The value of $\Delta_rG°$ for $AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$ is about
(a) 24.61 kJ mol^{-1} (b) 39.14 kJ mol^{-1} (c) 34.65 kJ mol^{-1} (d) 49.22 kJ mol^{-1}

(ii) The value of K_{eq} for the reaction $AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$ is about
(a) 8.46×10^{-7} (b) 8.46×10^{-5} (c) 8.46×10^{-3} (d) 0.846

(iv) The cell potential producing the reaction $AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$ at 298 K is about
(a) 0.359 V (b) – 0.359 V (c) 0.179 V (d) – 0.179 V

6. Given: $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-; \quad E° = -\,0.151 \text{ V}$

$$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O; \qquad E° = -\,0.359 \text{ V}$$

$$\Delta_fG°(AgCl) = -\,109.79 \text{ kJ mol}^{-1}, \qquad \Delta_fG°(Cl^-) = -\,131.23 \text{ kJ mol}^{-1}$$

$$\Delta_fG°(NH_4OH) = -\,263.62 \text{ kJ mol}^{-1}, \quad \Delta_fG°(H_2O) = -\,237.13 \text{ kJ mol}^{-1}$$

$E°$ for $AgCl + e^- = Ag^+ + Cl^-$ is 0.222 V

(i) The value of $\Delta_fG°(AgNH_3)_2^+)$ is about
(a) – 3.11 kJ mol^{-1} (b) – 6.22 kJ mol^{-1} (c) 3.11 kJ mol^{-1} (d) 6.22 kJ mol^{-1}

(ii) The value of $\Delta_fG°(NH_3)$ is about
(a) – 16.45 kJ mol^{-1} (b) 16.45 kJ mol^{-1} (c) – 32. 90 kJ mol^{-1} (d) 32.90 kJ mol^{-1}

(iii) The standard potential for the reaction $Ag(NH_3)_2^+ + 2H_2O + e^- = Ag + 2NH_4OH$ is about
(a) – 0.581 V (b) 0.581 V (c) 0.290 V (d) – 0.290 V

7. Cupric ions form blue complex with ammonia: $Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$
It is given that $Cu^{2+} + 2e^- = Cu; \quad E° = 0.337$ V
$Cu(NH_3)_4^{2+} + 2e^- = Cu + 4NH_3; \quad E° = -\,0.12$ V

(i) The cell potential producing the reaction $Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$ is
(a) 0.217 V (b) 0.457 V (c) – 0.217 V (d) – 0.457 V

(ii) The value of $\Delta_rG°$ for the reaction $Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$ is
(a) – 44.1 kJ mol^{-1} (b) 44.1 kJ mol^{-1} (c) – 88.2 kJ mol^{-1} (d) 88.2 kJ mol^{-1}

(iii) The value of K_{eq}° for the reaction $Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$ at 298 K is about
(a) 2.9×10^{15} (b) 1.9×10^{-8} (c) 5.4×10^{7} (d) 3.5×10^{-16}

8. Given is the following data.

$$\begin{tikzcd}
Cu^{2+} \arrow[r, "E°"] \arrow[rr, bend right, "0.34\text{ V}"'] & Cu^{+} \arrow[r, "0.52\text{ V}"] & Cu
\end{tikzcd}$$

(i) What is the change in Gibbs function when Cu^{2+} is converted into Cu^+ under standard conditions?
(a) – 17370 J mol^{-1} (b) – 82990 J mol^{-1} (c) – 15440 J mol^{-1} (d) – 67550 J mol^{-1}

(ii) The value of $E°$ shown in the above diagram is
(a) 0.18 V (b) 0.86 V (c) 0.36 V (d) 0.16 V

(iii) Which of the following can show disproportionation reaction?
(a) Cu^{2+} (b) Cu^+ (c) Cu (d) none of these

9. Given is the following data in alkaline medium.

$$\begin{tikzcd}
BrO_3^- \arrow[r, "0.54\text{ V}"] \arrow[rr, bend right, "E°"'] & BrO^- \arrow[r, "0.17\text{ V}"] & Br^-
\end{tikzcd}$$

(i) What is the change in Gibbs function when BrO_3^- is converted into Br^- in alkaline medium under standard conditions.
(a) – (0.71 V)F (b) – (0.37 V)F (c) – (2.5 V)F (d) (0.37 V)F

(ii) The value $E°$ shown in the above diagram is
(a) – 0.417 V (b) 0.71 V (c) 0.37 V (d) 0.417 V

(iii) Which of the following can show disproportionation reaction in alkaline medium?
(a) BrO_3^- (b) BrO^- (c) Br^- (d) none of these

10. Given is the following data.

$$\begin{tikzcd}
Sn^{4+} \arrow[r, "0.15\ V"] \arrow[rr, bend right, "E°"'] & Sn^{2+} \arrow[r, "-0.14\ V"] & Sn
\end{tikzcd}$$

(i) The change in Gibbs function when Sn^{4+} is converted into Sn under standard conditions is
(a) (0.29 V)F (b) – (0.01 V)F (c) – (0.02 V)F (d) – (0.29 V)F

(ii) The value of $E°$ shown in the above diagram is
(a) 0.02 V (b) 0.01 V (c) 0.005 V (d) 0.26 V

(iii) Which of the following can show the phenomenon of disproportionation?
(a) Sn^{4+} (b) Sn^{2+} (c) Sn (d) none of these

11. Given is the Latimer diagram.

$$\begin{tikzcd}
ClO_4^- \arrow[r, "0.36\ V"] \arrow[rr, bend right, "E°"'] & ClO_3^- \arrow[r, "0.33\ V"] & ClO_2^-
\end{tikzcd}$$

Based on this information, answer the following three questions.

(i) The value of $E°$ is
(a) 0.345 V (b) – 0.03 V (c) 0.69 V (d) 0.172 V

(ii) The cell potential producing the reaction $2ClO_3^- \rightleftharpoons ClO_4^- + ClO_2^-$ is
(a) 0.345 V (b) – 0.03 V (c) 0.69 V (d) 0.172 V

(iii) The ratio of $[ClO_4^-]/[ClO_3^-]$ in the reaction $2ClO_3^- \rightleftharpoons ClO_4^- + ClO_2^-$ when the reaction is initiated with 1.0 M ClO_3^- is
(a) 0.13 (b) 0.23 (c) 0.32 (d) 0.41

12. Tollens reagent (ammoniacal solution of silver nitrate) is used to test aldehydes. The following data are available

$$Ag^+(aq) + e^- \rightarrow Ag; \qquad E_1^\circ = 0.80\ V$$

$$C_6H_{12}O_7 + 2H^+ + 2e^- \rightarrow C_6H_{12}O_6 + H_2O; \qquad E_2^\circ = 0.05\ V$$

$$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag(s) + 2NH_3; \qquad E_3^\circ = 0.373\ V$$

Based on this information, answer the following three questions

(i) The value of $\log K_{eq}^\circ$ for the reaction $C_6H_{12}O_6 + 2Ag^+ + H_2O = C_6H_{12}O_7 + 2H^+ + Ag$ is
(a) 12.7 (b) 25.4 (c) 29.27 (d) 58.54

(ii) The use of NH_3 makes the pH of solution equal to 11. This causes
(a) decrease in the value of E_2 (b) increase in the value of E_2
(c) increase in the value of E_1 (d) increase in the value of E_1°

(iii) Ammonia is used in this reaction rather than any other base. This is due to the fact that
(a) $[Ag(NH_3)_2]^+$ is a weaker oxidising agent than Ag^+
(b) Ammonia prevents the decomposition of gluconic acid
(c) Silver precipitates gluconic acid as its silver salt.
(d) the standard reduction potential of $[Ag(NH_3)_2]^+$ is changed.

13. Redox reactions play a pivot role in chemistry and biology. The values of standard redox potential ($E°$) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E°$ (with respect to normal hydrogen electrode) values. Using this data, obtain the correct explanations to the following three questions.

$I_2 + 2e^- \rightarrow 2I^-$; $E° = 0.54$ V $Fe^{3+} + e \rightarrow Fe^{2+}$; $E° = 0.77$ V

$Cl_2 + 2e^- \rightarrow 2Cl^-$; $E° = 1.36$ V $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$; $E° = 1.23$ V

$Mn^{3+} + e^- \rightarrow Mn^{2+}$; $E° = 1.50$ V

(i) Among the following, identify the correct statement.
(a) Chloride ion is oxidized by O_2 (b) Fe^{2+} is oxidized by iodine
(c) Iodide ion is oxidized by chlorine (d) Mn^{2+} is oxidized by chlorine

(ii) While Fe^{3+} is stable, Mn^{3+} is not stable in acidic solution because
(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidizes H_2O to O_2
(d) Mn^{3+} oxidizes H_2O to O_2

(iii) Sodium fusion extract, obtained from aniline, on treatment with iron(II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of
(a) $Fe_4[Fe(CN)_6]$ (b) $Fe_3[Fe(CN)_6]_2$ (c) $Fe_3[Fe(FCN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

14. Questions (i) to (xviii) given below refer to a galvanic cell which makes use of the following reaction at 298 K.

$$Cr_2O_7^{2-} + 14H^+ + 6\,Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Given: $E°(Cr_2O_7^{2-}, H^+, Cr^{3+} \mid Pt) = 1.33$ V; $E°(Fe^{3+}, Fe^{2+} \mid Pt) = 0.77$ V

(i) The contribution made to the standard emf of the cell by oxidation half-cell is
(a) 0.77 V (b) − 0.77 V (b) 1.33 V (d) − 1.33 V

(ii) The contribution made to the standard emf of the cell by reduction half-cell is
(a) 0.77 V (b) − 0.77 V (c) 1.33 V (d) − 1.33 V

(iii) The standard emf of the cell is
(a) (1.33 + 0.77) V (b) (1.33 − 0.77) V (c) − (1.33 + 0.77) V (d) (−1.33 + 0.77) V

(iv) The cell emf could be increased above the standard emf by
(a) increasing $[Cr^{3+}]$ (b) increasing $[Fe^{3+}]$ (c) decreasing $[Cr_2O_7^{2-}]$ (d) decreasing the pH

(v) The anode of the cell might be
(a) Cr (b) Fe (c) Pt (d) diamond

(vi) The cathode of the cell might be
(a) Cr (b) Fe (c) Pt (d) diamond

(vii) Within the cell, it is important to prevent mixing or direct contact of
(a) $Cr_2O_7^{2-}$, Fe^{2+} (b) Cr^{3+}, Fe^{2+} (c) H_3O^+, Fe^{3+} (d) $Cr_2O_7^{2-}$, Cr^{3+}

(viii) The cell emf depends on
(a) size of anode (b) size of cathode (c) volume of solution (d) temperature

(ix) The cell emf is independent of
(a) temperature (b) size of cell (c) $[Cr_2O_7^{2-}]$ (d) $[Cr^{3+}]$

(x) Upon discharge of the cell for 80 min at one ampere, the anode was found to have decreased in mass by
(a) 5.4 g (b) 10.8 g (c) 8.2 g (d) zero

(xi) Reducing $[Fe^{3+}]$ to 0.50 M keeping all other concentrations at unity, the emf of the cell will be changed by
(a) − 0.059 V (b) − 0.0178 V (c) + 0.059 V (d) + 0.0178 V

(xii) Increasing $[Fe^{3+}]$ to 2.0 M keeping all other concentrations at unity, the emf of the cell is changed by
(a) −0.059 V (b) −0.0178 V (c) +0.059 V (d) + 0.0178 V

(xiii) Increasing $[H_3O^+]$ to 2.0 M, keeping all other concentrations at unity, will change the cell emf by
(a) 0.0414 V (b) − 0.0414 V (c) 0.0207 V (d) − 0.0207 V

(xiv) If $[Cr_2O_7^{2-}] = 1.0$ M, $[Cr^{3+}] = 0.5$ M, $[Fe^{2+}] = 0.5$ M, $[Fe^{3+}] = 2.0$ M and $[H_3O^+] = 2.0$ M, then the cell emf at 298 K would be
(a) 0.678 V (b) −0.678 V (c) 0.572 V (d) + 0.548 V

(xv) Reducing $[Cr^{3+}]$ to 0.50 M, keeping all other concentrations at unity, the emf of the cell would be changed by
(a) 5.92 mV (b) 2.96 mV (c) − 5.92 mV (d) − 2.96 mV

(xvi) The strongest oxidant is
(a) $Cr_2O_7^{2-}$ (b) Fe^{2+} (c) Cr^{3+} (d) Fe^{3+}

(xvii) The strongest reductant is

(a) $Cr_2O_7^{2-}$ (b) Fe^{2+} (c) Cr^{3+} (d) Fe^{3+}

15. Questions (i) to (xv) given below refer to a galvanic cell which makes use of the following reactions at 298 K:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Given: $E°(MnO_4^-, Mn^{2+}, H^+|Pt) = 1.51$ V and $E°(Fe^{3+}, Fe^{2+}|Pt) = 0.77$ V.

(i) The contribution made to the standard emf of the cell by the oxidation half-reaction, i.e. oxidation potential is

(a) 0.77 V (b) – 0.77 V (c) 1.51 V (d) – 1.51 V

(ii) The contribution made to the standard emf of the cell by the reduction half-reaction is

(a) 0.77 V (b) – 0.77 V (c) 1.51 V (d) – 1.51 V

(iii) The standard emf of the cell is

(a) 2.28 V (b) – 2.28 V (c) 0.74 V (d) – 0.74 V

(iv) The cell emf could be increased above the standard emf by

(a) increasing $[Mn^{2+}]$ (b) decreasing $[MnO_4^-]$ (c) increasing $[Fe^{3+}]$ (d) decreasing the pH

(v) The anode of the cell might be

(a) Mn (b) Fe (c) Pt (d) Hydrogen

(vi) The cathode of the cell might be made of

(a) Mn (b) Fe (c) Pt (d) Hydrogen

(vii) Within the cell it is important to prevent mixing or direct contact of

(a) MnO_4^-, Fe^{2+} (b) Mn^{2+}, Fe^{2+} (c) H_3O^+, Fe^{3+} (d) MnO_4^-, Mn^{2+}

(viii) The cell emf depends on

(a) temperature (b) the size of anode

(c) the size of cathode (d) volume of the electrolytic solution

(ix) The cell emf is independent of

(a) temperature (b) the size of the cell (c) $[MnO_4^-]$ (d) $[Mn^{2+}]$

(x) Upon discharge of the cell for 80 min at one ampere, the anode was found to have decreased in mass by

(a) 5.4 g (b) 10.8 g (c) zero (d) 8.2 g

(xi) Decreasing $[Fe^{3+}]$ to 0.50 M, keeping all other concentrations to unity, the emf of the cell will be increased by

(a) 0.059 V (b) 0.0116 V (c) 0.0178 V (d) 0.089 V

(xii) Increasing $[Fe^{3+}]$ to 2.0 M keeping all other concentrations at unity will decrease the cell emf by

(a) 0.301 V (b) 0.059 V (c) 0.0116 V (d) 0.0178 V

(xiii) Increasing $[H_3O^+]$ to 2.0 M keeping all other concentrations at unity will increase the cell emf by

(a) 0.142 V (b) 0.0178 V (c) 0.028 V (d) 0.059 V

(xiv) If $[MnO_4^-] = 1.0$ M, $[Mn^{2+}] = 0.5$ M, $[Fe^{2+}] = 0.5$ M, $[Fe^{3+}] = 2.0$ M and $[H_3O^+] = 2.0$ M, then the cell emf at 298 K would be

(a) 0.733 V (b) – 0.733 V (c) 0.747 V (d) – 0.747 V

(xv) Decreasing $[Mn^{2+}]$ to 0.50 M, keeping all other concentrations at unity, the emf of the cell will be increased by

(a) 0.018 V (b) 0.059 V (c) 3.55×10^{-3} V (d) 0.012 V

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explantation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	**Statement–2**
1.	Ionic molar conductivity at infinite dilution of Na^+ ion is smaller than that of K^+ ion.	Na^+ ion is more extensively hydrated as compared to K^+ ion.
2.	The ions Zn^{2+}, Na^+ and Mg^{2+} are not reducible with hydrogen gas under standard conditions.	The standard potential of hydrogen $H^+ \mid H_2$ is less than that of $M^{2+} \mid M$
3.	The reduction potential of mercurous/mercury decreases by 0.0295 V on diluting the solution ten times at 298 K.	The mercurous ion in solution exists as Hg_2^{2+} ion and not as Hg^+ ion.
4.	In the titration between Fe^{2+} ions versus $Cr_2O_7^{2-}$ ions, diphenylbenzene is used as the indicator in the presence of phosphoric acid.	Phosphoric acid helps changing the potential of ferric-ferrous system.
5.	Potentiometric titrations involving acid and base can be carried out by using quinhydrone electrode as the reference electrode.	Quinhydrone is equimolar mixture of quinone (Q) and hydroquinone (H_2Q). In solution, it exists as $Q + 2H^+ \rightleftharpoons H_2Q$
6.	Potential of Calomel electrode is sensitive to the concentration of Cl^- in solution.	Calomel electrode is $Cl^-(aq) \mid Hg_2Cl_2(s) \mid Hg(Pt)$
7.	Oxidation and reduction reactions occur at anode and cathode, respectively, in electrolytic as well as galvanic cell.	The sign of anode and cathode are identical in electrolytic as well as galvanic cell.
8.	In the cell diagram, the left half cell acts as anode.	The reduction reaction occurs at anode of a galvanic cell.
9.	The cell potential is obtained by by subtracting half-cell potential of cathode from that of anode.	Anode involves oxidation and cathode involves reduction.
10.	The half-cell potential of $Na^+(aq) \mid Na$ is negative while that of $Cl^-(aq) \mid Cl_2(g) \mid Pt$ is positive.	The half-cell potential of an electrode is a measure of reduction tendency of the reaction occurring at this electrode relative to that occurring at $H^+(aq) \mid H_2(g) \mid Pt$ half cell. The latter acts as reference half-cell whose potential is taken to be zero at standard conditions.
11.	The compounds of active metals such as Zn, Na and Mg are not reduced by hydrogen but the metal itself oxidiable by H^+ to yield H_2.	The cell potential of a cell producing the reaction $M^{n+} + \frac{n}{2} H_2 \rightarrow M + nH^+$ is negative because the half-cell potential $M^{n+} + ne^- \rightarrow M$ is negative.
12.	The entropy of reaction occurring in a cell can be determined by cell potentials at different temperatures.	ΔS of the reaction is given by the expression $\Delta S = nF\,(\partial E/\partial T)_p$
13.	The glass electrode is sensitive to $[H^+]$ in the solution.	The expression of cell potential of glass electrode is given by $E_{glass} = E^\circ_{glass} + \frac{RT}{F}$ pH

Matrix Match Type

1. A few characteristics of an electrolytic cell are given in Column I. Match correctly each of the these entries with those given in Column II

Column I	**Column II**
(a) Anode	(p) Positive electrode
(b) Cathode	(q) Negative electrode
(c) Cations move towards	(r) Oxidation reaction
(d) Anion move towards	(s) Attached to the negative terminal of the external cell
	(u) Attached to the positive terminal of the external cell

2. A few characteristics of a galvanic cell are given in Column I. Match correctly each of these entries with those given in Column II.

Column I	**Column II**
(a) Anode	(p) Positive electrode
(b) Cathode	(q) Negative electrode
(c) Cations move towards	(r) Oxidation reaction
(d) Anions move towards	(s) Reduction reaction

3. Column I lists some reduction reactions and Column II lists their standard reduction potentials. Match the correct entries from these two columns.

Column I	**Column II**
(a) $\frac{1}{2}F_2 + e^- \rightarrow F^-$	(p) 1.09 V
(b) $\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$	(q) 0.54 V
(c) $\frac{1}{2}Br_2 + e^- \rightarrow Br^-$	(r) 1.36 V
(d) $\frac{1}{2}I_2 + e^- \rightarrow I^-$	(s) 2.87 V

4. Column I lists some reduction reactions and Column II lists their standard reduction potentials. Match the correct entries from these two Columns

Column I	**Columns II**
(a) $AgI + e^- = Ag + I^-$	(p) 0.80 V
(b) $AgBr + e^- = Ag + Br^-$	(q) – 0.15
(c) $AgCl + e^- = Ag + Cl^-$	(r) 0.09 V
(d) $Ag^+ + e^- = Ag$	(s) 0.22 V

5. Column I lists some reduction reactions and Column II lists their standard reduction potentials. Match the correct entries from these two Columns.

Column I	**Column II**
(a) $Na^+ + e^- \rightarrow Na$	(p) 1.23 V
(b) $H^+ + e^- \rightarrow \frac{1}{2}H_2$	(q) 0.40 V
(c) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	(r) 0.0 V
(d) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	(s) – 2.71 V

ANSWER

Straight Objective Type

1. (b)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (d)
8. (b)	**9.** (d)	**10.** (a)	**11.** (b)	**12.** (a)	**13.** (a)	**14.** (a)
15. (a)	**16.** (c)	**17.** (b)	**18.** (a)	**19.** (a)	**20.** (b)	**21.** (a)
22. (d)	**23.** (c)	**24.** (a)	**25.** (c)	**26.** (b)	**27.** (a)	**28.** (a)
29. (b)	**30.** (a)	**31.** (d)	**32.** (a)	**33.** (a)	**34.** (b)	**35.** (c)
36. (d)	**37.** (b)	**38.** (a)	**39.** (c)	**40.** (b)	**41.** (c)	**42.** (c)

43. (b) **44.** (a) **45.** (c) **46.** (b) **47.** (d) **48.** (b) **49.** (d)
50. (b) **51.** (b) **52.** (b) **53.** (b) **54.** (d) **55.** (c) **56.** (a)
57. (b) **58.** (d) **59.** (c) **60.** (c) **61.** (b) **62.** (c) **63.** (d)
64. (a) **65.** (c) **66.** (d) **67.** (d) **68.** (a) **69.** (c) **70.** (b)
71. (d) **72.** (d) **73.** (c) **74.** (a) **75.** (c) **76.** (c) **77.** (a)
78. (b) **79.** (a) **80.** (d)

Multiple Correct Choice Type

1. (c), (d) **2.** (a), (b), (c), (d) **3.** (a), (c), (d)
4. (b), (c), (d) **5.** (a), (b) **6.** (a), (b), (c), (d)
7. (b), (d) **8.** (a), (c), (d) **9.** (a), (b), (c), (d)
10. (a), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (c) **(iii)** (b) **2.** **(i)** (d) **(ii)** (d) **(iii)** (d)
3. **(i)** (c) **(ii)** (b) **(iii)** (c) **4.** **(i)** (b) **(ii)** (a) **(iii)** (d)
5. **(i)** (c) **(ii)** (a) **(iii)** (b) **6.** **(i)** (c) **(ii)** (a) **(iii)** (b)
7. **(i)** (b) **(ii)** (c) **(iii)** (a) **8.** **(i)** (c) **(ii)** (d) **(iii)** (b)
9. **(i)** (c) **(ii)** (d) **(iii)** (d) **10.** **(i)** (c) **(ii)** (c) **(iii)** (d)
11. **(i)** (a) **(ii)** (b) **(iii)** (c) **12.** **(i)** (b) **(ii)** (a) **(iii)** (a)
13. **(i)** (c) **(ii)** (d) **(iii)** (a)
14. **(i)** (b) **(ii)** (c) **(iii)** (b) **(iv)** (d) **(v)** (c) **(vi)** (c)
(vii) (a) **(viii)** (d) **(ix)** (b) **(x)** (d) **(xi)** (d) **(xii)** (b)
(xiii) (a) **(xiv)** (c) **(xv)** (a) **(xvi)** (a) **(xvii)** (b)
15. **(i)** (b) **(ii)** (c) **(iii)** (c) **(iv)** (d) **(v)** (c) **(vi)** (c)
(vii) (a) **(viii)** (a) **(ix)** (b) **(x)** (c) **(xi)** (c) **(xii)** (d)
(xiii) (c) **(xiv)** (a) **(xv)** (c)

Assertion and Reason Type

1. (a) **2.** (c) **3.** (a) **4.** (b) **5.** (b) **6.** (b) **7.** (c)
8. (c) **9.** (d) **10.** (a) **11.** (a) **12.** (a) **13.** (c)

Matrix Match Type

1. (a) – (p), (r), (u) (b) – (q), (s), (t) (c) – (q) (d) – (p)
2. (a) – (q), (r) (b) – (p), (s) (c) – (p) (d) – (q)
3. (a) – (s) (b) – (r) (c) – (p) (d) – (q)
4. (a) – (q) (b) – (r) (c) – (s) (d) – (p)
5. (a) – (s) (b) – (r) (c) – (q) (d) – (p)

Hints and Solutions

Straight Objective Type

1. Left electrode is anode (negative terminal) and the reaction occurring here is the oxidation reaction.
2. Cathode is the positive terminal in a galvanic cell and is the negative terminal in an electrolytic cell. The reaction occurring at cathode is the reduction reaction in either of the cells.
3. In galvanic cell, the right electrode is cathode and carries positive sign.
4. Cathode is negative terminal in an electrolytic cell whereas it is positive terminal in a galvanic cell.
5. Oxidation occurs at anode in both galvanic and electrolytic cells.
6. Cations move towards cathode in both galvanic and electrolytic cells.
7. Anions move towards anode in both galvanic and electrolytic cells.

8. The electrode with more negative potential constitutes negative terminal (i.e. anode).

9. Electrons are given out in the external circuit from the anode because of oxidation reaction occurring at this electrode.

10. More negative potential will constitute negative terminal (i.e. anode) of the galvanic cell.

11. Electrode of more negative terminal will constitute negative terminal, i.e., anode.

17. Quantity of electricity passed = $9.65 \times 60 \times 60$ C

$$\text{Amount of electrons withdrawn} = \frac{9.65 \times 60 \times 60}{96500} \text{ mol}$$

$$\text{Amount of Zn oxidized or Cu}^{2+} \text{ reduced} = \frac{60 \times 60}{2 \times 10000} \text{ mol}$$

$$\text{Mass of Zn lost} = \frac{65.4 \times 60 \times 60}{2 \times 10000} \text{ g} = 11.77 \text{ g} \quad \text{and} \quad \text{Mass of Cu gain} = \frac{63.5 \times 60 \times 60}{2 \times 10000} \text{ g} = 11.43 \text{ g}$$

18. More negative the standard potential, least the reduction tendency of the ion. The corresponding atom has largest oxidation tendency and thus is a strong reducing agent. In the present case, Zn is the strongest reducing agent.

19. A positive potential implies that the given ion has a larger tendency to reduce as compared to H^+. Thus, Cu^{2+} ion can be reduced by H_2(g).

20. More negative the $E°$ value, larger the reducing power of the metal. In present case, K > Mg > Cr > Ag.

21. From the first reaction, we conclude $E_{\mathrm{Y^-|Y_2}} > E_{\mathrm{X^-|X_2}}$

From the second reaction, we conclude $E_{\mathrm{W^-|W_2}} > E_{\mathrm{Y^-|Y_2}}$

From the third reaction, we conclude $E_{\mathrm{X^-|X_2}} > E_{\mathrm{Z^-|Z_2}}$

Hence, $E_{\mathrm{W^-|W_2}} > E_{\mathrm{Y^-|Y_2}} > E_{\mathrm{X^-|X_2}} > E_{\mathrm{Z^-|Z_2}}$

22. If $E(\mathrm{M}^{n+}|\mathrm{M})$ is negative, it implies that M^{n+} has a lesser tendency to reduce as compared to H^+. In this case H^+ is reducible and M is oxidiazble.

If E $(\mathrm{M}^{n+} | \mathrm{M})$ is positive, it implies that M^{n+} has a larger tendency to reduce and H_2 is oxidizable. For a galvanic cell, the electrode with more negative potential serves as anode and the electrode with less negative potential or positive potential acts as cathode. Active metals have negative potentials and thus are not reducible by H_2. Noble metals have positive potentials and thus are reducible by H_2.

23. Fe^{3+} is more easily reducible than Mg^{2+} Thus, Mg will have larger reducing capability and thus will act as the best reducing agent.

24. Since $E^{\circ}_{\mathrm{Pb^{2+}|Pb}}$ is less negative, Pb^{2+} has more tendency to reduce as compared to Fe^{2+}. Hence Pb^{2+} will be reduced to Pb and Fe will be oxidised to Fe^{2+}. Thus, more of Pb and Fe^{2+} are formed.

25. Electrolysis will occur if $E_{\text{ext}} > E_{\text{galvanic}}$. The value of E_{galvanic} (in which metal is oxidized) is $E_{\mathrm{H_2O|O_2|Pt}} - E_{\mathrm{M^{n+}|M}}$. Hence, E_{ext} will be reached in the order Ag, Hg and Cu. Hence, the sequence of deposition of metals on the cathode will be Ag, Hg and Cu. Before Mg is deposited, H_2 gas will be obtained by the reduction of H_2O.

26. The standard potential of hydrogen electrode is assumed to be zero at all temperatures.

27. More negative the standard potential, least the tendency of the cation to be reduced. The corresponding atom has larger tendency for oxidation and hence larger reducing power.

28. The reduction tendencies is Z > Y > X. Hence, Y can oxidise X and not Z.

29. For the given cell, the reaction is

$$\begin{array}{l} \mathrm{X + e^- \rightarrow X^-} \\ \underline{\mathrm{M \rightarrow M^+ + e^-}} \\ \mathrm{X + M \rightarrow X^- + M^+} \end{array}$$

The cell potential is $E = E°(\mathrm{X|X^-}) - E°(\mathrm{M^+|M}) = 0.33 \text{ V} - 0.44 \text{ V} = -0.11 \text{ V}$

Since the cell potential is negative, the cell reaction is not spontaneous.

30. More positive potential will constitute positive terminal (i.e. cathode) and the ions will be reduced here. So Ag^+ is reduced by H_2 gas.

31. Since $E°(\mathrm{Fe^{3+}, Fe^{2+}|Pt})$, $E°(\mathrm{Cu^{2+}|Cu})$ and $E°(\mathrm{Ag^+|Ag})$ are greater than $E°(\mathrm{Co^{2+}|Co})$, Co metal will be able to reduce Fe^{3+} to Fe^{2+}, Cu^{2+} to Cu and Ag^+ to Ag.

32. The smaller the value of reduction potential, lesser the reduction tendency of the ion and larger the oxidation tendency of the corresponding metal. Larger oxidation tendency implies stronger reducing agent.

33. Cu^{2+} has larger tendency to reduce than H^+ and Sn^{2+} has lesser tendency to reduce than H^+.
Hence, Cu^{2+} ion can be reduced by $H_2(g)$.

34. For depositing metal ions, the emf of external battery must exceed the reduction potential.

36. $E°(Cu^{2+}|Cu) > E°(Fe^{2+}|Fe)$. The reaction $Fe^{2+} + Cu \rightarrow Fe + Cu^{2+}$ is not feasible.

37. Larger the reduction potential, larger the oxidation tendency of the ion being reduced. Hence, the oxidizing tendency follows the order $Pb^{4+} > Hg^{2+} > Sn^{4+}$.
Lesser the reduction potential, larger the reduction tendency of the ion formed in the reduction reaction. Hence, the reducing tendency follows the order $Sn^{2+} > Hg^{2+} > Pb^{2+}$.

39. The cell reaction giving $E°_{\text{cell}}$ positive is $Hg_2^{2+} + Sn \rightarrow 2Hg + Sn^{2+}$. $E°_{\text{cell}} = E°_{Hg_2^{2+}|Hg} - E°_{Sn^{2+}|Sn}$
From this, it follows that Hg_2^{2+} can oxidize Sn to Sn^{2+}.

40. More positive potential means more easily ion is reducible and more difficult is the oxidation of the corresponding atom. Reducing power of the metal means more easily the metal should be oxidizable.

41. H_2 is oxidized to H^+ and thus it will occur at anode, i.e., left-side electrode $Pt\,|H_2(g)|\,HCl(aq)$
AgCl is reduced to Ag and thus it will occur at cathode, i.e., right-side electrode $HCl\,(aq)|AgCl(s)|\,Ag(s)$. Hence, the cell with these reactions is $Pt \mid H_2(g) \mid HCl(aq) \mid AgCl(s) \mid Ag$

42. In the given reaction Zn is oxidised to Zn^{2+} and Fe^{2+} is reduced to Fe. Hence,

$$E_{\text{cell}} = E°_{Fe^{2+}|Fe} - E°_{Zn^{2+}|Zn} = -0.41\text{ V} - (-0.76\text{ V}) = 0.35\text{ V}.$$

45. For the reaction $H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2(g)$, the standard potential is given by $E = -\dfrac{RT}{nF} \ln \dfrac{(p_{H_2}/\text{bar})^{1/2}}{\left([H^+]/\text{mol dm}^{-3}\right)/c°}$
E will be negative if the numerical value of $p_{H_2}^{1/2}/[H^+] > 1$.

46. For the reaction $Cu^{2+} + 2e^- \rightarrow Cu$, Nernst equation is $E = E° - \dfrac{RT}{2F} \ln \dfrac{1}{[Cu^{2+}]/c°}$
If the solution is diluted 100 times, then we have

$$E_2 - E_1 = -\frac{RT}{2F} \ln \frac{[Cu^{2+}]}{(0.01)[Cu^{2+}]} = +\frac{RT}{2F} \ln (0.01) = -\frac{2 \times 0.059\text{ V}}{2} = -0.059\text{ V}$$

47. We have $E = -\dfrac{RT}{F} \ln \dfrac{\left(p_{H_2}^{1/2}/\text{bar}\right)}{\left([H^+]/\text{mol dm}^{-3}\right)}$

Since $E = 0$, we must have $(p_{H_2}/\text{bar})^{1/2}/([H^+]/\text{mol dm}^{-3}) = 1$. Thus $\dfrac{p_{H_2}}{\text{bar}} = \dfrac{[H^+]^2}{(\text{mol dm}^{-3})^2} = (10^{-7})^2$. Hence $p_{H_2} = 10^{-14}$ bar.

48. $E = -\dfrac{RT}{F} \ln \dfrac{\left(p_{H_2}/\text{bar}\right)^{1/2}}{[H^+]/\text{mol dm}^{-3}} = -\,(0.059\text{ V}) \log \dfrac{1}{(10^{-7})} = -7 \times 0.059\text{ V} = -0.413\text{ V}$

49. The half cell reaction is $H^+ + e^- \rightarrow \dfrac{1}{2}H_2$. Its potential is given by $E = -\,(RT\,/\,nF) \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{[H^+]/\text{mol dm}^{-3}}$.
In 1 M NaOH, $[H^+] = K_w/[OH^-] = 10^{-14}\text{ M}^2 / 1\text{ M} = 10^{-14}$ M. Hence, at 25 °C and 1 atm pressure $E = -\,(0.059\text{ V}) \log (1\,/\,10^{-14}) = -\,0.059 \times 14\text{ V} = -\,0.826\text{ V}$

50. For the reaction $H^+ + e^- \rightarrow (1/2)\,H_2$, we have $E = -\dfrac{RT}{F} \ln \dfrac{(p_{H_2}\,/\,\text{atm})^{1/2}}{([H^+]\,/\,\text{mol L}^{-1})}$ For $E = 0$, $p_{H_2} = \dfrac{[H^+]^2}{M^2}$ atm $= 10^{-14}$ atm

51. $E = -\dfrac{RT}{nF} \ln \dfrac{(p_{H_2}\,/\,\text{atm})^{1/2}}{[H^+]\,/\,\text{mol}^{-1}} = -\,(0.059\text{ V}) \log \left(\dfrac{1}{10^{-7}}\right) = +\,0.413\text{ V}$

52. $E_{H^+|H_2|Pt} = -\dfrac{RT}{F} \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{[H^+]/\text{mol dm}^{-3}}$. The combination $p(H_2) = 1$ atm and $[H^+] = 2$ M will make $E_{H^+|H_2|Pt}$ positive

53. $E_1 = E^\circ - \dfrac{RT}{2F}\ln\dfrac{1}{[\mathrm{Cu}^{2+}]_1/c^\circ}$

$$E_2 = E^\circ - \frac{RT}{2F}\ln\frac{1}{[\mathrm{Cu}^{2+}]_2/c^\circ} = E^\circ - \frac{RT}{2F}\ln\frac{1}{0.1[\mathrm{Cu}^{2+}]_1/c^\circ}$$

$$E_2 - E_1 = -\frac{RT}{2F}\ln\frac{1}{0.1[\mathrm{Cu}^{2+}]_1/c^\circ} + \frac{RT}{2F}\ln\frac{1}{[\mathrm{Cu}^{2+}]_1/c^\circ} = \frac{RT}{2F}\ln 0.1 = -\frac{2.303\,RT}{2F} = \frac{0.059\ \mathrm{V}}{2}$$

$$= -0.0295\ \mathrm{V} = -29.5\ \mathrm{mV}$$

55. The reaction to be considered is $2\mathrm{Hg}^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Hg}_2^{2+}$. Its Nernst equation is

$$E_1 = E^\circ - \frac{RT}{2F}\ln\frac{[\mathrm{Hg}_2^{2+}]/c^\circ}{[\mathrm{Hg}^{2+}]^2([\mathrm{Hg}^{2+}]/c^\circ)^2}$$

On diluting the concentration of $\mathrm{Hg_2Cl_2}$ ten times, we will have

$$E_2 = E^\circ - \frac{RT}{2F}\ln\frac{(0.1)[\mathrm{Hg}_2^{2+}]/c^\circ}{([\mathrm{Hg}^{2+}]^2/c^\circ)^2}$$

Hence $\quad E_2 - E_1 = \dfrac{RT}{2F}\ln(0.1) = \dfrac{RT}{2F} = 0.02915\ \mathrm{V}$

56. The reaction to be considered is $\mathrm{Hg_2Cl_2(s)} + 2\mathrm{e}^- \longrightarrow 2\mathrm{Hg(s)} + 2\mathrm{Cl^-(aq)}$. Its Nernst equation is

$$E_1 = E^\circ - \frac{RT}{2F}\ln([\mathrm{Cl}^-]/c^\circ)^2$$

On diluting the concentration of Cl^- by ten times, we have

$$E_2 = E^\circ - \frac{RT}{2F}\ln(0.01)([\mathrm{Cl}^-]/c^\circ)^2$$

Hence $\quad E_2 - E_1 = -\dfrac{RT}{2F}\ln(0.01) = \dfrac{2.303\,RT}{F} = 0.059\ \mathrm{V}$

58.

$$\begin{array}{ll}
\mathrm{Fe}^{3+} + 3\mathrm{e}^- \longrightarrow \mathrm{Fe} & \Delta G_1^\circ = -(3)\,F(-0.36\ \mathrm{V}) \\
\underline{\mathrm{Fe}^{2+} + 2\mathrm{e}- \longrightarrow \mathrm{Fe}} & \underline{\Delta G_2^\circ = -(2)\,F(-0.439\ \mathrm{V})} \\
\mathrm{Fe}^{3+} + \mathrm{e}^- \longrightarrow \mathrm{Fe}^{2+} & \Delta G = \Delta G_1^\circ - \Delta G_2^\circ = -F[3(-0.36 - 2(-0.439)]\ \mathrm{V}
\end{array}$$

Hence, $\quad E^\circ = [3\,(-0.36) - 2\,(-0.439)]\mathrm{V}$

59. Since $\Delta G^\circ = -nFE^\circ$, we have

$$\begin{array}{ll}
\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu} & \Delta G_1^\circ = -\,(2)(F)(0.337\ \mathrm{V}) \\
\underline{\mathrm{Cu}^{2+} + \mathrm{e}^- \rightarrow \mathrm{Cu}^+} & \Delta G_2^\circ = -\,(1)(F)(0.153\ \mathrm{V}) \\
\mathrm{Cu}^+ + \mathrm{e}^- \rightarrow \mathrm{Cu} & \Delta G^\circ = \Delta G_1^\circ - \Delta G_2^\circ = -\,(4)\ F\{(2\times 0.337 - 0.153)\ \mathrm{V}\}
\end{array}$$

$$E_{\mathrm{Cu^+|Cu}} = 2\times 0.337\ \mathrm{V} - 0.153\ \mathrm{V} = 0.521\ \mathrm{V}$$

60. The reactions are:

(1) $\mathrm{HNO_2} + \mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{NO} + \mathrm{H_2O}$; $\quad \Delta G_1^\circ = -\,FE_1^\circ$

(2) $2\mathrm{NO} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{N_2O} + \mathrm{H_2O}$; $\quad \Delta G_2^\circ = -\,2FE_2^\circ$

(3) $2\mathrm{HNO_2} + 4\mathrm{H}^+ + 4\mathrm{e}^- \rightarrow \mathrm{N_2O} + 3\mathrm{H_2O}$; $\quad \Delta G_3^\circ = -\,4FE_3^\circ$

The reaction (3) is obtained by the manipulations 2 Eq. (1) + Eq. (2).

Hence $\Delta G_3^\circ = 2\,\Delta G_1^\circ + \Delta G_2^\circ$. This gives

$$-\,4FE_3^\circ = 2(-\,FE_1^\circ) + (-\,2FE_2^\circ) \quad \text{or} \quad E_3^\circ = \frac{E_1^\circ - E_2^\circ}{2} = \frac{0.996\ \mathrm{V} + 1.59\ \mathrm{V}}{2} = 1.293\ \mathrm{V}$$

61. Given: In acidic medium $2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$

$$E = E_1^\circ - \frac{RT}{2F}\ \ln \frac{p_{N_2O}}{(p_{NO})^2\left[H^+\right]^2} = E_1^\circ - \frac{RT}{2F}\ \ln \frac{(p_{N_2O})\left[OH^-\right]^2}{(p_{NO})^2\ K_w^2}$$

In alkaline medium $2NO + H_2O + 2e^- \rightarrow N_2O + 2OH^-$

$$E = E_2^\circ - \frac{RT}{2F}\ \ln \frac{(p_{N_2O})[OH^-]^2}{(p_{NO})^2}$$

In the above two expressions, only the numerical values of physical quantities are to be used. Comparing the two expressions, we get

$$E_2^\circ = E_1^\circ - \frac{RT}{2F}\ \ln \frac{1}{K_w^2} = 1.59\ V - (0.0295\ V)\ \log\ \{1\ /\ (10^{-14})^2\} = 1.59\ V - 0.826\ V = 0.764\ V$$

62. The reactions are:

(1) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$; $\Delta G_1^\circ = -\ (2)\ FE_1^\circ$

(2) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$; $\Delta G_2^\circ = -\ (2)\ FE_2^\circ$

(3) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$; $\Delta G_3^\circ = -\ (4)\ FE_3^\circ$

The reaction (1) is obtained as Eq. (3) – Eq. (2). Hence

$\Delta G_1^\circ = \Delta G_3^\circ - \Delta G_2^\circ$ i.e. $-\ 2FE_1^\circ = -\ 4FE_1^\circ + 2FE_2^\circ \Rightarrow E_1^\circ = (2E_3^\circ - E_2^\circ) = 0.695\ V$

63. The reactions are:

(1) $HClO_2 + 2H^+ + 2e^- \rightarrow HClO + H_2O$; $\Delta G_1^\circ = -\ 2FE_1^\circ$

(2) $2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$; $\Delta G_2^\circ = -\ 2FE_2^\circ$

(3) $2HClO_2 + 6H^+ + 6e^- \rightarrow Cl_2 + 4H_2O$; $\Delta G_3^\circ = -\ 6FE_3^\circ$

The reaction (3) is obtained as 2 Eq. (1) + Eq. (2). Hence

$\Delta G_3^\circ = 2\Delta G_1^\circ + \Delta G_2^\circ$ i.e. $-\ 6FE_3^\circ = -\ 4FE_1^\circ - 2FE_2^\circ \Rightarrow E_3^\circ = (2E_1^\circ + E_2^\circ)\ /\ 3 = 1.659\ V$

64. The reactions are:

(1) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$; $\Delta G_1^\circ = -\ 3\ FE_1^\circ$

(2) $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$; $\Delta G_2^\circ = -\ 2\ FE_2^\circ$

(3) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$; $\Delta G_3^\circ = -\ 5\ FE_3^\circ$.

The reaction (1) is obtained as Eq. (3) – Eq. (2). Hence

$\Delta G_1^\circ = \Delta G_3^\circ - \Delta G_2^\circ$ i.e. $-\ 3FE_1^\circ = -\ 5FE_3^\circ + 2FE_2^\circ \Rightarrow E_1^\circ = (5\ E_3^\circ - 2E_2^\circ)\ /\ 3 = 1.696\ V$

65. The reactions are

(1) $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$; $\Delta G_1^\circ = -\ 2FE_1^\circ$

(2) $Hg_2^{2+} + 2e^- \rightarrow 2Hg$; $\Delta G_2^\circ = -\ 2FE_2^\circ$

(3) $Hg^{2+} + 2e^- \rightarrow Hg$; $\Delta G_3^\circ = -\ 2FE_3^\circ$

The reaction (2) is obtained as 2 Eq. (3) – Eq. (1). Hence

$\Delta G_2^\circ = 2\Delta G_3^\circ - \Delta G_1^\circ$ i.e. $-\ 2FE_2^\circ = 2(-\ 2FE_3^\circ) - (-\ 2FE_1^\circ)$

or $E^\circ_2 = 2E^\circ_3 - E^\circ_1 = 2(0.854\ V) - 0.911\ V = 0.797\ V$

66. Given:

(1) $HNO_2 + H^+ + e^- \rightarrow NO + H_2O$; $E_1^\circ = 0.996\ V$

(2) $HNO_2 \rightleftharpoons H^+ + NO_2^-$; $K_{eq} = 4.5 \times 10^{-4}$

(3) $NO_2^- + H_2O + e^- \rightarrow NO + 2OH^-$; $E_3^\circ = ?$

Equation (2) may be obtained as follows.

$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$ E_1°

$NO_2^- + H_2O + e^- \rightarrow NO + 2OH^-$ E_3°

Subtract

(4) $HNO_2 + H^+ + 2OH^- \rightarrow NO_2^- + 2H_2O;\ E = E_1^\circ - E_3^\circ$

To this reaction, adding $2H_2O \rightarrow 2H^+ + 2OH^-$, we get

(2) $HNO_2 \rightarrow H^+ + NO_2^-$ $K^\circ_{eq} = 4.5 \times 10^{-4}$

For Eq. (4), we have

$$K^{\circ\prime}_{eq} = \frac{K^\circ_{eq}}{K^{\circ 2}_{w}} = \frac{4.5 \times 10^{-4}}{(1.0 \times 10^{14})^2} = 4.5 \times 10^{24}$$

Hence $E^\circ_1 - E^\circ_3 = \frac{RT}{nF} \ln K^{\circ\prime}_{eq} = (0.059\ \text{V}) \log (4.5 \times 10^{24}) = (0.059\ \text{V})\ (24.65) = 1.454\ \text{V}$

Hence $E^\circ_3 = E^\circ_1 - 1.454\ \text{V} = 0.996\ \text{V} - 1.454\ \text{V} = -\ 0.458\ \text{V}$

67. $Fe^{3+} + 3e^- \rightarrow Fe$ $E^\circ_1 = -\ 0.036\ \text{V}$ $\Delta G^\circ_1 = -\ 3FE^\circ_1$

$Fe^{2+} + 2e^- \rightarrow Fe$ $E^\circ_2 = -\ 0.439\ \text{V}$ $\Delta G^\circ_2 = -\ 2FE^\circ_2$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^\circ_3 = ?$ $\Delta G^\circ_3 = -\ FE^\circ_3$

Third equation can be obtained by subtracting second from first. Hence

$$\Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2 \quad \Rightarrow \quad -\ FE^\circ_3 = -\ 3FE^\circ_1 + 2FE^\circ_2$$

or $E^\circ_3 = 3E^\circ_1 - 2E^\circ_2 = 3(-\ 0.036\ \text{V}) - 2(-\ 0.439\ \text{V})$

68. We have

$AgI + e^- = Ag + I^-$; $E^\circ = -\ 0.15\ \text{V}$

$Ag^+ + e^- = Ag$; $E^\circ = 0.80\ \text{V}$

Subtract

$AgI = Ag^+ + I^-$ $E^\circ = (-\ 0.15\ \text{V}) - 0.80\ \text{V} = -\ 0.95\ \text{V}$

Now $E^\circ = \frac{RT}{nF} \ln K_{sp}$. Hence

$$(-\ 0.95\ \text{V}) = (0.059\ \text{V}) \log K^\circ_{sp} \quad \log K^\circ_{sp} = -\ \frac{0.95}{0.059} = -\ 16.10 \quad \Rightarrow \quad K^\circ_{sp} = 7.9 \times 10^{-17}$$

70. $E^\circ_{cell} = 0.6264$ V. Cell reaction: $Sn^{2+} + Zn \rightarrow Sn + Zn^{2+}$

The given reaction is just opposite to the above reaction. Hence, the E°_{cell} producing the given reaction would be -0.6264 V. Thus

$$\log K^\circ_{eq} = \frac{nFE}{2.303\ RT} \quad \frac{nE}{(2.303\ RT/F)} = \frac{2 \times (-0.6264\ \text{V})}{(0.059\ \text{V})} = -\ 21.23$$

71. $K_{eq} = \text{antilog}\left(\frac{nE^\circ}{0.059\ \text{V}}\right) = \text{antilog}\left(\frac{2 \times 0.48}{0.059}\right) = \text{antilog}\ (16.27) = 1.80 \times 10^{16}$

72. $\Delta G^\circ = -\ nFE^\circ = -\ (2)\ (96500\ \text{C mol}^{-1})\ (0.48\ \text{V}) = -\ 92640\ \text{J mol}^{-1} = -\ 92.64\ \text{kJ mol}^{-1}$

74. The reduction reaction to be considered is $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$. Its Nernst equation is

$$E = E^\circ - \frac{RT}{F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

The addition of phosphoric acid forms the complex with ferric ion and thus lowering its concentration. Hence, the reduction potential becomes more negative.

75. The cell reaction is $Zn \rightarrow Zn^{2+} + 2e^-$

$Fe^{2+} + 2e^- \rightarrow Fe$

$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

The cell emf is given by $E = E^\circ - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Fe^{2+}]}$

Substituting the given data, we get $0.3495\ \text{V} = E° - \dfrac{(0.059\,\text{V})}{2}\ \log\left(\dfrac{0.001}{0.01}\right)$

This gives $E° = 0.3495\ \text{V} - 0.0295\ \text{V} = 0.32\ \text{V}$. Since $\Delta G° = -nFE° = -RT \ln K°_{\text{eq}}$, we get

$$\ln K°_{\text{eq}} = \frac{nF}{RT} E°$$

At 25 °C, we have $\log K°_{\text{eq}} = \left(\dfrac{1}{0.0295\ \text{V}}\right)(0.32\ \text{V}) = \dfrac{0.32}{0.0295}$. Hence $K°_{\text{eq}} = 10^{(0.32/0.0295)}$

76. From the given data, we have

$$2H^+(aq) + \tfrac{1}{2}\ O_2(g) + 2e^- \rightarrow H_2O(l);\quad E°_1 = 1.23\ \text{V}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\quad E°_2 = -\ 0.44\ \text{V}$$

Subtract

$$Fe(s) + 2H^+(aq) + \tfrac{1}{2}\ O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l)$$

$$E° = E°_1 - E°_2 = (1.23 + 0.44)\ \text{V} = 1.67\ \text{V}$$

The given reaction is obtained by multiplying the above reaction by 2. Hence, in the given reaction, the number of electrons is 4. Thus

$$\Delta G° = -\ nFE° = -\ (4)\ (96\ 500\ \text{C mol}^{-1})\ (1.67\ \text{V}) = -\ 644\ 620\ \text{J mol}^{-1} = -\ 644.62\ \text{kJ mol}^{-1}$$

77. We have $\underset{1.0\ \text{M} - x}{Cd^{2+}\ (aq)} + Fe(s) \rightleftharpoons Cd(s) + \underset{x}{Fe^{2+}(aq)}$

Hence $E = E° - \dfrac{RT}{2F} \ln \dfrac{[Fe^{2+}]}{[Cd^{2+}]}$

At equilibrium $E = 0$. Hence

$$E° = \frac{RT}{2F} \ln \frac{[Fe^{2+}]}{[Cd^{2+}]} \quad \text{i.e.} \quad \frac{x}{1.0\,\text{M} - x} = \text{antilog}\left(\frac{E^o}{RT/2F}\right)$$

or $$\frac{x}{1.0\text{M} - x} = \text{antilog}\left(\frac{0.037\ \text{V}}{0.0295\ \text{V}}\right) = 10^{1.254} \simeq 18 \quad \text{or} \quad x = \frac{18}{19}\ \text{M} = 0.95\ \text{M}$$

Thus, $[Fe^{2+}] = 0.95$ M and $Cd^{2+}(aq) = 0.05$ M

78. The equilibrium constant of the reaction $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$

is $$K_{\text{eq}} = \frac{[H_2O]}{[H^+]\,[OH^-]} = \frac{55.56\ \text{M}}{10^{-14}\ \text{M}^2} = 55.56 \times 10^{14}\ \text{M}^{-1}$$

Since $\Delta G° = -\ nFE° = -\ RT \ln K°$, we have

$$E° = \frac{RT \ln K°}{nF} = \left(\frac{2.303\ RT}{nF}\right) \log K° = (0.059\ \text{V}) \log (55.56 \times 10^{-14}) = -\ 0.723\ \text{V}$$

79. We have $Ag^+ + e^- = Ag$

$$E = E° - \frac{RT}{F} \ln \frac{1}{[Ag^+]/\text{M}} = E° - \frac{RT}{F} \ln \left(\frac{1}{[Ag^+]/\text{M}}\ \frac{[X^-]/\text{M}}{[X^-]/\text{M}}\right)$$

$$= [E° + \frac{RT}{F} \ln K°_{\text{sp}}(\text{Ag X})] - \frac{RT}{F} \ln ([X^-]/\text{M})$$

The last expression may be identified for the potential of $X^- \mid AgX(s) \mid Ag(s)$ half-cell.

Hence $E°_{X^- \mid AgCl \mid Ag} = E°_{Ag^+ \mid Ag} + \dfrac{RT}{F} \ln K°_{\text{sp}}(\text{AgX})$

Since $K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgBr}) > K_{\text{sp}}(\text{AgI})$ It follows that $E°_{Cl^- \mid AgCl \mid Ag} > E°_{Br^- \mid AgBr \mid Ag} > E°_{I^- \mid AgI \mid Ag}$

80. For the half-cell reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ we have

$$E_2 = E_2^\circ - \frac{RT}{4F} \ln \frac{1}{(p_{O_2}/\text{atm})([H^+]/M)^4} = E_2^\circ - \frac{RT}{4F} \ln \frac{1}{(p_{O_2}/\text{atm})([H^+]/M)^4} \left(\frac{[OH^-]/M}{[OH^-]/M}\right)^4$$

$$= \left(E_2^\circ + \frac{RT}{F} \ln K_w^\circ\right) - \frac{RT}{4F} \ln \frac{([OH^-]/M)^4}{(p_{O_2}/\text{atm})}$$

Identifying E with the half-cell reaction $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$, we find that

$$E_3^\circ = E_2^\circ + \frac{RT}{F} \ln K_w^\circ = E^\circ_2 - (0.059\ V)\ (14) = E_2^\circ - 0.826\ V$$

Since $E_2^\circ > 0.826$ V, E_3° will also be positive but less than E_2°. The standard potential of $H^+ \mid H_2 \mid Pt$ is zero.

Multiple Correct Choice Type

1. (a) It is Fe which can reduce Cu^{2+} to Cu.
(b) Standard electrode potentials are relative values. Reference is hydrogen half-cell whose standard potential is taken to be zero at 298 K.

2. (a) The correct expression is $E^\circ_{Cl^- \mid AgCl \mid Ag} = E^\circ_{Ag^+ \mid Ag} + \frac{RT}{F} \ln K_{sp}^\circ\,(AgCl)$
(b) The reverse is true.
(c) Pressure is fixed (= 1 bar). Temperature can have any value . But all measurements have been made at 298 K.
(d) The conventional value is at 298 K.

3. (a) Half-cell with higher potential involves reduction and thus provides an oxidizing agent.

4. (a) A positive half-cell potential implies that the species can be more readily reduced than H^+ ions.
(c) The Nernst equation for the given reaction is $E = E^\circ - \frac{RT}{nF} \ln \frac{[A^{x+}]}{[A^{(x+n)+}]}$

The variation of E with the ratio of concentrations of species can provide the value of n. In fact, one can plot E versus log $[A^{x+}] / [A^{(x+n)+}]$ which gives a straight line of slope - $RT/2.303\,nF$. From the latter, the value of n can be determined.

5. (a) Cell potential is an intensive property.
(b) The factor of 0.0591 V appears when temperature is 298 K and not 273 K.

Linked Comprehension Type

1. **(i)** In the given reaction Fe^{2+} is oxidized to Fe^{3+}. Since the standard reduction potential of $Fe^{3+}, Fe^{2+} \mid Pt$ is positive, the contribution made to the cell will be – 0.77 V.

(ii) In the given reaction, MnO_4^- is reduced to Mn^{2+}. Its contribution to the cell will be equal to $E^\circ(MnO_4^-, Mn^{2+}, H^+ \mid Pt)$, i.e. $\mid 1.51 \mid$ V.

(iii) Since H^+ ions appear in the reaction $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.

Its cell potential will be $E = E^\circ - \frac{RT}{nF} \ln \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$

Only the numerical values of concentrations are to be used in the above expression. Increasing pH implies decreasing $[H^+]$, this will cause E to decrease.

Since, $E_{cell} = E_{MnO_4^-, Mn^{2+}, H^+ \mid Pt} - E_{Fe^{3+}, Fe^{2+} \mid Pt}$, the decrease in $E_{MnO_4^-, Mn^{2+}, H^+ \mid Pt}$ will cause lowering of E_{cell}.

2. **(i)** The E_{cell} is given by $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{5F} \ln \dfrac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{H}^+]^8[\text{Fe}^{2+}]^5}$

Increasing $[\text{Mn}^{2+}]$ and $[\text{Fe}^{3+}]$ decreases E_{cell} while those appearing in denominator would increase E_{cell}. Decreasing pH means increasing $[\text{H}^+]$, hence, this causes increase in E_{cell}.

(ii) When all concentrations are 1 M, $E_{\text{cell}} = E^\circ_{\text{cell}}$

When $[\text{Fe}^{3+}] = 0.5$ M and all other unity, then

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{5F} \ln (0.5)^5 = E^\circ_{\text{cell}} - (0.059 \text{ V})(-0.3) = E^\circ_{\text{cell}} + 0.0178 \text{ V}$$

Thus, potential increases by 0.0178 V

(iii) When $[\text{MnO}_4^-]$ is to reduce to 0.50 M, then

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.059 \text{ V}}{5}\right) \log\left(\frac{1}{0.5}\right) = E^\circ_{\text{cell}} - \frac{0.3 \times 0.059}{5} \text{ V} = E^\circ_{\text{cell}} - 0.0036 \text{ V}$$

Hence, the potential is decreased by 0.0036 V

3. **(i)** The half-cell potential does not depend the way chemical equation is formulated.

(ii) We have

$$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- = 2\text{H}_2\text{O}(\text{l}) \qquad E = E^\circ - \frac{RT}{4F} \ln \left[\frac{1}{p_{\text{O}_2}[\text{H}^+]^4}\right]$$

Multiplying and dividing logarithm term by $[\text{OH}^-]^4$, we get

$$E = E^\circ - \frac{RT}{4F} \ln \left(\frac{[\text{OH}^-]^4}{p_{\text{O}_2} K_{\text{w}}^4}\right) = E^\circ - \frac{RT}{4F} \ln \left(\frac{[\text{OH}^-]^4}{p_{\text{o}_2}}\right) - \frac{RT}{4F} \ln \frac{1}{K_{\text{w}}^4}$$

The standard potential for $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = 4\text{OH}^-$ will be

$$E^\circ - \frac{RT}{4F} \ln \frac{1}{K_{\text{w}}^4} = 1.229 \text{ V} + (0.059 \text{ V})(-14) = 1.229 \text{ V} - 0.826 \text{ V} = 0.403 \text{ V}$$

(iii) Substituting $p_{\text{o}_2} = 1$ atm and $[\text{H}^+] = 10^{-7}$ M in the expression cell potential, we get

$$E = 1.229 \text{ V} - \left(\frac{0.059 \text{V}}{4}\right) \log \left(\frac{1}{10^{-7}}\right)^4 = 1.229 \text{ V} - 0.059 \times 7 \text{ V} = (1.229 - 0.413) \text{ V}$$

$$= 0.816 \text{ V}$$

4. **(i)** $E^\circ = E^\circ_{\text{Cl}^-|\text{AgCl}|\text{Ag}} - E^{\text{o}}_{\text{Ag(NH}_3)_2^+, \text{NH}_3|\text{Ag}} = 0.222 \text{ V} - 0.373 \text{ V} = -0.151 \text{ V}$

(ii) $\Delta G^\circ = -nFE^\circ = -(1)(96500 \text{ C mol}^{-1})(-0.151 \text{ V}) = 14572 \text{ J mol}^{-1} = 14.57 \text{ kJ mol}^{-1}$

(iii) $\Delta G^\circ = -nFE^\circ = -RT \ln K^\circ_{\text{eq}}$

$$K^\circ_{\text{eq}} = \text{antilog} \left(\frac{nFE^\circ}{RT}\right) = \text{antilog} \left(\frac{E^\circ}{RT/nF}\right) = \text{antilog} \left(-\frac{0.151 \text{V}}{0.059 \text{ V}}\right) = 2.76 \times 10^{-3}$$

5. **(i)** The given reaction is obtained as follows.

$\text{AgCl} + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)^{2+} + \text{Cl}^- \qquad \Delta G^\circ = 14.57 \text{ kJ mol}^{-1}$

$2[\text{NH}_4\text{OH} \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}] \qquad \Delta G^\circ = 2 \times 10.04 \text{ kJ mol}^{-1}$

Add $\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow \text{Ag(NH}_3)_2^{2+} + 2\text{H}_2\text{O} + \text{Cl}^- \Delta G^\circ = (14.57 + 2 \times 10.04) \text{ kJ mol}^{-1}$

$= 34.65 \text{ kJ mol}^{-1}$

(ii) Since $\Delta G^\circ = -\,RT \ln K^\circ_{\text{eq}}$, we get

$$K^\circ_{\text{eq}} = \text{antilog}\left(-\frac{\Delta G^{\text{o}}}{2.303\,RT}\right) = \text{antilog}\left[-\frac{34.65\times 10^3\,\text{J mol}^{-1}}{(2.303)\left(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298\,K)}\right]$$

$$= \text{antilog}\ (-\,6.07) = 8.51 \times 10^{-7}$$

(iii) The cell potential will be $E^\circ = \dfrac{\Delta G^{\text{o}}}{nF} = \dfrac{34650\ \text{J mol}^{-1}}{(1)\left(96500\ \text{C mol}^{-1}\right)} = -\,0.359\ \text{V}$

6. (i) For the reaction $\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow \text{Ag(NH}_3)^{2+} + \text{Cl}^- + 2\text{H}_2\text{O}$

$\Delta_r G^\circ = -\,(1)\,F(-\,0.359\ \text{V}) = (96500\ \text{C mol}^{-1})\ (0.359\ \text{V}) = 34643.5\ \text{J mol}^{-1} = 34.64\ \text{kJ mol}^{-1}$

Also $\Delta_r G^\circ = \Delta_f G^\circ(\text{Ag(NH}_3)_2^+) + \Delta_f G^\circ(\text{Cl}^-) + 2\Delta_f G^\circ(\text{H}_2\text{O}) - \Delta_f G^\circ(\text{AgCl}) - 2\Delta_f G^\circ(\text{NH}_4\text{OH})$

This gives

$\Delta_f G^\circ(\text{Ag(NH}_3)_2) = [34.64 + 131.23 + 2 \times 237.13 - 109.79 - 2 \times 263.62]\ \text{kJ mol}^{-1} = 3.1\ \text{kJ mol}^{-1}$

(ii) For the reaction $\text{AgCl} + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ + \text{Cl}^-$

$\Delta_r G = -\,(1)\,F(-\,0.151\ \text{V}) = (96500\ \text{C mol}^{-1})\ (0.151\ \text{V}) = 14571.5\ \text{J mol}^{-1} = 14.57\ \text{kJ mol}^{-1}$

$\Delta_r G^\circ = \Delta_f G^\circ(\text{Ag(NH}_3)^{2+}) + \Delta_f G^\circ(\text{Cl}^-) - \Delta_f G^\circ(\text{AgCl}) - 2\Delta_f G^\circ(\text{NH}_3)_2$

Hence $\Delta_f G^\circ(\text{NH}_3) = \frac{1}{2}\ [3.1 - 131.23 + 109.79 - 14.57]\ \text{kJ mol}^{-1} = -\,16.45\ \text{kJ mol}^{-1}$

(iii) $\Delta_r G^\circ = 2\Delta_f G^\circ(\text{NH}_4\text{OH}) - \Delta_f G^\circ(\text{Ag(NH}_3)_2^+) - 2\Delta_f G^\circ(\text{H}_2\text{O})$

$= [2 \times (-\,263.62) - 3.1 + 2 \times 237.13]\ \text{kJ mol}^{-1} = -\,56.08\ \text{kJ mol}^{-1}$

Since $\Delta G^\circ = -\,nFE^\circ$, we get $E^\circ = \dfrac{\Delta G^o}{nF} = \left(\dfrac{56080\,\text{J mol}^{-1}}{(1)\left(96500\ \text{C mol}^{-1}\right)}\right) = 0.581\ \text{V}$

7. (i) $E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{Cu}^{2+}|\text{Cu}} - E^\circ_{\text{Cu(NH}_3)_4^{2+},\ \text{NH}_3|\text{Cu}} = 0.337\ \text{V} + 0.12\ \text{V} = 0.457\ \text{V}$

(ii) $\Delta_r G^\circ = -\,nFE^\circ_{\text{cell}} = -\,(2)\ (96500\ \text{C mol}^{-1})\ (0.457\ \text{V}) = -\,88201\ \text{J mol}^{-1} = -\,88.20\ \text{kJ mol}^{-1}$

(iii) $K^\circ_{\text{eq}} = \text{antilog}\left(\dfrac{nFE^{\text{o}}}{2.303\,RT}\right) = \text{antilog}\left(\dfrac{nE^{\text{o}}}{2.303\,RT/F}\right) = \text{antilog}\left(\dfrac{2\times 0.457\ \text{V}}{0.059\ \text{V}}\right)$

$= \text{antilog}\ (15.49) = 3.1 \times 10^{15}$

8. (i) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \qquad \Delta G^\circ_1 = -\,(2)\ F(0.34\ \text{V})$

$\underline{\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}} \qquad \Delta G^\circ_2 = -\,(1)\ F(0.52\ \text{V})$

Subtract $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ $\Delta G^\circ = \Delta G^\circ{}_1 - \Delta G^\circ{}_2 = -\,F\ (2 \times 0.34 - 0.52)\ \text{V}$

$= -\,(1)\ F(0.16\ \text{V}) = -\,(96500\ \text{C mol}^{-1}) = -\,15440\ \text{J mol}^{-1}$

(ii) The value of E° as calculated in part (i) is 0.16 V.

(iii) The disproportionation reaction of Cu^+ is $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$

Its cell potential will be $E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^+|\text{Cu}} - E^\circ_{\text{Cu}^{2+},\text{Cu}^+|\text{Pt}} = 0.52\ \text{V} - 0.16\ \text{V} = 0.36\ \text{V}$

Since E°cell is positive, the disproportionation is feasible.

9. (i) The reaction to be considered is (a) $\text{BrO}_3^- + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{Br}^- + 6\text{OH}^- \qquad \Delta G^\circ_1 = ?$

The given data are as follows.

(b) $\text{BrO}_3^- + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{BrO}^- + 4\text{OH}^- \qquad \Delta G^\circ_2 = -\,4(F)\ (0.54\ \text{V})$

(c) $\text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}^- + 2\text{OH}^- \qquad \Delta G^\circ_3 = -\,2(F)\ (0.17\ \text{V})$

The reaction (a) is obtained by adding reactions (b) and (c). Hence
$\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ = -F(4 \times 0.54 + 2 \times 0.17)\ \text{V} = -(2.5\ \text{V})\ F$

(ii) $E^\circ = \dfrac{\Delta G_1^0}{nF} = -\dfrac{-(2.5\,\text{V})}{6F} = 0.417\ \text{V}$

(iii) Only BrO^- can be oxidized as well as reduced. $3BrO^- \rightarrow BrO_3^- + 2Br^-$
The cell producing this reaction is $Pt \mid BrO_3^-, BrO^-, OH^- \mid \mid BrO^-, Br^-, OH^- \mid Pt$
$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = E_{BrO^-,\ Br^-|Pt}^\circ - E_{BrO^{3-},\ BrO^-|Pt}^\circ = 0.17\ \text{V} - 0.54\ \text{V} = -0.37\ \text{V}$
Since E_{cell} is negative, the disproportionation of BrO^- is not possible.

10. **(i)** The given reactions are

(a) $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ $\qquad \Delta G_1^\circ = -(2)(F)(0.15\ \text{V})$

(b) $Sn^{2+} + 2e^- \rightarrow Sn$ $\qquad \Delta G_2^\circ = -(2)(F)(-0.14\ \text{V})$

The reaction $Sn^{4+} + 4e^- \rightarrow Sn$ can be produced by adding reactions (a) and (b). Hence
$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ = (F)\ [0.30\ \text{V} - 0.28\ \text{V}) = -(F)\ (0.02\ \text{V})$

(ii) $E^\circ = \dfrac{\Delta G^\circ}{nF} = -\dfrac{-(F)(0.02\,\text{V})}{(4)(F)} = 0.005\ \text{V}$

(iii) Considering the disproportionation reaction $2Sn^{2+} \rightarrow Sn^{4+} + Sn$
The cell potential this reaction is

$$E^\circ = E_R^\circ - E_L^\circ = E_{Sn^{2+}/Sn}^\circ - E_{Sn^{4+},\ Sn^{2+}/Pt}^\circ = -0.14\ \text{V} - 0.15\ \text{V} = -0.29\ \text{V}$$

Since the cell potential is negative, the disproportionation reaction is not feasible.

11. **(i)** $ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$ $\qquad \Delta G_1^\circ = -2F\ (0.36\ \text{V})$
$ClO_3^- + 2H^+ + 2e^- \rightarrow ClO_2^- + H_2O$ $\qquad \Delta G_2^\circ = -2F\ (0.33\ \text{V})$

Add $ClO_4^- + 4H^+ + 4e^- \rightarrow ClO_2^- + 2H_2O$ $\qquad \Delta G = \Delta G_1^\circ + \Delta G_2^\circ = -4FE^\circ$
Hence $\quad -4FE^\circ = -2F\ (0.36\ \text{V}) - 2F\ (0.33\ \text{V})$ i.e. $E^\circ = (0.36\ \text{V} + 0.33\ \text{V})/2 = 0.345\ \text{V}$

(ii) The reaction $2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$ involves the following half reactions

$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$

$ClO_3^- + H_2O \rightleftharpoons ClO_4^- + 2H^+ + 2e$

Hence $E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = E_{ClO_3^-,\, ClO_2^-,\, H^+|Pt}^\circ - E_{ClO_4^-,\, ClO_3^-,\, H^+|Pt}^\circ = 0.33\ \text{V} - 0.36\ \text{V} = -0.03\ \text{V}$

(iii) Since $\Delta G^\circ = -RT \ln K_{\text{eq}}^\circ = -nFE^\circ$, we have $RT \ln K_{\text{eq}}^\circ = nFE^\circ$

or $\quad K_{\text{eq}}^\circ = \text{antilog}\left(\dfrac{E^\circ}{2.303\,RT/nF}\right) = \text{antilog}\left(\dfrac{-0.03\ \text{V}}{0.0295\ \text{V}}\right) = 10^{-1} = 0.1$

Now $\quad \underset{0.1\ \text{M} - 2x}{2ClO_3^-} \rightleftharpoons \underset{x}{ClO_2^-} + \underset{x}{ClO_4^-}$

Hence $\quad K_{\text{eq}} = \dfrac{[ClO_2^-][ClO_4^-]}{[ClO_3^-]^2} = \dfrac{x^2}{(0.1\,\text{M} - 2x)^2}$ or $\dfrac{x}{1\,\text{M} - x} = \sqrt{K_{\text{eq}}} = \sqrt{0.1} = 0.32$

$x = \dfrac{0.32}{1.32}\ \text{M} = 0.24\ \text{M}.$ Thus $\dfrac{[ClO_4^-]}{[ClO_3^-]} = \dfrac{0.24\,\text{M}}{(1.0\,\text{M} - 0.24\,\text{M})} = 0.32$

12. **(i)** The value of E°_{cell} producing the given reaction is $E^\circ = E^\circ_1 - E^\circ_2 = 0.80\ \text{V} - 0.05\ \text{V} = 0.75\ \text{V}$

Thus $$\log K^\circ_{\text{eq}} = \frac{nFE^\circ}{2.303RT} = \frac{nE^\circ}{2.303RT/F} = \frac{2(0.75\ \text{V})}{(0.059\ \text{V})} = 25.4$$

(ii) The expression of E_2 is $E_2 = E^\circ{}_2 - \dfrac{RT}{2F}\ \ln \dfrac{[C_6H_{12}O_6]}{[C_6H_{12}O_7][H^+]^2}$

The addition of NH_3 causes increase in pH, i.e. decrease in $[H^+]$. This makes E_2 more negative. The expression of E_1 is $E_1 = E^\circ{}_1 - \dfrac{RT}{F}\ \ln \dfrac{1}{[Ag^+]}$

The addition of NH_3 forms the complex with Ag^+, decreasing its concentration and thus making E_1 more negative.

(iii) The value $E^\circ_3 < E^\circ_1$. This implies that $[Ag(NH_3)_2]^+$ is a weaker oxidising agent than Ag^+.

13. **(i)** Larger value of reduction potential implies larger reduction tendency hence larger oxidising ability. The reduction potential $Cl^-|Cl_2|Pt$ is larger than $I^-|I_2|Pt$. Hence, Cl_2 can oxidize I^- to I_2.

(ii) The reduction potential of Mn^{3+}, $Mn^{2+}|Pt$ is larger than $H_3O^+|O_2|Pt$. Hence, Mn^{3+} can oxidize H_2O to O_2.

(iii) The blue coloration is due to the formation of ferric ferrocyanide, $Fe_4[Fe(CN)_6]$.

14. **(i)** In the given reaction Fe^{2+} is oxidised to Fe^{3+}. Hence, contribution made to the standard emf of the cell is –0.77 V.

(ii) In the given reaction $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. Hence, contribution made to the standard emf of the cell is1.33 V.

(iii) The standard emf of the cell is $E^\circ = E^\circ_R - E^\circ_L = 1.33\ \text{V} - 0.77\ \text{V} = 0.56\ \text{V}$

(iv) Nernst equation for the reaction $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$ is

$$E = E^\circ - \frac{RT}{6F}\ln\frac{[Cr^{3+}]^2\,[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}\,[Fe^{2+}]^6}$$

Decreasing pH (i.e. increasing H^+) will make the logarithm term more negative. Hence, $E > E^\circ$.

(v) The anodic half-cell will be $Pt|Fe^{3+}$, Fe^{2+}. Hence, Pt is anode.

(vi) The cathodic half-cell will be $Cr_2O_7^{2-}$, Cr^{3+}, $H^+|Pt$. Hence, Pt is cathode.

(vii) Within the cell, it is important to prevent mixing of $Cr_2O_7^{2-}$ and Fe^{2+} as they will directly combine.

(viii) The emf of the cell will depends on temperature through Nernst equation.

(ix) The cell emf is independent of the size of the cell.

(x) Since the reaction at anode is $Fe^{2+} \rightarrow Fe^{3+} + e^-$ and both Fe^{2+} and Fe^{3+} appear in the solution, there will be no change in the mass of anode which is inert electrode.

(xi) Substituting $[Fe^{3+}] = 0.50$ M and all other species equal to 1 M in Nernst equation

$$E = E^\circ - \frac{RT}{6F}\ln\frac{[Cr^{3+}]^2\,[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}\,[Fe^{2+}]^6}$$

we get $$E = E^\circ - \frac{RT}{6F}\ln\,(0.50)^6 = E^\circ - \left(\frac{6\times0.059\ \text{V}}{6}\right)(-0.301) = E^\circ + 0.0178\ \text{V}$$

(xii) We have $$E = E^\circ - \frac{RT}{6F}\ln\,(2)^6 = E^\circ - \left(\frac{6\times0.059\ \text{V}}{6}\right)(0.301) = E^\circ - 0.0178\ \text{V}$$

(xiii) We have $$E = E^\circ - \frac{RT}{6F}\ln\frac{1}{(2)^{14}} = E^\circ + \left(\frac{14\times0.059\ \text{V}}{6}\right)(0.301) = 0.0414\ \text{V}$$

(xiv) We have

$$E = E^\circ - \frac{RT}{6F}\ln\frac{[Cr^{3+}]^2\,[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}\,[Fe^{2+}]^6} = E^\circ - \left(\frac{0.059\ \text{V}}{6}\right)\log\frac{(0.5)^2(2.0)^6}{(1.0)\,(2.0)^{14}\,(0.5)^6}$$

$$= (1.33\ \text{V} - 0.77\ \text{V}) - \left(\frac{0.059\ \text{V}}{6}\right)\log\left(\frac{1}{2^4}\right) = 0.56\ \text{V} + 4 \times \left(\frac{0.059\ \text{V}}{6}\right)(0.301)$$

$$= 0.56\ \text{V} + 0.012\ \text{V} = 0.572\ \text{V}$$

(xv) We have

$$E = E^\circ - \frac{RT}{6F}\ \ln\,(0.50)^2 = E^\circ - \left(\frac{2\times 0.059\ \text{V}}{6}\right)(-0.301) = E^\circ + 0.0059\ \text{V}$$

(xvi) The strongest oxidant is $\mathrm{Cr_2O_7{}^{2-}}$ as it oxidises $\mathrm{Fe^{2+}}$ to $\mathrm{Fe^{3+}}$.

(xvii) The strongest reductant is $\mathrm{Fe^{2+}}$ as it reduces $\mathrm{Cr_2O_7^{2-}}$.

15. (i) The cell producing the reaction is $\mathrm{Pt\ |Fe^{3+},\ Fe^{2+}||H^+,\ Mn^{2+},\ MnO^-_4|\ Pt}$

$$E^\circ_{\text{cell}} = E^\circ_{\mathrm{H^+,\ Mn^{2+},\ MnO_4^-\,|Pt}} - E^\circ_{\mathrm{Fe^{3+},\ Fe^{2+}|Pt}} = 1.51\ \text{V} - (0.77\ \text{V})$$

Contribution of oxidation half-reaction, i.e., oxidation potential towards cell potential = – 0.77 V

(ii) Contribution of reduction half-reaction towards cell potential = 1.51 V

(iii) $E^\circ_{\text{cell}} = 1.51\ \text{V} - 0.77\ \text{V} = 0.74\ \text{V}$

(iv) $E = E^\circ - \dfrac{RT}{5F}\ln\left(\dfrac{[\mathrm{Mn^{2+}}]\,[\mathrm{Fe^{3+}}]^5}{[\mathrm{MnO_4^-}]\,[\mathrm{H^+}]^8\,[\mathrm{Fe^{2+}}]^5}\right)$

Increasing $[\mathrm{Mn^{2+}}]$ and $[\mathrm{Fe^{3+}}]$ and decreasing $[\mathrm{MnO_4^-}]$ will make the term within the brackets more positive and the contribution in the E_{cell} will become more negative. The lowering pH means increasing $[\mathrm{H^+}]$. This will make the term within the brackets less positive and the contribution in the E_{cell} will become more positive.

(xi) $\Delta E = -\dfrac{RT}{F}\ \ln\,(0.5) = -\,(0.059\ \text{V})\ (-\,0.301) = 0.0178\ \text{V}$

(xiii) $\Delta E = -\dfrac{RT}{F}\ln\left(\dfrac{1}{2^8}\right) = +\left(\dfrac{0.059\ \text{V}}{5}\right)(8\times 0.301) = 0.028\ \text{V}$

(xiv) $E_{\text{cell}} = 0.74\ \text{V} - \dfrac{RT}{5F}\ln\left[\dfrac{(0.5)\,(2.0)^5}{(1.0)\,(2.0)^8\,(0.5)^5}\right] = 0.74\ \text{V} - \left(\dfrac{0.059\ \text{V}}{5}\right)\log\left[\dfrac{1}{(2.0)^3\,(0.5)^4}\right]$

$$= 0.74\ \text{V} - \left(\frac{0.059\ \text{V}}{5}\right)\ \log 2 = 0.74\ \text{V} - \frac{0.059\times 0.301}{5}\ \text{V} = 0.736\ \text{V}$$

(xv) $\Delta E = -\left(\dfrac{0.059\ \text{V}}{5}\right)\ \log\,(0.5) = +\,3.55\times 10^{-3}\ \text{V}$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. Consider the cell $\mathrm{Zn\ |\ Zn^{2+}(aq, 1.0\ M)\ ||\ Cu^{2+}(aq, 1.0\ M)\ |\ Cu}$. The standard reduction potentials are 0.350 V for $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu}$ and – 0.763 V for $\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn}$. (1982)

(i) Write down the cell reaction. (ii) Calculate the emf of the cell. (iii) Is the cell reaction spontaneous or not?

Solution We have

Anodic reaction $\mathrm{Zn \rightarrow Zn^{2+}(aq) + 2e^-}$ *Cathodic reaction* $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu}$

Overall reaction $\mathrm{Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu}$

EMF of the cell $E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = 0.350\ \text{V} - (-0.763\ \text{V}) = 1.113\ \text{V}$

Since E°_{cell} is positive, the cell reaction is spontaneous.

2. The emf of a cell corresponding to the reaction $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(0.1\ M) + H_2(g, 1\ bar)$ is 0.28 V at 25 °C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode. Given: $E^\circ_{Zn^{2+}\mid Zn} = -0.763$ V. (1986)

Solution The half-cell reactions are

$$\textit{Anodic reaction}\quad Zn \rightarrow Zn^{2+} + 2e^- \qquad \textit{Cathodic reaction}\quad 2H^+ + 2e^- \rightarrow H_2$$

The Nernst equation for the cell reaction is

$$E = E^\circ - \frac{RT}{2F}\ln\frac{[Zn^{2+}]\,p(H_2)}{[H^+]^2}$$

where $E^\circ = E^\circ_{H^+\mid H_2\mid Pt} - E^\circ_{Zn^{2+}\mid Zn} = 0 - (-0.763\ V) = 0.763\ V$

Substituting the given data in Nernst equation, we get

$$0.28\ V = 0.763\ V - \frac{0.05915\,V}{2}\log\frac{(0.1)\ (1)}{([H^+]/\text{mol dm}^{-3})^2}$$

This gives $-\log([H^+]/\text{mol dm}^{-3}) = \frac{1}{2}\left[\frac{2(0.763\ V - 0.28\ V)}{(0.05915\ V)} - \log(0.1)\right] = \frac{1}{2}[16.33 + 1] = 8.67$

Thus, the pH of the solution is 8.67.

3. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 V at 25 °C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution The given cell is $Pt \mid H_2(1\ bar) \mid H^+(10^{-6}M) \mid\mid H^+(?) \mid H_2(1\ bar) \mid Pt$ (1988)

The cell reactions are

$$\begin{array}{ll} \textit{Cathode} & (H^+)_R + e^- \rightarrow \tfrac{1}{2}H_2 \\ \textit{Anode} & \tfrac{1}{2}H_2 \rightarrow (H^+)_L + e^- \\ \text{Add} & \overline{(H^+)_R \rightarrow (H^+)_L\qquad\qquad} \end{array}$$

The cell potential is given as $E_{cell} = -\frac{RT}{F}\ln\frac{[H^+]_L}{[H^+]_R}$

which gives $0.118\ V = -(0.05915\ V)\log\frac{10^{-6}}{[H^+]_R/M}$

or $\log([H^+]_R/M) = (\log 10^{-6}) + 2 = -6 + 2 = -4$

i.e. $[H^+]_R = 10^{-4}$ M.

4. The standard reduction potential at 25 °C of the reaction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ is -0.8277 V. Calculate the equilibrium constant for the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25 °C. (1989)

Solution The reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ may be obtained by the addition of the following two half reactions.

$$\begin{array}{ll} \textit{Reduction} & H_2O + e^- \rightleftharpoons \tfrac{1}{2}H_2 + OH^- \\ \textit{Oxidation} & H_2O + \tfrac{1}{2}H_2 \rightleftharpoons H_3O^+ + e^- \\ \text{Add} & \overline{2H_2O \rightleftharpoons H_3O^+ + OH^-\qquad} \end{array}$$

The standard emf of the cell, producing the above reactions is

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = -0.8277\ V - 0\ V = -0.8277\ V$$

Now $\log K^\circ = \frac{nFE^\circ}{2.303RT} = \frac{(1)(96500\ C\ mol^{-1})(-0.8277\ V)}{(2.303)(8.314\ J\ K^{-1}\ mol^{-1})(298\ K)} = -13.9985$

i.e. $K^\circ = 1.1 \times 10^{-14}$.

5. The standard reduction potential of $Cu^{2+} \mid Cu$ and $Ag^+ \mid Ag$ electrodes are 0.337 V and 0.799 V, respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell be zero at 25 °C if the concentration of Cu^{2+} ions is 0.01 M? (1990)

Solution We have

$$\mathrm{Cu^{2+} + 2e^- \rightarrow Cu} \qquad E^\circ_{\mathrm{Cu^{2+}\,|\,Cu}} = 0.337\ \mathrm{V}$$

$$\mathrm{Ag^+ + e^- \rightarrow Ag} \qquad E^\circ_{\mathrm{Ag^+\,|\,Ag}} = 0.799\ \mathrm{V}$$

Since $E^\circ_{\mathrm{Ag^+\,|\,Ag}}$ is greater than $E^\circ_{\mathrm{Cu^{2+}|Cu}}$, the half cell $\mathrm{Ag^+\,|Ag}$ will constitute the cathode of the galvanic cell. Hence, the required cell is $\mathrm{Cu\,|\,Cu^{2+}\,||\,Ag^+\,|\,Ag}$

Its standard emf is $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{R}} - E^\circ_{\mathrm{L}} = 0.799\ \mathrm{V} - 0.337\ \mathrm{V} = 0.462\ \mathrm{V}$

The cell reaction may be obtained as follows.

Right half-cell $\mathrm{2Ag^+ + 2e^- \rightarrow 2Ag}$

Left half-cell $\mathrm{Cu \rightarrow Cu^{2+} + 2e^-}$

Add

$\mathrm{2\,Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}}$

Its Nernst equation is $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \dfrac{RT}{2F}\ln\dfrac{[\mathrm{Cu^{2+}}]}{[\mathrm{Ag^+}]^2}$

For $E = 0$, we will have

$$0 = 0.462\ \mathrm{V} - \left(\frac{0.059\,15\,\mathrm{V}}{2}\right)\log\frac{0.01}{([\mathrm{Ag^+}]/\mathrm{M})^2} \quad \text{or} \quad \log\frac{0.01}{([\mathrm{Ag^+}]/\mathrm{M})^2} = \frac{2\times 0.462}{0.059\,15} = 15.6345$$

or $\quad 2\log([\mathrm{Ag^+}]/\mathrm{M}) = \log 0.01 - 15.6345 \quad$ or $\quad \log([\mathrm{Ag^+}]/\mathrm{M}) = \dfrac{-2-15.6345}{2} = -8.8173$

or $\quad [\mathrm{Ag^+}] = 1.523 \times 10^{-9}\ \mathrm{M}.$

6. Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25 °C until equilibrium is reached. If the standard reduction potential of $\mathrm{Zn^{2+}\,|\,Zn}$ and $\mathrm{Ni^{2+}\,|\,Ni}$ are – 0.75 V and – 0.24 V, respectively, calculate the concentrations of $\mathrm{Ni^{2+}}$ in solution at equilibrium. (1991)

Solution The reaction to be considered is $\mathrm{Zn(s) + Ni^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Ni(s)}$

The cell producing this reaction would be $\mathrm{Zn(s)\,|\,Zn^{2+}(aq)\,||\,Ni^{2+}\,(aq)\,|\,Ni(s)}$

with standard cell potential as $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{R}} - E^\circ_{\mathrm{L}} = -0.24\ \mathrm{V} - (-0.75\ \mathrm{V}) = 0.51\ \mathrm{V}$

The equilibrium constant of the reaction would be given as

$$\log K_{\mathrm{eq}} = \frac{nFE^\circ}{2.303\,RT} = \frac{(2)\,(96\,500\,\mathrm{C\,mol^{-1}})\,(0.51\,\mathrm{V})}{(2.303)\,(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\,(298\mathrm{K})} = 17.25$$

Hence $\quad K_{\mathrm{eq}} = 1.78 \times 10^{-17}$

Let x be the concentration of $\mathrm{Ni^{2+}}$ ions that have been reduced to Ni at equilibrium.

We will have $\quad \mathrm{Zn(s)} + \underset{1.0\ \mathrm{M}\,-\,x}{\mathrm{Ni^{2+}(aq)}} \rightleftharpoons \underset{x}{\mathrm{Zn^{2+}(aq)}} + \mathrm{Ni(s)}$

Thus $\quad K_{\mathrm{eq}} = \dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ni^{2+}}]} = \dfrac{x}{1.0\mathrm{M} - x}$

Solving for x, we would get

$$x \simeq \frac{K_{\mathrm{eq}} \times 1.0\,\mathrm{M}}{1 + K_{\mathrm{eq}}} \simeq 1.0\ \mathrm{M}. \quad \text{Now} \quad [\mathrm{Ni^{2+}}] = \frac{[\mathrm{Zn^{2+}}]}{K_{\mathrm{eq}}} = \frac{1.0\ \mathrm{M}}{1.78\times 10^{17}} = 5.6 \times 10^{-18}\ \mathrm{M}.$$

7. For the galvanic cell $\mathrm{Ag\,|\,AgCl(s)\,|\,KCl(0.2\ M)\,||\,KBr\ (0.001\ M)\,|\,AgBr(s)\,|\,Ag}$. Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell at 25 °C. Given: $K^\circ_{\mathrm{sp}}(\mathrm{AgCl}) = 2.8 \times 10^{-10}$ and $K^\circ_{\mathrm{sp}}(\mathrm{AgBr}) = 3.3 \times 10^{-13}$. (1992)

Solution The cell reaction and its potential may be determined as follows.

Half-cell	*Reduction reaction*	*Reduction potential*
(i) LHC	$\mathrm{AgCl + e^- \rightarrow Ag + Cl^-}$	$E_{\mathrm{Cl^-\,|\,AgCl\,|\,Ag}} = E^\circ_{\mathrm{Cl^-\,|\,AgCl\,|\,Ag}} - \dfrac{RT}{F}\ln\,[\mathrm{Cl^-}]$
(ii) RHC	$\mathrm{AgBr + e^- \rightarrow Ag + Br^-}$	$E_{\mathrm{Br^-\,|\,AgBr\,|\,Ag}} = E^\circ_{\mathrm{Br^-\,|\,AgBr\,|\,Ag}} - \dfrac{RT}{F}\ln\,[\mathrm{Br^-}]$

Subtracting Eq. (i) from Eq. (ii), we get

Cell reaction $\quad Cl^- + AgBr \rightarrow Br^- + AgCl$

Cell potential $\quad E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{F}\ln\dfrac{[Br^-]}{[Cl^-]} \qquad (1)$

where $\quad E^\circ_{\text{cell}} = E^\circ_{Br^- | AgBr | Ag} - E^\circ_{Cl^- | AgCl | Ag}$.

The expression of $E^\circ_{Br^- | AgBr | Ag}$ (or $E^\circ_{Cl^- | AgCl | Ag}$) may be derived in terms of $E^\circ_{Ag^+ | Ag}$ and the corresponding solubility product constant of AgBr (or AgCl).

In the assembly $Br^- | AgBr | Ag$, some AgBr will dissolve in KBr solution whose solubility will be dictated through solubility product constant. The half-cell $Br^- | AgBr|Ag$ may be equivalently taken as $Ag^+|Ag$. The potential of half-cell computed through $Br^-|AgBr|Ag$ and $Ag^+ | Ag$ will be identical , i.e.

$$E_{Br^- |AgBr|Ag} = E_{Ag^+ | Ag}$$

or $$E^\circ_{Br^- |AgBr|Ag} - \frac{RT}{F}\ln[Br^-] = E^\circ_{Ag^+ | Ag} - \frac{RT}{F}\ln\frac{1}{[Ag^+]}$$

or $$E^\circ_{Br^-|AgBr|Ag} = E^\circ_{Ag^+ | Ag} + \frac{RT}{F}\ln[Ag^+][Br^-] = E^\circ_{Ag^+ | Ag} + \frac{RT}{F}\ln K^\circ_{sp}(AgBr)$$

Similarly, $$E^\circ_{Cl^- | AgCl | Ag} = E^\circ_{Ag^+ | Ag} + \frac{RT}{F}\ln K^\circ_{sp}(AgCl)$$

Thus $$E^\circ_{\text{cell}} = E^\circ_{Br^-|AgBr|Ag} - E^\circ_{Cl^- | AgCl | Ag} = \frac{RT}{F}\ln\frac{K^\circ_{sp}(Ag\,Br)}{K^\circ_{sp}(AgCl)}$$

Substituting the values, we get $\quad E^\circ_{\text{cell}} = (0.059\,15\text{ V})\log\left(\dfrac{3.3\times10^{-13}}{2.8\times10^{-10}}\right) = -\,0.173\,2\text{ V}$

With this, Eq. (1) becomes $\quad E^\circ_{\text{cell}} = (-\,0.173\,2\text{ V}) - (0.059\,15\text{ V})\log\left(\dfrac{0.001}{0.2}\right) = -\,0.037\,1\text{ V}$

Since the cell potential comes out to be negative, the cell reaction will be nonspontaneous. The spontaneous reaction will be $AgCl + Br^- \rightarrow AgBr + Cl^-$ with $Cl^- | AgCl | Ag$ serving as cathode (positive terminal) and $Br^- | AgBr | Ag$ serving as anode (negative terminal). The spontaneity is due to the fact that AgBr is less soluble than AgCl.

[Alternatively, the given cell may be written as $Ag|Ag^+(c_1), Cl^-(0.2\text{ M}) \| Ag^+(c_2), Br^-(0.001\text{ M}) | Ag$ with the cell reaction as $\quad (Ag^+)_{RHC} \rightarrow (Ag^+)_{LHC}$

and cell potential as $\quad E_{\text{cell}} = -\dfrac{RT}{F}\ln\dfrac{[Ag^+]_{LHC}}{[Ag^+]_{RHC}}$

Now $[Ag^+]_{LHC}$ and $[Ag^+]_{RHC}$ may be computed through solubility product expressions. Hence, we have

$$E_{\text{cell}} = -\frac{RT}{F}\ln\left(\frac{K_{sp}(AgCl)/[Cl^-]}{K_{sp}(AgBr)/[Br^-]}\right) = -\,(0.059\,15\text{ V})\log\left(\frac{2.8\times10^{-10}/0.2}{3.3\times10^{-13}/0.001}\right) = -\,0.037\text{ V.}]$$

8. The standard reduction potential for the half-cell $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O$ is 0.78 V

(a) Calculate the reduction potential at 8 M H^+.

(b) What will be the reduction potential of the half-cell in a neutral solution? Assume all other species to be at unit concentration. (1993)

Solution For the half-cell reaction $\quad NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$, the Nernst equation is (1)

$$E = E^\circ - \frac{RT}{F}\ln\frac{p_{NO_2}}{[NO_3^-][H^+]^2}$$

(a) In 8 M H^+, we have $\quad E = (0.78\text{ V}) - (0.059\,15\text{ V})\log\dfrac{1}{8^2} = 0.78 + (0.05915)(2)\log 8$

$$= 0.78 + (0.059\,15)(2)(0.903) = 0.887\text{ V}$$

(b) For a neutral solution at 25 °C, $[H^+] = 10^{-7}$ M.

Hence, $$E = 0.78\ \text{V} - (0.05915\ \text{V}) \log \frac{1}{(10^{-7})^2} = 0.78\ \text{V} + (0.05915\ \text{V})\,(2)\,(-7) = -0.046\ \text{V}.$$

9. The standard reduction potential of the $Ag^+ | Ag$ electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the $Ag^+ | Ag$ electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^- | AgI | Ag$ electrode. (1996)

Solution The concentration of Ag^+ in the saturated solution of AgI is

$$s = \sqrt{K_{sp}} = \sqrt{8.7 \times 10^{-17}\ \text{M}^2} = 9.33 \times 10^{-9}\ \text{M}$$

For the cell reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, the Nernst equation is

$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{[Ag^+]}$$

Hence, $$E = 0.799\ \text{V} - (0.05915\ \text{V}) \log \left(\frac{1}{9.33 \times 10^{-9}} \right)$$

$$= 0.799\ \text{V} - (0.05915\ \text{V})\,(8.030) = 0.799\ \text{V} - 0.475\ \text{V} = 0.324$$

The expression relating $E^\circ_{I^- | AgI | Ag}$ and $E^\circ_{Ag^+ | Ag}$ is

$$E^\circ_{I^- | AgI | Ag} = E^\circ_{Ag^+ | Ag} + \frac{RT}{F} \ln K_{sp}(AgI) = 0.799\ \text{V} + (0.05915\ \text{V}) \log (8.7 \times 10^{-17})$$

$$= 0.799\ \text{V} - (0.05915 \times 16.0605)\ \text{V} = 0.799\ \text{V} - 0.950\ \text{V} = 0.151\ \text{V}.$$

10. The Edison storage cell is represented as $Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3(s) | Ni(s)$

The half-cell reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-(aq) \qquad E^\circ = +0.40\ \text{V}$$

$$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-(aq) \qquad E^\circ = -0.87\ \text{V}$$

(i) What is the cell reaction?

(ii) What is the cell emf? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3? (1994)

Solution (i) The Edison storage cell is $Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3(s) | Ni(s)$

The cell reaction is obtained by subtracting reduction reaction of left half-cell from that of right half-cell.

Right half-cell $Ni_2O_3(s) + H_2O(l) + 2e^- = 2NiO(s) + 2OH^-(aq)$

Left half-cell $FeO(s) + H_2O(l) + 2e^- = Fe(s) + 2OH^-(aq)$

Subtract

$Fe(s) + Ni_2O_3(s) = FeO(s) + 2NiO(s)$

(ii) The cell emf is given as $E_{cell} = E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.40\ \text{V} - (-0.87\ \text{V}) = 1.27\ \text{V}$

The cell emf is independent of concentration of KOH as no OH^- appears in the cell reaction.

(iii) The maximum electrical energy obtained per mole of Ni_2O_3 (in the cell reaction, stoichimetric number of Ni_2O_3 is also one) would be

$$\Delta G = -nFE = -(2)\,(96500\ \text{C mol}^{-1})\,(1.27\ \text{V}) = -2.4511 \times 10^5\ \text{J mol}^{-1} = -245.11\ \text{kJ mol}^{-1}$$

11. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25 °C. Calculate $E^\circ(Hg_2^{2+} | Hg)$, assuming that the only reaction that occurs is $2Hg + 2Fe^{3+} \rightarrow Hg_2^{2+} + 2Fe^{2+}$. Given: $E^\circ(Fe^{3+} | Fe^{2+}) = 0.77$ V. (1995)

Solution The reaction occurring is

	2Hg	+	2 Fe^{3+}	$\rightleftharpoons$	Hg_2^{2+}	+	$2Fe^{2+}$
$t = 0$			1.0×10^{-3} M				0
t_{eq}	excess		$\frac{5}{100}$ $(1.0 \times 10^5$ M)		$\frac{1.0 \times 10^{-3} - 5.0 \times 10^{-5}}{2}$ M		$(1.0 \times 10^{-3} - 5.0 \times 10^{-5})$ M
			$= 5.0 \times 10^{-5}$ M		$= 4.75 \times 10^{-4}$ M		$= 9.5 \times 10^{-4}$ M

$$K_{\text{eq}} = \frac{[\text{Hg}_2^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} = \frac{(4.75\times10^{-4}\ \text{M})(9.5\times10^{-4}\ \text{M})^2}{(5.0\times10^{-5}\ \text{M})^2} = 0.171\,5\ \text{M}$$

The cell producing this chemical reaction is

$$\text{Pt} \mid \text{Hg(l)} \mid \text{Hg}_2^{2+}\text{(aq)} \parallel \text{Fe}^{3+}\text{(aq)},\ \text{Fe}^{2+}\text{(aq)} \mid \text{Pt}$$

with $$E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{Fe}^{3+},\ \text{Fe}^{2+} \mid \text{Pt}} - E^\circ_{\text{Hg}_2^{2+} \mid \text{Hg}} \qquad (1)$$

The standard cell potential, E°_{cell}, is related to K°_{eq} by the expression $E^\circ_{\text{cell}} = \dfrac{RT/F}{n} \ln K^\circ_{\text{eq}}$

For the given reaction, $n = 2$. At 298 K, we will have

$$E^\circ_{\text{cell}} = \frac{(0.05915\ \text{V})}{2} \log\,(0.171\,5) = -\,0.023\ \text{V} \qquad (2)$$

Equating Eqs. (1) and (2), we get

$$E^\circ_{\text{Fe}^{3+},\ \text{Fe}^{2+} \mid \text{Pt}} - E^\circ_{\text{Hg}_2^{2+} \mid \text{Hg}} = -\,0.023\ \text{V}$$

or $$E^\circ_{\text{Hg}_2^{2+} \mid \text{Hg}} = E^\circ_{\text{Fe}^{3+},\ \text{Fe}^{2+} \mid \text{Pt}} + 0.023\ \text{V} = 0.77\ \text{V} + 0.023\ \text{V} = 0.793\ \text{V}.$$

12. What pressure of H_2 would be required to make the potential of the hydrogen electrode zero in pure water at 25 °C?

Solution The half-cell reaction is $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Its Nernst equation is $$E = E^\circ - \frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{[\text{H}^+]^2}$$

Now since $E^\circ = 0$, we get $$E = -\frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{[\text{H}^+]^2}$$

To have $E = 0$, we must have

$$p_{\text{H}_2}/\text{bar} = \left([\text{H}^+]/\text{M}\right)^2 = (10^{-7})^2 = 10^{-14}.$$

$$p_{\text{H}_2} = 10^{-14}\ \text{bar}$$

13. Calculate the solubility product of AgI from the following data. $E^\circ_{\text{Ag}^+ \mid \text{Ag}} = 0.80$ V and $E^\circ_{\text{I}^- \mid \text{AgI} \mid \text{Ag}} = -\,0.15$ V

Solution The expression of solubility product constant for AgI is $\text{AgI(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{I}^-\text{(aq)}$

This reaction may be produced by the addition of the following two half-cell reactions.

Anode	$\text{Ag(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{e}^-$
Cathode	$\text{AgI(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{I}^-\text{(aq)}$

The cell producing these reactions would be $\text{Ag(s)} \mid \text{Ag}^+\text{(aq)} \parallel \text{I}^-\text{(aq)} \mid \text{AgI(s)} \mid \text{Ag(s)}$

The standard cell potential would be $E^\circ = E^\circ_{\text{I}^- \mid \text{AgI} \mid \text{Ag}} - E^\circ_{\text{Ag}^+ \mid \text{Ag}} = -\,0.15\ \text{V} - 0.80\ \text{V} = -\,0.95\ \text{V}$

Now using the expression $nFE^\circ = RT \ln K_{\text{sp}}$, we get

$$K_{\text{sp}} = \text{antilog}\left(\frac{nFE^\circ}{2.303\,RT}\right) = \text{antilog}\left(\frac{nE^\circ}{2.303\,RT/F}\right) = \text{antilog}\left(\frac{-0.95}{0.05915}\right) = \text{antilog}\,(-16.05)$$

$$= 8.9 \times 10^{-17}$$

14. The reversible reduction potential of pure water is – 0.414 V at 298 K and 1.0 bar hydrogen pressure. If the reduction reaction to be considered is $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, calculate the hydrogen ion concentration of pure water.

Solution The Nernst equation for the reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ is

$$E = -\,\frac{RT}{2F} \ln \frac{p_{\text{H}_2\text{O}}/\text{bar}}{([\text{H}^+]/\text{M})^2}$$

Substituting the given data, we get

$$-\,0.414\ \text{V} = -\left(\frac{0.05915}{2}\ \text{V}\right) \log \frac{1}{([\text{H}^+]/\text{M})^2}$$

which gives $$\log \frac{1}{[\text{H}^+]/\text{M}} = \frac{0.414}{0.05915} = 6.999 \qquad \text{i.e.} \qquad \text{pH} = 6.999$$

or $$[\text{H}^+] = \text{antilog}\,(-\,6.999) = 1.0 \times 10^{-7}\ \text{M}$$

15. A solution containing 1 M each of $AgNO_3$ and $Fe(NO_3)_2$ is allowed to come to equilibrium at 298 K. What are the values of $[Fe^{2+}]$, $[Fe^{3+}]$ and $[Ag^+]$ at this point? The reaction occurring is

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Given: $E^\circ_{Fe^{3+},\,Fe^{2+}\,|\,Pt} = 0.770\ V$ and $E^\circ_{Ag^{+}\,|\,Ag} = 0.7996\ V$.

Solution In the given reaction, Fe^{2+} is oxidized to Fe^{3+} and Ag^+ is reduced to Ag. The cell producing this reaction would be

$$Pt \,|\, Fe^{3+}(aq),\ Fe^{2+}(aq) \,||\, Ag^{+}(aq) \,|\, Ag$$

with $E^\circ_{cell} = E^\circ_{Ag^{+}\,|\,Ag} - E^\circ_{Fe^{3+},\,Fe^{2+}\,|\,Pt} = (0.7996 - 0.770)V = 0.0296\ V$

The equilibrium constant of the reaction will be given as

$$\log K^\circ_{eq} = \frac{nFE^\circ}{2.303RT} = \frac{nE^\circ}{(2.303RT/F)} = \frac{0.0296\,V}{0.05915\,V} \simeq \frac{1}{2}$$

$$K^\circ_{eq} = 3.16$$

At equilibrium, the concentrations of various species involved in the reactions will be as follows.

$$\begin{array}{ccccccc} Fe^{2+} & + & Ag^{+} & \rightleftharpoons & Fe^{3+} & + & Ag \\ 1.0\ M - x & & 1.0\ M - x & & x & & x \end{array}$$

Hence, $$K_{eq} = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{x}{(1.0\,M - x)^2}$$

Substituting the value of K_{eq} and solving for x, we get

$$x = 1.74\ M \quad \text{and} \quad x = 0.574\ M$$

As $x = 1.74$ M is greater than 1.0 M, it is a meaningless quantity. Hence,

$$x = 0.574\ M$$

Thus $[Fe^{2+}] = 1.0\ M - 0.574\ M = 0.426\ M$ $\quad [Fe^{3+}] = 0.574\ M$

$[Ag^{+}] = 1.0\ M - 0.574\ M = 0.426\ M.$

16. Two cells are constructed in which the $Ni^{2+}\,|\,Ni$ is one of the half-cells. When the other half-cell is $Cu^{2+}\,|\,Cu$, the E° is measured as 0.570 V with the nickel electrode as anode. When the $Mg^{2+}\,|\,Mg$ electrode is the other half-cell, the E° is measured as 2.145 V with the magnesium electrode as the anode. Calculate E° for the cell made of the magnesium and copper electrodes and designate the anode and cathode.

Solution In the first case, since nickel electrode is anode, the cell would be

$$Ni \,|\, Ni^{2+}(aq) \,||\, Cu^{2+}(aq) \,|\, Cu \quad \text{with} \quad E^\circ_1 = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Ni^{2+}\,|\,Ni} \tag{1}$$

In the second case, since magnesium electrode is anode, the cell would be

$$Mg \,|\, Mg^{2+}(aq) \,||\, Ni^{2+}(aq) \,|\, Ni \quad \text{with} \quad E^\circ_2 = E^\circ_{Ni^{2+}\,|\,Ni} - E^\circ_{Mg^{2+}\,|\,Mg} \tag{2}$$

Adding Eqs. (1) and (2), we get $E^\circ_1 + E^\circ_2 = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Mg^{2+}\,|\,Mg}$

Substituting the values of E°_1 and E°_2, we get

$$E^\circ = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Mg^{2+}\,|\,Mg} = E^\circ_1 + E^\circ_2 = (0.570 + 2.145)\ V = 2.715\ V$$

Since E° is positive, the cell made from $Cu^{2+}\,|\,Cu$ and $Mg^{2+}\,|\,Mg$ will have Cu electrode as cathode and magnesium electrode as anode.

17. Given that $K_{sp}(AgCl) > K_{sp}(AgBr) > K_{sp}(AgI)$, show that $E^\circ_{Cl^-\,|\,AgCl\,|\,Ag} > E^\circ_{Br^-\,|\,AgBr\,|\,Ag} > E^\circ_{I^-\,|\,AgI\,|\,Ag}$.

Solution Consider a half-cell assembly of silver dipped into a saturated solution of AgCl. This assembly may be viewed as $Ag^+\,|\,Ag$ half-cell or $Cl^-\,|\,AgCl\,|\,Ag$ half-cell. The potential of the half-cell calculated from the Nernst equation of either $Ag^+\,|\,Ag$ half-cell or $Cl^-\,|\,AgCl\,|\,Ag$ half-cell will come out to be identical. Hence, we have

$Ag^+\,|\,Ag$ *half-cell* $\quad Ag^{+}(aq) + e^{-} \rightleftharpoons Ag \quad$ $$E = E^\circ_{Ag^{+}\,|\,Ag} - \frac{RT}{F} \ln \frac{1}{[Ag^{+}]/M} \tag{1}$$

$Cl^-\,|\,AgCl\,|\,Ag$ *half-cell* $\quad AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}(aq) \quad$ $$E = E^\circ_{Cl^{-}\,|\,AgCl\,|\,Ag} - \frac{RT}{F} \ln [Cl^{-}]/M \tag{2}$$

Equating Eqs (1) and (2), we get

$$E^\circ_{\mathrm{Cl^-\,|\,AgCl\,|\,Ag}} - \frac{RT}{F}\ \ln\ [\mathrm{Cl^-}]/\mathrm{M} = E^\circ_{\mathrm{Ag^+\,|\,Ag}} - \frac{RT}{F}\ \ln\ \frac{1}{[\mathrm{Ag^+}]/\mathrm{M}}$$

or
$$E^\circ_{\mathrm{Cl^-\,|\,AgCl\,|\,Ag}} = E^\circ_{\mathrm{Ag^+\,|\,Ag}} + \frac{RT}{F}\ \ln\left(\frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{\mathrm{M^2}}\right) = E^\circ_{\mathrm{Ag^+\,|\,Ag}} + \frac{RT}{F}\ \ln\ K^\circ_{\mathrm{sp}}(\mathrm{AgCl})$$

In general, we have $E^\circ_{\mathrm{X^-\,|\,AgX\,|\,Ag}} = E^\circ_{\mathrm{Ag^+\,|\,Ag}} + \dfrac{RT}{F}\ \ln K^\circ_{\mathrm{sp}}(\mathrm{AgX})$

Now since $K^\circ_{\mathrm{sp}}(\mathrm{AgCl}) > K^\circ_{\mathrm{sp}}(\mathrm{AgBr}) > K^\circ_{\mathrm{sp}}(\mathrm{AgI})$ it follows that $E^\circ_{\mathrm{Cl^-\,|\,AgCl\,|\,Ag}} > E^\circ_{\mathrm{Br^-\,|\,AgBr\,|\,Ag}} > E^\circ_{\mathrm{I^-\,|\,AgI\,|\,Ag}}$.

18. Show that $E^\circ_{\mathrm{Cu^+\,|\,Cu}} = 2\ E^\circ_{\mathrm{Cu^{2+}\,|\,Cu}} - E^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}}$ Also calculate $E^\circ_{\mathrm{Cu^+\,|\,Cu}}$ if $E^\circ_{\mathrm{Cu^{2+}\,|\,Cu}} = 0.337$ V and $E^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}} = 0.153$ V.

Solution For the given three half-cells, we tabulate the following information.

Cell	*Cell-reaction*	*Standard cell potential*	ΔG° $(= -nFE^\circ)$
1. $\mathrm{Cu^+\,|\,Cu}$	$\mathrm{Cu^+ + e^- \rightarrow Cu}$	$E^\circ_{\mathrm{Cu^+\,|\,Cu}}$	$-F\,E^\circ_{\mathrm{Cu^+\,|\,Cu}}$
2. $\mathrm{Cu^{2+}\,|\,Cu}$	$\mathrm{Cu^{2+} + 2e^- \rightarrow Cu}$	$E^\circ_{\mathrm{Cu^{2+}\,|\,Cu}}$	$-2\,FE^\circ_{\mathrm{Cu^{2+}\,|\,Cu}}$
3. $\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}$	$\mathrm{Cu^{2+} + e^- \rightarrow Cu^+}$	$E^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}}$	$-F\,E^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}}$

Now the cell reaction of Eq. (1) can be obtained by subtracting the cell reaction of Eq. (3) from that of Eq. (2). Thus

$$\Delta G^\circ_{(1)} = \Delta G^\circ_{(2)} - \Delta G^\circ_{(3)}$$

$$-FE^\circ_{\mathrm{Cu^+\,|\,Cu}} = -2\ FE^\circ_{\mathrm{Cu^{2+}\,|\,Cu}} - (-FE^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}})$$

or
$$E^\circ_{\mathrm{Cu^+\,|\,Cu}} = 2\ E^\circ_{\mathrm{Cu^{2+}\,|\,Cu}} - E^\circ_{\mathrm{Cu^{2+},\,Cu^+\,|\,Pt}} = 2 \times 0.337\ \mathrm{V} - 0.153\ \mathrm{V} = 0.521\ \mathrm{V}.$$

19. Calculate the quantity of electricity delivered by a Daniell cell, initially containing 1.0 L each of 1.0 M copper(II) ions and 1.0 M zinc(II) ions, which is operated until its potential drops to 1.0 V. Given: $E^\circ(\mathrm{Zn^{2+}\,|\,Zn}) = -0.763$ V and $E^\circ(\mathrm{Cu^{2+}\,|\,Cu}) = 0.34$ V.

Solution The cell reaction is as follows.

Anode $\mathrm{Zn \rightarrow Zn^{2+} + 2e^-}$
Cathode $\mathrm{Cu^{2+} + 2e^- \rightarrow Cu}$
Cell-reaction $\mathrm{Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu}$

As the electricity is withdrawn from the cell, the concentration of $\mathrm{Cu^{2+}}$ ions decreases whereas that of $\mathrm{Zn^{2+}}$ ions increases. Because of these changes, the cell potential varies, which according to Nernst equation is given by

$$E = E^\circ - \frac{RT}{2F}\ \ln\ \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$$

When $E = 1.0$ V, we have

$$1.0\ \mathrm{V} = [0.34\ \mathrm{V} - (-0.763\ \mathrm{V})] - \frac{0.05915\ \mathrm{V}}{2}\ \log\ \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$$

which gives
$$\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]} = \text{antilog}\left[\frac{1.0 - 1.103}{(-0.05915/2)}\right] = \text{antilog}\ (3.483) = 3041$$

Let x be the amount of $\mathrm{Cu^{2+}}$ that is converted into Cu when the cell potential is 1.0 V. Thus, we have

$$\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]} = \frac{1.0\ \mathrm{mol} + x}{1.0\ \mathrm{mol} - x}$$

Hence,
$$\frac{1.0\ \mathrm{mol} + x}{1.0\ \mathrm{mol} - x} = 3041 \quad \text{which gives} \quad x = \frac{3040}{3042}\ \mathrm{mol} = 0.9993\ \mathrm{mol}$$

Now, since to change $\mathrm{Cu^{2+}}$ to Cu (or Zn to $\mathrm{Zn^{2+}}$), 2 electrons are required, we will have

Amount of electrons withdrawn $= 2 \times 0.9993$ mol

Quantity of electricity withdrawn $= 2 \times 0.9993 \times 96500\,\mathrm{C} = 1.929 \times 10^5\,\mathrm{C}$.

20. When metallic copper is shaken with a solution of a copper salt, the reaction $Cu + Cu^{2+} \rightleftharpoons 2Cu^+$ proceeds. When equilibrium is established at 298 K, $[Cu^{2+}]/[Cu^+]^2 = 1.66 \times 10^6\ M^{-1}$. If the standard potential of the $Cu^{2+} \mid Cu$ half-cell is +0.337 V, what is the standard potential of $Cu^+ \mid Cu$ half-cell?

Solution The cell producing the given reaction $Cu + Cu^{2+} \rightleftharpoons 2\,Cu^+$ is $Cu \mid Cu^+ \parallel Cu^+, Cu^{2+} \mid Pt$ and its standard emf is given by

$$E^\circ_{cell} = E^\circ_{Cu^{2+}, Cu^+ \mid Pt} - E^\circ_{Cu^+ \mid Cu} \qquad (1)$$

The equilibrium constant of the reaction is $K_{eq} = \dfrac{[Cu^+]^2}{[Cu^{2+}]} = \dfrac{1}{1.66 \times 10^6\ M^{-1}} = 6.024 \times 10^{-7}\ M$

Now using the expression $E^\circ_{cell} = \dfrac{RT}{nF} \ln K^\circ_{eq}$

we get $E^\circ_{cell} = \dfrac{0.05915\ V}{1} \log K^\circ_{eq} = (0.05915\ V) \log (6.024 \times 10^{-7})$

$$= (0.05915\ V)(-6.22) = -0.368\ V \qquad (2)$$

Now since
(i) $Cu^+ + e^- = Cu$ $\quad E^\circ_{Cu^+ \mid Cu}$
(ii) $Cu^{2+} + e^- = Cu^+$ $\quad E^\circ_{Cu^{2+}, Cu^+ \mid Pt}$
(iii) $Cu^{2+} + 2e^- = Cu$ $\quad E^\circ_{Cu^{2+} \mid Cu}$

we will have $\Delta G^\circ_{(iii)} = \Delta G^\circ_{(i)} + \Delta G^\circ_{(ii)}$

i.e.
$$E^\circ_{Cu^{2+} \mid Cu} = \frac{E^\circ_{Cu^+ \mid Cu} + E^\circ_{Cu^{2+}, Cu^+ \mid Pt}}{1+1} \qquad (3)$$

From Eqs. (1), (2) and (3), we get

$$E^\circ_{Cu^{2+}, Cu^+ \mid Pt} - E^\circ_{Cu^+ \mid Cu} = -0.368\ V \quad \text{and} \quad E^\circ_{Cu^{2+}, Cu^+ \mid Pt} + E^\circ_{Cu^+ \mid Cu} = 2 \times 0.337\ V = 0.674\ V$$

Solving for $E^\circ_{Cu^{2+}, Cu^+ \mid Pt}$ and $E^\circ_{Cu^+ \mid Cu}$, we get

$$E^\circ_{Cu^{2+}, Cu^+ \mid Pt} = 0.153\ V. \quad \text{and} \quad E^\circ_{Cu^+ \mid Cu} = 0.521\ V.$$

21. The half-cell potentials of a half-cell $A^{x+}, A^{(x+n)+} \mid Pt$ were found to be as follows.

per cent of reduced form	24.4	48.8
Cell potential/V	0.101	0.115

Determine the value of n.

Solution The half-cell reaction is $A^{(x+n)+} + ne^- \rightarrow A^{x+}$

Its Nernst equation is $E = E^\circ - \dfrac{RT}{nF} \ln \dfrac{[A^{x+}]}{[A^{(x+n)+}]} = E^\circ - \left(\dfrac{0.05915\ V}{n}\right) \log \dfrac{[\text{reduced form}]}{[\text{oxidized form}]}$

Substituting the given values, we get

$$0.101\ V = E^\circ - \left(\frac{0.05915\ V}{n}\right) \log \frac{24.4}{75.6} = E^\circ - \left(\frac{0.05915\ V}{n}\right)(0.491) \qquad (1)$$

$$0.115\ V = E^\circ - \left(\frac{0.05915\ V}{n}\right) \log \frac{48.8}{51.2} = E^\circ - \left(\frac{0.05915\ V}{n}\right)(0.021) \qquad (2)$$

Subtracting Eq. (1) from Eq. (2), we get

$$0.014\ V = \left(\frac{0.05915\ V}{n}\right)(0.491 - 0.021) \quad \text{or} \quad n = \frac{(0.05915\ V)(0.47)}{(0.014\ V)} \simeq 1.98 \simeq 2.$$

22. From the standard cell potentials given below, calculate the indicated cell potential E°.

$$\begin{tikzcd} BrO_3^-(aq) \arrow[r, "0.54\ V"] \arrow[rr, bend right, "E^\circ"'] & BrO^-(aq) \arrow[r, "0.45\ V"] & \frac{1}{2}\,Br_2(l) \end{tikzcd}$$

Solution The given half-cell reactions are

$$(1)\ \mathrm{BrO_3^- + 2H_2O + 4e^- = BrO^- + 4OH^-} \qquad E_1^\circ = 0.54\ \mathrm{V}$$

$$(2)\ \mathrm{BrO^- + H_2O + e^- = \tfrac{1}{2}\,Br_2 + 2OH^-} \qquad E_2^\circ = 0.45\ \mathrm{V}$$

$$(3)\ \mathrm{BrO_3^- + 3H_2O + 5e^- = \tfrac{1}{2}\,Br_2 + 6OH^-} \qquad E^\circ = ?$$

Equation (3) can be generated by adding Eqs. (1) and (2). Hence

$$\Delta G^\circ_{(3)} = \Delta G^\circ_{(1)} + \Delta G^\circ_{(2)} \qquad \text{i.e.} \quad -5FE^\circ = -4F(0.54\ \mathrm{V}) - F(0.45\ \mathrm{V})$$

$$E^\circ = \frac{4(0.54\,\mathrm{V}) + (0.45\,\mathrm{V})}{5} = 0.522\ \mathrm{V}$$

23. An excess of solid AgCl is added to a 0.1 M solution of $\mathrm{Br^-}$ ions at 298 K. Calculate the concentrations of $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ ions at equilibrium. Given: $E^\circ(\mathrm{Cl^-} \mid \mathrm{AgCl} \mid \mathrm{Ag}) = 0.222$ V and $E^\circ(\mathrm{Br^-} \mid \mathrm{AgBr} \mid \mathrm{Ag}) = 0.095$ V.

Solution When AgCl is added to a solution containing $\mathrm{Br^-}$ ions, the reaction to be considered is

$$\mathrm{AgCl(s) + Br^-(aq) \rightarrow AgBr(s) + Cl^-(aq)}$$

The two half-cell reactions and cell reaction are

Reduction $\mathrm{AgCl + e^- \rightarrow Ag + Cl^-}$
Oxidation $\mathrm{Ag + Br^- \rightarrow AgBr + e^-}$
Cell reaction $\mathrm{AgCl + Br^- \rightarrow AgBr + Cl^-}$

The cell producing the above reactions is $\mathrm{Ag(s) \mid AgBr(s) \mid Br^-(aq) \parallel Cl^-(aq) \mid AgCl(s) \mid Ag(s)}$

Its standard emf would be $E^\circ_{\text{cell}} = E^\circ_{\mathrm{Cl^- \mid AgCl \mid Ag}} - E^\circ_{\mathrm{Br^- \mid AgBr \mid Ag}} = 0.222\ \mathrm{V} - 0.095\ \mathrm{V} = 0.127\ \mathrm{V}$

Now using the expression $\log K_{\text{eq}} = \dfrac{nFE^\circ_{\text{cell}}}{2.303\,RT}$

we get $$\log K_{\text{eq}} = \frac{(1)(96\,500\,\mathrm{C})(0.127\,\mathrm{V})}{2.303(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(298\ \mathrm{K})} = 2.148$$

Hence, $K_{\text{eq}} = 140.6$

Let x be amount of $\mathrm{Br^-}$ that has converted to $\mathrm{Cl^-}$ at equilibrium. We have

$$K_{\text{eq}} = \frac{[\mathrm{Cl^-}]}{[\mathrm{Br^-}]} = \frac{x}{0.1\,\mathrm{M} - x} = 140.6$$

Solving for x, we get $x = 0.0993$ M

Hence $[\mathrm{Cl^-}] = 0.0993$ M and $[\mathrm{Br^-}] = 0.1\ \mathrm{M} - 0.0993\ \mathrm{M} = 0.0007$ M.

24. The standard reduction potential for $\mathrm{Cu^{2+}|Cu}$ is + 0.34 V. Calculate the reduction potential at pH = 14 for the above couple in a saturated solution of cupric hydroxide. K°_{sp} of $\mathrm{Cu(OH)_2}$ is 1.0×10^{-19}.

Solution For the reaction $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$

the reduction potential is $$E = E^\circ - \frac{RT}{2F}\ln\frac{1}{[\mathrm{Cu^{2+}}]/\mathrm{M}}$$

From the given data pH = 14 and $K^\circ_{\text{sp}}(\mathrm{Cu(OH)_2}) = 1.0 \times 10^{-19}$, we get

$$[\mathrm{H^+}] = 10^{-14}\ \mathrm{M}, \qquad [\mathrm{OH^-}] = \frac{K_{\text{w}}}{[\mathrm{H^+}]} = \frac{10^{-14}\,\mathrm{M^2}}{10^{-14}\ \mathrm{M}} = 1\ \mathrm{M}$$

$$[\mathrm{Cu^{2+}}] = \frac{K_{\text{sp}}}{[\mathrm{OH^-}]^2} = \frac{1.0\times10^{-19}\ \mathrm{M^2}}{1\,\mathrm{M}} = 1.0 \times 10^{-19}\ \mathrm{M}$$

Hence, $$E = 0.34\ \mathrm{V} - \left(\frac{0.059\ \mathrm{V}}{2}\right)\log\frac{1}{(1.0\times10^{-19})} = 0.34\ \mathrm{V} - \frac{0.059\times19\ \mathrm{V}}{2} = 0.34\ \mathrm{V} - 0.56\ \mathrm{V}$$

$$= -\,0.22\ \mathrm{V}$$

25. Calculate the equilibrium constant for the reaction $\mathrm{Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}}$. (1997)
(Given: $E^\circ_{\mathrm{Ce^{4+}|Ce^{3+}}} = 1.44$ V and $E^\circ_{\mathrm{Fe^{3+}|Fe^{2+}}} = 0.68$ V.)

Solution The cell producing the reaction $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$ is $Pt\ |Fe^{2+}, Fe^{3+}||Ce^{4+}, Ce^{3+}|\ Pt$

The standard cell potential is $E^\circ_{cell} = E^\circ_R - E^\circ_L = 1.44\ V - 0.68\ V = 0.76\ V$

Since $\Delta G^\circ = -\ nFE^\circ$ and $\Delta G^\circ = -\ RT \ln K^\circ_{eq}$, we get

$$\log K^\circ_{eq} = \frac{n\,FE^\circ}{2.303\,RT} = \frac{(1)\,(96500\ C\ mol^{-1})\,(0.76\ V)}{(2.303)(8.314\ J\ K^{-1}mol^{-1})(298\ K)} = 12.85$$

Hence $K^\circ_{eq} = 7.14 \times 10^{12}$

26. Calculate the equilibrium constant for the reaction $2\ Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for $Fe^{3+}|Fe^{2+}$ and $I_3^-|I^-$ couples. (1998)

Solution The given reaction is $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$

Its partial reactions are $2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$ and $3I^- \rightleftharpoons I_3^- + 2e^-$

The standard emf of the cell producing these reactions is

$$E^\circ_{cell} = E^\circ_{Fe^{3+},\ Fe^{2+}\ |Pt} - E^\circ_{I^-,\ I_3^-|\ Pt} = 0.77\ V - 0.54\ V = 0.23\ V$$

Now, using the expression $\log K^\circ = \dfrac{n\,E^\circ}{2.303\ RT/F}$ at 298 K, we get log

$$K^\circ = \frac{(2)\,(0.23\ V)}{(0.05915\ V)} = 7.777 \quad \text{or} \quad K^\circ = 5.98 \times 10^7$$

27. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag\ |Ag^+(\text{satd. } Ag_2CrO_4\ \text{soln.})||Ag^+(0.1\ M)|Ag$ is 0.164 V at 298 K. (1998)

Solution The given cell is $Ag\ |Ag^+(\text{saturated } Ag_2CrO_4\ \text{soln.})||Ag^+(0.1\ M)|\ Ag$

Cell Reaction Right half-cell $(Ag^+)_R + e^- \rightarrow Ag$

Left half-cell $Ag \rightarrow (Ag^+)_L + e^-$

Cell reaction $(Ag^+)_R \rightarrow (Ag^+)_L$

Cell potential $E_{cell} = -\dfrac{RT}{F} \ln \dfrac{[Ag^+]_L}{[Ag^+]_R}$

In the left half-cell, the concentration of Ag^+ will be related to the solubility product of Ag_2CrO_4 as shown in the following.

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

If x is the solubility of Ag_2CrO_4 in solution, then

$[Ag^+] = 2x$ and $[CrO^{2-}_4] = x$

and $K_{sp} = [Ag^+]^2\ [CrO_4^{2-}] = (2x)^2\ (x)$ or $x = (K_{sp}/4)^{1/3}$

$\Rightarrow$ $[Ag^+]_L = 2x = 2(K_{sp}/4)^{1/3} = (2K_{sp})^{1/3}$

With its, the cell potential becomes $E_{cell} = -\dfrac{RT}{F} \ln \dfrac{(2\,K_{sp})^{1/3}}{[Ag^+]_R}$

Substituting the given data, we get

$$0.164\ V = -\ (0.059\ V) \log \frac{(2\ K_{sp})^{1/3}}{(0.1\,M)} \quad \text{or} \quad \log\ (2\ K_{sp}/M^3)^{1/3} = -\frac{0.164}{0.059} + \log\ 0.1 = -\ 3.78$$

or $2\ K_{sp}/M^3 = \text{antilog}\ (-\ 3 \times 3.78) = 4.57 \times 10^{-12}$

or $K_{sp} = 2.29 \times 10^{-12}\ M^3$

28. A cell, $Ag\ |Ag^+||Cu^{2+}|Cu$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. (1999)

Solution Quantity of electricity passed is $Q = It = (9.65\ A)\ (60 \times 60\ s)$

Amount of electrons passed is $n = \dfrac{Q}{F} = \dfrac{(9.65\ A)\ (60 \times 60\ s)}{(96500\ C\ mol^{-1})} = 0.36\ mol$

The cell reaction is

Left half cell	$Ag(s) \rightarrow Ag^+(aq) + e^-$
Right half cell	$\frac{1}{2}Cu^{2+}(aq) + e^- \rightarrow \frac{1}{2}Cu(s)$
Cell reaction	$Ag(s) + \frac{1}{2}Cu^{2+}(aq) \rightarrow Ag^+(aq) + \frac{1}{2}Cu(s)$

The given data are

	$Ag(s)$	+	$\frac{1}{2}Cu^{2+}(aq)$	$\rightarrow$	$Ag^+(aq)$ + $\frac{1}{2}Cu(s)$
$t = 0$			1 M		1 M
After passing the current			(1 – 0.36/2) M		(1 + 0.36) M

The Nernst equation is $E = E° - \frac{RT}{F}\ \ln \frac{[Ag^+]}{[Cu^{2+}]^{1/2}}$

Substituting the given data, we get

$$E_1 = E° - (0.059\ V)\ \log \frac{1}{(1)^{1/2}} = E° \qquad \text{and} \qquad E_2 = E° - (0.059\ V)\ \log \frac{1.36}{\sqrt{0.82}} = E° - 0.010\ V$$

$$\Delta E = E_2 - E_1 = -\ 0.010\ V$$

29. The following electrochemical cell has been set up.

$$Pt(1)\ |\ Fe^{3+},\ Fe^{2+}\ (a = 1)||Ce^{4+},\ Ce^{3+}(a = 1)|\ Pt(2)$$

Given that $E°(Fe^{3+}, Fe^{2+}) = 0.77$ V and $E°(Ce^{4+}, Ce^{3+}) = 1.61$ V

If an ammeter is connected between two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? (2000)

Solution For the electrochemical cell $Pt(1)\ |Fe^{3+}, Fe^{2+}\ (a = 1)||Ce^{4+}, Ce^{3+}\ (a = 1)|\ Pt(2)$ the cell reactions are

Right half cell : reduction	$Ce^{4+} + e^- \rightarrow Ce^{3+}$
Left half cell : oxidation	$Fe^{2+} \rightarrow Fe^{3+} + e^-$
Add	$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

The net cell potential is $E°_{cell} = E°_R - E°_L = 1.61\ V - 0.77\ V = 0.84\ V$

Since $E°_{cell}$ is positive, the cell reaction is spontaneous. The current in the external circuit will flow from Pt(1) (which serves as anode) to Pt(2), which serves as cathode.

With the passage of time, E_{cell} will decrease and so is the current in the external circuit.

30. The standard potential of the following cell is 0.23 V at 15 °C and 0.21 V at 35 °C.

$$Pt\ |H_2(g)\ |\ HCl(aq)\ |\ AgCl(s)\ |\ Ag(s)$$

(i) Write the cell reaction.

(ii) Calculate $\Delta H°$ and $\Delta S°$ for the cell reaction by assuming that these quantities remain unchanged in the range 15 °C to 35 °C.

(iii) Calculate the solubility of AgCl at 25 °C. **Given:** The standard reduction potential of the $Ag^+(aq)|Ag(s)$ couple is 0.80 V at 25 °C. (2001)

Solution The given cell is $Pt\ |\ H_2(g)\ |\ HCl(aq)\ |\ AgCl(s)\ |\ Ag(s)$

(i) The cell reaction may be obtained as follows.

Right cell: reduction	$2AgCl(s) + 2e^-$	$\rightarrow$	$Ag(s) + 2Cl^-(aq)^-$
Left cell: oxidation	$H_2(g)$	$\rightarrow$	$2H^+(aq) + 2e^-$
Cell reaction	$2AgCl(s) + H_2(g)$	$\rightarrow$	$2Ag(s) + 2H^+(aq) + 2Cl^-(aq)$

(ii) $\Delta G^\circ_{15^\circ\mathrm{C}} = -\,nFE^\circ = -\,(2)\ (96500\ \mathrm{C\ mol^{-1}})\ (0.23\ \mathrm{V}) = -\,44390\ \mathrm{J\ mol^{-1}}$

$\Delta G^\circ_{35^\circ\mathrm{C}} = -\,nFE^\circ = -\,(2)\ (96500\ \mathrm{C\ mol^{-1}})\ (0.21\ \mathrm{V}) = -\,40530\ \mathrm{J\ mol^{-1}}$

Now $\Delta G^\circ_{15^\circ\mathrm{C}} = \Delta H^\circ - (288\ \mathrm{K})\ \Delta S^\circ = -\,44\ 390\ \mathrm{J\ mol^{-1}}$

$\Delta G^\circ_{35^\circ\mathrm{C}} = \Delta H^\circ - (308\ \mathrm{K})\ \Delta S^\circ = -\,40\ 530\ \mathrm{J\ mol^{-1}}$

Solving for ΔH° and ΔS°, we get

$\Delta H^\circ = -\,99974\ \mathrm{J\ mol^{-1}}$ and $\Delta S^\circ = -\,193\ \mathrm{J\ K^{-1}\ mol^{-1}}$

(iii) The value of ΔG° at 25 °C will be

$\Delta G^\circ = \Delta H^\circ - (298\ \mathrm{K})\ \Delta S^\circ = -\,99974\ \mathrm{J\ mol^{-1}} - (298\ \mathrm{K})\ (293\ \mathrm{J\ K^{-1}\ mol^{-1}})$

$= -\,42460\ \mathrm{J\ mol^{-1}}$

The value of $E^-_{\mathrm{Cl^-|Agcl|Ag}}$ at 25 °C will be $E^\circ = -\dfrac{\Delta G^\circ}{nF} = -\dfrac{(-\,42460\ \mathrm{J\ mol^{-1}})}{(2)(96500\ \mathrm{C\ mol^{-1}})} = 0.22\ \mathrm{V}$

Now using the expression $E^\circ_{\mathrm{Cl^-|Ag\ Cl|Ag}} = E^\circ_{\mathrm{Ag^+|Ag}} + \dfrac{RT}{F}\ \ln K^\circ_{\mathrm{sp}}$

we get $0.22\ \mathrm{V} = 0.80\ \mathrm{V} + (0.05915\ \mathrm{V})\log K^\circ_{\mathrm{sp}}$ or $\log K^\circ_{\mathrm{sp}} = \dfrac{(0.22-0.80)\,\mathrm{V}}{(0.05915\,\mathrm{V})} = -\,9.806$

and Hence $K^\circ_{\mathrm{sp}} = 1.56 \times 10^{-10}$ Solubility of AgCl $= \sqrt{K_{\mathrm{sp}}} = 1.25 \times 10^{-5}\ \mathrm{M}$

31. Two Daniell cells contain the same solution of $ZnSO_4$ but differ in the $CuSO_4$ solution. The emf of the cell containing 0.5 M $CuSO_4$ is higher than the other cell by 0.06 V. Calculate the concentration of $CuSO_4$ in the other cell. (2004)

Solution The reaction occurring in a Daniell cell is $\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$

Its cell emf is given by $E = E^\circ - \dfrac{RT}{2F}\ \ln \dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$

For the two cells, we have

$$E_1 = E^\circ - \frac{RT}{2F}\ \ln \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]_1} \quad \text{and} \quad E_2 = E^\circ - \frac{RT}{2F}\ \ln \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]_2}$$

Hence, $E_2 - E_1 = \dfrac{RT}{2F}\ \ln \dfrac{[\mathrm{Cu^{2+}}]_2}{[\mathrm{Cu^{2+}}]_1}$

If $E_2 > E_1$, then $[\mathrm{Cu^{2+}}]_2 > [\mathrm{Cu^{2+}}]_1$. Hence, we will have

$$0.06\ \mathrm{V} = \left(\frac{0.059\,\mathrm{V}}{2}\right)\ \log\ \left(\frac{0.5\,\mathrm{M}}{[\mathrm{Cu^{2+}}]_1}\right)$$

Hence $[\mathrm{Cu^{2+}}]_1 = (0.5\ \mathrm{M})\ \text{antilog}\ \left(-\dfrac{2\times 0.06}{0.059}\right) = (0.5\ \mathrm{M})\ (0.01) = 0.005\ \mathrm{M}$

32. Determine the standard equilibrium constant at 298 K for the reaction

$$\mathrm{Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^{+}(aq) + In^{3+}(aq)}$$

Given that $E°(Cu^{2+} \mid Cu) = 0.335$ V, $E°(Cu^{+} \mid Cu) = 0.52$ V, $E°(In^{3+}, In^{+} \mid Pt) = -0.42$ V and $E°(In^{2+}, In^{+} \mid Pt) = -0.40$ V. (2004)

Solution In the given reaction In^{2+} is oxidised to In^{3+} and Cu^{2+} is reduced to Cu^{+}. The cell producing this reaction is

$$Pt \mid In^{3+}, In^{2+} \mid \mid Cu^{2+}, Cu^{+} \mid Pt$$

Its standard cell potential is given by $E°_{cell} = E°_{R} - E°_{L} = E°_{Cu^{2+},Cu^{+}|Pt} - E°_{In^{3+},In^{+}|Pt}$

From the given data, we write

(i) $In^{3+} + 2e^{-} = In^{+}$ $\quad \Delta G°_1 = -(2)\,FE°_{In^{3+},In^{+}|Pt} = -2F(-0.42\text{ V})$

$In^{2+} + e^{-} = In^{+}$ $\quad \Delta G°_2 = -(1)\,FE°_{In^{2+},In^{+}|Pt} = -F(-0.40\text{ V})$

From these reactions, we get

$$In^{3+} + e^{-} = In^{2+} \qquad \Delta G° = \Delta G°_1 - \Delta G°_2 = -F(-0.84\text{ V} + 0.40\text{ V})$$
$$= -F(-0.44\text{ V})$$

For this reaction, $\Delta G° = -FE°_{In^{2+},In^{+}|Pt}$. Hence $E°_{In^{2+},In^{+}|Pt} = -0.44$ V

(ii)
$$\begin{array}{lll} & Cu^{2+} + 2e^{-} \rightarrow Cu & \Delta G° = -2F(0.335\text{ V}) \\ & Cu^{+} + e^{-} \rightarrow Cu & \Delta G° = -F(0.52\text{ V}) \\ \hline \text{Subtract} & Cu^{2+} + e^{-} \rightarrow Cu^{+} & \Delta G° = -F(0.15\text{ V}) \end{array}$$

Hence, $E°_{Cu^{2+},Cu^{+}|Pt} = 0.15$ V

Thus, for the given reaction $E°_{cell} = E°_{Cu^{2+},Cu^{+}|Pt} - E°_{In^{3+},In^{2+}|Pt} = 0.15\text{ V} - (-0.44\text{ V}) = 0.59$ V

Finally, from the expression $\Delta_r G° = -nFE° = -RT\ln K°$ we get

$$\log K° = \frac{n}{(2.303\,RT/F)}E° = \frac{1}{(0.059\text{ V})}(0.59\text{ V})$$

Hence, $K° = 10^{10}$

UNSOLVED PROBLEMS

1. Explain why does copper(I) sulphate not exist in an aqueous solution. Given:
   $Cu^{+} + e^{-} \rightarrow Cu \quad E° = 0.53$ V and $Cu^{2+} + e^{-} \rightarrow Cu^{+} \quad E° = 0.15$ V.
2. Chlorine can undergo the following two reactions in an alkaline medium.
   $Cl_2 + 2e^{-} \rightleftharpoons 2\,Cl^{-} \quad E° = 1.36$ V
   $2ClO^{-} + 2H_2O + 2e^{-} \rightleftharpoons Cl_2 + 4OH^{-} \quad E° = 0.40$ V.
   Predict whether or not Cl_2 would disproportionate in alkaline medium.
3. What pressure of H_2 would be required to make the potential of the hydrogen half-cell zero in pure water at 25 °C?
4. Evaluate the standard equilibrium constant for the formation of triodide ion, $I_2 + I^{-} \rightleftharpoons I_3^{-}$, at 298 K from the knowledge that
   $I_2(aq) + 2e^{-} \rightarrow 2I^{-} \quad E° = 0.6197$ V and $I_3^{-} + 2e^{-} \rightarrow 3I^{-} \quad E° = 0.5355$ V.
5. A galvanic cell consisting of two silver electrodes, one in a saturated solution of AgCl and the other in a saturated solution of Ag_2CrO_4, is prepared. What is the value of E_{cell} at 298 K? Given: $K_{sp}(AgCl) = 1.6 \times 10^{-10}\text{ M}^2$ and $K_{sp}(Ag_2CrO_4) = 2.4 \times 10^{-12}\text{ M}^3$?
6. Estimate the standard reduction potential of $S^{2-} \mid CuS \mid Cu$ from the following data:
   $K_{sp}(CuS) = 8.5 \times 10^{-36}\text{ M}^2$ and $E°(Cu^{2+} \mid Cu) = 0.34$ V.
7. Determine the potential of a Daniell cell, initially containing 1.0 L each of 1.0 M copper(II) and 1.0 M zinc(II) ion after 100 kC of charge is withdrawn from it. Given: $E°(Zn^{2+} \mid Zn) = -0.763$ V and $E°(Cu^{2+} \mid Cu) = 0.34$ V.

8. Show that $E^\circ_{\mathrm{Cl^-|AgCl|Ag}} = E^\circ_{\mathrm{Ag^+|Ag}} + \dfrac{RT}{F} \ln K^\circ_{\mathrm{sp}}(\mathrm{AgCl})$.

9. Show that at 298 K $E^\circ_{\mathrm{OH^-|H_2|Pt}} = -0.828$ V

10. Show that $E^\circ_{\mathrm{Fe^{3+}, Fe^{2+}|Pt}} = 3\ E^\circ_{\mathrm{Fe^{3+}|Fe}} - 2\ E^\circ_{\mathrm{Fe^{2+}|Fe}}$

Also calculate $E^\circ_{\mathrm{Fe^{3+}, Fe^{2+}|Pt}}$ if $E^\circ_{\mathrm{Fe^{3+}|Fe}} = -0.036$ V and $E^\circ_{\mathrm{Fe^{2+}|Fe}} = -0.439$ V.

11. Calculate the equilibrium constant at 298 K of the following reactions.

(a) $2\,\mathrm{MnO_4^-} + 6\mathrm{H^+} + 5\mathrm{H_2} \rightarrow 2\mathrm{Mn^{2+}} + 8\mathrm{H_2O}$
(b) $2\mathrm{Cr^{3+}} + 6\ \mathrm{Fe^{3+}} + 7\mathrm{H_2O} \rightarrow 6\mathrm{Fe^{2+}} + \mathrm{Cr_2O_7^{2-}} + 14\ \mathrm{H^+}$
(c) $\mathrm{Hg_2Cl_2(s)} \rightarrow 2\mathrm{Hg(l)} + \mathrm{Cl_2(g)}$

Given: $E^\circ_{\mathrm{MnO_4^-, Mn^{2+}, H^+|Pt}} = 1.51$ V; $E^\circ_{\mathrm{Cr_2O_7^{2-}, Cr^{3+}, H^+|Pt}} = 1.33$ V
$E^\circ_{\mathrm{Fe^{3+}, Fe^{2+}|Pt}} = 0.77$ V; $E^\circ_{\mathrm{Cl^-|Cl_2|Pt}} = 1.3583$ V
$E^\circ_{\mathrm{Cl^-|Hg_2Cl_2|Hg}} = 0.2676$ V;

12. A sample of lead weighing 1.05 g was dissolved in a small quantity of nitric acid to produce an aqueous solution of $\mathrm{Pb^{2+}}$ and $\mathrm{Ag^+}$ (which is present as impurity). The volume of the solution was increased to 350 mL by adding water, a pure silver electrode was immersed in the solution and the potential difference between this electrode and a standard hydrogen electrode was found to be 0.503 V. What was the percentage of silver in the lead metal?

13. The K_{sp} of CuI is $1.1 \times 10^{-12}\ \mathrm{M^2}$. Determine E° for the cell $\mathrm{Cu(s)\,|\,CuI(s)\,|\,I^-(1M)\,||\,Cu^+(1M)\,|\,Cu}$.

14. Show that $E^\circ_{\mathrm{H^+|O_2|Pt}} = 1.229$ V. Given: Half-cell reaction is $\mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow 2\mathrm{H_2O}$.

15. Compute E° for the following reactions at 298 K.

$\mathrm{Ag(NH_3)_2^+} + \mathrm{e^-} \rightleftharpoons \mathrm{Ag} + 2\mathrm{NH_3}$
$\mathrm{Ag(CN)_2^-} + \mathrm{e^-} \rightleftharpoons \mathrm{Ag} + 2\mathrm{CN^-}$

Given: $E^\circ_{\mathrm{Ag^+|Ag}} = 0.799$ V
$\mathrm{Ag^+} + 2\mathrm{NH_3} \rightarrow \mathrm{Ag(NH_3)_2^+}$ $K^\circ = 1.661 \times 10^7$
$\mathrm{Ag^+} + 2\mathrm{CN^-} \rightarrow \mathrm{Ag(CN)_2^-}$ $K^\circ = 5.013 \times 10^{18}$

16. (a) The standard potentials of the two reactions

$\mathrm{M}^{n+} + n\mathrm{e}^- \rightarrow \mathrm{M}$ and $\mathrm{M}^{m+} + m\mathrm{e}^- \rightarrow \mathrm{M}$

are $E^\circ_{\mathrm{M}^{n+}|\mathrm{M}}$ and $E^\circ_{\mathrm{M}^{m+}|\mathrm{M}}$, respectively. Assuming n to be greater than m, show that the standard potential of the reaction

$\mathrm{M}^{n+} + (n - m)\ \mathrm{e}^- = \mathrm{M}^{m+}$

is given as $E^\circ_{\mathrm{M}^{n+},\,\mathrm{M}^{m+}|\mathrm{Pt}} = \dfrac{n\,E^\circ_{\mathrm{M}^{n+}|\mathrm{M}} - mE^\circ_{\mathrm{M}^{m+}|\mathrm{M}}}{n - m}$

(b) If $E^\circ_{\mathrm{Cr^{3+}|Cr}} = -0.74$ V and $E^\circ_{\mathrm{Cr^{3+}, Cr^{2+}|Pt}} = -0.40$ V, determine $E^\circ_{\mathrm{Cr^{2+}|Cr}}$.

17. The emf of the cell $\mathrm{Pt\,|\,H_2(g, 1\ bar)\,|\,HA_1(0.1\ M)\,||\,HA_2\,(0.1\ M)\,|\,H_2\,(g, 1\,bar)\,|\,Pt}$ is found to be 0.032 V. Which of the two weak acids is stronger and how many times?

Unsolved Problems (Galvanic cells)

1. $2\mathrm{Cu^+} \rightarrow \mathrm{Cu^{2+}} + \mathrm{Cu}$ $E^\circ_{\mathrm{cell}} = 0.38$ V
2. $\mathrm{Cl_2} + 2\mathrm{OH^-} \rightarrow \mathrm{Cl_2} + \mathrm{ClO^-} + \mathrm{H_2O}$ $E^\circ_{\mathrm{cell}} = 0.96$ V
3. 10^{-14} bar
4. 703.1
5. 0.0666 V
6. – 0.70 V
7. 1.088 V
10. 0.770 V
11. (a) 2.4×10^{255} (b) 1.98×10^{-57} (c) 1.39×10^{-37}
12. 0.036% Ag
13. 0.71
15. 0.372 V, – 0.307 V
16. – 0.91 V
17. $\mathrm{HA_2}$ is 3.5 time stronger than $\mathrm{HA_1}$.

CHAPTER 9

SOLUTIONS

COMPOSITION OF A SOLUTION

A solution may be defined as a homogeneous mixture of a single phase containing two or more of the chemical species dispersed on a molecular state. The composition of a solution may be specified in different ways. Some of them are described in the following.

Let a solution contain the amounts n_1 and n_2 of solvent and solute, respectively, and let ρ be the density of the solution. We will have

$$\text{Volume of solution} = \frac{n_1 M_1 + n_2 M_2}{\rho}$$

$$\text{Molarity of the solution, } M = \frac{\text{amount of solute}}{\text{volume of solution in dm}^3} = \frac{n_2}{(n_1 M_1 + n_2 M_2)/\rho}$$

$$\text{Molality of solution, } m = \frac{\text{amount of solute}}{\text{mass of solvent in kg}} = \frac{n_2}{n_1 M_1}$$

$$\text{Mole fraction of solute, } x_2 = \frac{n_2}{n_1 + n_2}.$$

The symbols M_1 and M_2 in the above expressions are the molar masses of solvent and solute, respectively. The composition of solution expressed as molarity is temperature dependent owing to the variation of volume of the solution with temperature. Molality and mole fraction are temperature independent. The expressions relating molality and molarity, molality and mole fraction of solute, molarity and mole fraction of solute, and vice versa are expressed below.

$$m = \frac{M}{\rho - M M_2} \quad \text{and} \quad M = \frac{m\rho}{1 + m M_2}$$

$$m = \frac{x_2}{x_1 M_1} \quad \text{and} \quad x_2 = \frac{m M_1}{1 + m M_1}$$

$$M = \frac{x_2 \rho}{x_1 M_1 + x_2 M_2} \quad \text{and} \quad x_2 = \frac{M M_1}{M(M_1 - M_2) + \rho}.$$

HENRY'S LAW

The solubility of a gas in a liquid is governed by Henry's law which states that at a given temperature, the mass of dissolved gas in a given volume of solvent is proportional to the pressure of the gas with which it is in equilibrium, Mathematically, $m \propto p$ or $m = k_H p$ where k_H is known as Henry's law constant.

IDEAL LIQUID SOLUTION

A liquid solution is said to be an ideal solution if its constituents follow Raoult's law in whole of the composition range. According to this, the partial pressure of the vapours of a constituent is proportional to the mole fraction of the latter in the solution. Mathematically, this law is written as

$$p_\mathrm{i} \propto x_\mathrm{i} \qquad \text{or} \qquad p_\mathrm{i} = x_\mathrm{i}\, p_\mathrm{i}^*$$

where p_i^* is the constant of proportionality and is equal to the vapour pressure of the pure constituent. The total vapour pressure of the solution is given as

$$p_\mathrm{total} = \sum_\mathrm{i} p_\mathrm{i} = \sum_\mathrm{i} x_\mathrm{i}\, p_\mathrm{i}^*$$

For a binary ideal solution, we have $p_\mathrm{total} = p_\mathrm{A} + p_\mathrm{B} = x_\mathrm{A} p_\mathrm{A}^* + x_\mathrm{B} p_\mathrm{B}^* = p_\mathrm{B}^* + (p_\mathrm{A}^* - p_\mathrm{B}^*)\, x_\mathrm{A}$
The mole fraction of the constituent *i* in vapour phase is given as

$$y_i = \frac{p_i}{p_\mathrm{total}} = \frac{x_i\, p_i^*}{\sum x_i\, p_i^*}$$

For a binary solution, we get $\quad y_\mathrm{A} = \dfrac{x_\mathrm{A}\, p_\mathrm{A}^*}{p_\mathrm{B}^* + (p_\mathrm{A}^* - p_\mathrm{B}^*)\, x_\mathrm{A}}$

The expression of x_A in terms of y_A is $\quad x_\mathrm{A} = \dfrac{y_\mathrm{A}\, p_\mathrm{B}^*}{p_\mathrm{A}^* + (p_\mathrm{B}^* - p_\mathrm{A}^*)\, y_\mathrm{A}} \qquad$ or $\qquad \dfrac{1}{x_\mathrm{A}} = \dfrac{p_\mathrm{A}^*}{p_\mathrm{B}^*}\dfrac{1}{y_\mathrm{A}} + \dfrac{p_\mathrm{B}^* - p_\mathrm{A}^*}{p_\mathrm{B}^*}$

that is, a plot of $1/x_\mathrm{A}$ versus $1/y_\mathrm{A}$ is linear with the slope and intercept equal to $p_\mathrm{A}^*/p_\mathrm{B}^*$ and $(p_\mathrm{B}^* - p_\mathrm{A}^*)/p_\mathrm{B}^*$, respectively.

If the solution contains a nonvolatile solute in a volatile solvent, then the vapour pressure of such a solution is due to the solvent alone and is given as $p = x_1\, p_1^*$ where $x_1 = 1 - x_2$ and p_1^* is the vapour pressure of the pure solvent.

In the formation of an ideal solution, the change in enthalpy and change in volume on mixing the constituents are zero. The change in Gibbs energy is negative while the change in entropy is positive.

NONIDEAL LIQUID SOLUTIONS

Nonideal liquid solutions show deviations from Raoult's law. Two types of deviations are observed.

Positive Deviation In this case, the vapour pressures of the constituents and also that of the solution are larger than those expected for an ideal solution. Such a solution is formed when the forces of attraction between unlike molecules are weaker than those existing between like molecules. This causes an increase in molecular tendency of each constituent to escape from the solution as compared to that prevailing in an ideal solution. Examples include carbon tetrachloride-heptane, ethyl ether-acetone and heptane-ethanol solutions. If the deviations are large, a maximum in the vapour pressure versus composition curve is observed. Because of increase in vapour pressure, the boiling point versus composition curve of the solution exhibits an minimum at which compositions of solution and vapour pressure are identical. The temperature corresponding to this minimum boiling point is known as *azeotropic temperature* and the composition is known as *azeotropic composition*.

Negative Deviation In this case, the vapour pressure of the constituents and also that of the solution are lesser than those expected for an ideal solution. Such a solution is formed when the forces of attraction between unlike molecules are stronger than those existing between like molecules. This causes a decrease in molecular tendency of each constituent to escape from the solution as compared to that prevailing in an ideal solution. Examples include pyridine-formic acid, chloroform-acetone and aqueous solutions of halogen acids, nitric acid and perchloro acids. If the deviations are large, a minimum in the vapour pressure versus composition curve is observed. Because of decrease in vapour pressure, the boiling point versus composition curve of the solution exhibits a maximum at which compositions of solution and vapour pressure are identical. The temperature corresponding to this maximum boiling point is known as *azeotropic temperature* and the composition is known as *azeotropic composition*.

COLLIGATIVE PROPERTIES

By definition, colligative properties are those which depend on the number of nonvolatile solute species relative to the total number of species present in the solution. These properties do not depend upon the nature of solute species.

Examples of such properties are (1) the relative lowering of vapour pressure, (2) the elevation of boiling point, (3) the depression of freezing point, and (4) the osmotic pressure. The relevant expressions are

$$-\frac{\Delta p_1}{p_1^*} = x_2 \qquad -\Delta T_\mathrm{f} = K_\mathrm{f} m \quad \text{where} \quad K_\mathrm{f} = \frac{M_1 R T_\mathrm{f}^{*2}}{\Delta_\mathrm{fus} H_\mathrm{m}}$$

$$\Delta T_\mathrm{b} = K_\mathrm{b} m \quad \text{where} \quad K_\mathrm{b} = \frac{M_1 R T_\mathrm{b}^{*2}}{\Delta_\mathrm{vap} H_\mathrm{m}} \qquad \Pi = cRT$$

where the subscripts 1 and 2 respectively stand for solvent and solute in the solution. These expressions have been used in determining the molar mass of the solute. For a dilute solution where $n_2 << n_1$, the approximate expressions are

$$M_2 = \frac{m_2}{(m_1/M_1)(-\Delta p_1/p_1^*)} \qquad M_2 = \frac{K_\mathrm{b}}{\Delta T_\mathrm{b}}\frac{m_2}{m_1}$$

$$M_2 = \frac{K_\mathrm{f}}{(-\Delta T_\mathrm{f})}\frac{m_2}{m_1} \qquad M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\Pi}$$

where m and M stand for mass and molar mass, respectively. Of these, osmotic pressure measurement has been used to determine the molar mass of either slightly soluble or comparatively bigger solute molecules (such as proteins, polymers, colloids). It is because even small concentration produces significant osmotic pressure which can be measured experimentally. In other colligative properties, the effect produced is small and cannot be measured experimentally with great precision.

The colligative properties of an electrolytic solution are found to be larger than those of a nonelectrolytic solution of the same concentration. This is due to the dissociation of an electrolyte in the solution causing increase in the number of species irrespective of its nature. The colligative properties of an electrolytic solution in terms of those of a nonelectrolytic solution are expressed in terms of van't Hoff factor i defind as

$$i = \frac{-\Delta T_\mathrm{f}}{(-\Delta T_\mathrm{f})_0} = \frac{\Delta T_\mathrm{b}}{(\Delta T_\mathrm{b})_0} = \frac{\Pi}{\Pi_0} = \frac{-\Delta p}{(-\Delta p)_0}$$

where the quantities without subscripts refer to an electrolytic solution and those with subscripts refer to a nonelectrolytic solution of the same concentration. The value of i is determined from the experimental data.

For a weak electrolyte, the expression connecting the degree of dissociation and van't Hoff factor is determined as follows.

Let α be the degree of dissociation of a weak electrolyte $\mathrm{A}_x\mathrm{B}_y$. Then

$$\underset{n_0(1-\alpha)}{\mathrm{A}_x\mathrm{B}_y} \rightleftharpoons \underset{n_0(x\alpha)}{x\mathrm{A}^{y+}} + \underset{n_0(y\alpha)}{y\mathrm{B}^{x-}}$$

Total amount of species in the solution = $n_0(1-\alpha) + n_0(x\alpha) + n_0(y\alpha) = n_0(x+y-1)\alpha + n_0$
Hence, the van't Hoff factor is

$$i = \frac{\text{Total amount of species in solution}}{\text{Amount of } \mathrm{A}_x\mathrm{B}_y \text{ without dissociation}} = \frac{n_0(x+y-1)\alpha + n_0}{n_0} = (x+y-1)\alpha + 1$$

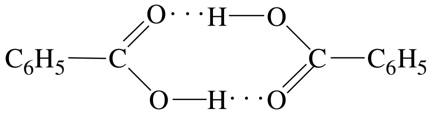
Thus, $$\alpha = \frac{i-1}{(x+y-1)} = \frac{i-1}{\nu - 1}$$

where ν is the total stoichiometric number of the electrolyte.

If the solution contains more than one species, then the molar mass determined from any of the colligative properties is the number average molar mass and is given by

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + \ldots}{n_1 + n_2 + \ldots} = \frac{\sum n_\mathrm{i} M_\mathrm{i}}{\sum n_\mathrm{i}}$$

where n_i is the number of species having molar mass M_i. Benzoic acid in benzene produces molar mass twice of the actual molar mass, since benzoic acid dimerizes in benzene and thus the number of benzoic acid species becomes half of the actual number. The dimer formed is



Straight Objective Type

Composition of a Solution

1. A molal solution is one that contains one mole of a solute in
(a) 1000 g of the solvent (b) one litre of the solvent
(c) one litre of the solution (d) 22.4 litres of the solution (1986)

2. In which mode of expression the concentration of a solution remains independent of temperature?
(a) Molarity (b) Normality (c) Formality (d) Molality (1988)

3. The expression relating molarity (M) and molality (m) of a solution is
(a) $m = \dfrac{M}{\rho + M M_2}$ (b) $m = \dfrac{M}{\rho - M M_2}$ (c) $m = \dfrac{\rho + M M_2}{M}$ (d) $m = \dfrac{\rho - M M_2}{M_2}$
where ρ is the density of solution and M_2 is the molar mass of solute.

4. The expression relating molality (m) and mole fraction of solute (x_2) in a solution is
(a) $x_2 = \dfrac{m M_1}{1 + m M_1}$ (b) $x_2 = \dfrac{m M_1}{1 - m M_1}$ (c) $x_2 = \dfrac{1 + m M_1}{m M_1}$ (d) $x_2 = \dfrac{1 - m M_1}{m M_1}$
where M_1 is the molar mass of solvent.

5. The expression relating mole fraction of solute (x_2) and molarity (M) of the solution is
(a) $x_2 = \dfrac{M M_1}{M(M_1 - M_2) + \rho}$ (b) $x_2 = \dfrac{M M_1}{M(M_1 - M_2) - \rho}$
(c) $x_2 = \dfrac{M(M_1 - M_2) + \rho}{M M_1}$ (d) $x_2 = \dfrac{M(M_1 - M_2) - \rho}{M M_1}$

6. The density of a 10.0% by mass KCl solution in water is 1.06 g cm^{-3}. Its molarity is
(a) 1.489 M (b) 1.420 M (c) 1.420 mol kg^{-1} (d) 1.489 mol kg^{-1}

7. What mass of ethanol be added to 1.0 kg water to have the mole fraction of ethanol equal to 0.20?
(a) 63.89 g (b) 6.39 g (c) 638.89 g (d) 683.89 g

8. The volume of 96% H_2SO_4 (density 1.83 g mL^{-1}) required to prepare 2.0 L of 3.0 M H_2SO_4 solution is
(a) 33.47 mL (b) 3.347 mL (c) 334.7 mL (d) 343.7 mL

9. An aqueous solution of HCl has 2% mass of HCl and a density of 1.02 g cm^{-3}. The numerical values of molarity and molality, respectively, are
(a) 0.542, 0.652 (b) 0.652, 0.542 (c) 0.559, 0.652 (d) 0.559, 0.559

10. The volume required to prepare 2.0 L of 3.0 M H_2SO_4 solution from 96% H_2SO_4 solution (density 1.83 g mL^{-1}) is
(a) 242.0 mL (b) 334.7 mL (c) 385.2 mL (d) 450.1 mL

Ideal and Nonideal Liquid Solutions

11. For a dilute solution, Raoult's law states that
(a) the lowering of vapour pressure is equal to the mole fraction of solute
(b) the relative lowering of vapour pressure is equal to the mole fraction of solute
(c) the relative lowering of vapour pressure is proportional to the amount of solute in the solution
(d) the vapour pressure of the solution is equal to the mole fraction of solvent (1985)

12. For a binary ideal liquid solution, the total pressure of the solution is given as

(a) $p_{\text{total}} = p_A^* + (p_A^* - p_B^*)\, x_B$ (b) $p_{\text{total}} = p_B^* + (p_A^* - p_B^*)\, x_A$

(c) $p_{\text{total}} = p_A^* + (p_B^* - p_A^*)\, x_A$ (d) $p_{\text{total}} = p_B^* + (p_B^* - p_A^*)\, x_B$

13. Which of the following plots does not represent the behaviour of an ideal binary liquid solution?

(a) Plot of p_A versus x_A (mole fraction of A in liquid phase) is linear

(b) Plot of p_B versus x_B is linear

(c) Plot of p_{total} versus x_A (or x_B) is linear

(d) Plot of p_{total} versus x_A is nonlinear

14. Which of the following plots represents the behaviour of an ideal binary liquid solution?

(a) Plot of p_{total} versus y_A (mole fraction of A in vapour phase) is linear

(b) Plot of p_{total} versus y_B is linear

(c) Plot of $1/p_{\text{total}}$ versus y_A is linear

(d) Plot of $1/p_{\text{total}}$ versus y_B is nonlinear

15. Which of the following plots correctly represents the behaviour of an ideal binary liquid solution?

(a) Plot of x_A (mole fraction of A in liquid phase) versus y_A (mole fraction of A in vapour phase) is linear

(b) Plot of x_A versus y_B is linear

(c) Plot of $1/x_A$ versus $1/y_A$ is linear

(d) Plot of $1/x_A$ versus $1/y_B$ is linear

16. The plot of $1/x_A$ versus $1/y_A$ (where x_A and y_A are the mole fractions of A in a binary liquid and vapour phases, respectively) is linear with slope and intercept respectively are given as

(a) p_A^*/p_B^*, $(p_A^* - p_B^*)/p_B^*$ (b) p_A^*/p_B^*, $(p_B^* - p_A^*)/p_B^*$

(c) p_B^*/p_A^*, $(p_A^* - p_B^*)/p_B^*$ (d) p_B^*/p_A^*, $(p_B^* - p_A^*)/p_B^*$

17. For an ideal solution containing a nonvolatile solute, which of the following expressions represents the vapour pressure of the solution?

(a) $p = x_2\, p_2^*$ (b) $p = x_1\, p_2^*$ (c) $p = x_1\, p_1^*$ (d) $p_1^* - p = x_2$

where the subscripts 1 and 2 stand for solvent and solute, respectively.

18. For an ideal solution containing a nonvolatile solute, which of the following expressions is correctly represented?

(a) $-\dfrac{\Delta p_1}{p_1^*} = x_1$ (b) $-\dfrac{\Delta p_1}{p_2^*} = x_2$ (c) $-\dfrac{\Delta p_1}{p_1^*} = x_2$ (d) $-\dfrac{\Delta p_1}{p_2^*} = x_1$

where the subscripts 1 and 2 stand for solvent and solute, respectively.

19. For an ideal binary liquid solution with $p_A^* > p_B^*$, which of the following relations between x_A (mole fraction of A in liquid phase) and y_A (mole fraction of A in vapour phase) is correctly represented?

(a) $x_A = y_A$ (b) $x_A > y_A$

(c) $x_A < y_A$ (d) x_A and y_A cannot be correlated with each other

20. Which of the following is true?

(a) The ideal behaviour of a liquid solution is due to the fact that the different molecules present in it do not interact with one another.

(b) Henry's law deals with the variation of solubility of gas with temperature.

(c) The constituents of an ideal solution follow Raoult's law under all conditions.

(d) The addition of a nonvolatile solute to a volatile solvent decreases the boiling point of the latter.

21. An azeotropic solution of two liquids has a boiling point lower than either of them when it

(a) shows negative deviation from Raoult's law

(b) shows no deviation from Raoult's law

(c) shows positive deviation from Raoult's law

(d) is saturated (1985)

22. A binary liquid solution of *n*-heptane and ethyl alcohol is prepared. Which of the following statements correctly represents the behaviour of this liquid solution?

(a) The solution formed is an ideal solution

(b) The solution formed is nonideal solution with positive deviations from Raoult's law

(c) The solution formed is nonideal solution with negative deviations from Raoult's law

(d) *n*-Heptane exhibits positive deviation whereas ethyl alcohol exhibits negative deviation from Raoult's law

23. A binary liquid solution of chloroform and acetone is prepared. Which of the following statements correctly represents the behaviour of this liquid solution?
(a) The solution formed is an ideal solution
(b) The solution formed is nonideal solution with positive deviations from Raoult's law
(c) The solution formed is nonideal solution with negative deviations from Raoult's law
(d) Chloroform exhibits positive deviation whereas acetone exhibits negative deviation from Raoult's law

24. Raoult's law is obeyed by each constituent of a binary liquid solution when
(a) the forces of attractions between like molecules are greater than those between unlike molecules
(b) the forces of attractions between like molecules are smaller than those between unlike molecules
(c) the forces of attractions between like molecules are more or less identical with those between unlike molecules
(d) the volume occupied by unlike molecules are different

25. An azeotropic solution of two liquids has a boiling point higher than either of the boiling points of the two liquids when it
(a) shows negative deviation from Raoult's law (b) shows positive deviation from Raoult's law
(c) shows no deviation from Raoult's law (d) is saturated

26. The vapour-pressure lowering of a solvent is proportional to
(a) the mole fraction of the solute (b) the mole fraction of the solvent
(c) the molality of the solvent (d) the normality of the solution

27. The vapour pressure of a solvent in a solution is proportional to
(a) the mole fraction of the solute (b) the mole fraction of the solvent
(c) the molality of the solvent (d) the normality of the solute

28. Which of the following solutions is expected to show positive deviations from Raoult's law?
(a) Pyridine-formic acid (b) Ethanol-hexane
(c) Acetone-chloroform (d) Hydrochloric acid-water

29. Which of the following solutions is expected to show negative deviations from Raoult's law?
(a) Ethanol-hexane (b) Ethanol-water (c) Acetone-chloroform (d) Ethyl ether-acetone

30. The vapour pressure of pure liquid is 70 Torr at 27 °C. The vapour pressure of a solution of this liquid and another liquid (mole fraction 0.2) is 84 Torr at 27 °C. The vapour pressure of pure liquid B at 27 °C is
(a) 140 Torr (b) 280 Torr (c) 160 Torr (d) 200 Torr

31. The vapour pressure of pure benzene and toluene are 160 Torr and 60 Torr, respectively. The mole fraction of benzene in vapour phase in contact with equimolar solution of benzene and toluene would be
(a) 0.50 (b) 0.84 (c) 0.73 (d) 0.27

32. The vapour pressures of *n*-hexane and *n*-heptane are 46 and 13 mmHg. If the vapour pressure of a solution of these two liquids is 38 mmHg, the mole fraction of *n*-hexane in solution is
(a) 0.24 (b) 0.56 (c) 0.66 (d) 0.76

33. A binary solution contains 4 mol of A and 6 mol of B. Its vapour pressure is found to be 460 mmHg. To this solution, when 10 mol of B is added, its vapour pressure becomes 480 mmHg. The vapour pressures of pure A and pure B, respectively, are
(a) 300 mmHg, 600 mmHg (b) 400 mmHg and 500 mmHg
(c) 300 mmHg, 500 mmHg (d) 400 mmHg and 600 mmHg.

34. The vapour pressure of a pure liquid A is 80 mmHg at 300 K. It forms an ideal solution with liquid B. When the mole fraction of B is 0.4, the total pressure was found to be 88 mmHg. The vapour pressure of liquid A would be
(a) 84 mmHg (b) 90 mmHg (c) 100 mmHg (d) 120 mmHg.

Relative Lowering of Vapour Pressure

35. The vapour pressure of a solvent is found to be 400 mmHg at 300 K. When a certain amount of a nonvolatile solute is added to 50 mol of the solvent its vapour pressure decreases to 360 mmHg. The amount of solute added is
(a) 2.41 mol (b) 3.42 mol (c) 4.54 mol (d) 5.45 mol

36. 5 g of a nonvolatile compound (molar mass 50 g mol^{-1}) is added to 100 g of water. If the decrease of vapour pressure is 11.31 Torr, the vapour pressure of water will be
(a) 480 Torr (b) 640 Torr (c) 840 Torr (d) 988 Torr

Depression in Freezing Point

37. When mercuric iodide is added to an 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 (1987)

38. Which of the following 0.1 M aqueous solutions will have the lowest freezing point?
(a) Potassium sulphate (b) Sodium chloride (c) Urea (d) Glucose (1989)

39. The freezing point of equimolal aqueous solutions will be highest for
(a) $C_6H_5NH_3Cl$(anilinium chloride) (b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$ (d) $C_6H_{12}O_6$(glucose) (1990)

40. For an ideal solution containing a nonvolatile solute, which of the following expressions is correctly represented?
(a) $-\Delta T_f = K_f m$ with $K_f = M_1 R T_f^{*2}/\Delta_{fus}H_m$ (b) $-\Delta T_f = K_f m$ with $K_f = R T_f^{*2}/M_1\Delta_{fus}H_m$
(c) $-\Delta T_f = K_f m$ with $K_f = M_1 T_f^{*2}/R\Delta_{fus}H_m$ (d) $-\Delta T_f = K_f m$ with $K_f = \Delta_{fus}H_m/M_1 R T_f^{*2}$

41. A solution contains 0.1 mol of acetamide in 1 L of glacial acetic acid. When the solution is cooled, the first crystals that appeared at the freezing point contain the molecules of
(a) acetamide only
(b) acetic acid only
(c) both acetamide and acetic acid
(d) either acetamide or acetic acid depending upon the conditions of the experiment.

42. Assuming 100% ionization, the increasing order of the freezing point of the solution will be
(a) 0.10 mol kg^{-1} $Ba_3(PO_4)_2$ < 0.10 mol kg^{-1} Na_2SO_4 < 0.10 mol kg^{-1} KCl
(b) 0.10 mol kg^{-1} KCl < 0.10 mol kg^{-1} Na_2SO_4 < 0.10 mol kg^{-1} $Ba_3(PO_4)_2$
(c) 0.10 mol kg^{-1} Na_2SO_4 < 0.10 mol kg^{-1} $Ba_3(PO_4)_2$ < 0.10 mol kg^{-1} KCl
(d) 0.10 mol kg^{-1} KCl < 0.10 mol kg^{-1} $Ba_3(PO_4)_2$ < 0.10 mol kg^{-1} Na_2SO_4

43. Pure Benzene freezes at 5.4 °C. A solution of 0.223 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene (K_f = 5.12 K kg mol^{-1}) freezes at 4.47 °C. From this observation, one can conclude that
(a) phenyl acetic acid exists as such in benzene
(b) phenyl acetic acid undergoes partial ionization in benzene
(c) phenyl acetic acid undergoes complete ionization in benzene
(d) phenyl acetic acid dimerizes in benzene

44. When a sugar-solution is slowly frozen, the first solid which separates out is
(a) ice (b) solid solution of sugar and ice
(c) sugar (d) a compound formed from sugar and water

45. Which of the following exhibits the greatest freezing-point lowering?
(a) 0.1 mol kg^{-1} NaCl (b) 0.1 mol kg^{-1} $CaCl_2$ (c) 0.1 mol kg^{-1} $HC_2H_3O_2$ (d) 0.1 mol kg^{-1} $NaC_2H_3O_2$

46. The freezing point of equimolal solution will be lowest for
(a) anilinium chloride (b) calcium nitrate (c) glucose (d) sodium phosphate

47. The molar mass of acetic acid dissolved in benzene determined from the depression in freezing point is found to be
(a) 30 g mol^{-1} (b) 60 g mol^{-1} (c) 120 g mol^{-1} (d) 240 g mol^{-1}

48. The freezing point of a 0.05 molal solution of a nonelectrolyte in water is
(a) – 1.86 °C (b) – 0.93 °C (c) – 0.093 °C (d) 0.93 °C

49. The unit of freezing point depression constant is
(a) K mol^{-1} (b) K kg^{-1} mol^{-1} (c) K kg mol^{-1} (d) K kg^{-1}

50. 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) 3 (2007)

51. For water, $\Delta_{\text{fus}}H^\circ_{\text{m}}$ = 6.09 kJ mol^{-1}. The value of freezing point depression constant at 1 atm pressure would be about
(a) 4.71 K kg mol^{-1} (b) 1.2 K kg mol^{-1} (c) 1.83 K kg mol^{-1} (d) 2.5 K kg mol^{-1}

52. If the freezing point depression constant of a solvent is 20.0 K kg mol^{-1}. If its $\Delta_{\text{fus}}H^\circ_{\text{m}}$ = 2.74 kJ mol^{-1} and its molar mass is 84.2 g mol^{-1}, the normal freezing point of the solvent would be about
(a) 308.2 K (b) 298.1 K (c) 249.8 K (d) 279.8 K

53. The molar mass and the freezing point of camphor are 152.2 g mol^{-1} and 178.4 °C, respectively. The cryoscopic constant of camphor is 37.7 K kg mol^{-1}, the molar enthalpy of fusion of camphor is about
(a) 5.24 kJ K^{-1} mol^{-1} (b) 6.84 kJ K^{-1} mol^{-1}
(c) 8.24 kJ K^{-1} mol^{-1} (d) 9.8 kJ K^{-1} mol^{-1}

54. Which of the following solvents has he largest value of K_f?
(a) Water (b) Benzene (c) Camphor (d) Hexane

Elevation of Boiling Point

55. For an ideal solution containing a nonvolatile solute, which of the following expressions is correctly represented?
(a) $\Delta T_b = K_b m$ where $K_b = M_1 R T_b^{*2}/\Delta_{\text{vap}}H_m$ (b) $\Delta T_b = K_b m$ where $K_b = R T_b^{*2}/M_1\Delta_{\text{vap}}H_m$
(c) $\Delta T_b = K_b m$ where $K_b = M_1 T_b^{*2}/R\Delta_{\text{vap}}H_m$ (d) $\Delta T_b = K_b m$ where $K_b = M_1 R T_b^{*2}\Delta_{\text{vap}}H_m$

56. The boiling point of water at 735 Torr is 99.07 °C. The mass of NaCl added in 100 g water (K_b = 0.51 K kg mol^{-1}) to make its boiling point 100 °C is
(a) 10.68 g (b) 5.34 g (c) 2.67 g (d) 26.7 g

57. The elevation of boiling point of water produced by dissolving 1.17 g sodium chloride in 100 g water (K_b = 0.512 K kg mol^{-1}) is
(a) 0.103 K (b) 0.205 K (c) 0.309 K (d) 0.410 K

58. When mercuric iodide is added to an aqueous solution of potassium iodide, the
(a) boiling point is raised (b) boiling point is lowered
(c) freezing point does not change (d) effect on freezing point cannot be predicted

59. The elevation in boiling point when 20.16 g of freshly prepared $CuCl_2$ (relative molar mass : 134.4) is dissolved in 1 kg of water (K_b = 0.52 kg K mol^{-1}) is
(a) 0.075 °C (b) 0.150 °C (c) 0.234 °C (d) 0.468 °C (2005)

60. An involatile solute A dimerizes in a solvent as $2A \rightleftharpoons A_2$. If m is the molarity of solute in the solution, then the equilibrium constant of the reaction is given as

(a) $\dfrac{K_b(K_b m + \Delta T_b)}{(2\Delta T_b - K_b m)^2}$ (b) $\dfrac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$ (c) $\dfrac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$ (d) $\dfrac{K_b(K_b m + \Delta T_b)}{(2\Delta T_b + K_b m)^2}$

61. A sucrose solution in 50 g water boils at 100.15 °C. If this solution is heated till its temperature is 100.375°C, how much of water is evaporated? Given: K_b(water) = 0.52 K kg mol^{-1}.
(a) 30 g (b) 25 g (c) 15 g (d) 10 g.

62. A solvent of molar mass 84.2 g mol^{-1} and boiling point 81.4 °C has boiling-point elevation constant equal to 2.79 K kg mol^{-1}. Its molar enthalpy of vapourization will be about
(a) 22.7 kJ mol^{-1} (b) 25.7 kJ mol^{-1} (c) 30.7 kJ mol^{-1} (d) 35.7 kJ mol^{-1}

63. The solvent CS_2 has enthalpy of vapourization of 352 J g^{-1} and boiling point equal to 320 K. The value of K_b for this solvent is about
(a) 0.51 K kg mol^{-1} (b) 0.86 K kg mol^{-1} (c) 1.23 K kg mol^{-1} (d) 2.42 K kg mol^{-1}

64. A solution containing 0.5 g of a solute (molar mass 130 g mol^{-1}) in 50 g CCl_4 yields a boiling point elevation of 0.4 K. While a solution of 0.6 g of an unknown solute in the same mass of solvent yields 0.6 K of elevation of boiling point. The molar mass of solute is about
(a) 85 g mol^{-1} (b) 96 g mol^{-1} (c) 106 g mol^{-1} (d) 121 g mol^{-1}

Osmotic Pressure

65. A semipermeable membrane used in the measurement of osmotic pressure of a solution allows the passage of
(a) solvent molecules through it.
(b) solute molecules through it.

(c) both solvent and solute molecules through it.
(d) either solvent or solute and not both through it.

66. The osmotic pressure of a solution (density = 1.02 g $\mathrm{cm^{-3}}$) containing 50 g glucose ($C_6H_{12}O_6$) in 1 kg of water at 300 K is
(a) 67.39 kPa (b) 673.85 kPa (c) 6.74 kPa (d) 673.85 Pa

67. The osmotic pressure of 0.1 M sodium chloride solution at 27 °C is
(a) 4.0 atm (b) 2.46 atm (c) 4.92 atm (d) 1.23 atm

68. In the phenomenon of osmosis through the semipermeable membrane
(a) solvent molecules pass from solution to solvent
(b) solvent molecules pass from solvent to solution
(c) solute molecules pass from solution to solvent
(d) solute molecules pass from solvent to solution

69. Which of the following pairs of solutions are expected to be isotonic?
(a) 0.1 M urea and 0.1 M NaCl (b) 0.1 M urea and 0.1 M $MgCl_2$
(c) 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4 (d) 0.1 M NaCl and 0.1 M glucose

70. A 0.004 M solution of K_2SO_4 is isotonic with a 0.010 M solution of glucose at the same temperature. The apparent per cent degree of dissociation of K_2SO_4 is
(a) 25% (b) 50% (c) 75% (d) 100% (2004)

Van't Hoff Factor

71. The degree of dissociation (α) of a weak electrolyte A_xB_y is related to van’t Hoff factor (i) by the expression
(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) $\alpha = \dfrac{x+y+1}{i-1}$

72. The van’t Hoff factor of benzoic acid in benzene is found to be
(a) 1 (b) 2 (c) 0.5 (d) 1.5

73. Which of the following electrolytes would have the same van’t Hoff factor as that of potassium ferricyanide?
(a) NaCl (b) Na_2SO_4 (c) $Al_2(SO_4)_3$ (d) $Al(NO_3)_3$

74. The van’t Hoff factor for 0.1 molal $Ba(NO_3)_2$ solution is 2.74. Its degree of dissociation is
(a) 0.74 (b) 0.87 (c) 0.91 (d) 1.0

75. The van’t Hoff factor of acetic acid in water will be
(a) equal to one (b) equal to two
(c) in between one and two (d) more than two

76. The van’t Hoff factor of the compound $K_3Fe(CN)_6$ in dilute solution is
(a) 1 (b) 2 (c) 3 (d) 4

Determination of Molar Mass

77. For a dilute solution containing a nonvolatile solute, which of the following expressions correctly represents the molar mass of solute?
(a) $M_2 = \dfrac{m_2}{(m_1/M_1)}$ (b) $M_2 = \dfrac{m_2}{(m_1/M_1)(-\Delta p_1/p_1^*)}$
(c) $M_2 = \dfrac{m_2}{(M_1/m_1)(-\Delta p_1/p_1^*)}$ (d) $M_2 = \left(\dfrac{m_2 M_1}{m_1}\right)(-\Delta p_1/p_1^*)$

78. For a dilute solution containing a nonvolatile solute, the molar mass of solute evaluated from the elevation of boiling point is given by the expression
(a) $M_2 = \dfrac{\Delta T_b}{K_b}\dfrac{m_1}{m_2}$ (b) $M_2 = \dfrac{\Delta T_b}{K_b}\dfrac{m_2}{m_1}$ (c) $M_2 = \dfrac{K_b}{\Delta T_b}\dfrac{m_2}{m_1}$ (d) $M_2 = \dfrac{K_b}{\Delta T_b}\dfrac{m_1}{m_2}$

79. For a dilute solution containing a nonvolatile solute, the molar mass of solute evaluated from the osmotic pressure measurement is given as
(a) $M_2 = \dfrac{m_2}{V}\dfrac{RT}{\Pi}$ (b) $M_2 = \dfrac{m_2}{V}\dfrac{\Pi}{RT}$ (c) $M_2 = m_2\dfrac{RT}{\Pi}$ (d) $M_2 = m_2\dfrac{\Pi}{RT}$

80. Which of the following colligative properties can provide molar mass of proteins (or polymers or colloids) with greater precision?
(a) Relative lowering of vapour pressure (b) Elevation of boiling point
(c) Depression in freezing point (d) Osmotic pressure

81. The Molar Mass of benzoic acid in benzene as determined by depression in freezing point method corresponds to
(a) ionization of benzoic acid (b) dimerization of benzoic acid
(c) trimerization of benzoic acid (d) solvation of benzoic acid (1996)

82. The vapour pressure of a solution having 2.0 g of a solute X (molar mass 32 g mol^{-1}) in 100 g of CS_2 (vapour pressure 854 Torr) is 848.9 Torr. The molecular formula of the solute is
(a) X (b) X_2 (c) X_4 (d) X_8

83. The vapour pressure of a solution of 5 g of a nonelectrolyte in 100 g water at a particular temperature is 2950 Pa and that of pure water at the same temperature is 3000 Pa. The molar mass of the solute is
(a) 54 g mol^{-1} (b) 119 g mol^{-1} (c) 179 g mol^{-1} (d) 229 g mol^{-1}

84. The vapour pressure of a pure liquid A is 10.0 Torr. at 27 °C. One gram of B is dissolved in 20 g of A, the vapour pressure is lowered to 9.0 Torr. If the molar mass of A is 200 g mol^{-1}, the molar mass of B is
(a) 75 g mol^{-1} (b) 85 g mol^{-1} (c) 100 g mol^{-1} (d) 115 g mol^{-1}

85. A solution contains 10 g of a solute and 116 g of acetone at 30 °C. Its vapour pressure is 290 Torr. If the vapour pressure of pure acetone is 300 Torr at 30 °C, the molar mass of solute is
(a) 75 g mol^{-1} (b) 100 g mol^{-1} (c) 125 g mol^{-1} (d) 150 g mol^{-1}

86. The freezing point of a solution containing 36 g of a compound (empirical formula : CH_2O) in 1.20 kg of water is found to be – 0.93 °C. The molecular formula of the solute is
(a) CH_2O (b) $C_2H_4O_2$ (c) $C_3H_6O_3$ (d) $C_4H_8O_4$

87. The molar mass of sodium chloride determined by osmotic pressure would be
(a) 58.5 g mol^{-1} (b) more than 58.5 g mol^{-1}(c) less than 58.5 g mol^{-1} (d) 117.0 g mol^{-1}

88. A solution containing 8.6 g L^{-1} of urea (molar mass 60 g mol^{-1}) is isotonic with a 5% solution of unknown solute. The molar mass of the solute will be
(a) 348.9 g mol^{-1} (b) 174.5 g mol^{-1} (c) 87.3 g mol^{-1} (d) 34.89 g mol^{-1}

89. Twenty grams of hemoglobin in 1 L solution at 300 K is separated from pure water by a semipermeable membrane. At equilibrium, the height of solution (density 1 g cm^{-3}) in a tube dipped in solution is found to be 83.1 mm higher than in the tube dipped in water. If g = 10 m s^{-2}, the molar mass of hemoglobin is about
(a) 30 kg mol^{-1} (b) 40 kg mol^{-1} (c) 60 kg mol^{-1} (d) 80 kg mol^{-1}

90. The Henry's law constant for the solubility of N_2 gas in water is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The amount of N_2 from air dissolved in 10 mol of water at 298 K and 5 atm pressure is
(a) 4.0×10^{-4} mol (b) 4.0×10^{-5} mol (c) 5.0×10^{-4} mol (d) 4.0×10^{-6} mol (2009)

Multiple Correct Choice Type

In Q. 1 to Q. 4, the symbols used are
m : molality of the solution. M : molarity of the solution.
x_1 and x_2 : mole fractions of solvent and solute respectively.
M_1 and M_2 : molar masses of solvent and solute, respectively.
ρ : density of solution. n_1 and n_2 : amounts of the solvent and solute, respectively.

1. Which of the following conversion expressions is/are correctly depicted?
(a) $m = M/(\rho - MM_2)$ (b) $M = (1 + mM_2)/m\rho$
(c) $x_2 = mM_1/(1 + mM_1)$ (d) $M = x_2\rho/(x_1M_1 + x_2M_2)$

2. Which of the following conversion expressions is/are correctly depicted?
(a) $M = m\rho/(1 + mM_2)$ (b) $m = x_2/x_1M_1$
(c) $x_2 = \{M(M_1 - M_2) + \rho\}/MM_1$ (d) $x_1 = mM_1/(1 + mM_1)$

3. Which of the following conversion expressions is/are correctly depicted?
(a) $m = x_1/x_2M_2$ (b) $x_1 = MM_1/\{M(M_1 - M_2) + \rho\}$
(c) $x_1 = mM_2/(1 + mM_2)$ (d) $M = m\rho/(1 + mM_2)$

4. Which of the following expressions is/are correctly depicted?
(a) $x_2 = mx_1M_1$
(b) $x_2 = mM_1/(1 + mM_1)$
(c) $x_2 = MM_1/(M(M_1 - M_2) + \rho)$
(d) $x_2 = mM_2/M_1$

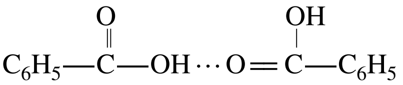
5. Which of the following expressions is/are correctly depicted?
(a) $m = n_2/n_1M_1$
(b) $M = n_2/V$
(c) $x_1 = n_1/n_2$
(d) $x_1 + x_2 = 1$

6. For an ideal binary liquid solution, which of the following statements is/are correct?
(a) The plot of $1/y_A$ (where y_A is the mole fraction of A in vapour phase) versus $1/x_A$ (where x_A is the mole fraction of A in liquid phase) is linear.
(b) The plot of $1/p_{total}$ versus y_A is linear.
(c) The plot of $1/p_{total}$ versus x_A is linear.
(d) y_A is greater than x_A if the component A is more volatile.

7. For an ideal binary liquid solution, which of the following statements is/are correct?
(a) The plot of temperature versus x_A (where x_A is the mole fraction of A in liquid phase) is linear.
(b) The plot of temperature versus y_A (where y_A is the mole fraction of A in vapour phase) is linear.
(c) The two components can be separated by the method of fractional distillation.
(d) The vapour phase is more rich in the more volatile component as compared to the liquid phase.

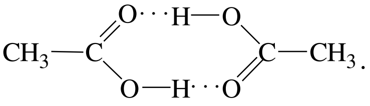
8. Which of the following statements are correct?
(a) Water has maximum density at 4 °C.
(b) The unit of K_f is K kg^{-1}.
(c) Isotonic solutions have identical osmotic pressures.
(d) Osmotic pressure of 0.1 molar sodium chloride solution is identical with that of 0.1 molar glucose solution.

9. Which of the following statements are not correct?
(a) The value of K_b for water is larger than that of K_f.
(b) The elevation of boiling point of a solvent when a nonvolatile solute is added to it is larger than its depression in freezing point.
(c) Osmotic pressure measurement is preferred over any other colligative properties in determining the molar mass of proteins and polymers.
(d) The dimerized form of benzoic acid in benzene is



$C_6H_5-\overset{\overset{O}{\|}}{C}-OH\cdots O{=}\overset{\overset{OH}{|}}{C}-C_6H_5$.

10. Which of the following statements are correct?
(a) The dimerized form of acetic acid in benzene is



(b) Lowering of vapour pressure is a colligative property.
(c) The value of K_b or K_f depends only on the type of solvent and not solute dissolved in it.
(d) For a very dilute solution, mole fraction of a solute is directly proportional to the molality of the solution.

11. Which of the following statements are correct?
(a) The increasing order of osmotic pressure of 0.1 M aqueous solution containing different electrolyte is as follows. 0.1 M Glucose < 0.1 M Sodium chloride < 0.1 M Magnesium chloride.
(b) Density of a solution is independent of temperature.
(c) Camphor has comparatively larger value of K_f as compared to other common solvents.
(d) Limiting value of van't Hoff factor of $K_4Fe(CN)_6$ is 11.

12. Which of the following statements are correct?
(a) A solution contains two non-volatile solutes. The molar mass of such a solution determined through colligative property is the mass average molar mass.
(b) The vapour pressure of an ideal solution may be predicted by using Raoult's law.
(c) The molarity of a solution is independent of temperature
(d) The relative lowering of vapour pressure of a solution containing nonvolatile solutes is a colligative property.

13. Which of the following statements are not correct?
   (a) 3 g of a salt of molar mass 30 g mol^{-1} is dissolved in 250 g of water. The molality of the solution is 0.2 mol kg^{-1}.
   (b) The molality of a solution is dependent on temperature.
   (c) The molarity of a solution is dependent on temperature.
   (d) The density of a solution is dependent on temperature.

14. Which of the following statements are correct?
   (a) The mole fraction of a constituent in a solution is independent of the total mass of the system.
   (b) The enthalpy of mixing during the formation of an ideal solution is zero.
   (c) For a nonideal solution exhibiting positive deviations from Raoult's law, $\Delta_{mix}H$ has a negative (nonzero) value.
   (d) For a nonideal solution exhibiting negative deviation from Raoult's law, $\Delta_{mix}H$ has a positive (nonzero) value.

15. Which of the following statements are correct?
   (a) If in a binary solution, forces of attraction between like molecules are stronger than those prevailing between unlike molecules, the solution is expected to exhibit positive deviations from Raoult's law.
   (b) If in a binary solution, forces of attraction between like molecules are weaker than those prevailing between unlike molecules, the solution is expected to exhibit negative deviations from Raoult's law.
   (c) An azeotropic solution boils at a constant temperature.
   (d) The boiling point elevation constant depends on the characteristics of solute only.

16. Which of the following statements are correct?
   (a) A semipermeable membrane allows the passage of solvent molecules through it.
   (b) For a azeotropic solution, the compositions of liquid and vapour at its boiling point are identical.
   (c) For an ideal binary liquid solution, the plot of p_{total} versus x_A (mole fraction of A in liquid) is nonlinear.
   (d) For an ideal binary liquid solution, the plot of $1/p_{total}$ versus y_A (mole fraction of A in vapour) is nonlinear.

17. Which of the following statements are **not** correct?
   (a) For an ideal binary liquid solution, the plot of $1/x_A$ versus $1/y_A$ (where x_A and y_A are the mole fractions of A in liquid and vapour phases, respectively) is linear.
   (b) According to Raoult's law, the relative lowering of vapour pressure is equal to the mole fraction of solvent in the solution.
   (c) The cryoscopic constant K_f is defined as $K_f = M_1RT_f^{*2}/\Delta_{fus}H_m$
   (d) Benzoic acid dimerizes in benzene. The value of van't Hoff factor of this solute would be two.

18. Which of the following statements are correct?
   (a) The van't Hoff factor of a weak electrolyte AB in a solution is 1.1. Its degree of dissociation would be 0.1.
   (b) An ideal solution contains more than one solute. The molar mass determined from its colligative properties would be number average molar mass of solutes.
   (c) The density of a solution expressed in g cm^{-3} and kg dm^{-3} have different values.
   (d) The units of boiling point elevation constant K_b are K kg mol^{-1}.

19. In the depression of freezing point experiment, it is found that the
   (a) vapour pressure of the solution is less than that of pure solvent
   (b) vapour pressure of the solution is more than that of pure solvent
   (c) only solute molecules solidify at the freezing point
   (d) only solvent molecules solidify at the freezing point

20. In the formation of an ideal solution, which of the following facts hold good?
   (a) The entropy of mixing of constituents is positive
   (b) The change in Gibbs energy is positive
   (c) The enthalpy of mixing is zero
   (d) The volume of mixing is nonzero.

Link Comprehension Type

1. Properties such as boiling point, freezing point and vapour pressure of pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given:

Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol^{-1}

Freezing point depression constant of ethanol (K_f^{ethanol}) = 2.0 K kg mol^{-1}

Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}

Boiling point elevation constant of ethanol (K_b^{ethanol}) = 1.2 K kg mol^{-1}

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mmHg

Vapour pressure of pure ethanol = 40 mmHg

Molar mass of water = 18 g mol^{-1}

Molar mass of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

(i) The freezing point of the solution **M** is
(a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K

(ii) The vapour pressure of the solution **M** is
(a) 39.3 mmHg (b) 36.0 mmHg (c) 29.5 mmHg (d) 28.8 mmHg

(iii) Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. the boiling point of this solution is
(a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K (2008)

2. The density of 20 mass per cent acetic acid solution in water is 1.03 g cm^{-3}. Based on this information, attempt the following three questions.

(i) The mole fraction of acetic acid in solution is
(a) 0.05 (b) 0.07 (c) 0.09 (d) 0.11

(ii) The molality of acetic acid solution is
(a) 3.4 mol kg^{-1} (b) 3.8 mol kg^{-1} (c) 4.2 mol kg^{-1} (d) 4.8 mol kg^{-1}

(iii) The molarity of acetic acid solution is
(a) 3.4 M (b) 3.8 M (c) 4.2 M (d) 4.8 M

3. 1.21 g of benzoic acid (molar mass 121 g mol^{-1}) when dissolved in 100 cm^3 solution produces osmotic pressure of 1.73 atm at 300 K. Benzoic acid is known to form dimer in benzene. Based on this information, attempt the following three questions.

(i) The number average molar mass of benzoic acid in the solution is
(a) 150 g mol^{-1} (b) 181 g mol^{-1} (c) 172.1 g mol^{-1} (d) 198 g mol^{-1}

(ii) The percentage of benzoic acid in the associated state is
(a) 41% (b) 48% (c) 53% (d) 59%

(iii) The equilibrium constant of the dimerization reaction is
(a) 1.5 M^{-1} (b) 1.75 M^{-1} (c) 2.5 M^{-1} (d) 3.5 M^{-1}

4. Ethanol and methanol form very nearly ideal solutions. The vapour pressures of ethanol and methanol are 44.5 Torr and 88.7 Torr, respectively. Based on this information, answer the following three questions.

(i) The mole fraction of methanol in a solution obtained by mixing 100 g of each is
(a) 0.41 (b) 0.48 (c) 0.56 (d) 0.68

(ii) The total vapour pressure of the solution is
(a) 36.37 Torr (b) 46.26 Torr (c) 62.63 Torr (d) 52.52 Torr

(iii) The mole fraction of methanol in the vapour phase is
(a) 0.48 (b) 0.58 (c) 0.68 (d) 0.78

5. The vapour pressure of the constituent in an ideal binary liquid solution is given by Raoult's law, $p_i = x_i\, p_i^*$ where x_i is the mole fraction of the constituent i in the liquid phase and p_i^* is the vapour pressure of the pure constituent. The composition of vapour phase is given by $y_i = p_i/p_{\text{total}}$. Based on these information, answer correctly the following three questions.

(i) The composition of A in the liquid phase for which $y_A - x_A$ has a maximum value is given by the expression

(a) $\dfrac{\sqrt{p_A^* p_B^*} + p_B^*}{p_A^* + p_B^*}$ (b) $\dfrac{\sqrt{p_A^* p_B^*} - p_B^*}{p_A^* - p_B^*}$ (c) $\dfrac{\sqrt{p_A^* p_B^*} - p_B^*}{p_A^* - p_B^*}$ (d) $\dfrac{\sqrt{p_A^* p_B^*} + p_B^*}{p_A^* - p_B^*}$

(ii) The expression of vapour pressure when $y_A - x_A$ has a maximum value is

(a) $\sqrt{p_A^* p_B^*}$ (b) p_A^*/p_B^* (c) p_B^*/p_A^* (d) $p_A^*\, p_B^*$

(iii) The composition of A in the vapour phase when $y_A - x_A$ exhibits a maximum is

(a) $\left(\dfrac{\sqrt{p_A^*} + \sqrt{p_B^*}}{p_A^* + p_B^*}\right)\sqrt{p_A^*}$ (b) $\left(\dfrac{\sqrt{p_A^*} + \sqrt{p_B^*}}{p_A^* - p_B^*}\right)\sqrt{p_A^*}$ (c) $\left(\dfrac{\sqrt{p_A^*} - \sqrt{p_B^*}}{p_A^* - p_B^*}\right)\sqrt{p_A^*}$ (d) $\left(\dfrac{\sqrt{p_A^*} - \sqrt{p_B^*}}{p_A^* + p_B^*}\right)\sqrt{p_A^*}$

6. The vapour pressures of two pure liquids A and B which form an ideal solution are 300 and 800 Torr, respectively, at temperature T. A liquid solution of A and B for which the mole fraction of A is 0.60 is contained in a cylinder closed by a piston on which the pressure can be varied. The solution is slowly vapourized at temperature T by decreasing the applied pressure, starting with a pressure of about 1 atm. Based on this information, answer the following three questions

(i) The composition of the first bubble of vapour will be

(a) $y_A = 0.36$ (b) $y_A = 0.64$ (c) $y_A = 0.46$ (d) $y_A = 0.54$

(ii) The composition of the last droplet of liquid will be

(a) $x_A = 0.40$ (b) $x_A = 0.60$ (c) $x_A = 0.80$ (d) $x_A = 0.90$

(iii) The pressure of the vapour when the last droplet of liquid remains will be

(a) 300 Torr (b) 400 Torr (c) 500 Torr (d) 600 Torr

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explantation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	**Statement–2**
1.	The molality of a solution changes with change in temperature.	The volume of the solution changes with change in temperature.
2.	The solution of carbon tetrachloride in heptane shows positive deviations from Raoult's law.	The forces of attraction between unlike molecules are stronger than those between like molecules in the solution.
3.	The osomotic pressure of 0.01 M benzoic acid in water is smaller than that of 0.01 M glucose in water.	Benzoic acid ionizes in solution so as to give larger number of species as compared to the glucose solution.
4.	The relative lowering of vapour pressure of solvent in a solution containing a nonvolatile solute is directly proportional to the mole fraction of solvent in the solution.	The vapour pressure of a solution containing a nonvolatile solute is only due to solvent molecules.
5.	The boiling point elevation constant of a solvent at sea level is higher than at a mountain height of 10 km.	The boiling point of a solvent is higher at sea level as compared to that at a height of 10 km.

6.	The molar mass determined from any one of the colligative properties is the number average molar mass.	The number average molar mass is defined as $M_{\text{av}} = \dfrac{N_1M_1 + N_2M_2 + \cdots}{N_1 + N_2 + \cdots}$
7.	The boiling point of chloroform-acetone solution is larger than expected from ideal behaviour.	The forces of attraction between unlike molecules are stronger than those between like molecules in the solution. This results in lower vapour as compared to an ideal solution which is responsible for the higher boiling point.
8.	Pure hydrochloric acid can be distilled off from its aqueous solution.	The aqueous solution of hydrochloric acid exhibits the formation of azeotropic solution.
9.	The vapour pressure of KI solution decreases initially with the addition of HgI_2.	HgI_2 forms complex with KI: $2KI + HgI_2(s) \rightarrow K_2[HgI_4]$ There is net decrease in the amount of species in solution resulting larger mole fraction of solvent.
10.	Osmosis involves the movement of solvent through semipermeable membrane from a solution of higher concentration to a solution of lower concentration.	The free energy per mole of solvent in a concentrated solution is lesser than that in a dilute solution.
11.	The van't Hoff factor for a weak electrolyte in water is dependent of its concentration.	The degree of dissociation of a weak electrolyte increases on dilution.
12.	The solubility of NH_3 in water is directly proportional to the pressure of NH_3 with which it is in equilibrium.	Henry's low is not applicable to the gases in a solvent in which there exist interaction between gases and solvent.
13.	The formation of an ideal liquid solution involves $\Delta_{\text{mix}}V = 0$ and $\Delta_{\text{mix}}H = 0$.	There exists no forces of interaction between the molecules in an ideal liquid solution.

ANSWERS

Straight Objective Type

1. (a) **2.** (d) **3.** (b) **4.** (a) **5.** (a) **6.** (b) **7.** (c)
8. (c) **9.** (d) **10.** (b) **11.** (b) **12.** (b) **13.** (d) **14.** (c)
15. (c) **16.** (b) **17.** (c) **18.** (c) **19.** (c) **20.** (c) **21.** (c)
22. (b) **23.** (c) **24.** (c) **25.** (a) **26.** (a) **27.** (b) **28.** (b)
29. (c) **30.** (a) **31.** (c) **32.** (d) **33.** (b) **34.** (c) **35.** (c)
36. (b) **37.** (a) **38.** (a) **39.** (d) **40.** (a) **41.** (b) **42.** (a)
43. (d) **44.** (a) **45.** (b) **46.** (d) **47.** (c) **48.** (c) **49.** (c)
50. (a) **51.** (c) **52.** (d) **53.** (b) **54.** (c) **55.** (a) **56.** (b)
57. (b) **58.** (b) **59.** (c) **60.** (b) **61.** (a) **62.** (c) **63.** (d)
64. (b) **65.** (a) **66.** (b) **67.** (c) **68.** (b) **69.** (c) **70.** (c)
71. (a) **72.** (c) **73.** (d) **74.** (b) **75.** (c) **76.** (d) **77.** (c)
78. (c) **79.** (a) **80.** (d) **81.** (b) **82.** (d) **83.** (a) **84.** (c)
85. (d) **86.** (b) **87.** (c) **88.** (a) **89.** (c) **90.** (a)

Multiple Correct Choice Type

1. (a), (c), (d) **2.** (a), (b) **3.** (c), (d) **4.** (a), (b), (c)
5. (a), (b), (d) **6.** (a), (b), (c), (d) **7.** (c), (d) **8.** (a), (c)
9. (a), (b), (d) **10.** (a), (c), (d) **11.** (a), (c) **12.** (b), (d)
13. (a), (b) **14.** (a), (b) **15.** (a), (b), (c) **16.** (a), (b)
17. (b), (d) **18.** (a), (b), (d) **19.** (a), (d) **20.** (a), (c)

Linked Comprehension Type

1. **(i)** (d) **(ii)** (b) **(iii)** (b) **2.** **(i)** (b) **(ii)** (c) **(iii)** (a)
3. **(i)** (c) **(ii)** (d) **(iii)** (b) **4.** **(i)** (a) **(ii)** (c) **(iii)** (b)
5. **(i)** (b) **(ii)** (a) **(iii)** (c) **6.** **(i)** (a) **(ii)** (c) **(iii)** (b)

Assertion and Reason Type

1. (d) **2.** (c) **3.** (c) **4.** (d) **5.** (b) **6.** (b) **7.** (a)
8. (d) **9.** (d) **10.** (d) **11.** (a) **12.** (d) **13.** (c)

Hints and Solutions

Straight Objective Type

1. Molality involves 1000 g of solvent.

2. Molality involved a fixed mass of solvent. Hence, this is independent of temperature.

3. $$m = \frac{n_2}{m_1} = \frac{n_2}{m_{\text{total}} - m_2} = \frac{n_2}{m_{\text{total}} - (m_2/M_2)M_2} = \frac{n_2}{\rho V - n_2 M_2} = \frac{n_2/V}{\rho - (n_2/V)M_2} = \frac{M}{\rho - MM_2}$$

4. $$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{(m_1/M_1) + n_2} = \frac{n_2 M_1}{m_1 + n_2 M_1} = \frac{(n_2/m_1)M_1}{1 + (n_2/m_1)M_1} = \frac{m}{1 + mM_1}$$

5. $$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{(m_1/M_1) + n_2} = \frac{n_2 M_1}{m_1 + n_2 M_1} = \frac{n_2 M_1}{(m_1 + m_2) + n_2 M_1 - m_2} = \frac{n_2 M_1}{V\rho + n_2(M_1 - M_2)}$$

$$= \frac{(n_2/V)M_1}{\rho + (n_2/V)(M_1 - M_2)} = \frac{M\,M_1}{\rho + M\,(M_1 - M_2)}$$

6. $$M = \frac{(10\text{ g}/74.5\text{ g mol}^{-1})}{(100\text{ g}/1.06\text{ g cm}^{-3})} = 1.42 \times 10^{-3}\text{ mol cm}^{-3} = 1.42\text{ mol dm}^{-3}$$

7. $$0.2 = \frac{(m/46\text{ g mol}^{-1})}{(m/46\text{ g mol}^{-1}) + (1000\text{ g}/18\text{ g mol}^{-1})} \Rightarrow \frac{m}{46\text{ g}} = \frac{0.2 \times 1000}{18} \times \frac{1}{0.8} = 13.89$$

$m = 13.89 \times 46\text{ g} = 638.89\text{ g}$

8. $$\text{Volume of 96\% H}_2\text{SO}_4 = (2.0\text{ L})(3.0\text{ mol L}^{-1})(98\text{ g mol}^{-1})\left(\frac{100}{96}\right)\left(\frac{1}{1.83\text{ g mL}^{-1}}\right) = 334.7\text{ mL}$$

9. Mass of HCl = 2 g. Mass of water = 98 g

Amount of HCl = (2 g/36.5 g mol^{-1}) = 0.0548 mol

Volume of 100 g HCl solution = $100\text{ g}/1.02\text{ g mL}^{-1}$ = 98.03 mL

Molarity of HCl = $n/V = 0.0548\text{ mol}/98.08 \times 10^{-3}\text{ L}$ = 0.559 mol L^{-1}

Molality of HCl = $n/m_1 = 0.0548\text{ mol}/98 \times 10^{-3}\text{ kg}$ = 0.559 mol kg^{-1}

10. Amount of HCl in 2.0 L of 3.0 M solution = (2.0 L) (3.0 mol L^{-1}) = 6.0 mol

Mass of H_2SO_4 in this solution = (6.0 mol) (98 g mol^{-1}) = 588 g

Mass of 96% H_2SO_4 solution containing 588 g of H_2SO_4 $= 588 \times 100\text{ g}/96$ = 612.5 g

Volume of 96% H_2SO_4 solution weighing 612.5 g = $612.5\text{ g}/1.83\text{ g mL}^{-1}$ = 334.7 mL

11. Relative lowering of vapour pressure, $-\Delta p/p^* = -(p - p^*)/p^* = 1 - p/p^* = 1 - x_1 = x_2$

12. $P_{\text{total}} = p_A + p_B = x_A\, p_A^* + x_B\, p_B^* = x_A\, p_A^* + (1 - x_A)\, p_B^* = p_B^* + x_A\,(p_A^* - p_B^*)$

13. Plot of p_{total} versus x_A is linear. The choice d is not correct.

14. Plot of $1/p_{\text{total}}$ versus y_A is linear.

15. Plot of $1/x_A$ versus $1/y_A$ is linear.

16. The slope is p_A^*/p_B^* and intercept is $(p_B^* - p_A^*)/p_B^*$.

17. From Raoult's law, $p = x_1\, p_1^*$.

18. Relative lower of vapour pressure is given by $-\Delta p_1/p_1^* = x_2$.

19. The vapour contains more of the volatile component as compared to that present in the solution, i.e. $x_A < y_A$.

21. Positive deviation from Raoult's law implies higher vapour pressure and thus lower boiling point.

22. Escaping tendencies of both *n*-heptane and ethyl alcohol increase as compared to an ideal solution. The solution exhibits positive deviations from Raoult's law. This is due to less attraction between *n*-heptane and ethyl alcohol as compared to those existing separately between *n*-heptane and ethyl alcohol molecules.

23. Escaping tendencies of both chloroform and acetone decrease as compared to an ideal solution. The solution exhibits negative deviations from Raoult's law. This is primarily due to more attraction between chloroform and acetone (because of hydrogen bonding) as compared to those existing separately between chloroform and acetone molecules.

24. Raoult's law is applicable when the forces of attractions between like molecules are more or less identical with those between unlike molecules.

28. $p = x_A\, p_A^* + x_B\, p_B^* \;\Rightarrow\; 84 \text{ Torr} = (0.8)\,(70 \text{ Torr}) + (0.2)\,(p^*_B) \;\Rightarrow\; p^*_B = 140 \text{ Torr}$

29. $p_b = x_b\, p_b^* = (0.5)\,(160 \text{ Torr}) = 80 \text{ Torr}$

$$p_{\text{total}} = x_b\, p_b^* + x_t\, p_t^* = (0.5)\,(160 \text{ Torr}) + (0.5 \text{ Torr})\,(60 \text{ Torr}) = 110 \text{ Torr}$$

$$y_b = p_b / p_{\text{total}} = 80/110 = 0.73$$

32. $38 = x(46) + (1 - x)\, 13 \quad\Rightarrow\quad x = (38 - 13)/(46 - 13) = 25/33 = 0.76$

33. Initially, mole fractions of A and B in liquid solutions are 0.4 and 0.6, respectively. The addition of 10 mol of B changes mole fractions to 0.2 and 0.8, respectively. With these mole fractions, p_A^* and p_B^* of the choice (b) generates the given vapour pressures.

34. $x_A\, p_A^* + x_B\, p_B^* = p \;\Rightarrow\; 0.6 \times 80 \text{ mmHg} + 0.4\, p_B^* = 88 \text{ mmHg};\;$ Hence $p_B^* = \dfrac{(88 - 0.6 \times 80)\text{mmHg}}{0.4}$

$= 100$ mmHg

35. $-\Delta p = (400 - 360) \text{ mmHg} = 40 \text{ mmHg}. \quad x_2 = \dfrac{-\Delta p}{p_1^*} = \dfrac{40 \text{ mmHg}}{400 \text{ mmHg}} = 0.1$

Thus $\quad x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{n_2}{500 \text{ mol} + n_2} = 0.1 \quad$ or $\quad n_2 = \dfrac{5 \text{ mol}}{1.1} = 4.54 \text{ mol}$

37. The reaction is $HgI_2 + 2KI \rightarrow K_2HgI_4$. Hence, $2K^+$ and $2I^-$ are replaced by $2K^+$ and HgI_4^{2-}. There is a decrease in the number of species in the solution. The value of $-\Delta T_f$ decreases, hence, freezing point is raised.

38. Potassium sulphate produces larger number of species and hence larger value of $-\Delta T_f$.

39. Glucose being nonelectrolyte produces lesser value of $-\Delta T_f$ and hence higher freezing point.

40. The correct expressions are $-\Delta T_f = K_f m$ where $K_f = M_1 R T_f^{*2}/\Delta_{\text{fus}} H_m$

41. It is the solvent that crystallizes, i.e. acetic acid.

42. Assuming complete dissociation $(-\Delta T_f)_{Ba_3(PO_4)_2} > (-\Delta T_f)_{Na_2SO_4} > (-\Delta T_f)_{KCl}$

Hence $\quad (T_f)_{Ba_3(PO_4)_2} < (T_f)_{Na_2SO_4} < (T_f)_{KCl}$

43. $m = \dfrac{(-\Delta T_f)}{K_f} = \dfrac{(5.4 - 4.47)}{5.12} \text{ mol kg}^{-1} = \dfrac{0.97}{5.12} \text{ mol kg}^{-1}. \quad$ Hence $\quad \dfrac{0.223 \text{ g}/M}{(4.4/1000) \text{ kg}} = \dfrac{0.97}{5.12} \text{ mol kg}^{-1}$

Solving for M, we get $M = 279 \text{ g mol}^{-1}$. Number of molecules of phenyl acetic acid = 279/136 = 2

47. Acetic acid dimerizes in benzene. Its molar mass would be $2 \times 60\ \mathrm{g\ mol^{-1}}$, i.e. $120\ \mathrm{g\ mol^{-1}}$.

48. $-\Delta T_f = K_f\, m = (1.86\ \mathrm{K\ kg\ mol^{-1}})\ (0.05\ \mathrm{mol\ kg^{-1}}) = 0.093\ \mathrm{K}$. Freezing point = – 0.093 °C

49. Unit of $K_f = \dfrac{\text{unit of } \Delta T_f}{\text{unit of molality}} = \dfrac{\mathrm{K}}{\mathrm{mol\ kg^{-1}}} = \mathrm{K\ kg\ mol^{-1}}$

50. Amount of naphthoic acid = $20\ \mathrm{g}/172\ \mathrm{g\ mol^{-1}} = (20/172)\ \mathrm{mol}$

Molality of naphthoic acid = $(20/172)\ \mathrm{mol}/0.05\ \mathrm{kg} = (400/172)\ \mathrm{mol\ kg^{-1}}$

Using the expression $(-\Delta T_f) = i\, K_f\, m$, we get

$$i = \frac{(-\Delta T_f)}{K_f m} = \frac{(2\ \mathrm{K})}{(1.72\ \mathrm{K\ kg\ mol^{-1}})\{(400/172)\ \mathrm{mol\ kg^{-1}}\}} = 0.5$$

51. $$K_f = \frac{M_1 R T_f^{*2}}{\Delta_{\mathrm{fus}} H_m} = \frac{(0.018)\ \mathrm{kg\ mol^{-1}})\ (8.314\ \mathrm{J\ K^{-1} mol^{-1}})\ (273.15\ \mathrm{K})^2}{(6.09 \times 10^3\ \mathrm{J\ mol^{-1}})} = 1.83\ \mathrm{K\ kg\ mol^{-1}}$$

52. $$T_f^* = \left[\frac{K_f \Delta_{\mathrm{fus}} H_{\mathrm{m}}}{M_1 R}\right]^{1/2} = \left[\frac{(20\ \mathrm{K\ kg\ mol^{-1}})\ (2.74 \times 10^3\ \mathrm{J\ mol^{-1}})}{(84.2 \times 10^{-3}\ \mathrm{kg\ mol^{-1}})\ (8.314\ \mathrm{J\ K^{-1} mol^{-1}})}\right]^{1/2} = 279.8\ \mathrm{K}$$

53. $$\Delta_{\mathrm{fus}} H_{\mathrm{m}}^{\circ} = \frac{M_1 R T_f^{*2}}{K_f} = \frac{(152.2 \times 10^{-3}\ \mathrm{kg\ mol^{-1}})(8.314\ \mathrm{J\,K^{-1}\ mol^{-1}})(451.5\ \mathrm{K})^2}{(37.7\ \mathrm{K\ kg\ mol^{-1}})}$$

$$= 6842.2\ \mathrm{J\ K^{-1}\ mol^{-1}} = 6.84\ \mathrm{kJ\ K^{-1}\ mol^{-1}}$$

55. The correct expressions are $\Delta T_b = K_b m$ and $K_b = M_1 R T_b^{*2}/\Delta_{\mathrm{vap}} H_{\mathrm{m}}$.

56. $m = \dfrac{T_b}{K_b} = \dfrac{(100 \quad 99.07)}{0.51}\ \mathrm{mol\ kg^{-1}}$; Molality of NaCl = $\dfrac{1}{2}\left(\dfrac{100 - 99.07}{0.51}\ \mathrm{mol\ kg^{-1}}\right)$

Mass of NaCl in 100 g water = $\dfrac{1}{2}\left(\dfrac{1}{10}\right)\left(\dfrac{0.93}{0.51}\right)(58.5)\ \mathrm{g} = 5.33\ \mathrm{g}$

57. Molality of sodium chloride = $\dfrac{(1.17/58.5)\ \mathrm{mol}}{0.1\ \mathrm{kg}} = 0.2\ \mathrm{mol\ kg^{-1}}$

Molality of ions in solution = $2 \times 0.2\ \mathrm{mol\ kg^{-1}}$. $\Delta T_b = K_b\, m = (0.512)\ (2 \times 0.2)\ \mathrm{K} = 0.205\ \mathrm{K}$

58. From the reaction $HgI_2 + 2KI \rightarrow K_2[HgI_4]$

The total number of species is lowered from 4 (= 2 (K^+) + 2(I^-)) to 3 (= 2 (K^+) + 1 (HgI_4^{2-})). Hence, there is less increase in the boiling point.

59. Molality of given solution is $m = \dfrac{n_2}{m_1} = \dfrac{m_2/M_2}{m_1} = \dfrac{(20.16\ \mathrm{g})/(134.4\ \mathrm{g\ mol^{-1}})}{1\ \mathrm{kg}} = 0.15\ \mathrm{mol\ kg^{-1}}$

Molality of ions in solution is $3\,m$, that is $0.45\ \mathrm{mol\ kg^{-1}}$

$$\Delta T_b = K_b\, m = (0.52\ \mathrm{kg\ K\ mol^{-1}})\ (0.45\ \mathrm{mol\ kg^{-1}}) = 0.234\ \mathrm{K} \equiv 0.234\ ^{\circ}\mathrm{C}$$

60. $2A \rightleftharpoons A_2$

$(1 - \alpha)$ $(\alpha/2)$; Total amount = $(1 - \alpha/2)$

The van't Hoff factor is $i = \dfrac{\text{Total amount in solution}}{\text{Amount of A to start with}} = \dfrac{(1 - \alpha/2)}{1} = 1 - \alpha/2$ or $\alpha = 2(1 - i)$

Hence $K_{\mathrm{eq}} = \dfrac{m(\alpha/2)}{m^2 (1-\alpha)^2} = \dfrac{(1-i)}{m(2i-1)^2}$ where $i = \dfrac{\Delta T_b}{(\Delta T_b)_0} = \dfrac{\Delta T_b}{K_b m}$

Thus $$K_{\text{eq}} = \frac{(1-\Delta T_{\text{b}}/K_{\text{b}}m)}{m[(2\Delta T_{\text{b}}/K_{\text{b}}m)-1]^2} = \frac{K_{\text{b}}(K_{\text{b}}m-\Delta T_{\text{b}})}{(2\Delta T_{\text{b}}-K_{\text{b}}m)^2}$$

61. Since $\Delta T_{\text{b}} = K_{\text{b}}\,m = K_{\text{b}}\left(\frac{n_2}{m_1}\right)$, we have $0.15\text{ K} = K_{\text{b}}\left(\frac{n_2}{0.05\text{ kg}}\right)$ and $0.375\text{ K} = K_{\text{b}}\left(\frac{n_2}{m_1}\right)$

Thus $$\frac{0.15\text{ K}}{0.375\text{ K}} = \frac{m_1}{0.05\text{ kg}} \quad \text{or} \quad m_1 = \left(\frac{0.15\text{ K}}{0.375\text{ K}}\right)(0.05\text{ kg}) = 0.02\text{ kg}$$

Mass of water evaporated = 50 g – 20 g = 30 g.

62. Since $K_{\text{b}} = (M_1RT_{\text{b}}^{*2}/\Delta_{\text{vap}}H_{\text{m}})$, we have

$$\Delta_{\text{vap}}H_{\text{m}} = \frac{M_1RT_{\text{b}}^{*2}}{K_{\text{b}}} = \frac{(0.082\text{ kg mol}^{-1})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(354.55\text{ K})^2}{(2.79\text{ K kg mol}^{-1})} = 30717\text{ J mol}^{-1} = 30.72\text{ kJ mol}^{-1}$$

63. $$K_{\text{b}} = \frac{M_1RT_{\text{b}}^{*2}}{\Delta_{\text{vap}}H_{\text{m}}} = \frac{(0.076\text{ kg mol}^{-1})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(320\text{ K})^2}{(352\text{ J g}^{-1})(76\text{ g mol}^{-1})} = 2.42\text{ K kg mol}^{-1}$$

64. $$0.4\text{ K} = K_{\text{b}}\,\frac{(0.5\text{ g})/(130\text{ g mol}^{-1})}{(50\text{ g})} \quad \text{and} \quad 0.65\text{ K} = K_{\text{b}}\,\frac{(0.6\text{ g})/M}{(50\text{ g})}$$

From these, we get $$\frac{0.4}{0.65} = \frac{0.5/(130\text{ g mol}^{-1})}{0.6/M} \Rightarrow M = \frac{0.4\times 0.6\times 130}{0.65\times 0.5}\text{ g mol}^{-1} = 96\text{ g mol}^{-1}$$

65. A semipermeable membrane allows the passage of solvent molecules only

66. Concentration of glucose = $\dfrac{(50/180)\text{ mol}}{(1.05\text{ kg}/1.02\text{ kg L}^{-1})} = 0.27\text{ mol L}^{-1}$

Osmotic pressure, $\Pi = cRT = (0.27\text{ mol L}^{-1})\,(8.314\text{ kPa L K}^{-1}\text{ mol}^{-1})\,(300\text{ K}) = 673.85\text{ kPa}$

67. Osmotic pressure, $\Pi = cRT = (2\times 0.1\text{ mol L}^{-1})\,(0.082\text{ atm L K}^{-1}\text{ mol}^{-1})\,(300\text{ K}) = 4.92\text{ atm}$.

69. Isotonic solutions have the same osmotic pressures. The same osmotic pressures implies the same concentrations. 0.1 M $Ca(NO_3)_2$ produces 0.3 M species (0.1 M Ca^{2+} + 0.2 M NO_3^-) and also 0.1 M Na_2SO_4 produces 0.3 M species (0.2 M Na^+ and 0.1 M SO_4^{2-}).

70. The dissociation of K_2SO_4 may be written as

$$\underset{c(1-\alpha)}{K_2SO_4} \rightleftharpoons \underset{c(2\alpha)}{2K^+} + \underset{c\alpha}{SO_4^{2-}}$$

The concentration of species in the solution is $c(1-\alpha) + c(2\alpha) + c\alpha = c(1+2\alpha)$, (where $c = 0.004$ M).

Hence $c(1+2\alpha) = 0.01$ M or $\alpha = \dfrac{1}{2}\left(\dfrac{0.01}{0.004}-1\right) = 0.75$

The per cent dissociation is 0.75 × 100, i.e. 75%

71. The correct expression is $\alpha = \dfrac{i-1}{(x+y-1)}$

72. Benzoic acid dimerizes in benzene. Its van't Hoff factor will be 1/2.

73. $K_3[Fe(CN)_6]$ and $Al(NO_3)_3$ produce the same number of species.

74. $$\alpha = \frac{i-1}{(x+y)-1} = \frac{2.74-1}{3-1} = 0.87$$

75. Acetic acid ionizes as $$\underset{1-\alpha}{CH_3COOH} \rightleftharpoons \underset{\alpha}{CH_3COO^-} + \underset{\alpha}{H^+}$$

It produces 1 + α species from one CH_3COOH. Since $\alpha < 1$, the van't Hoff factor will lie in between 1 and 2.

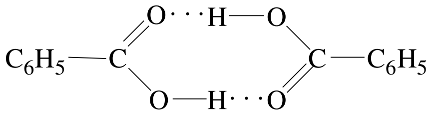
77. $-\dfrac{\Delta p_1}{p_1^*} = x_2 = \dfrac{n_2}{n_1 + n_2} \simeq \dfrac{n_2}{n_1} = \dfrac{(m_2/M_2)}{(m_1/M_1)}$. Hence, $M_2 = \dfrac{m_2}{(m_1/M_1)(-\Delta p_1/p_1^*)}$

78. $\Delta T_b = K_b m = K_b \dfrac{n_2}{m_1} = K_b \dfrac{(m_2/M_2)}{m_1}$. Hence, $M_2 = \dfrac{K_b}{\Delta T_b}\dfrac{m_2}{m_1}$

79. $\Pi = cRT = \dfrac{n_2}{V} RT = \dfrac{(m_2/M_2)}{V} RT.$ Hence, $M_2 = \dfrac{m_2}{V}\dfrac{RT}{\Pi}$

80. Osmotic pressure measurement is used to determine molar mass of proteins or polymers or colloids.

81. Benzoic acid in benzene dimerizes as



82. Mole fraction of solvent = $\dfrac{(100\text{ g}/76\text{ g mol}^{-1})}{(100\text{ g}/76\text{ g mol}^{-1}) + (2\text{ g}/M)}$

Hence 848.9 Torr = $\dfrac{(100/76\text{ mol}^{-1})}{(100/76\text{ mol}^{-1}) + (2\text{ g}/M)}$ (854 Torr)

Solving for M, we get $M = \dfrac{0.994 \times 2\text{ g}}{1.316\,(1 - 0.994)\text{ mol}} = 251.8\text{ g mol}^{-1}$

Number of S atoms in a molecule of solute = $\dfrac{251.8\text{ amu}}{32\text{ amu}} = 8$

83. $x_2 = -\dfrac{\Delta p}{p_1^*} = \dfrac{(3000 - 2950)\text{ Torr}}{3000\text{ Torr}} = \dfrac{1}{60}$. Now $x_2 \simeq \dfrac{(m_2/M_2)}{(m_1/M_1)}$. Hence $\dfrac{1}{60} = \dfrac{(5\text{ g}/M)}{(100\text{ g}/18\text{ g mol}^{-1})}$.

This gives $M = 54\text{ g mol}^{-1}$

84. $x_2 = -\dfrac{\Delta p}{p_1^*} = \dfrac{1\text{ Torr}}{10\text{ Torr}} = \dfrac{1}{10}$. Now $x_2 \simeq \dfrac{(m_2/M_2)}{(m_1/M_1)}$. Hence $\dfrac{1}{10} = \dfrac{(1\text{ g}/M_2)}{(20\text{ g}/200\text{ g mol}^{-1})}$.

This gives $M_2 = 100\text{ g mol}^{-1}$

85. $x_2 = -\dfrac{\Delta p}{p_1^*} = \dfrac{10\text{ Torr}}{300\text{ Torr}} = \dfrac{1}{30}$. Now $x_2 \simeq \dfrac{(m_2/M_2)}{(m_1/M_1)}$. Hence $\dfrac{1}{30} = \dfrac{(10\text{ g}/M_2)}{(116\text{ g}/58\text{ g mol}^{-1})}$

This gives $M_2 = 150\text{ g mol}^{-1}$

86. $-\Delta T_f = K_f\, m \Rightarrow 0.93\text{ K} = (1.86\text{ K kg mol}^{-1})\left(\dfrac{36\text{ g/M}}{1.20\text{ kg}}\right)$

This gives $M = \dfrac{1.86 \times 36}{0.93 \times 1.20}\text{ g mol}^{-1} = 60\text{ g mol}^{-1}$. $n = \dfrac{\text{Molar mass}}{\text{Empirical molar mass}} = \dfrac{60\text{ g mol}^{-1}}{30\text{ g mol}^{-1}} = 2$

Hence, molecular formula is $C_2H_4O_2$

87. The molar mass obtained from a colligative property is the number average molar mass. This mass for NaCl will be $(23 + 35.5)\text{ g mol}^{-1}/2 = 29.25\text{ g mol}^{-1}$.

88. Isotonic solution has the same osmotic pressure and hence the same concentration in the solution.

$$\frac{(8.6\text{ g}/60\text{ g mol}^{-1})}{1\text{ L}} = \frac{(5\text{ g}/M)}{0.1\text{ L}}.\quad \text{Hence}\quad M = \frac{5 \times 60}{8.6 \times 0.1}\text{ g mol}^{-1} = 348.8\text{ g mol}^{-1}$$

89. The osmotic pressure of solution becomes

$$\Pi = h\rho g = (83.1 \times 10^{-3}\ \text{m})\ (10^{3}\ \text{kg m}^{-3})\ (10\ \text{m s}^{-2}) = 831\ \text{kg m}^{-1}\ \text{s}^{-2} = 831\ \text{Pa}$$

Using the expression $\Pi = cRT = \dfrac{m/M}{V}\ RT$, we get

$$831\ \text{Pa} = \left(\frac{20\ \text{g}}{M}\,\frac{1}{1\ \text{dm}^{3}}\right)(8.314 \times 10^{3}\ \text{Pa dm}^{3}\ \text{K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})$$

$$M = \left(\frac{20\ g \times 8.314 \times 10^{3} \times 300}{831}\right)\ \text{g mol}^{-1} = 60{,}000\ \text{g mol}^{-1} = 60\ \text{kg mol}^{-1}$$

90. Partial pressure of N_2 in 5 atm pressure, $p_{N_2} = (0.8)\ (5\ \text{atm}) = 4\ \text{atm}$

By definition, Henry's law is $p_{N_2} = K_H\, x_{N_2}$. This gives $x_{N_2} = \dfrac{p_{N_2}}{K_H} = \dfrac{4\ \text{atm}}{1.0 \times 10^{5}\ \text{atm}} = 4.0 \times 10^{-5}$

Since $x_{N_2} = n_{N_2}/(n_{N_2} + n_{H_2O})$, in 10 mol of water, the amount of N_2 will be given by the expression

$4.0 \times 10^{-5} = \dfrac{n_{N_2}}{n_{N_2} + (10\ \text{mol})}$. Solving for n_{N_2}, we get $n_{N_2} = \dfrac{4.0 \times 10^{-5}\ (10\ \text{mol})}{1 - 4.0 \times 10^{-5}} = 4.0 \times 10^{-4}\ \text{mol}$

Multiple Correct Choice Type

6. The expression is $\dfrac{1}{y_A} = \dfrac{p_B^*}{p_A^*}\dfrac{1}{x_A} + \dfrac{p_A^* - p_B^*}{p_A^*}$

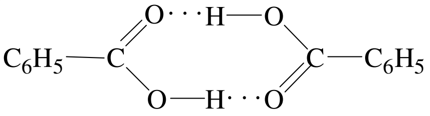
8. (b) The unit is K mol kg^{-1}.

(d) Sodium chloride is an electrolyte, it dissociates in solution to give Na^+ and Cl^- ions. The total concentration of species in sodium chloride solution will be 0.2 M. Hence, its osmotic pressure will be twice than 0.1 M glucose solution.

9. (a) The value of K_f is always larger than K_b.

(b) ΔT_b is always smaller than ΔT_f as $K_b < K_f$.

(d) The dimerzied benzoic acid is



10. (b) Relative lowering of vapour pressure, $-\Delta p/p^*$, is a colligative property.

11. (a) The total concentration of species in $MgCl_2$ solution will be 0.3 M and in NaCl solution it will be 0.2 M. Glucose is a nonelectrolyte, hence concentration of glucose solution will be 0.1 M.

(b) Density is defined as mass per unit volume and the volume of the solution varies with temperature.

(d) In solution, $K_4Fe(CN)_6$ ionizes as $K_4Fe(CN)_6 \rightleftharpoons 4K^+ + Fe(CN)_6^{4-}$. Hence, the limiting value of van't Hoff factor will be 5.

12. (a) Colligative property provides number average molar mass.

Link Comprehension Type

1. **(i)** In solution **M**, water acts as solute and ethanol as a solvent. Consider a solution with 0.9 mol of ethanol and 0.1 mol of water. In this solution, we have

Amount of water, $n_2 = 0.1$ mol

Mass of ethanol, $m_1 = n_1 M_1 = (0.9\ \text{mol})\ (46\ \text{g mol}^{-1}) = 41.4\ \text{g} = 0.0414\ \text{kg}$

Molality of water, $m = n_2/m_1 = 0.1\,\text{mol}/0.0414\ \text{kg}$

$$-\Delta T_f = K_f^{\text{ethanol}}\, m = (2\ \text{K kg mol}^{-1})\ (0.1\,\text{mol}/0.0414\ \text{kg}) = 4.83\ \text{K}$$

$$T_f = T_f^* + \Delta T_f = 155.7\ \text{K} - 4.83\ \text{K} = 150.9\ \text{K}$$

(ii) Since the solute is considered to be nonvolatile, $p_{\text{solution}} = p_1^* x_1 = (40\ \text{mmHg})\ (0.9) = 36\ \text{mmHg}$.

(iii) Amount of water = 0.9 mol

Mass of water, $m_1 = (0.9\ \text{mol})\ (18\ \text{g mol}^{-1}) = 16.2\ \text{g} = 0.0162\ \text{kg}$

Molality of ethanol, $m = \dfrac{0.1\,\text{mol}}{0.0162\,\text{kg}}$; $\Delta T_b = K_b^{\text{water}} m = (0.52\ \text{K kg mol}^{-1})\ (0.1\ \text{mol}/0.0162\ \text{kg}) = 3.2\ \text{K}$

$$T_b = T^*_b + \Delta T_b = 373\ \text{K} + 3.2\ \text{K} = 376.2\ \text{K}$$

2. In 100 g of the solution, we have

Mass of acetic acid = 20 g and Mass of water = 80 g

(i) Amount of acetic acid ($M = 60\ \text{g mol}^{-1}$), $n_1 = (20\ \text{g})/(60\ \text{g mol}^{-1}) = 0.333\ \text{mol}$

Amount of water, $n_2 = 80\ \text{g}/18\ \text{g mol}^{-1} = 4.444\ \text{mol}$

$$\text{Mole fraction of acetic acid} = \frac{n_1}{n_1 + n_2} = \frac{0.333}{0.333 + 4.444} = \frac{0.333}{4.777} = 0.07$$

(ii) $$\text{Molality of solution} = \frac{n_2}{m_1} = \frac{0.333\ \text{mol}}{80 \times 10^{-3}\ \text{kg}} = 4.16\ \text{mol kg}^{-1}$$

(iii) $$\text{Volume of solution} = \frac{m}{\rho} = \frac{100\ \text{g}}{1.03\ \text{g cm}^{-3}} = 97.1\ \text{cm}^3$$

3. **(i)** Since $\Pi = cRT$, we have $\Pi = \dfrac{n}{V} RT = \dfrac{(m/M)}{V} RT$

$$\text{or} \quad M = \frac{mRT}{\Pi V} = \frac{(1.21\ \text{g})\ (0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})}{(1.73\ \text{atm})\ (0.1)} = 172.1\ \text{g mol}^{-1}$$

(ii) $$\underset{n(1-\alpha)}{2C_6H_5COOH} \rightleftharpoons \underset{n(\alpha/2)}{(C_6H_5COOH)_2}$$

$$\text{Number average molar mass} = \frac{n\,(1-\alpha)\,(121\ \text{g mol}^{-1}) + n\,(\alpha/2)\,(242\ \text{g mol}^{-1})}{n\,(1-\alpha) + n\,(\alpha/2)}$$

This gives $\dfrac{(121\ \text{g mol}^{-1})}{1-\alpha/2} = 172.1\ \text{g mol}^{-1}$ or $\alpha = 2\left(1 - \dfrac{121}{172.1}\right) = 2\ (1 - 0.703) = 0.59$

(iii) $$K_{\text{eq}} = \frac{n(\alpha/2)/V}{[n(1-\alpha)/V]^2} = \frac{\alpha}{(1-\alpha)^2}\frac{V}{2n} = \frac{0.59}{(0.41)^2}\frac{0.1\ \text{L}}{2(1.21\ \text{g}/121\ \text{g mol}^{-1})} = 1.75\ \text{M}^{-1}$$

4. **(i)** Molar mass of methanol (CH_3OH), $M_1 = 32\ \text{g mol}^{-1}$; Molar mass of ethanol (C_2H_5OH), $M_2 = 46\ \text{g mol}^{-1}$

Amount of methanol = (100/32) mol; Amount of ethanol = (100/46) mol

$$\text{Mole fraction of methanol in solution} = \frac{(100/32)}{(100/32) + (100/46)} = \frac{46}{46/32} = 0.41$$

(ii) $p_1 = x_1\, p_1^* = (0.41)\ (88.7)\ \text{Torr} = 36.37\ \text{Torr}$

$p_2 = (1 - x_1)\, p_2^* = (0.59)\ (44.5)\ \text{Torr} = 26.26\ \text{Torr}$

$p_{\text{total}} = p_1 + p_2 = (36.37 + 26.26)\ \text{Torr} = 62.63\ \text{Torr}$

(iii) Mole fraction of methanol in vapour phase $y_1 = \dfrac{p_1}{p_1 + p_2} = \dfrac{36.37}{36.37 + 26.26} = \dfrac{36.37}{62.63} = 0.58$

5. **(i)** The composition of A in vapour phase is $y_A = \dfrac{p_A}{p_{\text{total}}} = \dfrac{x_A\, p_A^*}{x_A\, p_A^* + x_B\, p_B^*} = \dfrac{x_A\, p_A^*}{p_B^* + \left(p_A^* - p_B^*\right)x_A}$

Hence, $$y_A - x_A = \frac{x_A\, p_A^*}{p_B^* + \left(p_A^* - p_B^*\right)x_A} - x_A$$

For the maximum value of $y_A - x_A$, we set $d(y_A - x_A)/dx_A = 0$. This gives

$$\frac{p_A^*}{p_B^* + \left(p_A^* - p_B^*\right)x_A} - \frac{x_A p_A^*\left(p_A^* - p_B^*\right)}{\left[p_B^* + \left(p_A^* - p_B^*\right)\right]^2} - 1 = 0$$

Solving for x_A, we get $$x_A = \frac{\sqrt{p_A^*\, p_B^*} - p_B^*}{p_A^* - p_B^*}$$

(ii) $p_{\text{total}} = p_B^* + (p_A^* - p_B^*)\, x_A = p_B^* + \left(\sqrt{p_A^*\, p_B^*} - p_B^*\right) = \sqrt{p_A^*\, p_B^*}$

(iii) $y_A = \dfrac{p_A}{p_{\text{total}}} = \dfrac{x_A\, p_A^*}{\sqrt{p_A^*\, p_B^*}} = \left(\dfrac{\sqrt{p_A^*\, p_B^*} - p_B^*}{p_A^*\, p_B^*}\right)\left(\dfrac{p_A^*}{p_B^*}\right)^{1/2} = \left(\dfrac{\sqrt{p_A^*} - \sqrt{p_B^*}}{p_A^* - p_B^*}\right)\sqrt{p_A^*}$

6. **(i)** Total pressure of the first bubble of vapour is

$$p_{\text{total}} = x_A\, p_A^* + x_B\, p_B^* = (0.6 \times 300 + 0.4 \times 800)\ \text{Torr} = 500\ \text{Torr}$$

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{x_A p_A^*}{p_{\text{total}}} = \frac{0.6 \times 300\ \text{Torr}}{500\ \text{Torr}} = 0.36$$

(ii) When the last drop of liquid remains the composition of A in vapour phase will be equal to 0.60 as most of the liquid has vapourized. Hence

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{x_A p_A^*}{x_A\, p_A^* + x_B\, p_B^*} = \frac{x_A p_A^*}{p_B^* + \left(p_A^* - p_B^*\right)x_A} \quad \text{i.e } 0.60 = \frac{x_A\,(300\ \text{Torr})}{800\ \text{Torr} - (300\ \text{Torr} - 800\ \text{Torr})\,x_A}$$

Solving for x_A, we get $x_A = 0.80$.

(iii) The pressure of the vapour when the last liquid remains would be

$$p = x_A\, p_A^* + x_B\, p_B^* = (0.8 \times 300 + 0.2 \times 800)\ \text{Torr} = 400\ \text{Torr}.$$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The vapour pressure of pure benzene at 25 °C is 639.7 mmHg and the vapour pressure of a solution of a solute in benzene at the same temperature is 631.9 mmHg. Calculate the molality of the solution. (1981)

Solution Using Raoult's law ($p_1 = x_1\, p_1^*$), we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{631.9\ \text{mmHg}}{639.7\ \text{mmHg}} = 0.988$$

Now molality of the solution is given as

$$m = \frac{n_2}{n_1\, M_1} = \frac{x_2}{x_1}\frac{1}{M_1} = \frac{0.012}{0.988} \times \frac{1}{0.078\ \text{kg mol}^{-1}} = 0.156\ \text{mol kg}^{-1}.$$

2. Two liquids A and B form ideal solutions. At 300 K, the vapour pressure of solution containing 1 mol of A and 3 mol of B is 550 mmHg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mmHg. Determine the vapour pressures of A and B in their pure states. (1982)

Solution Since $p = x_A\, p_A^* + x_B\, p_B^*$, we have

$$\left(\frac{1}{1+3}\right) p_A^* + \left(\frac{3}{1+3}\right) p_B^* = 550 \text{ mmHg} \quad \text{and} \quad \left(\frac{1}{1+4}\right) p_A^* + \left(\frac{4}{1+4}\right) p_B^* = 560 \text{ mmHg}$$

That is, $0.25\, p_A^* + 0.75\, p_B^* = 550$ mmHg and $0.20\, p_A^* + 0.8\, p_B^* = 560$ mmHg

Solving for p_A^* and p_B^*, we get $p_A^* = 400$ mmHg and $p_B^* = 600$ mmHg.

3. The density of a 3 molal sodium thiosulphate solution is 1.25 g cm^{-3}. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate, and (iii) molarities of Na^+ and $S_2O_3^{2-}$ ions. (1983)

Solution For a 3 molal solution, we will have

Amount of sodium thiosulphate = 3 mol Mass of sodium thiosulphate = 3 × 248 g = 744 g

Amount of water = $\dfrac{1000\text{ g}}{18\text{ g mol}^{-1}} = 55.56$ mol Total mass of solution = (1000 + 744) g = 1744 g

$$\text{Volume of 1744 g of solution} = \frac{1744\text{ g}}{1.25\text{ g cm}^{-3}} = 1395.2 \text{ cm}^3$$

$$\text{Mass per cent of sodium thiosulphate} = \frac{744\text{ g}}{1744\text{ g}} \times 100 = 42.7$$

$$\text{Mole fraction of sodium thiosulphate} = \frac{3}{3+55.56} = 0.051$$

$$\text{Molarity of Na}^+ = \frac{2\times 3\text{ mol}}{1.395\text{ dm}^3} = 4.30 \text{ mol dm}^{-3} \quad \text{and} \quad \text{Molarity of } S_2O_3^{2-} = \frac{3\text{ mol}}{1.395\text{ dm}^3} = 2.15 \text{ mol dm}^{-3}$$

4. The vapour pressures of ethanol and methanol are 44.5 mmHg and 88.7 mmHg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol and 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986)

Solution Let A be ethanol and B be methanol.

Amount of A = $\dfrac{60\text{ g}}{46\text{ g mol}^{-1}} = 1.304$ mol Amount of B = $\dfrac{40\text{ g}}{32\text{ g mol}^{-1}} = 1.25$ mol

$$\text{Mole fraction of A in solution, } x_A = \frac{1.304}{1.304+1.25} = 0.511$$

Mole fraction of B in solution, $x_B = 1 - x_A = 1 - 0.511 = 0.489$

Partial pressure of A, $p_A = x_A\, p_A^* = (0.511)(44.5 \text{ mmHg}) = 22.74$ mmHg

Partial pressure of B, $p_B = x_B\, p_B^* = (0.489)(88.7 \text{ mmHg}) = 43.37$ mmHg

Total vapour pressure, $p = p_A + p_B = (22.74 + 43.37)$ mmHg = 66.11 mmHg

$$\text{Mole fraction of B in vapour phase, } y_B = \frac{p_B}{p} = \frac{43.37\text{ mmHg}}{66.11\text{ mmHg}} = 0.656.$$

5. A sugar syrup of mass 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate (i) molality, and (ii) mole fraction of sugar in the syrup. (1988)

Solution Mass of water in the syrup = (214.2 − 34.2) g = 180.0 g

$$\text{Molality of the solution} = \frac{n_2}{m_1} = \frac{(34.2\text{ g}/342\text{ g mol}^{-1})}{(180.0\times 10^{-3}\text{ kg})} = 0.556 \text{ mol kg}^{-1}$$

$$\text{Mole fraction of sugar} = \frac{34.2/342}{(34.2/342)+(180/18)} = 0.0099.$$

6. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mmHg at 373 K. Calculate (i) molality and (ii) mole fraction of the solute. (1989)

Solution From Raoult's law, we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{750\ \text{mmHg}}{760\ \text{mmHg}} = 0.987$$

Mole fraction of solute, $x_2 = 1 - x_1 = 1 - 0.987 = 0.013$

$$\text{Now, Molality of solute} = \frac{n_2}{m_1} = \frac{n_2}{n_1 M_1} = \frac{0.013\ \text{mol}}{(0.987\ \text{mol})(18\times 10^{-3}\ \text{kg mol}^{-1})} = 0.732\ \text{mol kg}^{-1}.$$

7. Calculate the molality of a 1 litre solution of 93% H_2SO_4 (mass/volume). The density of the solution is 1.84 g mL^{-1}. (1990)

Solution Mass of 1 L solution = $\rho V = (1.84\ \text{g mL}^{-1})\ (1000\ \text{mL}) = 1840\ \text{g}$

$$\text{Mass of } H_2SO_4 \text{ in 1 L solution} = \frac{93\ \text{g}}{100\ \text{mL}} \times 1000\ \text{mL} = 930\ \text{g}$$

$$\text{Amount of } H_2SO_4 \text{ in 1 L solution} = \frac{930\ \text{g}}{98\ \text{g mol}^{-1}} = 9.49\ \text{mol}$$

Mass of H_2O in 1 L solution = 1840 g – 930 g = 910 g

$$\text{Molality of solution} = \frac{9.49\ \text{mol}}{(910/1000)\ \text{kg}} = 10.43\ \text{mol kg}^{-1}.$$

8. The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A nonvolatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molar mass of the solid substance? (1990)

Solution From the Raoult's law, we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{600\ \text{mmHg}}{640\ \text{mmHg}} = 0.9375$$

Now $$x_1 = \frac{n_1}{n_1 + n_2} \quad \text{i.e.} \quad 0.9375 = \frac{(39.0/78.0)\ \text{mol}}{(39.0/78.0)\ \text{mol} + (2.175\ \text{g}/M)}$$

which gives $$M = \frac{2.175\ \text{g}}{0.5(1 - 0.9375)\ \text{mol}} = 69.6\ \text{g mol}^{-1}.$$

9. Addition of 0.643 g of a compound to 50 mL of benzene (density: 0.879 g mL^{-1}) lowers the freezing point from 5.51 °C to 5.03 °C. If K_f for benzene is 5.12 K kg mol^{-1}, calculate the molar mass of the compound. (1992)

Solution We have

$$\text{Amount of the compound} = \frac{0.643\ \text{g}}{M}$$

Mass of the solvent = $\rho V = (0.879\ \text{g mL}^{-1})\ (50\ \text{mL}) = 43.95\ \text{g}$

$$\text{Molality of the solution} = \frac{(0.643\ \text{g}/M)}{(43.95/1000)\ \text{kg}}$$

Lowering of the freezing point, $-\Delta T_f = (5.51 - 5.03)\ °C = 0.48\ °C \equiv 0.48\ K$

Now using the expression $-\Delta T_f = K_f m$ we get

$$0.48\ \text{K} = (5.12\ \text{K kg mol}^{-1})\left(\frac{0.643\times 1000}{43.95\ M}\ \frac{\text{g}}{\text{kg}}\right)$$

or $$M = \frac{5.12\times 0.643\times 1000}{0.48\times 43.95}\ \text{g mol}^{-1} = 156.06\ \text{g mol}^{-1}.$$

10. What mass of the non-volatile solute urea (NH_2CONH_2) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993)

Solution The vapour pressure of water is to be decreased by 25%.

Hence, $$-\frac{\Delta p_1}{p_1^*} = 0.25$$

According to Raoult's laws $-\dfrac{\Delta p_1}{p_1^*} = x_2$ where x_2 is the mole fraction of solute, i.e. $x_2 = \dfrac{n_2}{n_1 + n_2}$

Substituting $x_2 = 0.25$, we get

$$n_2 = \frac{1}{3} n_1 = \frac{1}{3}\left(\frac{100\ \text{g}}{18\ \text{g mol}^{-1}}\right) = \frac{50}{27}\ \text{mol};\quad \text{Mass of urea dissolved} = \left(\frac{50}{27}\ \text{mol}\right)(60\ \text{g mol}^{-1}) = \frac{1000}{9}\ \text{g}$$

$$\text{Molality of solution} = \frac{(50/27)\ \text{mol}}{0.1\ \text{kg}} = \frac{500}{27}\ \text{mol kg}^{-1}.$$

11. How much of concentrated H_2SO_4 of density 1.84 g cm^{-3} and containing 98 mass per cent of H_2SO_4 must be diluted to prepare 100 cm^3 of the 20 mass per cent H_2SO_4 of density 1.14 g cm^{-3}?

Solution Let V be the required volume of concentrated H_2SO_4.

Mass of H_2SO_4 in the volume V of concentrated solution, $m = (V)\,(1.84\ \text{g cm}^{-3})\left(\dfrac{98}{100}\right)$ (1)

This must be equal to the mass of the H_2SO_4 in the required dilute solution which is given as

$$m = (100\ \text{cm}^3)\,(1.14\ \text{g cm}^{-3})\left(\frac{20}{100}\right) \tag{2}$$

Equating Eqs (1) and (2), we get

$$V = \frac{(100\ \text{cm}^3)(1.14\ \text{g cm}^{-3})(20/100)}{(1.84\ \text{g cm}^{-3})\,(98/100)} = 12.64\ \text{cm}^3.$$

12. $8.057\,5 \times 10^{-2}$ kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1 077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution. (1994)

Solution Glauber's salt is $Na_2SO_4 \cdot 10H_2O$.

Molar mass of Glauber's salt = {2 × 23.00 + 32.10 + 4 × 16.00 + 10 (2 × 1.01 + 16.00)} g mol^{-1} = 322.3 g mol^{-1}

Amount of Galuber's salt dissolved, $n_2 = \dfrac{m}{M} = \dfrac{8.0575 \times 10^{-2}\ \text{kg}}{322.3 \times 10^{-3}\ \text{kg mol}^{-1}} = 0.25\ \text{mol}$

Mass of 1 dm^3 of solution = $\rho V = (1077.2\ \text{kg m}^{-3})\,(10^{-3}\ \text{m}^3) = 1.0772\ \text{kg}$

Mass of Na_2SO_4 in 1 dm^3 solution $= n_2\, M_{Na_2SO_4} = (0.25\ \text{mol})\,(2 \times 23.00 + 32.10 + 4 \times 16.00)\ \text{g mol}^{-1}$

$= 35.525\ \text{g} \equiv 3.5525 \times 10^{-2}\ \text{kg}.$

Mass of solvent in 1 dm^3 solution = $(1.0772 - 3.5525 \times 10^{-2})$ kg = 1.0417 kg

$$\text{Molarity of } Na_2SO_4 \text{ in solution} = \frac{n_2}{V} = \frac{0.25\ \text{mol}}{1\ \text{dm}^3} = 0.25\ \text{mol dm}^{-3}$$

$$\text{Molality of } Na_2SO_4 \text{ in solution} = \frac{n_2}{m_{\text{solvent}}} = \frac{0.25\ \text{mol}}{1.0417\ \text{kg}} = 0.24\ \text{mol kg}^{-1}$$

$$\text{Amount of solvent in 1 dm}^3 \text{ solution},\quad n_1 = \frac{1.0417 \times 10^3\ \text{g}}{18\ \text{g mol}^{-1}} = 57.87\ \text{mol}$$

$$\text{Mole fraction of } Na_2SO_4 \text{ in solution},\ \frac{n_1}{n_1 + n_2} = \frac{0.25}{0.25 + 57.87} = 0.004\,3$$

13. Calculate the (a) molar concentration and (b) molality of a sulphuric acid solution of density 1.198 g cm^{-3}, containing 27 mass per cent of sulphuric acid. To what volume should 100 mL of this acid be diluted to prepare 1.5 N solution?

Solution We have

Mass of sulphuric acid = 27 g   Mass of water = 73 g

$$\text{Amount of sulphuric acid} = \frac{27\ \text{g}}{98\ \text{g mol}^{-1}} = 0.276\ \text{mol}$$

$$\text{Volume of 100 g solution} = \frac{100\ \text{g}}{1.198\ \text{g cm}^{-3}} = 83.47\ \text{cm}^3$$

$$\text{Molarity of solution} = \frac{0.276\ \text{mol}}{(83.47/1000)\ \text{dm}^3} = 3.307\ \text{mol dm}^{-3}$$

$$\text{Molality of solution} = \frac{0.276\ \text{mol}}{(73/1000)\ \text{kg}} = 3.78\ \text{mol kg}^{-1}$$

Since sulphuric acid contains 2 replaceable H^+ ions, we will have Normality of solution = 6.614 eq dm^{-3}
Applying normality equation, we get

$$(100\ \text{mL})\ (6.614\ \text{N}) = V\ (1.5\ \text{N}) \quad \text{or} \quad V = \frac{100 \times 6.614}{1.5}\ \text{mL} = 440.9\ \text{mL}.$$

14. What volume of 1.0 M HCl must be added to 50.0 mL of 0.50 M HCl to give a solution whose concentration is 0.6 M?

Solution Let V be the volume of 1.0 M HCl that has been added to 50.0 mL of 0.50 M HCl to give a solution whose concentration is 0.6 M. We will have

$$(V)\ (1.0\ \text{M}) + (50.0\ \text{mL})\ (0.50\ \text{M}) = (V + 50.0\ \text{mL})\ (0.6\ \text{M})$$

Solving for V, we get $(V)\ (1.0\ \text{M} - 0.6\ \text{M}) = (50.0\ \text{mL})\ (0.6\ \text{M} - 0.50\ \text{M})$

or $V = (0.1/0.4) \times 50.0\ \text{mL} = 12.5\ \text{mL}.$

15. To what volume must 250 mL of 1.40 M H_2SO_4 be diluted to give a solution, 25.0 mL of which is able to completely react with 15.0 mL of 0.75 M NaOH solution?

Solution Let M be the molarity of diluted sulphuric acid solution. We will have

$$(25.0\ \text{mL})\ (2\ M) = (15.0\ \text{mL})\ (0.75\ \text{M}) \quad \text{or} \quad M = \frac{15.0 \times 0.75}{25.0 \times 2}\ \text{M}$$

If V is the volume to which the original sulphuric acid is diluted, we will have

$$(V)\left(\frac{15.0 \times 0.75}{25.0 \times 2}\ \text{M}\right) = (250\ \text{mL})\ (1.40\ \text{M}) \quad \text{or} \quad V = (250 \times 1.40)\left(\frac{25.0 \times 2}{15.0 \times 0.75}\right)\ \text{mL} = 1555.56\ \text{mL}.$$

16. Determine the volume of dilute nitric acid (density 1.11 g cm^{-3}, 19 mass % HNO_3) that can be prepared by diluting 50.0 cm^3 of concentrated acid (density 1.42 g cm^{-3}, 69.8 mass % HNO_3). Calculate the molarities and molalities of concentrated and dilute acids.

Solution *Concentrated Acid*

69.8 mass % HNO_3 implies that 69.8 g of HNO_3 is present in 100 g of total solution. Thus, we have

Mass of HNO_3 = 69.8 g $\qquad \text{Amount of } HNO_3 = \dfrac{69.8\ \text{g}}{63\ \text{g mol}^{-1}} = 1.1075\ \text{mol}$

Mass of solution = 100 g $\qquad \text{Volume of solution} = \dfrac{100\ \text{g}}{1.42\ \text{g cm}^{-3}} = 70.42\ \text{cm}^3$

Mass of water = 100 g − 69.8 g = 30.2 g

Hence, $\quad \text{Molarity of solution} = \dfrac{1.1075\ \text{mol}}{70.42 \times 10^{-3}\ \text{dm}^3} = 15.73\ \text{mol dm}^{-3}$

$$\text{Molality of solution} = \frac{1.1075\ \text{mol}}{30.2 \times 10^{-3}\ \text{kg}} = 36.67\ \text{mol kg}^{-1}$$

Dilute Acid

Here, we have

Mass of HNO_3 = 19 g $\qquad \text{Amount of } HNO_3 = \dfrac{19\ \text{g}}{63\ \text{g mol}^{-1}} = 0.3016\ \text{mol}$

Mass of solution = 100 g $\qquad \text{Volume of solution} = \dfrac{100\ \text{g}}{1.11\ \text{g cm}^{-3}} = 90.05\ \text{cm}^3$

Mass of water = 100 g – 19 g = 81 g

Hence, Molarity of solution $= \dfrac{0.3016 \text{ mol}}{90.05 \times 10^{-3} \text{ dm}^{-3}} = 3.35 \text{ mol dm}^{-3}$

Molality of solution $= \dfrac{0.3016 \text{ mol}}{81 \times 10^{-3} \text{ kg}} = 3.72 \text{ mol kg}^{-1}$

Let V be the obtained volume of diluted nitric acid. We will have,

$$M_1 V_2 = M_2 V_2 \quad \text{i.e.} \quad (3.35 \text{ mol dm}^{-3})\,(V) = (15.73 \text{ mol dm}^{-3})\,(50.0 \text{ cm}^3)$$

or $V = \dfrac{15.73 \times 50.0}{3.35} \text{ cm}^3 = 234.8 \text{ cm}^3.$

17. At 100 °C, benzene and toluene have vapour pressures of 1375 and 558 Torr, respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm and 100 °C. What is the composition of vapour issuing at these conditions?

Solution Let x_1 be the mole fraction of benzene in the solution. We will have

$$p = x_1 p_1^* + (1 - x_1)\, p_2^* \quad \text{i.e.} \quad 760 \text{ Torr} = x_1\,(1375 \text{ Torr}) + (1 - x_1)\,(558 \text{ Torr})$$

which gives $x_1 = \dfrac{760 - 558}{1375 - 558} = 0.247$

Now, the mole fraction of benzene in the vapour phase is given as

$$y = \frac{p_1}{p} = \frac{x_1 p_1^*}{p_1} = \frac{0.247\,(1375 \text{ Torr})}{760 \text{ Torr}} = 0.447$$

Hence, Mole fraction of benzene in solution = 0.247 Mole fraction of toluene in solution = 0.753

Mole fraction of benzene in vapour phase = 0.447 Mole fraction of toluene in vapour phase = 0.553.

18. (a) The vapour pressure of *n*-hexane and *n*-heptane at 273 K are 45.5 mmHg and 11.4 mmHg, respectively. What is the composition of a solution of these two liquids if its vapour pressure at 273 K is 37.3 mmHg. (b) The mole fraction of *n*-hexane in the vapour above a soluton of *n*-hexane and *n*-heptane is 0.75 at 273 K. What is the composition of the liquid solution?

Solution (a) Let x_1 be the mole fraction of *n*-hexane in the solution. We will have

$$p = x_1 p_1^* + (1 - x_1)\, p_2^* \quad \text{i.e.} \quad 37.3 \text{ mmHg} = x_1(45.5 \text{ mmHg}) + (1 - x_1)\,(11.4 \text{ mmHg})$$

which gives $x_1 = \dfrac{(37.3 - 11.4) \text{ mmHg}}{(45.5 - 11.4) \text{ mmHg}} = 0.76$ and hence $x_2 = 1 - x_1 = 1 - 0.76 = 0.34$

(b) If y_1 be the mole fraction of *n*-hexane in vapour phase, we will have

$$y_1 = \frac{x_1 p_1^*}{p}. \quad \text{Thus} \quad 0.75 = \frac{x_1\,(45.5 \text{ mmHg})}{(37.3 \text{ mmHg})} \quad \text{or} \quad x_1 = \frac{0.75 \times 37.3}{45.5} = 0.61.$$

19. A solution is prepared from 26.7 g of an unknown compound and 116.0 g of acetone at 313 K. The vapour pressure of pure acetone at this temperature is 0.526 atm and that of the acetone above the solution is 0.501 atm. Calculate the molar mass of the unknown compound.

Solution Using Raoult's law, we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{0.501 \text{ atm}}{0.526 \text{ atm}} = 0.9525$$

If M is the molar mass of the unknown compound, we will have

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{(116.0 \text{ g}/58 \text{ g mol}^{-1})}{(116.0 \text{ g}/58 \text{ g mol}^{-1}) + (26.7 \text{ g}/M)}$$

which gives $M = \dfrac{x_1\,(26.7 \text{ g})}{(2 \text{ mol})\,(1 - x_1)} = \dfrac{(0.9525)\,(26.7 \text{ g})}{(2 \text{ mol})\,(1 - 0.9527)} = 267.7\text{g mol}^{-1}.$

20. A solution containing 30 g of a nonvolatile solute in exactly 90 g water has a vapour pressure of 21.85 mmHg at 25 °C. Further 18 g of water is then added to the solution. The resulting solution has vapour pressure of 22.18 mmHg at 25 °C. Calculate (a) molar mass of the solute, and (b) vapour pressure of water at 25°C.

Solution If M is the molar mass of solute, we will have

$$p_1 = x_1\, p_1^*$$

$$21.85 \text{ mmHg} = \frac{(90\text{ g}/18\text{ g mol}^{-1})}{(90\text{ g}/18\text{ g mol}^{-1}) + (30\text{ g}/M)}\, p_1^* \qquad (1)$$

$$22.18 \text{ mmHg} = \frac{(108\text{ g}/18\text{ g mol}^{-1})}{(108\text{ g}/18\text{ g mol}^{-1}) + (30\text{ g}/M)}\, p_1^* \qquad (2)$$

Dividing Eq. (2) by Eq. (1), we get

$$\frac{22.18}{21.85} = \frac{6\text{ mol}}{6\text{ mol} + (30\text{ g}/M)} \cdot \frac{5\text{ mol} + (30\text{ g}/M)}{5\text{ mol}} = \frac{30\text{ mol} + 180\text{ g}/M}{30\text{ mol} + 150\text{ g}/M}$$

or $$22.18\ (30\text{ mol} + 150\text{ g}/M) = 21.85\ (30\text{ mol} + 180\text{ g}/M)$$

or $$M = \frac{(21.85 \times 180 - 22.18 \times 150)\text{ g}}{(22.18 \times 30 - 21.85 \times 30)\text{ mol}} = \frac{(3933 - 3327)\text{ g}}{(665.4 - 655.5)\text{ mol}} = \frac{606}{9.9}\text{ g mol}^{-1} = 61.21\text{ g mol}^{-1}$$

Substituting this value of M in Eq. (1), we get

$$21.85\text{ mmHg} = \frac{5\text{ mol}}{5\text{ mol} + (30\text{ g}/61.21\text{ g mol}^{-1})}\, p_1^* \quad \text{or} \quad p_1^* = \frac{21.85\,(5 + 0.49)}{5}\text{ mmHg} = 23.99\text{ mmHg.}$$

21. The freezing point of ether was lowered by 0.60 °C on dissolving 2.0 g of phenol in 100 g of ether. Calculate the molar mass of phenol and comment on the result. Given : K_f(ether) = 5.12 K kg mol^{-1}.

Solution Let M be the molar mass of phenol in ether. We will have

$$\text{Molality of solution} = \frac{2.0\text{ g}/M}{(100/1000)\text{ kg}}$$

Now using the expression $-\Delta T_f = K_f\, m,$ we get

$$0.60\text{ K} = (5.12\text{ K kg mol}^{-1})\left(\frac{20}{M}\,\frac{\text{g}}{\text{kg}}\right) \quad \text{which gives} \quad M = \frac{5.12 \times 20}{0.60}\text{ g mol}^{-1} = 170.7\text{ g mol}^{-1}$$

Since the calculated molar mass is about twice its actual molar mass (94 g mol^{-1}), it may be concluded that the phenol in ether is almost present in the dimerized form.

22. Two elements A and B form compounds having molecular formulae AB_2 and AB_4. When dissolved in 2.0 g of benzene 1.0 g of AB_2 lowers the freezing point by 2.3 °C whereas 1.0 g of AB_4 lowers the freezing point by 1.3 °C. Calculate the molar masses of A and B. Given : K_f(benzene) = 5.1 K kg mol^{-1}.

Solution Let M_A and M_B be the molar masses of A and B, respectively. Now from the expression $-\Delta T_f = K_f\, m$ we get

$$2.3\text{ K} = (5.1\text{ K kg mol}^{-1})\left[\frac{1.0\text{ g}/(M_A + 2M_B)}{(20/1000)\text{ kg}}\right] \quad \text{and} \quad 1.3\text{ K} = (5.1\text{ K kg mol}^{-1})\left[\frac{1.0\text{ g}/(M_A + 4M_B)}{(20/1000)\text{ kg}}\right]$$

That is $$M_A + 2\,M_B = \frac{5.1 \times 1000}{2.3 \times 20}\text{ g mol}^{-1} = 110.9\text{ g mol}^{-1}$$

$$M_A + 4\,M_B = \frac{5.1 \times 1000}{1.3 \times 20}\text{ g mol}^{-1} = 196.2\text{ g mol}^{-1}$$

Solving the M_A and M_B, we get

$$M_A = 25.60\text{ g mol}^{-1} \quad \text{and} \quad M_B = 42.65\text{ g mol}^{-1}.$$

23. A solution of a nonvolatile solute in water has a boiling point of 375.3 K. Calculate the vapour pressure of water above this solution at 338 K. Given: p^*(water) = 0.2467 atm at 338 K, and K_b(water) = 0.51 K kg mol^{-1}.

Solution From the expression $\Delta T_b = K_b\, m$, we get

$$m = \frac{\Delta T_b}{K_b} = \frac{(375.3 - 373.15)\text{ K}}{0.51\text{ K kg mol}^{-1}} = 4.216 \text{ mol kg}^{-1}$$

Now, the mole fraction of water in solution will be

$$x_1 = \frac{(1000\text{ g}/18\text{ g mol}^{-1})}{(1000\text{ g}/18\text{ g mol}^{-1}) + 4.216\text{ mol}} = 0.9295$$

Hence, $p_1 = x_1 p_1^* = (0.9295)\ (0.2467 \text{ atm}) = 0.2293$ atm.

24. The osmotic pressure of a solution containing 0.10 g of haemoglobin in 10.0 cm^3 of solution is 2.67 Torr at 1 °C. Estimate the molar mass of haemoglobin.

Solution Since $\Pi V = nRT$, we have

$$\Pi V = \frac{m}{M}\, RT \qquad \text{or} \qquad M = \frac{mRT}{\Pi V}$$

Substituting the given values, we get

$$M = \frac{(0.10\text{ g})\,(0.0821\text{ L atm K}^{-1}\text{ mol}^{-1})\,(274\text{ K})}{\{(2.67/760)\text{ atm}\}\,\{(10.0/1000)\text{ L}\}} = 64 \times 10^3 \text{ g mol}^{-1}.$$

25. The density of a 9.5% by mass solution of fructose ($C_6H_{12}O_6$) is 1.036 g cm^{-3} at 293 K. Calculate the osmotic pressure of the solution.

Solution We have

Molar mass of fructose = 180 g mol^{-1}

9.5% mass solution of fructose implies that 9.5 g of fructose is present in 100 g solution. Hence, we have

Volume of solution, $V = \dfrac{100\text{ g}}{1.036\text{ g mol}^{-3}} = 96.53 \text{ cm}^3$ Amount of fructose, $n_2 = \dfrac{9.5\text{ g}}{180\text{ g mol}^{-1}} = 0.0528$ mol

Concentration of solution, $c = \dfrac{n_2}{V} = \dfrac{0.0528\text{ mol}}{(96.53/1000)\text{ dm}^3} = 0.547 \text{ mol dm}^{-3}$

Hence, $\Pi = cRT = (0.547 \text{ mol dm}^{-3})\ (0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})\ (293 \text{ K}) = 13.16$ atm.

26. A solution contains 3.22 g of $HClO_2$ in 47.0 g of water. The freezing point of the solution is 271.10 K. Calculate the fraction of $HClO_2$ that undergoes dissociation to H^+ and ClO_2^-. Given: K_f(water) = 1.86 K kg mol^{-1}.

Solution We have

$$\begin{array}{ccccc} HClO_2 & \rightleftharpoons & H^+ & + & ClO_2^- \\ m(1-\alpha) & & m\alpha & & m\alpha \end{array}$$

Total molality of species in solution = $m(1 + \alpha)$. Now, using the expression $-\,\Delta T_f = K_f m$ we get,

$$(273.15 - 271.10)\text{ K} = (1.86 \text{ K kg mol}^{-1}) \left[\frac{(3.22\text{ g}/68.5\text{ g mol}^{-1})(1+\alpha)}{(47.0/1000)\text{ kg}}\right]$$

$$\text{or} \qquad 2.05 = \frac{1.86 \times 3.22 \times 1000}{47.0 \times 68.5}\,(1+\alpha) = 1.86\,(1+\alpha) \quad \text{or} \quad \alpha = \frac{2.05}{1.86} - 1 = 0.102.$$

27. A 0.1 molar solution of NaCl is found to be isotonic with 1% urea solution. Calculate (a) van't Hoff factor, and (b) degree of dissociation of sodium chloride. Assume density of 1% urea equal to 1 g cm^{-3}.

Solution We have

$$\begin{array}{ccccc} NaCl & \rightleftharpoons & Na^+ & + & Cl^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

Total concentration of species in solution = $c(1 + \alpha) = (0.1\ \text{M})(1 + \alpha)$

Now, Osmotic pressure of NaCl solution = $(0.1\ \text{M})\ (1 + \alpha)\ RT$

Osmotic pressure of urea solution = $\dfrac{(1/60)\ \text{mol}}{0.1\ \text{L}}\ RT$

Since the two solutions are isotonic, we will have

$$(0.1\ \text{M})(1 + \alpha)RT = \left(\frac{1}{60 \times 0.1}\ \text{mol L}^{-1}\right) RT \quad \text{or} \quad \alpha = \frac{1}{60 \times 0.1 \times 0.1} - 1 = 1.667 - 1 = 0.667$$

Now, van't Hoff factor = $\dfrac{c(1+\alpha)}{c} = 1.667$

28. The freezing point depression of a 0.109 M aqueous solution of formic acid is –0.21 °C. Calculate the equilibrium constant for the equation $\text{HCOOH(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{HCOO}^-\text{(aq)}$

The molality of the solution is 0.110 mol kg^{-1} and K_f(water) = 1.86 K kg mol^{-1}.

Solution If α is the degree of dissociation of HCOOH, we will have

$$\underset{m(1-\alpha)}{\text{HCOOH}} \rightleftharpoons \underset{m\alpha}{\text{H}^+} + \underset{m\alpha}{\text{HCOO}^-} \qquad \text{Total molality of the solution} = m(1 + \alpha)$$

Hence, $0.21\ \text{K} = m(1 + \alpha)(1.86\ \text{K kg mol}^{-1})$ which gives $\alpha = \dfrac{0.21}{0.11 \times 1.86} - 1 = 0.0264$

Thus $$K = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{(0.109\,\text{M})\,(0.0264)^2}{(1-0.0264)} = 7.8 \times 10^{-5}\ \text{M}.$$

29. When 2 g of a nonvolatile hydrocarbon containing 94.4 per cent carbon is dissolved in 100 g benzene, the vapour pressure of benzene is lowered from 74.66 Torr to 74.01 Torr. Determine the molecular formula of the hydrocarbon.

Solution According to Raoult's law, $\dfrac{-\Delta p}{p^*} = x_2$ where $-\Delta p = (74.01 - 74.66)$ Torr and $p^* = 74.66$ Torr.

If M is the molar mass of hydrocarbon, then

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{(2\,\text{g}/M)}{(100\,\text{g}/78\,\text{g mol}^{-1}) + (2\,\text{g}/M)} \qquad \text{Hence,} \quad \frac{(74.66 - 74.01)\ \text{Torr}}{74.66\ \text{Torr}} = \frac{(2\,\text{g}/M)}{(100\ \text{mol}/78) + (2\,\text{g}/M)}$$

Solving for M, we get $M = 177.6\ \text{g mol}^{-1}$

Thus atomic ratio is $N_\text{C} : N_\text{H} :: \dfrac{94.4}{12} : \dfrac{5.6}{1} \Rightarrow 7.87 : 5.6 \Rightarrow 1.4 : 1 \Rightarrow 7 : 5$

Hence, Empirical formula is C_7H_5. Molar empirical mass = 89 g mol^{-1}

$$\text{Number of C}_7\text{H}_5 \text{ unit in the given molecule} = \frac{\text{Molar mass}}{\text{Molar empirical mass}} = \frac{177.6}{89} \simeq 2$$

Thus, molecular formula is $\text{C}_{14}\text{H}_{10}$.

30. The addition of 3 g of a substance to 100 g CCl_4 (M = 154 g mol^{-1}) raises the boiling point of CCl_4 by 0.60 °C. If $K_b(\text{CCl}_4)$ is 5.03 K mol^{-1} kg, calculate (a) the freezing point depression, (b) the relative lowering of vapour pressure, (c) the osmotic pressure at 298 K and (d) the molar mass of the substance. Given: $K_f(\text{CCl}_4)$ = 31.8 K kg mol^{-1} and ρ(solution) = 1.64 g cm^{-3}.

Solution The molality of the given solution is $m = \dfrac{\Delta T_\text{b}}{K_\text{b}} = \dfrac{0.60\ \text{K}}{5.03\ \text{K kg mol}^{-1}} = 0.12\ \text{mol kg}^{-1}$

(a) $-\Delta T_\text{f} = K_\text{f}\, m = (31.8\ \text{K kg mol}^{-1})\ (0.12\ \text{mol kg}^{-1}) = 3.816\ \text{K}$

(b) If M_2 is the molar mass of the substance, then

$$\frac{-\Delta p}{p^*} = x_2 = \frac{n_2}{n_1+n_2} = \frac{(3\,\text{g}/M_2)}{(100\,\text{g}/154\ \text{g mol}^{-1})+(3\,\text{g}/M_2)} \qquad (1)$$

Now, from the molality of the solution we get

$$\text{molality} = \frac{n_2}{m_1} = \frac{m_2/M_2}{m_1} \quad \text{i.e.} \quad 0.12\ \text{mol kg}^{-1} = \frac{3\,\text{g}/M_2}{100\,\text{g}}$$

or $$M_2 = \left(\frac{3}{100}\right)\left(\frac{1}{0.12\ \text{mol kg}^{-1}}\right) = 0.25\ \text{kg mol}^{-1} = 250\ \text{g mol}^{-1}$$

Substituting this in Eq. (1), we get $$\frac{-\Delta p}{p^*} = \frac{(3/250)}{(100/154)+(3/250)} = 0.01814$$

(c) For calculating osmotic pressure, we use the expression $\varPi = cRT = \left(\frac{n_2}{V}\right) RT$ where

$$n_2 = \frac{m_2}{M_2} = \frac{3\ \text{g}}{250\ \text{g mol}^{-1}} = 0.012\ \text{mol} \quad \text{and} \quad V = \frac{\text{mass of solution}}{\text{density of solution}} = \frac{(100+3)\ \text{g}}{1.64\ \text{g cm}^{-3}} = 62.8\ \text{cm}^3 = 0.0628\ \text{dm}^3$$

Hence, $$\varPi = \frac{(0.012\ \text{mol})\,(0.082\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})\,(298\ \text{K})}{(0.0628\ \text{dm}^3)} = 4.669\ \text{atm}$$

(d) Molar mass of the substance as calculated above is 250 g mol^{-1}.

31. The freezing point of 0.02 mole fraction solution of acetic acid in benzene is 277.4 K. Assuming molality equal to molarity, calculate K_c for the equilibrium reaction $2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$
Given: T_f^*(benzene) = 278.4 K and K_f(benzene) = 5.0 K kg mol^{-1}.

Solution From the expression $-\Delta T_f = K_f m$, we get

$$m = \frac{-\Delta T_f}{K_f} = \frac{(278.4-277.4)\ \text{K}}{5.0\ \text{K kg mol}^{-1}} = 0.2\ \text{mol kg}^{-1} \quad \text{i.e.} \quad c = 0.2\ \text{mol dm}^{-3}$$

From the given mole fraction, we calculate the initial concentration of acetic acid had there been no equilibrium reaction. We have

$$x_2 = \frac{n_2}{n_1+n_2} \simeq \frac{n_2}{n_1} = \frac{n_2}{(m_1/M_1)} = (n_2/m_1)\ (M_1) = m_0\, M_1$$

or $$m_0 = \frac{x_2}{M_1} = \frac{0.02}{78\times10^{-3}\ \text{kg mol}^{-1}} = 0.257\ \text{mol kg}^{-1} \quad \text{i.e.} \quad c_0 = 0.257\ \text{mol dm}^{-3}$$

Now for the equilibrium reaction $$\underset{c_0-2x}{2\ CH_3COOH} \rightleftharpoons \underset{x}{(CH_3COOH)_2}$$

we get $$c = c_0 - 2x + x = c_0 - x \qquad \text{i.e.} \qquad 0.2\ \text{M} = 0.257\ \text{M} - x \qquad \text{or} \qquad x = 0.057\ \text{M}$$

Thus $$K_c = \frac{[(CH_3COOH)_2]}{[CH_3COOH]^2} = \frac{x}{(c_0-2x)^2} = \frac{0.057\ \text{M}}{\{(0.257-2\times0.057)\ \text{M}\}^2} = 2.787\ \text{M}^{-1}.$$

32. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20 °C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20 °C. A solution of benzene and toluene at 20 °C has vapour prossure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. (1996)

Solution Molar volume of liquid benzene $= \frac{M}{\rho} = \frac{78\ \text{g mol}^{-1}}{0.877\ \text{g mL}^{-1}} = 88.94\ \text{mL}$

Molar volume of benzene vapour at its vapour pressure = (2750) (88.94 mL) = 224585 mL = 244.585 L

Vapour pressure pure benzene $$p_b^* = \frac{nRT}{V} = \frac{(1\ \text{mol})\,(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{(244.585\ \text{L})} = 0.0982\ \text{atm}$$

Molar volume of liquid toluene $= \dfrac{M}{\rho} = \dfrac{92\ \text{g mol}^{-1}}{0.867\ \text{g mL}^{-1}} = 106.11\ \text{mL}$

Molar volume of toluene vapour at its vapour pressure = (7720) (106.11 mL) = 819169 mL = 819.169 L

Vapour pressure of toluene, $p_\text{t}^* = \dfrac{nRT}{V} = \dfrac{(1\ \text{mol})(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{(819.169\ \text{L})} = 0.0293\ \text{atm}$

Let x_b be the mole fraction of benzene in the liquid phase. We will have

$$p_\text{total} = x_\text{b}\, p_\text{b}^* + (1 - x_\text{b})\, p_\text{t}^* = p_\text{t}^* + (p_\text{b}^* - p_\text{t}^*)x_\text{b}$$

or $$x_\text{b} = \frac{p_\text{total} - p_\text{t}^*}{p_\text{b}^* - p_\text{t}^*} = \frac{(46.0/760)\ \text{atm} - 0.0293\ \text{atm}}{0.0982\ \text{atm} - 0.0293\ \text{atm}} = 0.453$$

Mole fraction of benzene in vapour phase, $y_\text{b} = \dfrac{p_\text{b}}{p_\text{total}} = \dfrac{x_\text{b}\, p_\text{b}^*}{p_\text{total}^*} = \dfrac{(0.453)(0.0982\ \text{atm})}{(46/760)\ \text{atm}} = 0.735$

33. A very small amount of a nonvolatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mmHg while that of benzene is 100 mmHg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree Celsius lower than that of benzene, what is the value of molal freezing point depression constant of benzene? (1997)

Solution Using Raoult's law $p_1 = x_1\, p_1^*$ we get (98.88 mmHg) = x_1 (100 mmHg) or $x_1 = 0.9888$
Let 1 mol of the total amount of solvent and solute. We will have

$n_1 = 0.9888$ mol and $n_2 = 0.0112$ mol; $m_1 = n_1 M = (0.9888\ \text{mol})\ (78\ \text{g mol}^{-1}) = 77.126\ \text{g}$

The molality of the solution is $m = \dfrac{n_1}{m_1} = \dfrac{0.0112\ \text{mol}}{77.126 \times 10^{-3}\ \text{kg}} = 0.1452\ \text{mol kg}^{-1}$

Freezing point depression constant of benzene would be

$$K_\text{f} = \frac{-\Delta T_\text{f}}{m} = \frac{0.73\ \text{K}}{0.1452\ \text{mol kg}^{-1}} = 5.028\ \text{K kg mol}^{-1}$$

34. A solution of a non-volatile solute in water freezes at – 30 °C. The vapour pressure of pure water at 298 K is 23.51 mmHg and K_f for water is 1.86 K kg mol^{-1}. Calculate the vapour pressure of this solution at 298 K. (1998)
Solution From the data on the depression in freezing point, we get

$$m = \frac{-\Delta T_\text{f}}{K_\text{f}} = \frac{0.30\ \text{K}}{1.86\ \text{K kg mol}^{-1}} = 0.1613\ \text{mol kg}^{-1}$$

Mole fraction of solvent in the solution would be $x_1 = \dfrac{n_1}{n_1 + n_2} = \dfrac{(1000/18)}{(1000/18) + 0.1613} = 0.9971$

Vapour pressure of the solution would be $p = x_1\, p_1^* = (0.9971)\ (23.51\ \text{mmHg}) = 23.44\ \text{mmHg}$.

35. To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 2.3% of acetic acid is dissociated, what will be the depression of freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3}, respectively. (2000)
Solution

Mass of acetic acid = 3×10^{-3} kg = 3 g; Amount of acetic acid, $n_2 = \dfrac{3\ \text{g}}{60\ \text{g mol}^{-1}} = 0.05\ \text{mol}$

Volume of water, $V = 500\ \text{cm}^3$; Mass of water, $m_1 = V\rho = (500\ \text{cm}^3)\ (0.997\ \text{g cm}^{-3}) = 498.5\ \text{g} = 0.4985\ \text{kg}$

Molality of acetic acid, $m = \dfrac{n_2}{m_1} = \dfrac{0.05\ \text{mol}}{0.4985\ \text{kg}} = 0.1003\ \text{mol kg}^{-1}$

Since 23% acetic acid is dissociated, its degree of dissociation will be 0.23. Hence, in solution we have

$$\begin{array}{ccc} CH_3COOH & \rightleftharpoons & CH_3COO^- + H^+ \\ m(1-\alpha) & m\alpha & m\alpha \end{array}$$

Molality of species in solution = $m(1 - \alpha) + m\alpha + m\alpha = m(1 + \alpha)$

Hence, $-\Delta T_f = m(1 + \alpha)K_f = (0.1003\ \text{mol kg}^{-1})(1 + 0.23)\quad(1.86\ \text{K kg mol}^{-1}) = 0.23\ \text{K}$

36. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100° C is 70 per cent. If the vapour pressure of water at 100 °C is 760 mmHg, calculate the vapour pressure of the solution. (1991)

Solution We have

Mass of $Ca(NO_3)_2$ = 7.0 g; Molar mass of $Ca(NO_3)_2$ = 164 g mol^{-1}

Amount $Ca(NO_3)_2$ = (7.0/164) mol; Amount of water = (100/80) mol

The dissociation of $Ca(NO_3)_2$ along with the amounts of different species are as follows.

$$\begin{array}{lcccc} & Ca(NO_3)_2 & \rightleftharpoons & Ca^{2+} & 2NO_3^- \\ \textit{Amount} & \frac{7.0}{164}\,(1-0.7)\ \text{mol} & & \frac{7.0}{164}\,(0.7)\ \text{mol} & \frac{7.0}{164}\,(2\times 0.7)\ \text{mol} \end{array}$$

Total amount of the solution, $n_{\text{total}} = n(H_2O) + n(Ca(NO_3)_2) + n(Ca^{2+}) + n(NO_3^-)$

$$= \left\{\frac{100}{18} + \frac{7.0}{164}(0.3 + 0.7 + 1.4)\right\}\ \text{mol} = (5.556 + 0.102)\ \text{mol} = 5.658\ \text{mol}$$

Mole fraction of solvent, x_1 = 5.556/5.658

Hence, $p_1 = x_1 p^*_1 = \left(\frac{5.556}{5.658}\right)(760\ \text{mmHg}) = 746.3\ \text{mmHg}$

37. Match the following if the molar mass of X, Y and Z are the same

Solvent	t_b/°C	K_b/kg K mol^{-1}
X	127	0.73
Y	27	0.53
Z	253	0.98

(2003)

Solution

Since $K_b = MRT_b^{*2}/\Delta_{\text{vap}}H$, we have $K_b = \dfrac{MRT_b^*}{\Delta_{\text{vap}}H/T_b} = (\text{constant})\ T_b^*$

Note that $\Delta_{\text{vap}}H/T_b^*$ is taken to be constant (Trouton's rule). Hence, $K_b \propto T_b^*$

Thus, we have

K_b(X) = 0.73 Kg K mol^{-1}; K_b(Y) = 0.53 kg K mol^{-1}; K_b(Z) = 0.98 kg K mol^{-1}

Verification

$$\frac{K_b(X)}{K_b(Y)} = \frac{0.73}{0.53} = 1.38 \qquad \text{also} \qquad \frac{T_b^*(X)}{T_b^*(Y)} = \frac{400}{300} = 1.33$$

$$\frac{K_b(X)}{K_b(Z)} = \frac{0.73}{0.98} = 0.74 \qquad \text{also} \qquad \frac{T_b^*(X)}{T_b^*(Z)} = \frac{400}{526} = 0.76$$

38. 12.2 g of benzoic acid is dissolved in (i) 1 kg acetone (K_b = 1.7 K kg mol^{-1}) and (ii) 1 kg benzene (K_b = 2.6 K kg mol^{-1}). The elevation of boiling points are 0.17 °C and 0.13 °C, respectively.

(a) What are the molar masses of benzoic acid in the two solutions?

(b) What are the structures of benzoic acid in the two solutions? (2004)

Solution Let M be the molar mass of benzoic acid in the solution. The molality of the solution is

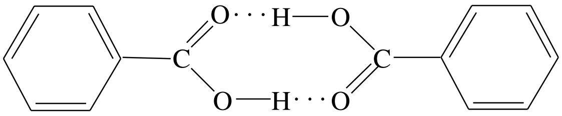
$$m = \frac{n}{m_1} = \frac{(12.2\ \text{g})/M}{1\ \text{kg}}$$

Since $\Delta T_b = K_b\, m$, we get

(a) *Acetone solution* $0.17\ \text{K} = (1.7\ \text{K kg mol}^{-1})\left[\frac{12.2\ \text{g}/M_1}{1\ \text{kg}}\right]$; $M_1 = \frac{1.7 \times 12.2}{0.17}\ \text{g mol}^{-1} = 122\ \text{g mol}^{-1}$

Benzene solution $0.13\ \text{K} = (2.6\ \text{K kg mol}^{-1})\left[\frac{12.2\ \text{g}/M_2}{1\ \text{kg}}\right]$; $M_2 = \frac{2.6 \times 12.2}{0.13}\ \text{g mol}^{-1} = 244\ \text{g mol}^{-1}$

(b) The actual molar mass of benzoic acid (C_6H_5COOH) is 122 g mol^{-1}. This means benzoic acid is present as monomer in acetone solution while it dimerises in benzene solution. The structure of dimerised benzoic acid is



39. In 1 kg of a solvent (K_f = 14 K kg^{-1} mol), 75.2 g of phenol was dissolved. The depression in freezing point of the solvent was found to be 7 K. Determine the degree of dimerization of phenol. (2006)

Solution We have

$$\underset{m(1-\alpha)}{2\,\text{PhOH}} \rightleftharpoons \underset{m\alpha/2}{(\text{PhOH})_2}$$

where $$m = \frac{n_2}{m_1} = \frac{75.2\ \text{g}/(94\ \text{g mol}^{-1})}{1\ \text{kg}} = 0.8\ \text{mol kg}^{-1}$$

Molality of solution $= m(1 - \alpha) + m\,\alpha/2 = m(1 - \alpha/2)$

Since $\Delta T_f = K_f\, m$, we get

$$7\ \text{K} = (14\ \text{K kg}^{-1}\ \text{mol})\,(0.8\ \text{mol kg}^{-1})\,(1 - \alpha/2) \quad \text{This gives} \quad \alpha = 2\left[1 - \frac{1}{2 \times 0.8}\right] = 0.75$$

UNSOLVED PROBLEMS

1. What volume of 95 mass per cent of alcohol (density 0.809 g cm^{-3}) must be used to prepare 150 cm^3 of 30 mass per cent alcohol (density 0.987 g cm^{-3})?
2. Concentrated HNO_3 has a specific gravity of 1.42 and is 69 mass % in HNO_3. What mass of HNO_3 is contained in 500 mL of this reagent? What volume of this concentrated HNO_3 be diluted to obtain 800 mL of 0.20 M HNO_3?
3. What would be the molality of a solution made by mixing equal volumes of 30 mass % H_2SO_4 (density 1.218 g cm^{-3}) and 70 mass % H_2SO_4 (density 1.610 g cm^{-3})? If the density of the resulting solution is 1.425 g cm^{-3}, what is its molarity?
4. The molality of a 1 M solution of sodium nitrate is 0.858 mol kg^{-1}. Determine the density of the solution.
5. The molarity of NH_3 in an aqueous solution is 11.8 mol dm^{-3}. The density of the solution is 0.916 g cm^{-3}. Determine : (a) molality, (b) mass per cent and (c) mole fraction of NH_3.
6. What is the mole fraction of benzene in a benzene-toluene solution that is in equilibrium with a vapour phase containing 60.0 mol % C_6H_6? Given: p^*(benzene) = 95.1 mmHg and p^*(toluene) = 28.4 mmHg.
7. *n*-Butane and *n*-pentane form a nearly ideal solution. At 25 °C, the vapour pressure of *n*-butane is 1823 Torr and that of *n*-pentane is 521 Torr.
   (a) Find the vapour pressure at 25°C of a liquid solution containing 10 mass % of *n*-butane.
   (b) Find the mole fraction of *n*-butane of a solution having vapour pressure of 760 Torr at 25 °C.
   (c) What is the mass percentage of *n*-butane in the vapour phase in (b)?

8. Assuming ideal behaviour, what mass of a volatile liquid of molar mass 128 g mol^{-1} would have to be dissolved in 228 g octane (C_8H_{18}) to lower the vapour pressure of octane by 20%.

9. The density of a 3.742 M solution of glycerol ($C_3H_8O_3$) in water at 298 K is 1.077 g cm^{-3}. The vapour pressure of pure water at this temperature is 23.76 Torr. Calculate the vapour pressure of water above the solution.

10. Two alcohols, isopropyl alcohol and propyl alcohol, have the same molecular formula (C_3H_8O). A solution of the two containing 2/3 by mass of isopropyl alcohol has a vapour pressure of 0.110 atm at 313 K. A solution that is 1/3 by mass of isopropyl alcohol has a vapour pressure of 0.089 atm at 313 K. Calculate the vapour pressure of each pure alcohol at this temperature.

11. In 804 g of water, 30 g sucrose ($C_{12}H_{22}O_{11}$) and 30 g glucose ($C_6H_{12}O_6$) were dissolved. What is the vapour pressure of this solution at 303 K if the vapour pressure of pure water is 31.82 mmHg?

12. At 30 °C, pure benzene (C_6H_6) has a vapour pressure of 121.8 Torr. Dissolving 15 g of a nonvolatile solute in 250 g of benzene produced a solution having a vapour pressure of 120.2 Torr. Determine the molar mass of solute.

13. The vapour pressure of dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 Torr at 100 °C. Calculate (a) mole fraction of the solute, and (b) molality of the solution.

14. An unknown compound contains 42.4% C, 2.4% H, 16.6% N and 37.8% O. The addition of 6.45 g of this compound to 50.0 cm^3 benzene (density 0.879 g cm^{-3}) lowers the freezing point from 5.51 to 1.35 °C. What is the molecular formula of this substance? Given: K_f (benzene) = 5.07 K kg mol^{-1}.

15. An aqueous solution containing 288 g of a nonvolatile compound ($C_nH_{2n}O_n$) in 90.0 g of water boils at 101.24 °C at 1 atm pressure. What is the molecular formula of the compound? Given : K_b(water) = 0.516 K kg mol^{-1}.

16. A 250 cm^3 water solution containing 48.0 g of sucrose ($C_{12}H_{22}O_{11}$) at 300 K is separated from pure water by means of a semipermeable memberane. What is the minimum pressure that has to be applied above the solution to prevent osmosis?

17. The average osmotic pressure of human blood is 7.7 atm at 40 °C. What should be the total concentration of various solutes in the blood?

18. Sea water is 3.5 mass per cent of a salt and has a density of 1.04 g cm^{-3} at 293 K. Assuming the salt to be sodium chloride, calculate the osmotic pressure of sea water.

19. Equal volumes of ethylene glycol and water are mixed. Calculate the freezing point of such a solution Given: ρ(ehylene glycol, $C_2H_4(OH)_2$) = 1.113 g cm^{-3} and K_f(water) = 1.86 K kg mol^{-1}.

20. 1.0 kg of an aqueous solution of sucrose is cooled and maintained at – 3.534 °C. How much ice will separate out if the solution molality is 1 mol kg^{-1}. K_f(water) = 1.86 K kg mol^{-1}.

21. Chloroacetic acid has $K_a = 1.36 \times 10^{-3}$ M. Calculate the freezing point of 0.1 M solution of this acid. Assume that molarity and molality have identical values. K_f(water) = 1.86 K kg mol^{-1}.

ANSWERS

1. 56.0 cm^3
2. 490 g HNO_3, about 10.3 mL
3. 11.4 mol kg^{-1}, 7.66 mol dm^{-3}
4. 1.25 g cm^{-3}
5. 16.5 mol kg^{-1}, 0.219, 0.229
6. 0.31
7. 677.24 Torr, 0.183, 38.76
8. 64 g
9. 19.63 Torr
10. 0.067 atm for propyl alcohol
0.132 atm for isopropyl alcohol
11. 31.64 mmHg
12. 350 g mol^{-1}
13. 0.0132, 0.741 mol kg^{-1}
14. $C_6H_4N_2O_4$
15. $C_{44}H_{88}O_{44}$
16. 13.82 atm
17. 0.3 mol L^{-1}
18. 29.90 atm
19. – 33.4 °C
20. 353 g
21. – 0.21 °C

CHAPTER 10

CHEMICAL KINETICS

Chemical kinetics deals with the rate of chemical reactions including its dependence on the concentrations of the reacting species and the experimental conditions.

Average Rate of a Reaction By the term average rate of change of concentration of a reactant or a product, we mean the decrease in concentration of a reactant or increase in concentration of a product occurring in a unit interval of time. For example, for the reaction

$$\nu_1 A_1 + \nu_2 A_2 \rightarrow \nu_3 A_3 + \nu_4 A_4$$

the average of rate of change of the concentration of reactant A over the time interval Δt is given by the expression

$$r_{av} = -\frac{\Delta[A]}{\Delta t}$$

Similar expressions can be written for other species appearing in the chemical equation. These terms will be interrelated through the expression

$$-\frac{1}{\nu_1}\frac{\Delta[A_1]}{\Delta t} = -\frac{1}{\nu_2}\frac{\Delta[A_2]}{\Delta t} = \frac{1}{\nu_3}\frac{\Delta[A_3]}{\Delta t} = \frac{1}{\nu_4}\frac{\Delta[A_4]}{\Delta t}$$

Each of these individual terms represents the average rate of reaction over the time interval Δt.

Instantaneous Rate of a Reaction In chemical kinetics, the rate at any particular instant rather than the average rate over a time interval has much more practical application and importance. This rate is known as the instantaneous rate (or simply as rate) and is defined as

$$r_{\text{ins}, t} = \lim_{\Delta t \rightarrow 0} (r_{av})$$

or

$$r_{\text{ins}, t} = -\frac{1}{\nu_1}\frac{d[A_1]}{dt} = -\frac{1}{\nu_2}\frac{d[A_2]}{dt} = \frac{1}{\nu_3}\frac{d[A_3]}{dt} = \frac{1}{\nu_4}\frac{d[A_4]}{dt}$$

In the above expression, the term $-d[A_1]/dt$ is known as rate of disappearance of the concentration of A_1. When this term is divided by the stoichiometric coefficient ν_1, we get the rate of reaction. Similarly, the terms $-d[A_2]/dt$, $d[A_3]/dt$ and $d[A_4]/dt$ stand for the rate of disappearance/appearance of the species A_2, A_3 and A_4, respectively. When each of these terms is divided by the corresponding stoichiometric coefficient in the balanced chemical equation, we get the rate of reaction.

The rate of reaction can also be defined in terms of the rate of change of extent of reaction divided by volume of a chemical reaction. By definition, the extent of reaction divided by volume when multiplied by the stoichiometric number of a chemical species in the balanced chemical equation gives the change in concentration of the species during the progress of the chemical reaction. For example, for the reaction

$$\nu_1 A_1 + \nu_2 A_2 \rightarrow \nu_3 A_3 + \nu_4 A_4$$

if x is the extent of reaction divided by volume, then we have

$$\begin{array}{cccccccc} & \nu_1 A_1 & + & \nu_2 A_2 & \rightarrow & \nu_3 A_3 & + & \nu_4 A_4 \\ t = 0 & [A_1]_0 & & [A_2]_0 & & 0 & & 0 \\ t & [A_1]_0 - \nu_1 x & & [A_2]_0 - \nu_2 x & & \nu_3 x & & \nu_4 x \end{array}$$

Hence,
$$r = -\frac{1}{\nu_1}\frac{\mathrm{d}[\mathrm{A}_1]}{\mathrm{d}t} = -\frac{1}{\nu_1}\frac{\mathrm{d}([\mathrm{A}_1]_0 - \nu_1 x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}; \qquad r = -\frac{1}{\nu_2}\frac{\mathrm{d}[\mathrm{A}_2]}{\mathrm{d}t} = -\frac{1}{\nu_2}\frac{\mathrm{d}([\mathrm{A}_2]_0 - \nu_2 x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$
$$r = \frac{1}{\nu_3}\frac{\mathrm{d}[\mathrm{A}_3]}{\mathrm{d}t} = \frac{1}{\nu_3}\frac{\mathrm{d}(\nu_3 x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}; \qquad r = \frac{1}{\nu_4}\frac{\mathrm{d}[\mathrm{A}_4]}{\mathrm{d}t} = \frac{1}{\nu_4}\frac{\mathrm{d}(\nu_4 x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

Thus, rate of reaction can be defined in terms of change of concentration of one of either reactants or products.

Order of a Reaction In general, if the rate of a reaction $\nu_1\mathrm{A}_1 + \nu_2\mathrm{A}_2 \rightarrow$ products can be written in a form

$$r = k\,[\mathrm{A}_1]^a\,[\mathrm{A}_2]^b$$

then the exponents a, b, ... are known as the *orders of the reaction* with respect to A_1, A_2, ..., respectively. The overall order of the reaction is equal to $a + b + ...$ The constant k is known as the *rate constant*.

Both the rate constant and order are experimentally determined quantities. The unit of rate constant is $(\mathrm{mol\ L^{-1}})^{1-n}\ \mathrm{s^{-1}}$ where n is the order of the reaction. For example, when

order = 0 unit of k is $\mathrm{mol\ L^{-1}\ s^{-1}}$. order = 1 unit of k is $\mathrm{s^{-1}}$.

order = 2 unit of k is $\mathrm{mol^{-1}\ L\ s^{-1}}$. order = 3 unit of k is $\mathrm{mol^{-2}\ L^2\ s^{-1}}$.

The order of the reaction is never greater than three. In fact, only limited reactions with order equal to three are observed.

The order n of a reaction may be fractional, zero, positive or negative. It is always determined experimentally.

Integrated Rate Expressions In the study of chemical kinetics, it is worth knowing how the concentrations of species in the rate law vary with the progress of the reaction. The expression representing such a relation is known as integrated rate law and is obtained by integrating the corresponding differential rate law. The expressions for the zero- and first-order reactions are given below.

Zero-Order Reactions The integrated rate expression for A $\rightarrow$ products is

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$$

that is, the variation of A is linear with time. The time of completion of the reaction is given as

$$t_{\text{completion}} = [\mathrm{A}]_0/k$$

First-Order Reactions The integrated rate expression for A $\rightarrow$ products is

$$\ln\,\{[\mathrm{A}]_t/[\mathrm{A}]_0\} = -\,kt$$

that is, the variation of $\ln\,[\mathrm{A}]_t$ with time is linear or the variation of $[\mathrm{A}]_t$ with time is exponential. The half-life of a reaction is defined as the time taken to decrease the concentration of A to its half value. For the first-order reaction, half-life is given as

$$t_{0.5} = 0.693/k$$

and is independent of the initial concentration of A.

Since the integrated rate expression of first order kinetics involves the ratio $[\mathrm{A}]_t/[\mathrm{A}]_0$, the time taken for any fraction of reaction (say 1/4, 1/6 or 1/10) to occur is independent of initial concentration $[\mathrm{A}]_0$, i.e. the reaction takes the same time to complete the given fraction of the reaction.

All radioactive decay follows first-order kinetics.

Second-Order Reactions In this case, we have

$$\mathrm{A} \xrightarrow{k_2} \text{products}; \qquad \frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_2 t; \qquad t_{0.5} = \frac{1}{k_2\,[\mathrm{A}]_0}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \text{products}; \qquad \log\left(\frac{[\mathrm{B}]_0 - x}{[\mathrm{A}]_0 - x}\right) = \log\left(\frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\right) + \left(\frac{[\mathrm{B}]_0 - [\mathrm{A}]_0}{2.303}\right) k_2 t$$

Third-Order Reactions The simplest example is

$$\mathrm{A} \xrightarrow{k_3} \text{products}; \qquad \frac{1}{[\mathrm{A}]_t^2} - \frac{1}{[\mathrm{A}]_0^2} = 2\,k_3 t$$

Only five homogeneous gas reaction involving NO(g) as one of the reacting species are known to follow third order reaction.

General Expression For a reaction A → products following n^{th} order ($n \neq 1$), we have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_n\,([\mathrm{A}]_0 - x)^n; \qquad \frac{1}{(n-1)}\left[\frac{1}{[\mathrm{A}]_t^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right] = k_n t$$

$$t_{0.5} = \frac{1}{k_n(n-1)}\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}}$$

The reaction of the type $a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightarrow$ products with $\frac{[\mathrm{A}]_0}{a} = \frac{[\mathrm{B}]_0}{b} = \frac{[\mathrm{C}]_0}{c}$ also belongs to this category. The integrated rate expression is

$$\frac{1}{(n-1)}\left[\frac{1}{[\mathrm{A}]_t^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right] = k\frac{b^\beta c^\gamma}{a^{n-\alpha-1}}t; \qquad \text{where } n = \alpha + \beta + \gamma$$

The half-life time is

$$t_{0.5} = \frac{1}{k(n-1)}\frac{a^{n-\alpha-1}}{b^\beta c^\gamma}\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}}$$

Ostwald Isolation Method In a reaction A + B → products following the rate law $r = k\,[\mathrm{A}]^\alpha\,[\mathrm{B}]^\beta$ if one of the reacting species (say, A) has very large concentrations in comparing to the other species, its concentration virtually remains constant (or the charge is negligible), the rate expression can be written as

$$r = k'[\mathrm{B}]^\beta \qquad \text{where } k' = k\,[\mathrm{A}]^\alpha = \text{constant}$$

This method reduces the order of a reaction. One of the examples is the acid hydrolysis of an ester which follows the rate law

$$r = k\,[\text{ester}]\,[\mathrm{H_2O}]\,[\mathrm{H^+}]$$

here $\mathrm{H^+}$ ions act as a catalyst (its concentration remains constant throughout the hydrolysis) and $\mathrm{H_2O}$ is present in excess. Hence, the rate law is reduced to

$$r = k'\,[\text{ester}] \qquad \text{where } k' = k\,[\mathrm{H_2O}]\,[\mathrm{H^+}]$$

Variation of Rate Constant with Temperature The rate of a reaction depends on the temperature of the system. The Arrhenius equation describing the temperature dependence is

$$k = A\,\exp(-\,E_\mathrm{a}/RT)$$

where A is known as pre-exponential term and E_a is the energy of activation. The latter is definied as the difference between the minimum energy required to bring about molecular rearrangement and the average energy of the reactant species. The logarithmic form of Arrhenius equation is

$$\log\frac{k_2}{k_1} = -\frac{E_\mathrm{a}}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k_2 and k_1 are the rate constants at temperatures T_2 and T_1, respectively.

Effect of a Catalyst on a Reaction Sometimes, the rate of a chemical reaction is altered in the presence of a substance called the catalyst. Though the catalyst is involved in the reaction, it does not appear in the overall reaction.

Broadly, two types of catalysts are known, namely, *homogeneous* and *heterogeneous* catalysts. A homogeneous catalyst is present in the same phase as the reaction and a heterogeneous catalyst exists in different phase from the reaction it catalyzes. The rate of catalytic reaction is usually proportional to the concentration of the homogeneous catalyst or the surface area of the heterogeneous catalyst. It is because of this reason, the latter is usually taken in a finally divided form.

For a reversible reaction, the rates of forward as well as reverse directions are increased with the result that the equilibrium stage is reached more quickly. The catalyst has no effect on the equilibrium amounts of reactants and products. Thus, the equilibrium constant of the reaction is not affected in the presence of a catalyst.

In general, the reaction proceeds via an alternate path in the presence of a catalyst. The energies of activation of both forward and backward directions are decreased. In general, the homogeneous catalyst is involved in an equilibrium reaction with one of the reactants. The catalyst is recovered in the subsequent reactions. The heterogeneous catalyst involves the adsorption of reactants on active sites available on the surface of the catalyst. This process activates the molecules and thus reaction can proceed with faster speed.

Radioactive Decay All radioactive decays follow the first-order kinetics.

Straight Objective Type

General Characteristics

1. The rate constant of a reaction depends on
(a) temperature
(b) initial concentration of the reactants
(c) time of reaction
(d) extent of reaction (1981)

2. The rate constant of a first-order reaction depends on the
(a) concentration of the reactant
(b) concentration of the product
(c) time
(d) temperature (1983)

3. The terms rate of reaction and rate of appearance (or disappearance) of reactant (or product)
(a) represent one and the same physical quantity
(b) differ by a constant factor
(c) are positive parameters and have same value
(d) may or may not have same value depending upon the stoichiometric coefficient of reactant (or product) in the balanced chemical equation

4. For the reaction $2A + 3B \rightarrow 4C$ the rate of reaction may be represented as
(a) $r = -2\frac{d[A]}{dt} = -3\frac{d[B]}{dt} = 4\frac{d[C]}{dt}$
(b) $r = -6\frac{d[A]}{dt} = -4\frac{d[B]}{dt} = 3\frac{d[C]}{dt}$
(c) $r = -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$
(d) $r = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$

5. The unit of rate of a reaction is
(a) s^{-1}
(b) mol s^{-1}
(c) mol L^{-1} s^{-1}
(d) mol^{-1} L s^{-1}

6. The order of a reaction is
(a) never zero
(b) never fraction
(c) always equal to the total stoichiometric number of reactants
(d) is an experimentally determined quantity

7. The units of rate of reaction and rate constant are identical for a
(a) fractional-order reaction
(b) zero-order reaction
(c) first-order reaction
(d) second-order reaction

8. The order of an elementary reaction
(a) is equal to the total stoichiometric number of reactants
(b) is equal to the total stoichiometric number of products
(c) can be greater than three
(d) is equal to the difference in the total stoichiometric numbers of reactants and products

9. The order of a reaction with respect to OH^- is -1. The OH^- species
(a) act as a catalyst
(b) act as an inhibitor
(c) act as a promotor
(d) always appear in the chemical equation

10. For a chemical reaction $X \rightarrow Y$, the rate of reaction increases by a factor of 1.837 when the concentration of X is increased by 1.5 times. The order of the reaction with respect to X is
(a) 1
(b) 1.5
(c) 2
(d) -1

11. For a reaction $A \rightleftharpoons B$ if k_1 and k_{-1} are the rate constants of forward and backward directions, respectively, the equilibrium constant of the reaction is given as
(a) $K_{eq} = k_1/k_{-1}$ (b) $K_{eq} = k_{-1}/k_1$ (c) $K_{eq} = k_1\, k_{-1}$ (d) $K_{eq} = 1/k_1\, k_{-1}$

12. The units of rate of a reaction and its rate constant
(a) are identical
(b) are quite independent of each other
(c) depend on the experimental conditions of the reaction
(d) are related to each other through a definite expression depending upon the order of the reaction

13. The order of an elementary reaction
(a) is equal to its molecularity (b) cannot be predicted
(c) depends upon temperature (d) depends on the experimental conditions

14. During the course of a chemical reaction, the rate of a reaction
(a) remains constant throughout (b) increases as the reaction proceeds
(c) decreases as the reaction proceeds (d) first increases followed by a decrease

15. In a reaction $2A + B \longrightarrow A_2B$, the reactant A will disappear at
(a) half the rate at which B disappears (b) the same rate as that of B
(c) the same rate as that of appearance of A_2B (d) twice the rate at which B decreases

16. In a reaction $2X + Y_2 \longrightarrow 2XY$, the reactant X disappears at
(a) half the rate as that of disappearance of Y_2 (b) the same rate as that of disappearance of Y_2
(c) the same rate as that of appearance of XY (d) twice the rate as that of appearance of XY

17. For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of formation of ammonia was found to be 2.0×10^{-4} mol $dm^{-3}\,s^{-1}$. The rate of consumption of H_2 will be
(a) 1.0×10^{-4} mol dm^{-3} s^{-1} (b) 2.0×10^{-4} mol dm^{-3} s^{-1}
(c) 3.0×10^{-4} mol dm^{-3} s^{-1} (d) 4.0×10^{-4} mol dm^{-3} s^{-1}

18. The reaction $2A + B \longrightarrow D + E$ involves the following mechanism
$A \longrightarrow B$ (fast); $B \longrightarrow C$ (slow); $A + C \longrightarrow D + E$
The rate expression would be
(a) $k[A]^2\,[B]$ (b) $k[B]$ (c) $k[A]$ (d) $k[A][B]$

19. The equilibrium reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$ is started with A such that initially one can write $A \xrightarrow{k'_f} B$. In such a case, which of the following will be correct?
(a) $k_f = k'_f$ (b) $k_f > k'_f$
(c) $k_f < k'_f$ (d) k_f may be greater or smaller than k'_f depending upon the concentration of A

20. The equilibrium reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$ is started with A such that initially one can write $B \xrightarrow{k'_b} A$. In such a case, which of the following will be correct?
(a) $k_b = k'_b$ (b) $k_b > k'_b$
(c) $k_b < k'_b$ (d) k_b may be greater or smaller than k'_b depending upon the concentration of B

21. If '*I*' is the intensity of absorbed light and '*c*' is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to
(a) c (b) I (c) I^2 (d) $c.I$ (2001)

22. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions
(a) Rate $= -\, d[N_2]/dt = -\,(1/3)\, d[H_2]/dt = (1/2)\, d[NH_3]/dt$
(b) Rate $= d[N_2]/dt = -\,3\, d[H_2]/dt = 2\, d[NH_3]/dt$
(c) Rate $= d[N_2]/dt = (1/3)\, d[H_2]/dt = (1/2)\, d[NH_3]/dt$
(d) Rate $= -\, d[N_2]/dt = -\, d[H_2]/dt = d[NH_3]/dt$ (2002)

23. Which of the following statements is incorrect about order of a reaction?
(a) Order of a reaction can never be equal to zero or fractional value
(b) It is always determined experimentally
(c) It is equal to the molecularity of an elementary reaction
(d) It is sum of the powers of concentration terms in the differential rate law of a reaction. (2005)

24. Consider a reaction $a\text{G} + b\text{H} \rightarrow$ Products. When concentrations of both the reactants G and H are doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3 (2007)

25. The decomposition of $N_2O_5(g)$ may be represented by the chemical equations

(i) $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ (ii) $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$

If r_1 and r_2 are the rates of first and second reactions, respectively, then which of the following expressions is correct?
(a) $r_1 = r_2$ (b) $r_1 = 2r_2$ (c) $2r_1 = r_2$ (d) $2r_1 = 3r_2$

Zero-Order Reactions

26. For a zero-order reaction, the plot of $[A]_t$ versus t for the reaction $A \rightarrow B$ is linear with a
(a) positive slope and zero intercept (b) positive slope and nonzero intercept
(c) negative slope and zero intercept (d) negative slope and nonzero intercept

27. The slope of the plot of $[A]_t$ versus t for a zero-order reaction $A \rightarrow B$ is
(a) k (b) $k/2.303$ (c) $-k$ (d) $-k/2.303$

28. A substance (initial concentration a) reacts according to zero-order kinetics. The time it takes for the completion of the reaction is
(a) a/k (b) $a/2k$ (c) k/a (d) $2k/a$

29. The reaction $\nu A \rightarrow$ products is zero order with respect to A with rate constant equal to k_0. The concentration of A with time is given as
(a) $[A]_t = [A]_0 - k_0 t$ (b) $[A]_t = [A]_0 - \nu k_0 t$ (c) $[A]_t = [A]_0 + k_0 t$ (d) $[A]_t = [A]_0 - k_0 t/\nu$

30. For the reaction $\nu A \rightarrow$ products, the half-life time is given as
(a) $[A]_0/\nu_1\, k_0$ (b) $[A]_0/k_0$ (c) $[A]_0/2\nu k_0$ (d) $\nu[A]_0/2k_0$

31. The half-life of a zero order reaction $A \rightarrow B$ is
(a) directly proportional to the concentration of A
(b) independent of the concentration of A
(c) inversely proportional to the concentration of A
(d) determined by the concentration of B

First-Order Reactions

32. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
(a) (1/2) g (b) (1/4) g (c) (1/8) g (d) (1/16) g (1986)

33. For a first-order reaction $A \rightarrow B$ the plot of $\log([A]_t/1\text{M})$ versus t is linear with a
(a) positive slope and zero intercept (b) positive slope and nonzero intercept
(c) negative slope and zero intercept (d) negative slope and nonzero intercept

34. The slope of the plot of $\log\{[A]_t/\text{M}\}$ versus t for a first-order reaction $A \rightarrow B$ is
(a) k (b) $k/2.303$ (c) $-k$ (d) $-k/2.303$

35. The half-life of a first-order reaction $A \rightarrow B$ is
(a) $t_{1/2} = 0.693\, k$ (b) $t_{1/2} = 0.693/k$ (c) $t_{1/2} = 0.693 \ln k$ (d) $t_{1/2} = 0.693/\ln k$

36. For the first-order decomposition reaction of N_2O_5, it is found that

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g); \qquad -\frac{d[N_2O_5]}{dt} = k\,[N_2O_5]$$

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g); \qquad -\frac{d[N_2O_5]}{dt} = k'\,[N_2O_5]$$

which of the follows facts is true?
(a) $k = k'$ (b) $k > 2k'$ (c) $k > k'$ (d) $2k = k'$

37. For the first-order decomposition reaction of N_2O_5 written as

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \qquad \text{rate} = k\,[N_2O_5]$$
$$N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g) \qquad \text{rate} = k'\,[N_2O_5]$$

which of the following facts is true?

(a) $k = k'$ (b) $k > k'$ (c) $k > 2k'$ (d) $2k = k'$

38. The gaseous reaction $A(g) \rightarrow 2\,B(g) + C(g)$ is found to be first-order with respect to A. If the reaction is started with $p_A = 90$ mmHg, the pressure after 10 min is found to be 180 mmHg. The rate constant of the reaction is

(a) $1.15 \times 10^{-3}\ s^{-1}$ (b) $2.30 \times 10^{-3}\ s^{-1}$ (c) $3.45 \times 10^{-3}\ s^{-1}$ (d) $4.60 \times 10^{-3}\ s^{-1}$

39. A substance A reacts according to a first-order rate law with rate constant equal to $5.0 \times 10^{-5}\ s^{-1}$. The rate of the reaction $A \rightarrow B$ after 3.85 h when the reaction is started with 1.0 M of A will be

(a) 4.0×10^{-5} mol $L^{-1}\ s^{-1}$ (b) 3.0×10^{-5} mol $L^{-1}\ s^{-1}$

(c) 2.5×10^{-5} mol $L^{-1}\ s^{-1}$ (d) 2.0×10^{-5} mol $L^{-1}\ s^{-1}$

40. For a first-order reaction, the time taken to reduce initial concentration by a factor of 1/4 is 10 min. The time required to reduce initial concentration by a factor of 1/16 will be

(a) 10 min (b) 20 min (c) 30 min (d) 40 min

41. For a first-order reaction $A \rightarrow B$, the ratio of times to complete 99.9% and half of the reaction is

(a) 8 (b) 9 (c) 10 (d) 12

42. The reaction $\nu_1 A + \nu_2 B \rightarrow$ products is first-order with respect to A and zero-order with respect to B. If the reaction is started with $[A]_0$ and $[B]_0$, the integrated rate expression of this reaction would be

(a) $\ln \dfrac{[A]_0}{[A]_0 - x} = k_1 t$ (b) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = k_1 t$

(c) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = \nu_1 k_1 t$ (d) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = -\,\nu_1 k_1 t$

43. The radioactive decay follows

(a) first-order kinetics

(b) second-order kinetics

(c) a complicated kinetics with temperature dependence behaviour

(d) zero-order kinetics

44. A first order reaction is 20% complete in 10 min. The rate constant of the reaction $A \rightarrow B$ is

(a) 0.223 min^{-1} (b) 0.0223 min^{-1} (c) 2.23 min^{-1} (d) 22.3 min^{-1}

45. The half-life of a radioactive isotope is 3 h. What mass out of 100 g is left after 15 h?

(a) 12.5 g (b) 6.25 g (c) 3.125 g (d) 1.562 g

46. For a first order reaction $2N_2O_5 \xrightarrow{k} 4NO_2 + O_2$, the half-life period is given by

(a) $2.303/k$ (b) $0.693/k$ (c) $2.303/2k$ (d) $0.693/2k$

47. If the concentration of a reactant decreases from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^5 s in a first order reaction $A \rightarrow B$, the rate constant of the reaction would be

(a) 2×10^{-5} s (b) 1.386×10^{-5} s (c) 3.45×10^{-5} s (d) 2×10^{5} s (2003)

48. The reaction, $A \rightarrow$ products, follows first order kinetics. In 45 min, the concentration of A changes from 0.1 M to 0.0125 M. The rate of reaction when [A] = 0.001 M is

(a) 2.31×10^{-5} mol L^{-1} min^{-1} (b) 4.62×10^{-5} mol L^{-1} min^{-1}

(c) 2.31×10^{-4} mol L^{-1} min^{-1} (d) 4.62×10^{-4} mol L^{-1} min^{-1} (2004)

49. Under the same reaction condition of $A \rightarrow B$, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constants for first order (k_1) and zero order (k_0) of the reactions is

(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol dm^{-3} (c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^3 (2008)

50. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is 2.40×10^{-5} mol $L^{-1}\ s^{-1}$, then the concentration of N_2O_5 (in mol L^{-1}) is

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8 (2000)

51. The hydrolysis of an ester was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4. Which of the following will be true?

(a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{HCl} < k_{H_2SO_4}$ (c) $k_{HCl} = k_{H_2SO_4}$ (d) $k_{H_2SO_4} = 2k_{HCl}$

52. The hydrolysis of an ester was carried out separately with 0.05 N HCl and 0.05 N H_2SO_4. Which of the following will be true?

(a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{HCl} < k_{H_2SO_4}$ (c) $k_{HCl} = k_{H_2SO_4}$ (d) $k_{H_2SO_4} = 2k_{HCl}$

53. A gaseous reaction A(g) → products involves $\Delta\nu_g$ change in gaseous species in going from reactants to products. If the reaction follows first order kinetics, which of the following integrated rate expressions holds good?

(a) $\ln\left(\dfrac{\Delta\nu_g\, p_0}{(\Delta\nu_g + 1)p_0 + p_t}\right) = kt$ (b) $\ln\left(\dfrac{\Delta\nu_g\, p_0}{(\Delta\nu_g - 1)p_0 + p_t}\right) = kt$

(c) $\ln\left(\dfrac{\Delta\nu_g\, p_0}{(\Delta\nu_g + 1)p_0 + p_t}\right) = kt$ (d) $\ln\left(\dfrac{\Delta\nu_g\, p_0}{(\Delta\nu_g - 1)p_0 - p_t}\right) = kt$

54. The reaction $(CH_3)_3COOC(CH_3)_3(g) \rightarrow 2CH_3COCH_3(g) + C_2H_6(g)$ is carried out at constant volume with p_0 as the pressure of $(CH_3)_3COOC(CH_3)_3$. Which of the following expressions holds good if the reaction follows first order kinetics.

(a) $\ln\left(\dfrac{3p_0 + p}{2p_0}\right) = -\,kt$ (b) $\ln\left(\dfrac{3p_0 - p}{2p_0}\right) = -\,kt$ (c) $\ln\left(\dfrac{2p_0 + 3p}{2p_0}\right) = -kt$ (d) $\ln\left(\dfrac{2p_0 - 3p}{2p_0}\right) = -\,kt$

55. The reaction $2NO(g) + H_2(g) = N_2O(g) + H_2O(g)$ follows the rate law $\dfrac{d\,p(N_2O)}{dt} = k\,(p_{NO})^2\, p_{H_2}$

If the reaction is initiated with p_{NO} = 1000 mmHg and p_{H_2} = 10 mmHg. The reaction may be considered to follow

(a) first order kinetics (b) second order kinetics (c) zero order kinetics (d) third order kinetics

56. The reaction A → product follows the rate law $dx/dt = k\,[A]^n$; $(n \neq 1)$

The half-life of this reaction is given by

(a) $t_{0.5} = \dfrac{1}{k_n(n+1)}\,\dfrac{2^{n+1}-1}{[A]_0^{n-1}}$ (b) $t_{0.5} = \dfrac{1}{k_n(n-1)}\,\dfrac{2^{n-1}-1}{[A]_0^{n-1}}$

(c) $t_{0.5} = \dfrac{1}{k_n(n+1)}\,\dfrac{2^{n-1}+1}{[A]_0^{n-1}}$ (d) $t_{0.5} = \dfrac{1}{k_n(n+1)}\,\dfrac{2^{n+1}-1}{[A]_0^{n+1}}$

57. For a reaction $aA + bB + cC \rightarrow$ products with initial concentrations related to each other through the expression

$$\frac{[A]_0}{a} = \frac{[B]_0}{b} = \frac{[C]_0}{c}$$

the rate law is given as $-\dfrac{1}{a}\dfrac{d[A]}{dt} = k\,[A]^{\alpha}\,[B]^{\beta}\,[c]^{\gamma}$; $n = \alpha + \beta + \gamma$

The half life for this reaction is given by the expression

(a) $t_{1/2} = \dfrac{1}{k(n-1)}\,\dfrac{a^{n-\alpha-1}}{b^{\beta}c^{\gamma}}\,\dfrac{2^{n-1}-1}{[A]_0^{n-1}}$ (b) $t_{1/2} = \dfrac{1}{k(n+1)}\,\dfrac{a^{n-\alpha-1}}{b^{\beta}c^{\gamma}}\,\dfrac{2^{n+1}-1}{[A]_0^{n+1}}$

(c) $t_{1/2} = \dfrac{1}{k(n-1)}\,\dfrac{a^{n-\alpha-1}}{b^{\beta}c^{\gamma}}\,\dfrac{2^{n+1}-1}{[A]_0^{n+1}}$ (d) $t_{1/2} = \dfrac{1}{k(n+1)}\,\dfrac{a^{n-\alpha-1}}{b^{\beta}c^{\gamma}}\,\dfrac{2^{n-1}-1}{[A]_0^{n+1}}$

58. The reaction A → product following the rate law $dx/dt = k\,(a_0 - x)^n$; $(n \neq 1)$
was studied with two different initial concentrations a_{01} and a_{02}. The expression to be used to determine its half life is

(a) $n = 1 - \dfrac{\log\{(t_{1/2})_1/(t_{1/2})_2\}}{\log(a_{01}/a_{02})}$ (b) $n = 1 + \dfrac{\log\{(t_{1/2})_1/(t_{1/2})_2\}}{\log(a_{01}/a_{02})}$

(c) $n = 1 - \dfrac{\log\{(t_{1/2})_1/(t_{1/2})_2\}}{\log(a_{02}/a_{01})}$ (d) $n = 1 + \dfrac{\log\{(t_{1/2})_1/(t_{1/2})_2\}}{\log(a_{02}/a_{01})}$

Second-Order Reactions

59. For a second-order reaction of the type rate = $k\,[A]^2$, the plot of $1/[A]_t$ versus t is linear with a
(a) positive slope and zero intercept
(b) positive slope and nonzero intercept
(c) negative slope and zero intercept
(d) negative slope and nonzero intercept

60. For a second-order reaction of the type rate = $k\,[A]^2$, the slope of plot of $1/[A]_t$ versus t is
(a) k
(b) $k/2.303$
(c) $-k$
(d) $-k/2.303$

61. The half-life of a second-order reaction is
(a) $t_{1/2} = 0.693/k$
(b) $t_{1/2} = k/[A]_0$
(c) $t_{1/2} = [A]_0/k$
(d) $t_{1/2} = 1/k\,[A]_0$

62. The volume of the reacting system $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is suddenly reduced to half its value. If the reaction is second order with respect to NO and first order with respect to O_2, the rate of reaction will
(a) diminish to one-fourth of its initial value
(b) diminish to one-eighth of its initial value
(c) increase eight times of its initial value
(d) decrease four times of its initial value

63. The half-life of a reaction $A \longrightarrow B$ varies as the inverse of concentration of A. The order of the reaction would be
(a) zero
(b) first
(c) second
(d) third

64. In which of the following ways, the rate of reaction $2NO(g) + O2(g) \longrightarrow 2NO_2(g)$ get affected if the volume of the reacting system is doubled? Given that the reaction is second order with respect to NO and first order with respect to O_2.
(a) Diminishes to one-fourth of its initial value
(b) Diminishes to one-eighth of its initial value
(c) Increases four times
(d) Increases eight times

65. The reaction $\nu A \xrightarrow{k}$ products is second order with respect to A. Its half-life is given by
(a) $\nu\,[A]_0 k$
(b) $2/([A]_0 k)$
(c) $1/(\nu\,[A]_0 k)$
(d) $\nu\,[A]_0/k$

66. For the reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$, the following data are obtained.

When p_{H2} constant		When p_{NO} constant	
p_{NO} = 360 Torr	r = 1.60 Torr s^{-1}	p_{H2} = 360 Torr	r = 1.2 Torr s^{-1}
p_{NO} = 180 Torr	r = 0.40 Torr s^{-1}	p_{H2} = 180 Torr	r = 0.6 Torr s^{-1}

The order of the reaction is
(a) 0
(b) 1
(c) 2
(d) 3

Temperature Dependence

67. For an endothermic reaction where ΔH represents the enthalpy of the reaction, the minimum value for the energy of activation will be
(a) less than ΔH
(b) zero
(c) more than ΔH
(d) equal to ΔH (1992)

68. The plot of log k versus $1/T$ is linear with a slope of
(a) E_a/R
(b) $-E_a/R$
(c) $E_a/2.303R$
(d) $-E_a/2.303R$

69. The unit of activation energy is
(a) kJ
(b) kJ mol^{-1}
(c) kJ K^{-1}
(d) kJ K^{-1} mol^{-1}

70. The activation energy in a chemical reaction is defined as
(a) the difference in average energies of reactants and products
(b) the difference in average energies of reactants and intermediate product
(c) the difference in average energies of products and intermediate product
(d) the sum of energies of reactants and products

71. For the decomposition of $N_2O_5(g)$, it is given that

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ activation energy E_a

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ ctivation energy E_a'

then
(a) $E_a = E_a'$
(b) $E_a > E_a'$
(c) $E_a < E_a'$
(d) $E_a = 2E_a'$

72. The plot of log k versus $1/T$ of a reaction is linear with a
(a) positive slope and zero intercept
(b) positive slope and nonzero intercept
(c) negative slope and zero intercept
(d) negative slope and nonzero intercept

73. The activation energy for a reaction which doubles the rate when the temperature is raised from 300 K to 310 K is

(a) 50.6 kJ mol^{-1} (b) 53.6 kJ mol^{-1} (c) 56.6 kJ mol^{-1} (d) 59.6 kJ mol^{-1}

74. The logarithm of rate constant of a reaction

(a) increases linearly with increase in inverse of temperature
(b) decreases linearly with increase in inverse of temperature
(c) increases linearly with increase in temperature
(d) decreases linearly with increase in temperature

75. By increasing the temperature by 10 °C, the rate of forward reaction at equilibrium is increased by a factor of 2. The rate of backward reaction by this increase in temperature

(a) remains unaffected (b) increases by a factor greater than two
(c) decreases by a factor lesser than two (d) is also increased by a factor of two

76. The rate constant of a reaction follows

(a) exponential increase with increase in temperature
(b) exponential decrease with increase in temperature
(c) linear increase with increase in temperature
(d) linear decrease with increase in temperature

77. For an exothermic reaction $A \longrightarrow B$, the activation energy is 65 kJ mol^{-1} and enthalpy of reaction is 42 kJ mol^{-1}. The activation energy for the reaction $B \longrightarrow A$ would be

(a) 23 kJ mol^{-1} (b) 107 kJ mol^{-1} (c) 65 kJ mol^{-1} (d) 42 kJ mol^{-1}

78. The rate constant, the activation energy and the Arrhenius parameters of a chemical reaction at 25 °C are 2.0×10^{-5} s^{-1}, 100 kJ mol^{-1} and 6.0×10^{14} s^{-1}, respectively. The value of rate constant at very high temperature approaches

(a) 2.0×10^{-5} s^{-1} (b) infinity (c) 6.0×10^{14} s^{-1} (d) 12×10^{-9} s^{-1}

79. The rate constant of a reaction (activation energy E_1) increases twice as fast as the rate constant of a second reaction (activation energy E_2). Which of the following conditions will hold good?

(a) $E_1 = E_2$ (b) $E_1 < E_2$ (c) $E_1 > E_2$ (d) $E_1 = (1/2)\,E_2$

80. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation

$$\log (k/\mathrm{s}) = -\frac{2000\,\mathrm{K}}{T} + 6.0$$

The pre-exponential factor A and the activation energy E_a, respectively, are

(a) 1.0×10^{6} s^{-1} and 9.2 kJ mol^{-1} (b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) 1.0×10^{6} s^{-1} and 16.6 kJ mol^{-1} (d) 1.0×10^{6} s^{-1} and 38.3 kJ mol^{-1} (2009)

81. For most reactions, rate of a reaction increases about two times when its temperature is raised by 10 K. This fact is due to

(a) increase in number of collisions per unit volume
(b) increase in number of molecule having energy E_A or more
(c) lowering of activation energy
(d) lowering of pre-exponential factor in Arrhenius equation

82. The half-life of a first order reaction

(a) increases with increasing temperature
(b) increases with decreasing temperature
(c) is not affected by changing temperature
(d) increases firstly followed by a decrease on increasing temperature.

83. For the reaction $A(g) \rightleftharpoons B(g)$ $\Delta H = -40$ kJ mol^{-1}, If $E_f/E_b = 2/3$, then

(a) $E_f = 60$ kJ mol^{-1}; $E_b = 100$ kJ mol^{-1} (b) $E_f = 30$ kJ mol^{-1}; $E_b = 70$ kJ mol^{-1}
(c) $E_f = 80$ kJ mol^{-1}; $E_b = 120$ kJ mol^{-1} (d) $E_f = 70$ kJ mol^{-1}; $E_b = 30$ kJ mol^{-1}

84. Given are the information: Reaction 1; $k = A\ e^{-E_1/RT}$ and Reaction 2; $k' = A\ e^{-E_2/RT}$
If $E_1 = 2E_2$, then the ratio $\ln(k_{T+10K}/k_T)$ for the reaction 1 will be
(a) equal to that of reaction 2
(b) greater than that of reaction 2
(c) lesser than that of reaction 2
(d) may be greater or lesser than reaction 2 depending upon the temperature T.

Catalyst

85. A catalyst is a substance which
(a) increases the equilibrium concentration of the product
(b) changes the equilibrium constant of the reaction
(c) shortens the time to reach equilibrium
(d) supplies energy to the reaction (1983)

86. A catalyst is a substance which
(a) increases the equilibrium constant of the reaction
(b) increases the equilibrium concentrations of the products
(c) does not alter the reaction mechanism
(d) changes the activation energy of the reaction

87. A catalyst lowers the activation energy of the forward reaction by 20 kJ mol^{-1}. It also changes the activation energy of the backward reaction by an amount
(a) equal to that of the forward reaction
(b) equal to twice that of the forward reaction
(c) which is determined only by the average energy of products
(d) which is determined by the average energy of products relative to that of reactants

88. The use of a catalyst helps in increasing the
(a) rate of forward direction only
(b) rate of backward direction only
(c) rates of both forward as well as backward directions
(d) relative amounts of products

89. Which of the following statements is **not** true?
(a) Catalyst is not involved in the reaction
(b) The concentration of a catalyst remains constant throughout the progress of chemical reaction
(c) The mechanism of catalytic reaction may vary from reaction to reaction
(d) Nitric oxide acts as a homogeneous catalyst in the oxidation of SO_2 into SO_3

90. Which of the following statements is **not** correct?
(a) The efficiency of a solid catalyst depends upon its surface area
(b) Catalyst operates by providing alternate path for the reaction that involves a lower activation energy
(c) Catalyst lowers the energy of activation of the forward direction without affecting the energy of activation of the backward direction
(d) Catalyst does not affect the overall enthalpy change of the reaction

91. Which of the following statements is **not** correct?
(a) The catalyst changes not only the rate of forward direction but also that of backward direction
(b) The catalyst changes the value of equilibrium constant of the reaction
(c) The mechanism of a catalytic reaction depends on the type of catalyst, i.e. whether it is homogeneous or heterogeneous
(d) Enzymes are essentially proteins which catalyze reaction occurring in living matter

92. Which of the following statements is **not** correct?
(a) Most heterogeneous catalytic reactions involve the solid surface of the catalyst
(b) Heterogeneous catalysts primarily function by lowering the activation energy of the reaction
(c) A solid catalyst present in the powder form is more effective as it has larger surface area
(d) The catalyst may be deactivated by heating it to high temperature

93. The increase in the rate of a reaction with increase in temperature is mainly due to
(a) the increase in collision frequency
(b) the decrease in activation energy
(c) the increase in the number of molecules having threshold energy
(d) the increase in the pre-exponential factor

94. The activation energies of two reactions are E_{a1} and E_{a2} with $E_{a1} > E_{a2}$. If the temperature of the reacting systems is increased from T_1 to T_2, predict which of the following alternatives is correct?
(a) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (b) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (c) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (d) $\frac{k_1'}{k_1} < 2\,\frac{k_2'}{k_2}$
where k' s are the rate constants at higher temperatures.

95. A catalyst lowers the activation energy of the forward reaction by 10 kJ mol^{-1}. What effect it has on the activation energy of the backward reaction?
(a) Increase by 10 kJ mol^{-1} (b) Decrease by 10 kJ mol^{-1}
(c) Remains unaffected (d) Cannot be predicted

96. A catalyst is a substance which
(a) increases the equilibrium concentrations of the products
(b) decreases the energy of activation
(c) does not alter reaction mechanism
(d) increases the frequency of collision of reacting species

Multiple Correct Choice Type

1. A catalyst
(a) increases the average kinetic energy of reacting molecules
(b) decrease the activation energy
(c) alters the reaction mechanism
(d) increases the frequency of collisions of reacting species

2. The rate law for the reaction RCl + NaOH(aq) → ROH + NaCl is given by, Rate = k_1 [RCl]. The rate of the reaction will be
(a) doubled on doubling the concentration of sodium hydroxide
(b) halved on reducing the concentration of alkyl halide to one half
(c) increased on increasing the temperature of the reaction
(d) unaffected by increasing the temperature of the reaction

3. For a first-order reaction A → B, (1988)
(a) the degree of dissociation is equal to $(1 - e^{-kt})$.
(b) a plot of reciprocal concentration of the reactant versus time gives a straight line.
(c) the time taken for the completion of 75% reaction is thrice that of $t_{1/2}$ of the reaction.
(d) the pre-exponential factor in the Arrhenius equation has the dimension of time T^{-1}. (1998)

4. Which of the following statements is/are correct?
(a) The order of an elementary reaction is equal to its molecularity.
(b) The order of a reaction is a theoretical physical quantity.
(c) The order of a reaction can be equal to zero.
(d) The order of an acid hydrolysis of an ester is two.

5. The use of a catalyst helps in
(a) increasing the rate of forward reaction. (b) increasing the rate of backward reaction.
(c) increasing the relative amounts of products. (d) changing the activation energy of the reaction.

6. For a second order reaction A → B,
(a) the degree of dissociation is equal to $1 - 1/(1 + a_0kt)$.
(b) a plot of reciprocal concentration of the reactant versus times gives a straight line.
(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction.
(d) The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}.

7. For the reaction $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$, which of the following expression(s) is/are correct?

(a) $\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t}$ (b) $\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = \frac{2}{3}\frac{\Delta[H_2O]}{\Delta t}$

(c) $-\frac{\Delta[O_2]}{\Delta t} = \frac{5}{4}\frac{\Delta[NO]}{\Delta t} = \frac{5}{6}\frac{\Delta[H_2O]}{\Delta t}$ (d) $-\frac{\Delta[NH_3]}{\Delta t} = \frac{5}{4}\frac{\Delta[O_2]}{\Delta t} = \frac{3}{2}\frac{\Delta[H_2O]}{\Delta t}$

8. For a zero order reaction A → product,

(a) the integrated rate expression is $[A] = [A]_0 - kt$. (b) the unit of rate constant is mol L^{-1} s^{-1}.

(c) the time to complete the reaction is $[A]_0/k$. (d) the half-life is $0.693/k$.

9. For a first order reaction A → product

(a) the integrated rate expression is $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ (b) the unit of rate constant is s^{-1}.

(c) the reaction in principle is never completed. (d) the half-life is $0.693/k$.

10. For a first order reaction νA → product

(a) the differential rate law is $-\frac{1}{\nu}\frac{d[A]}{dt} = k[A]$ (b) the integrated rate law is log $([A]/[A]_0) = -t$

(c) the half-life period is $t_{1/2} = 0.693/\nu k$ (d) the plot of ln [A] versus t is linear with slope equal to νk.

11. The reaction $2NO_2 + F_2 \underset{}{\overset{K_{eq}}{\rightleftharpoons}} 2NO_2F$ involves two steps.

$$NO_2 + F_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2F + F; \qquad F + NO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO_2F$$

The equilibrium constant of the reaction is given by

(a) $K_{eq} = \frac{k_1}{k_{-1}}\frac{k_2}{k_{-2}}$ (b) $K_{eq} = \frac{k_1}{k_{-1}}\frac{k_{-2}}{k_2}$ (c) $K_{eq} = K_{eq1} K_{eq2}$ (d) $K_{eq} = K_{eq1}/K_{eq2}$

12. Which of the following statements is/are correct?

(a) The rate constant of an exothermic reaction decreases with increase in temperature.

(b) The rate constant of an endothermic reaction increases with increase in temperature.

(c) The rate constant of forward and backward directions of a reversible reaction increases with increase in temperature.

(d) The rate constant of forward direction increases while that of backward direction decreases with increase in temperature.

13. Which of the following statements are correct?

(a) The half-life period of a reaction is independent of temperature.

(b) The half-life period of a first-order reaction is independent of initial concentration of the reacting species.

(c) The half-life period of a second order reaction is directly proportional to the initial concentration of the reacting species.

(d) Hydrolysis of an ester is a first-order reaction.

14. Which of the following statements are correct?

(a) Saponification of an ester is a first-order reaction.

(b) Acid hydrolysis of an ester is first-order with respect to H^+ and first order with respect to ester.

(c) An elementary step has an order equal to its molecularity.

(d) The order of a reaction is never greater than two.

15. Which of the following statements are correct?

(a) For a first-order reaction, the time required to reduce successively the concentration of reactant to a constant fraction is always same.

(b) A catalyst decreases the enthalpy change of a chemical reaction.

(c) A first-order reaction never reaches the completion stage.
(d) The rate constant of a reaction increases with increase in temperature. It is primarily due to the decrease in the activation energy of the reaction.

16. Which of the following statements are **not** correct?
(a) An autocatalytic reaction is the one in which the reaction is catalyzed by one of the reactants.
(b) A catalyst never enters into the chemical reaction.
(c) An endothermic reaction can, in principle, have zero activation energy.
(d) An exothermic reaction can, in principle, have zero activation energy.

17. Which of the following statements are correct?
(a) A reaction with zero activation energy is practically independent of temperature.
(b) A heterogeneous catalyst is more effective if it is present in the powder form.
(c) A catalyst changes the relative amounts of products and reactants of an equilibrium reaction.
(d) In a first-order reaction, the concentration of A after n half-times is $[A]_0\ (1/2)^{n-1}$.

18. Which of the following statements are correct?
(a) A higher order reaction may be reduced to a lower order by taking one of the rate determining reacting species in excess amounts.
(b) The rate of decomposition of N_2O_5 depends on the way the reaction is written, such as

$$2N_2O_5 \rightarrow 2N_2O_5 + O_2; \qquad N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}\ O_2$$

(c) The rate of reaction $SO_3 \rightarrow SO_2 + \frac{1}{2}\ O_2$ defined in terms of appearance of concentration of O_2 is written as $\frac{1}{2}\,d[O_2]/dt$.
(d) A catalyst helps in attaining equilibrium more rapidly.

19. Which of the following statements are correct?
(a) The slope of straight-line plot of log [A] versus t for a first-order reaction is $-\ k$.
(b) The stoichiometry of a reaction tells nothing about the order of the reaction unless it is an elementary step.
(c) Half-life period for a zero-order reaction is directly proportional to the initial concentration of the reacting species.
(d) For a given reaction, the rate constant is found to be $k = 1.6 \times 10^{-2}\ \text{min}^{-1}\ \text{mol L}^{-1}$. The reaction is of second-order.

20. Which of the following statements are **not** correct?
(a) The average speed of reaction increases with time.
(b) For a reaction A → 2B, the rate of disappearance of concentration B and rate of reaction represent one and the same thing.
(c) For the reaction, $2N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, the rate law is given as $-\ (1/2)\ d[N_2]/dt$.
(d) The unit of rate constant for zero order reaction is mol $dm^{-3}\ s^{-1}$.

21. Which of the following statements are correct?
(a) The rate of chemical change is directly proportional to temperature.
(b) The hydrolysis of ethyl ethonate in acidic medium is a first order reaction.
(c) The decolorization of $KmnO_4$ by oxalic acid is catalyzed by Mn^{2+}.
(d) The half-life of a first-order reaction increases with increase in temperature.

22. Which of the following statements are correct?
(a) The unit of rate constant of a reaction having order 1.5 would be $(\text{mol L}^{-1})^{-1/2}\ s^{-1}$
(b) The rate of a chemical reaction remains constant with increase in the concentration(s) of the reacting species. Its order would be zero.
(c) The order of a enzymatic reaction with resect to enzyme is second order.
(d) The order of a reaction is never greater than two.

23. Which of the following statements are correct?
(a) The fractional-order reaction cannot take place in one elementary step.
(b) In a reaction involving more than one elementary reaction, the slowest elementary step is the rate determining reaction.
(c) The radioactive decay always follows first order kinetics.
(d) The decay constant of a radioactive disintegration is temperature independent.

24. Which of the following statements are **not** correct?
(a) For a reaction (1/2)A → 2B, the rate of reaction in terms of disappearance of A is – d[A]/d*t*.
(b) For a reaction $(1/2)A_2 \rightarrow 2B$, the rate of disappearance of A_2 is related to the rate of appearance of B through an expression $-\,d[A_2]/dt = 4\,d[B]/dt$.
(c) Reactions with small activation energies slow a lesser increase in rate with rise in temperature as compared to that having high activation energy.
(d) The half-life for a given reaction is doubled as the initial concentration of a reactant was doubled. The order of the reaction would be zero.

25. Which of the following statements are **not** correct?
(a) A reaction has $k = 1.2 \times 10^{-4}$ mol^{-1} L s^{-1}. Its order is two.
(b) The average rate of appearance of concentration of a product increases with the progress of a chemical reaction.
(c) The rate constant and order of a reaction are experimentally determined quantities.
(d) The rate constant of a zero order gaseous reaction is dependent of the gaseous pressure.

26. Which of the following statements are correct?
(a) A plot of log K_p° versus $1/T$ is linear
(b) A plot of log {[X]/M} versus time is linear for a first order reaction, X → P
(c) A plot of log (p/p°) versus $1/T$ is linear at constant volume
(d) A plot of p versus $1/V$ is linear at constant temperature

Linked Comprehension Type

1. The reaction $2NO(g) + H_2(g) = N_2O(g) + H_2O(g)$ follows the rate law

$$\frac{dp(N_2O)}{dt} = k\,(p_{NO})^2\,p_{H_2}$$

The following data have been obtained.

Expt. No.	$\frac{(p_{NO})_0}{\text{mmHg}}$	$\frac{(p_{H_2})_0}{\text{mmHg}}$	$\frac{\textit{Half-life time}}{s}$	$\frac{\textit{Temperature}}{^\circ C}$
1.	600	10	19.2	827
2.	600	20	?	827
3.	10	600	830	827
4.	20	600	?	827
5.	600	10	9.6	847

Based on these informations, answer the following three questions.
(i) The values of half-life time not shown above in the run 2 and 4, respectively, are
(a) 19.2 s, 8.30 s (b) 19.2 s, 415 s (c) 38.4 s, 830 s (d) 38.4 s, 415 s
(ii) The rate constant of the reaction is
(a) 10^{-5} mmHg^{-2} s^{-1} (b) 10^{-6} mmHg^{-2} s^{-1} (c) 10^{-7} mmHg^{-2} s^{-1} (d) 10^{-8} mmHg^{-2} s^{-1}
(iii) The energy of activation of the reaction is about
(a) 250 kJ mol^{-1} (b) 280 kJ mol^{-1} (c) 315 kJ mol^{-1} (d) 355 kJ mol^{-1}

2. The following data were obtained for the decomposition of dimethyl ether:

$$CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$$

t/s	0	1600	3200
$p_{\text{total/Torr}}$	300	600	750

Based on this information, answer the following three questions.
(i) The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3
(ii) The rate constant of the reaction is
(a) 4.33×10^{-2} s^{-1} (b) 4.33×10^{-3} s (c) 4.33×10^{-4} s (d) 4.33×10^{-5} s

(iii) The time required to reduce the partial pressure of CH_3COCH_3 to one eight will be
(a) 3000 s (b) 4000 s (c) 4800 s (d) 6400 s

3. The following data were obtained on the half-life time of a reaction

$t_{0.5}$/s	425	275
p_0/mmHg	350	540

Based on this information, answer the following three questions.

(i) The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

(ii) When p is expressed in mmHg and t in s, then the numerical value of rate constant of the reaction is
(a) 6.72×10^{-5} (b) 6.72×10^{-6} (c) 6.72×10^{-7} (d) 6.22×10^{-4}

(iii) If the reaction is started with $p_0 = 400$ mmHg, how much time it will take to reduce the partial pressure of the reactant to 300 mmHg?
(a) 124 s (b) 105 s (c) 94 s (d) 82 s

4. The formation of AB_2 from A and B_2 is a reversible reaction $A(g) + B_2(g) \rightleftharpoons AB_2(g)$
The variation of k_f and k_b follow the following Arrhenius equations.

$$\log\,(k_f/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = 8.848 - \frac{(26000\ \text{K})}{4.157}\frac{1}{T}$$

$$\log\,(k_b/\text{s}^{-1}) = 30.0 - \frac{(52500\ \text{K})}{4.375}\frac{1}{T}$$

Based on these informations, answer the following three questions.

(i) The activation energies of the forward and backward reactions at 300 K, respectively, are
(a) 120 kJ mol^{-1}, 100 kJ mol^{-1} (b) 52 kJ mol^{-1}, 230 kJ mol^{-1}
(c) 120 kJ mol^{-1}, 230 kJ mol^{-1} (d) 52 kJ mol^{-1}, 100 kJ mol^{-1}

(ii) The value of $\Delta_r H$ of the reaction at 300 K is
(a) 20 kJ mol^{-1} (b) – 110 kJ mol^{-1} (c) – 178 kJ mol^{-1} (d) 48 kJ mol^{-1}

(iii) The equilibrium constant of the reaction at 300 K is
(a) 10 M^{-1} (b) 100 M^{-1} (c) 1000 M^{-1} (d) 10^4 M^{-1}

5. The table given below gives kinetic data for the following reaction at 300 K.

$$OCl^- + I^- = OI^- + Cl^-$$

Expt. No	$\frac{[OCl^-]}{\text{mol dm}^{-3}}$	$\frac{[I^-]}{\text{mol dm}^{-3}}$	$\frac{[OH^-]}{\text{mol dm}^{-3}}$	$\frac{\frac{d[IO^-]}{dt}}{\text{mol dm}^{-3}\text{s}^{-1}}$
1	0.0017	0.0017	1.0	1.75×10^{-4}
2	0.0034	0.0017	1.0	3.50×10^{4}
3	0.0017	0.0034	1.0	3.50×10^{4}
4	0.0017	0.0017	0.5	3.50×10^{4}

Based on these informations, answer the following three questions.

(i) The rate law is
(a) $r = k\,[I^-]\,[OCl^-]$ (b) $r = k\,[I^-]\,[OCl^-]\,[OH^-]$
(c) $r = k\,[I^-]\,[OCl^-]/[OH^-]$ (d) $r = k\,[I^-]\,[OH^-]/[OCl^-]$

(ii) The value of rate of reaction is
(a) 40.5 s^{-1} (b) 60.5 s^{-1} (c) 80.5 s^{-1} (d) 100 s^{-1}

(iii) The rate of reaction when $[OCl^-] = 0.004$ M, $[I^-] = 0.002$ M and $[OH^-] = 0.5$ M is
(a) $2.27 \times 10^{-4}\ M^{-1}\ s^{-1}$ (b) $4.21 \times 10^{-4}\ M^{-1}\ s^{-1}$
(c) $6.11 \times 10^{-3}\ M^{-1}\ s^{-1}$ (d) $9.7 \times 10^{-4}\ M^{-1}\ s^{-1}$

6. The gaseous reaction $A(g) \rightarrow 2B(g) + C(g)$ is observed to be of the first order. On starting with pure A, it is found that at the end of 10 min, the total pressure of the system is 176 mmHg and after a very long time it is 270 mmHg.
Based on these information, select the correct choice for each of the following three questions.

(i) The initial pressure of A is

(a) 60 mmHg (b) 90 mmHg (c) 150 mmHg (d) 210 mmHg

(ii) The partial pressure of A after 10 min is

(a) 25 mmHg (b) 35 mmHg (c) 47 mmHg (d) 51 mmHg

(iii) The rate constant of the reaction is

(a) 0.11 s^{-1} (b) $1.3 \times 10^{-2}\ s^{-1}$ (c) $1.5 \times 10^{-2}\ s^{-1}$ (d) $1.1 \times 10^{-3}\ s^{-1}$

7. The substance X decomposes in two different ways as shown in the following.

$$X \rightarrow A \quad ; \quad k_1 = A_1 e^{-E_1/RT} \quad \text{with} \quad A_1 = 10^{15} s^{-1} \quad \text{and} \quad E_1 = 126\ \text{kJ mol}^{-1}$$

$$X \rightarrow B \quad ; \quad k_2 = A_2 e^{-E_2/RT} \quad \text{with} \quad A_2 = 10^{13} s^{-1} \quad \text{and} \quad E_2 = 83\ \text{kJ mol}^{-1}$$

Based on these informations, answer correctly the following three questions.

(i) The activation energy E for the disappearance in terms of E_1 and E_2 is

(a) $\dfrac{k_1E_1 + k_2E_2}{k_1 + k_2}$ (b) $\dfrac{k_1E_1 + k_2E_2}{k_1 - k_2}$ (c) $\dfrac{k_1E_1 - k_2E_2}{k_1 + k_2}$ (d) $\dfrac{k_1E_1 - k_2E_2}{k_1 - k_2}$

(ii) The temperature at which the two products A and B are formed at the same rate is about

(a) 950 K (b) 1085 K (c) 1150 K (d) 1210 K

(iii) The rate at which A is formed is given as

(a) $k_1\ [X]_0\ [1 - e^{-k_1 t}]$ (b) $k_1\ [X]_0\ [1 - e^{(k_1+k_2)t}]$

(c) $\dfrac{k_1}{k_1 + k_2}[X]_0$ (d) $\dfrac{k_1}{k_1 + k_2}[X]_0\ [1 - e^{-(k_1+k_2)t}]$

Assertion and Reason Type

The questions below consist of Statement-1 and Statement-2. Use the following key to choose the appropriate answer.

(a) If both statement-1 and statement-2 are correct, and statement-2 is the correct expnanation of the statement-1.

(b) If both statement-1 and statement -2 are correct, but statement -2 is not the correct explanation of the statement-1.

(c) If statement-1 is correct and statement-2 is incorrect.

(d) If statement-1 is incorrect and statement-2 is correct.

	Statement–1	**Statement–2**
1.	For each ten degree rise in temperature the rate an constant is nearly doubled.	Energy wise distribution of molecules in a gas is exponential function of temperature. (1989)
2.	A first-order reaction never reaches the completion state.	The concentration of reactant decreases exponentially.
3.	Acatalyst helps attaining equilibrium more rapidly.	A catalyst is not involved in a chemical reaction.
4.	A catalyst increases rates of both forward and backward reaction	A catalyst has no effect on energy of activation of forward and backward reactions.
5.	The reactions of order more than three are not observed.	The probability of more than three particles collicing together is very remote.
6.	A reaction $A(g) \rightleftharpoons$ products is second order at low pressures, and is first order at high pressures.	At low pressure, the rate determining step is the bimolecular formation of the excited molecules and at high pressure, the rate-determining step is the dissociated of the excited molecule.
7.	The half-life time of a second order reaction $A \rightarrow$ products depends on the initial concentration of A.	The half life time for second order reaction is given as $t_{0.5} = 1/[A]_0^2\ k$.

8.	The unit of rate constant depends on the order of the reaction.	The unit of rate of reaction is independent of the order of the reaction.
9.	The rate constant of a reaction increases with increase in temperature.	The increase in the rate constant is primarily due to increase in the rate of bimolecular collisions of reacting moleculer.
10.	Fractional-order reactions are not possible. plex	Noninteger orders are generally due to the com- nature of reactions involving more than one elementary step.
11.	The order of an elementary step is alway equal to its molecularity.	The molecularity of an elementary step is never greater than three.
12.	The study of first-order reaction can be studied from any time after the reaction is initiated.	The integrated rate expression involves the ratio of $[A]_t/[A]_0$ and zero time can be taken any time after the reaction is initiated.
13.	The first-order reaction, in principle, is completed.	The integrated rate expression involves the never expanential decay of concentration with time.

Matrix Match Type

Column I lists the order of the reactions and column II lists some characteristics of these reaction. Match correctly the each entry in Column I with those listed in Column II.

1.

Column I	**Column II**
(a) Zero-order reaction	(p) Unit of rate constant: $\text{mol}^{-1}\ \text{L s}^{-1}$
(b) First-order reaction	(q) Half-life time, $t_{0.5} = 1/[A]_0^2\, k$
(c) Second-order reaction	(r) Unit of rate of reaction: $\text{mol L}^{-1}\ \text{s}^{-1}$
(d) Third-Order reaction	(s) Unit of rate constant: s^{-1}
	(t) Half-life time, $t_{0.5} = 0.693/k$
	(u) Unit of rate constant: $\text{mol L}^{-1}\ \text{s}^{-1}$

2. Column I lists the order of the reactions and Column II lists some of the reactions. Match correctly the each entry in Column I with those listed in Column II.

Column I	**Column II**
(a) Zero-order reaction	(p) Acid hydrolysis of an ester
(b) First-order reaction	(q) Saponification of an ester
(c) Second-order reaction	(r) $2NO + Cl_2 \rightarrow 2NOCl$
(d) Third-order reaction	(s) Substrate in an enzyme reaction
	(t) Persulphate-Iodide reaction
	(u) Hydrolysis of cane sugar
	(v) Radioactive decay

ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (d)	**4.** (d)	**5.** (c)	**6.** (d)	**7.** (b)
8. (a)	**9.** (b)	**10.** (b)	**11.** (a)	**12.** (d)	**13.** (a)	**14.** (c)
15. (d)	**16.** (c)	**17.** (c)	**18.** (b)	**19.** (a)	**20.** (a)	**21.** (b)
22. (a)	**23.** (a)	**24.** (d)	**25.** (c)	**26.** (d)	**27.** (c)	**28.** (a)
29. (b)	**30.** (c)	**31.** (a)	**32.** (d)	**33.** (d)	**34.** (d)	**35.** (b)
36. (a)	**37.** (d)	**38.** (a)	**39.** (c)	**40.** (b)	**41.** (c)	**42.** (c)
43. (a)	**44.** (b)	**45.** (c)	**46.** (d)	**47.** (b)	**48.** (b)	**49.** (a)
50. (d)	**51.** (b)	**52.** (a)	**53.** (c)	**54.** (b)	**55.** (a)	**56.** (b)

57. (a) **58.** (d) **59.** (b) **60.** (a) **61.** (d) **62.** (c) **63.** (c)
64. (b) **65.** (c) **66.** (d) **67.** (c) **68**. (d) **69.** (b) **70.** (b)
71. (a) **72.** (d) **73.** (b) **74.** (b) **75.** (d) **76.** (a) **77.** (b)
78. (c) **79.** (b) **80.** (d) **81.** (b) **82.** (b) **83.** (c) **84.** (b)
85. (c) **86.** (d) **87.** (a) **88.** (c) **89.** (a) **90.** (c) **91.** (b)
92. (d) **93.** (c) **94.** (b) **95.** (b) **96.** (b)

Multiple Correct Choice Type

1. (b), (c) **2.** (b), (c) **3.** (a), (d) **4.** (a), (c), (d)
5. (a), (b), (d) **6.** (a), (b), (c) **7.** (b), (c) **8.** (a), (b), (c)
9. (b), (c), (d) **10.** (a), (c), (d) **11.** (a), (c) **12.** (b), (c)
13. (b), (d) **14.** (b), (c) **15.** (a), (c) **16.** (a), (b), (c)
17. (a), (b) **18.** (a), (d) **19.** (b), (c) **20.** (a), (b)
21. (b), (c) **22.** (a), (b) **23.** (a), (b), (c) **24.** (a), (b)
25. (b), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (c) **(iii)** (d) **2.** **(i)** (b) **(ii)** (c) **(iii)** (c)
3. **(i)** (c) **(ii)** (b) **(iii)** (a) **4.** **(i)** (c) **(ii)** (b) **(iii)** (b)
5. **(i)** (c) **(ii)** (b) **(iii)** (d) **6.** **(i)** (b) **(ii)** (c) **(iii)** (d)
7. **(i)** (a) **(ii)** (b) **(iii)** (d)

Reason and Assertion Type

1. (a) **2.** (a) **3.** (c) **4.** (c) **5.** (a) **6.** (a) **7.** (c)
8. (b) **9.** (c) **10.** (d) **11.** (b) **12.** (a) **13.** (a)

Matrix Match Type

1. (a)-(r), (u) (b)-(r), (s), (t) (c)-(p), (r) (d)-(q), (r)
2. (a)-(s) (b)-(p), (u), (v) (c)-(q), (t) (d)-(r)

Hints and Solutions

Straight Objective Type

1. The rate constant of a reaction depends on temperature.

2. Same answer as Q.1.

3. The rate of reaction and rate of appearance (or disappearance) of a reactant (or product) are different quantities unless its stoichiometric number in chemical equation is one.

4. For the reaction $2A + 3B \rightarrow 4C$, the rate of reaction is represented as

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$$

5. The unit of rate of reaction is mol L^{-1} s^{-1}.

6. The order of a reaction is an experimentally determined quantity.

7. The units of rate of reaction and rate constant are identical for a zero-order reaction.

8. For an elementary reaction, order is equal to the molecularity (i.e. sum of stoichiometric number of reactants).

9. The species OH^- with order -1 is an inhibitor.

10. $1.837 = (1.5)^{1.5}$

11. We have $K_{eq} = k_1/k_{-1}$.

16. Rate = $-\frac{1}{2}\frac{d[X]}{dt}=\frac{1}{2}\frac{d[XY]}{dt}$ or $-\frac{d[X]}{dt}=\frac{1}{2}\left(\frac{d[XY]}{dt}\right)$

17. We will have $-\frac{d[N_2]}{dt}=-\frac{1}{3}\frac{d[H_2]}{dt}=\frac{1}{2}\frac{d[NH_3]}{dt}$

Its is given that $\frac{d[NH_3]}{dt}$ = 2×10^{-4} mol dm^{-3} s^{-1}. Hence, $-\frac{d[H_2]}{dt}=\frac{3}{2}\frac{d[NH_3]}{dt}$ = 3×10^{-4} mol dm^{-3} s^{-1}

18. Slow step is the rate determining step.

19. k_f does not depend upon the concentration of A.

22. Individual rate of appearance of a product or disappearance of a reactant becomes identical when devided by the corresponding stoichiometric coefficient.

23. Order of a reaction may have zero or fractional value.

24. Let the order of the reaction with respect to G and H be m and n, respectively. The given informations are as follows

$$r = k\,[G]^m\,[H]^n$$

$$8r = k\,\{2\,[G]\}^m\,\{2\,[H]\}^n = 2^{m+n}\,(k\,[G]^m\,[H]^n) = 2^{m+n}r.\ \text{Hence, } m + n = 3$$

[Note: It is also given that $2r = k\ \{2\,[G]\}^m\,[H]^n = 2^m\,(k\,[G]^m\,[H]^n) = 2^m\,r$

This gives $m = 1$. Hence, $n = 3 - m = 2$. Thus, the reaction is first order with respect to G and second order with respect to H and the overall order of the reaction is three.

25. $r_1 = -\frac{1}{2}\frac{d[N_2O_5]}{dt}$ and $r_2 = -\frac{d[N_2O_5]}{dt}$ Obviously $2r_1 = r_2$.

26. For a zero-order reaction, $[A]_t - [A]_0 = -kt$, the plot of $[A]_t$ versus t is linear with negative slope and nonzero intercept.

27. The slope of the plot of $[A]_t$ versus t is $-k$.

28. For a zero-order kinetics, the time of completion is $[A]_0/k$.

29. $\nu A \rightarrow$ products

Rate of reaction = $-\frac{1}{\nu}\frac{d[A]}{dt}$ = $k\,[A]^0 = k$ or $d[A] = -\,\nu k\,dt$

Integrating, we get $[A]_t - [A]_0 = -\,\nu\,kt$

30. For half-life time, $[A]_t = [A]_0/2$. Hence $t_{0.5} = \frac{[A]_0/2}{\nu k}$

32. A radioactive decay follows first-order kinetics. 560 Days are equivalent to four half-lives. Hence, the mass of radioactive element left is $(1/2^4)$g, i.e. (1/16)g.

33. For a first-order reaction, the rate expression is $\log\{[A]_t/M\} - \log\{[A]_0/M\} = -(k/2.303)_t$

The plot of $\log\{[A]_t/M\}$ versus t is a straight line with negative slope and nonzero intercept.

34. The slope of the plot of $\log\{[A]_t/M\}$ versus t for a first-order reaction is $-k/2.303$.

35. The half-life of a first-order kinetics is $t_{1/2} = 0.693/k$.

36. Rate of disappearance of N_2O_5 does not depend upon the way a chemical reaction is formulated. Hence, $k = k'$.

37. The rate of reaction will be given by

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = k\,[N_2O_5] \quad \text{and} \quad -\frac{d[N_2O_5]}{dt} = k'\,[N_2O_5]$$

Since $-d\,[N_2O_5]/dt$ has the same value, we will have $2k = k'$.

38. We have

$$\begin{array}{lll} A(g) \rightarrow & 2B(g) + & C(g); \\ p_0 - p & 2p & p \end{array}$$

$$p_t = p_0 + 2p = 180 \text{ mmHg}; \quad p = (180 \text{ mmHg} - 90 \text{ mmHg})/2 = 45 \text{ mmHg}$$

$$\ln\frac{p_0 - p}{p_0} = -\,kt \quad \Rightarrow \quad k = -\frac{1}{t}\ln\left(\frac{45\text{ mmHg}}{90\text{ mmHg}}\right) \quad \text{i.e.} \quad k = \frac{0.693}{10 \times 60\text{ s}} = 1.15 \times 10^{-3}\text{ s}^{-1}$$

39. $\ln \dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt \quad \Rightarrow \quad \ln([\mathrm{A}]_t/\mathrm{M}) = \ln([\mathrm{A}]_0/\mathrm{M}) - kt$

$\ln([\mathrm{A}]_t/\mathrm{M}) = \ln(1.0) - (5.0 \times 10^{-5}\ \mathrm{s}^{-1})(3.85 \times 60 \times 60\ \mathrm{s}) = -0.693$

$[\mathrm{A}]_t = 0.50\ \mathrm{M}$

Rate of reaction $= k[\mathrm{A}]_t = (5.0 \times 10^{-5}\ \mathrm{s}^{-1})(0.50\ \mathrm{M}) = 2.5 \times 10^{-5}\ \mathrm{M\ s}^{-1}$

40. One fourth is two half-lives and 1/16 is four half-lives. One half-life is equal to 5 min, four half-lives will be equal to 20 min.

41. $t_{1/2} = 0.693/k$ and $t_{99.9\%} = \ln(0.1/100)/k = 6.91/k$. Hence, $t_{99.9\%}/t_{1/2} = 10$.

42. The integrated rate expression is $\ln [\mathrm{A}]_0/([\mathrm{A}]_0 - \nu_1 x) = \nu_1 k_1 t$.

43. A radioactive decay follows first-order kinetics.

44. $\log \dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = \dfrac{k}{2.303}t$ i.e. $\log 0.8 = -\dfrac{k}{2.303}(10\ \mathrm{min})$ or $k = \dfrac{2.303}{10\ \mathrm{min}}\log(0.8) = 0.0223\ \mathrm{min}^{-1}$

45. 15 h is five times the half-life of 3 h. Hence, $[\mathrm{A}] = \dfrac{[\mathrm{A}]_t}{2^5} = \dfrac{100\ \mathrm{g}}{32} = 3.125\ \mathrm{g}$

46. For $2\mathrm{N_2O_5} \longrightarrow 4\mathrm{NO_2} + \mathrm{O_2}$, we have $-\dfrac{1}{2}\dfrac{\mathrm{d[N_2O_5]}}{\mathrm{d}t} = k[\mathrm{N_2O_5}]$ or $-\dfrac{\mathrm{d[N_2O_5]}}{[\mathrm{N_2O_5}]} = 2k\,\mathrm{d}t$

On integrating, we get $\quad \ln \dfrac{[\mathrm{N_2O_5}]_0}{[\mathrm{N_2O_5}]_t} = 2kt$

For a half-life, $[\mathrm{N_2O_5}]_t = (1/2)[\mathrm{N_2O_5}]_0$. Hence $t_{1/2} = \dfrac{\ln 2}{2k} = \dfrac{0.693}{2k}$

47. We have $\ln\left(\dfrac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = kt$. Hence $2.303 \log\left(\dfrac{800}{50}\right) = k(2 \times 10^5\ \mathrm{s})$

or $k = \dfrac{1}{2\times10^5\ \mathrm{s}}\,2.303\log(16) = \dfrac{2.303}{2\times10^5\ \mathrm{s}}\log(2^4) = \dfrac{2.303\times4\times0.3010}{2\times10^5\ \mathrm{s}} = 1.386 \times 10^{-5}\ \mathrm{s}$

48. The concentration changes from 0.1 M to 0.0125 M is equivalent to three half lives. Hence,

$$3\,t_{1/2} = 45\ \mathrm{min} \quad \text{or} \quad t_{1/2} = 15\ \mathrm{min} \quad \text{and} \quad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{15\ \mathrm{min}} = 0.0462\ \mathrm{min}^{-1}$$

Rate of reaction $= \lambda[\mathrm{A}] = (4.62 \times 10^{-2}\ \mathrm{min}^{-1})(0.001\ \mathrm{mol\ L}^{-1}) = 4.62 \times 10^{-5}\ \mathrm{mol\ L^{-1}\ min^{-1}}$

49. The rate expressions are:

First order $\quad \ln\{[\mathrm{A}]_t/[\mathrm{A}]_0\} = -k_1 t$ and *Zero order* $\quad [\mathrm{A}]_t - [\mathrm{A}]_0 = k_0 t$

Hence, for first order reaction $\quad t_{1/2} = \dfrac{1}{k_1}\,\text{In}\,\dfrac{1}{2} = \dfrac{0.693}{k_1} = 40\ \mathrm{s}$

For zero order reaction $\quad t_{1/2} = \dfrac{[\mathrm{A}]_0}{2k_0} = 20\ \mathrm{s}$

Thus $\quad \dfrac{k_1}{k_0} = \dfrac{0.693/(40\,\mathrm{s})}{\left(1.386\,\mathrm{mol\ dm^{-3}}\right)/(2\times20\,\mathrm{s})} = 0.5\ \mathrm{mol^{-1}\ dm^3}$

50. $[\mathrm{N_2O_5}] = r/k = (2.4 \times 10^{-5}\ \mathrm{mol\ L^{-1}\ s^{-1}})/(3.0 \times 10^{-5}\ \mathrm{s}^{-1}) = 0.8\ \mathrm{mol\ L}^{-1}$

51. The rate of hydrolysis of an ester is directly proportional to $[\mathrm{H}^+]$. Since $\mathrm{H_2SO_4}$ contains more H^+, it follows that $k_{\mathrm{HCl}} < k_{\mathrm{H_2SO_4}}$.

52. For equinormal solutions H^+ in HCl is larger than $\mathrm{H_2SO_4}$. Hence, $k_{\mathrm{HCl}} > k_{\mathrm{H_2SO_4}}$.

53. Let p_0 and p_t be the pressures of the system at $t = 0$ and $t = t$, respectively. If at time t, the concentration of A decreases by x, we will have $\quad p_0 \propto [\mathrm{A}]_0$ and $p_t \propto [\mathrm{A}]_0 + (\Delta\nu_\mathrm{g})x$

Hence $[\mathrm{A}]_0 \propto p_0$ and $x \propto (p_t - p_0)/\Delta\nu_g$. Thus $[\mathrm{A}]_t = [\mathrm{A}]_0 - x \propto p_0 - \dfrac{p_t - p_0}{\Delta\nu_g} = \dfrac{(\Delta\nu_g + 1)p_0 - p_t}{\Delta\nu_g}$

With these, equation $\ln \dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = kt$ becomes $\ln \left(\dfrac{(\Delta\nu_g)p_0}{(\Delta\nu_g + 1)p_0 - p_t}\right) = kt$

54. For the given reaction, $\Delta\nu_g = 2$. Substituting this in the equation derived in Q.53, we get

$$\ln\left(\frac{2p_0}{3p_0 - p_t}\right) = kt$$

55. Here $p_{\mathrm{NO}} >> p_{\mathrm{H_2}}$. Hence, the given rate reaction can be approximated as $\dfrac{\mathrm{d}p_{\mathrm{N_2O}}}{\mathrm{d}t} = k' p_{\mathrm{H_2}}$ where $k' = k(p_{\mathrm{NO}})^2$.

56. $\underset{[\mathrm{A}]_0 - x.}{\mathrm{A}} \rightarrow \text{product}$ Hence $\dfrac{\mathrm{d}x}{\mathrm{d}t} = k([\mathrm{A}]_0 - x)^n$ or $\dfrac{\mathrm{d}x}{([\mathrm{A}]_0 - x)^n} = k\,\mathrm{d}t$

On integrating, we get

$\dfrac{1}{(n-1)}\left[\dfrac{1}{([\mathrm{A}]_0 - x)^{n-1}} - \dfrac{1}{[\mathrm{A}]_0}\right] = kt$. For half-life, $x = [\mathrm{A}]_0/2$. Hence $\dfrac{1}{(n-1)}\dfrac{2^{n-1}}{[\mathrm{A}]_0^{n-1}} = k\,t_{1/2}$

57. We have

$$\underset{[\mathrm{A}]_0 - ax}{a\mathrm{A}} + \underset{[\mathrm{B}]_0 - bx}{b\mathrm{B}} + \underset{[\mathrm{C}]_0 - cx}{c\mathrm{C}} \rightarrow \text{products.} \quad \text{Also, } \frac{[\mathrm{A}]_0}{a} = \frac{[\mathrm{B}]_0}{b} = \frac{[\mathrm{C}]_0}{c}$$

The rate law gives

$$-\frac{1}{a}\frac{\mathrm{d}([\mathrm{A}]_0 - ax)}{\mathrm{d}t} = k([\mathrm{A}]_0 - ax)^{\alpha}([\mathrm{B}]_0 - bx)^{\beta}([\mathrm{C}]_0 - cx)^{\gamma}$$

$$= k([\mathrm{A}]_0 - ax)^{\alpha}\left(\frac{b}{a}[\mathrm{A}]_0 - bx\right)^{\beta}\left(\frac{c}{a}[\mathrm{A}]_0 - cx\right)^{\gamma} = \frac{k b^{\beta}c^{\gamma}}{a^{\beta+\gamma}}([\mathrm{A}]_0 - ax)^n;$$

where $n = \alpha + \beta + \gamma$

On integrating, we get $\dfrac{1}{(n-1)}\left[\dfrac{1}{([\mathrm{A}]_0 - ax)^{n-1}} - \dfrac{1}{[\mathrm{A}]_0^{n-1}}\right] = k\dfrac{b^{\beta}c^{\gamma}}{a^{n-\alpha-1}}t$

For half-life time, $ax = [\mathrm{A}]_0/2$. Hence $t_{1/2} = \dfrac{1}{k(n-1)}\dfrac{a^{n-\alpha-1}}{b^{\beta}c^{\gamma}}\dfrac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}}$

58. The half-life time as given in Q.56 is

$$t_{1/2} = \frac{1}{k_n(n-1)}\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}}. \quad \text{Hence} \quad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{[\mathrm{A}]_{02}}{[\mathrm{A}]_{01}}\right)^{n-1}$$

or $\log[(t_{1/2})_1/(t_{1/2})_2] = (n-1)\log[[\mathrm{A}]_{02}/[\mathrm{A}]_{01})$ or $n = 1 + \dfrac{\log[(t_{1/2})_1/(t_{1/2})_2]}{\log[[\mathrm{A}]_{02}/[\mathrm{A}]_{01}]}$

59. For a second-order reaction $\dfrac{1}{[\mathrm{A}]_t} - \dfrac{1}{[\mathrm{A}]_0} = kt$. The plot of $1/[\mathrm{A}]_t$ versus t is linear with positive slope and nonzero intercept.

60. The slope of $1/[\mathrm{A}]_t$ versus t for a second-order reaction is k.

61. The half-life of a second-order kinetics is $t_{1/2} = 1/k[\mathrm{A}]_0$.

62. The rate law is $r = k\,[\mathrm{NO}]^2[\mathrm{O_2}]$. Reducing volume to half, the concentration changes to double values. Hence, rate will increase by eight times of its initial value.

63. For second order reaction $\mathrm{A} \rightarrow \mathrm{B}$, $t_{1/2} = 2/k[\mathrm{A}]_0$

64. On increasing the volume to a twice value, the concentrations of each species is reduced by a factor of 2. Hence

$$\text{rate}_1 = k\,[\mathrm{NO}]^2\,[\mathrm{O_2}] \quad \text{and} \quad \text{rate}_2 = k\left(\frac{[\mathrm{NO_2}]}{2}\right)^2\left(\frac{[\mathrm{O_2}]}{2}\right) \quad \text{i.e.} \quad \frac{\text{rate}_2}{\text{rate}_1} = \frac{1}{8}$$

65. $\underset{a_0 - \nu x}{\nu\mathrm{A}} \xrightarrow{k}$ products

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - \nu x)^2 \quad \text{or} \quad \frac{\mathrm{d}x}{(a_0 - \nu x)^2} = k\,\mathrm{d}t. \quad \text{Thus} \quad \frac{1}{\nu}\left(\frac{1}{a_0 - \nu x} - \frac{1}{a_0}\right) = kt$$

For half-life time, $\nu x = a_0/2$. This gives $t_{1/2} = 1/\nu a_0 k$

66. For p_{H2} = constant, we have

$$\frac{r_1}{r_2} = \left[\frac{(p_{\mathrm{NO}})_1}{(p_{\mathrm{NO}})_2}\right]^m$$. This gives $m = 2$ when the values of data are substituted in the expression.

For p_{NO} = constant, we have

$$\frac{r_1}{r_2} = \left[\frac{(p_{\mathrm{H_2}})_1}{(p_{\mathrm{H_2}})_2}\right]^n$$. This gives $n = 1$ when the values of data are substituted in the expression.

The over-all order is $n + m = 3$.

67. The energy of activation will be more than ΔH.

68. The variation of rate constant is given by $k = A\exp(-E_\mathrm{a}/RT)$ or $\log k = \log A - E_\mathrm{a}/(2.303\,RT)$. The slope of plot of $\log k$ versus $1/T$ is $-E_\mathrm{a}/2.303\,R$.

69. The unit of activation energy is $\mathrm{kJ\ mol^{-1}}$.

70. The activation energy of a reaction is the difference in energies of intermediate product and average energies of reactants.

71. Activation energy does not depend on the way a reaction is formulated in the chemical equation.

72. The plot of $\log k$ versus $1/T$ has a negative slope and nonzero intercept.

73. We have $\mathrm{e}^{-E_\mathrm{a}/(310\ \mathrm{K})R} = 2\,\mathrm{e}^{-E_\mathrm{a}/(300\ \mathrm{K})\,R}$

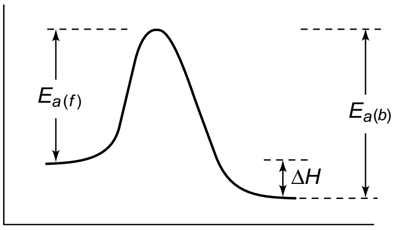
$$\text{or} \quad -\frac{E_\mathrm{a}}{(310\,\mathrm{K})\,R} = \ln 2 - \frac{E_\mathrm{a}}{(300\,\mathrm{K})\,R} \quad \text{or} \quad \frac{E_\mathrm{a}}{R}\left(\frac{1}{300\,\mathrm{K}} - \frac{1}{310\,\mathrm{K}}\right) = \ln 2$$

$$\text{or} \quad E_\mathrm{a} = \frac{(0.693)\,(300\,\mathrm{K})\,(310\,\mathrm{K})\,(8.314\,\mathrm{J\,K^{-1}\ mol^{-1}})}{(10\,\mathrm{K})} = 53\,583\ \mathrm{J\ mol^{-1}}$$

75. At equilibrium, Rate of forward reaction = Rate of backward reaction

76. Acoording to the Arrhenius equation $k = A\exp(-E_\mathrm{a}/RT)$, that is, k increases exponentially with increase in temperature.

77. The given data are shown in the figure.
Obviously, $E_{\mathrm{a(b)}} = E_{\mathrm{a(f)}} + \Delta H = (65 + 42)\ \mathrm{kJ\ mol^{-1}}$



78. We have $k = Ae^{-Ea/RT}$. When $T \rightarrow \infty$, $k \rightarrow A$.

80. The Arrhenius equation, $k = A \exp(-E_a/RT)$, may be written as

$$\log\left(\frac{k}{\text{s}}\right) = \log\left(\frac{A}{\text{s}}\right) - \frac{E_a}{2.303\,RT}$$

On comparing this expression with the given expression, we find that

$$\log(A/\text{s}) = 6.0 \quad \Rightarrow \quad A = 10^6\text{s}$$

$$\frac{E_a}{2.303\,R} = 2000\ \text{K} \quad \Rightarrow \quad E_a = (2.303)\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (2000\ \text{K}) = 3.829 \times 10^4\ \text{J mol}^{-1}$$

82. On decreasing temperature, the rate constant k decreases and hence half-life time (= $0.693/k$) increases.

83. $\Delta H = E_f - E_b = -40\ \text{kJ mol}^{-1}$. Since $E_f/E_b = 2/3$, we get $E_f = 2E_b/3$
Thus $(2E_B/3) - E_b = -40\ \text{kJ mol}^{-1}$. This gives $E_b = 120\ \text{kJ mol}^{-1}$
and $E_f = (2/3)E_b = (2/3)(120\ \text{kJ mol}^{-1}) = 80\ \text{kJ mol}^{-1}$

84. We have $\ln k_T = \ln A - \dfrac{E_1}{RT}$ or $\ln k_{T+10\text{K}} = \ln A - \dfrac{E_1}{R(T+10\text{K})}$

Hence $\quad \ln k_{T+10\text{K}} - \ln k_T = \dfrac{E_1}{R}\left[\dfrac{1}{T} - \dfrac{1}{T+10\text{K}}\right]$ or $\ln\left(\dfrac{k_{T+10\text{K}}}{k_T}\right) = \dfrac{E_1(10\text{K})}{RT\,(T+10\text{K})}$

Similarly, $\ln\left(\dfrac{k'_{T+10\text{K}}}{k'_T}\right) = \dfrac{E_2(10\text{K})}{RT\,(T+10\text{K})}$

Dividing these two, we get $\dfrac{\text{In}\left(k_{T+10\text{K}}/k_T\right)}{\text{In}\left(k'_{T+10\text{K}}/k'_T\right)} = \dfrac{E_1}{E_2} = \dfrac{2E_2}{E_2} = 2$

85. A catalyst shortens the time to reach equilibrium.

86. A catalyst changes the activation energy of the reaction.

87. The lowering of activation energy of the backward reaction is same as that of forward reaction.

88. A catalyst increases rates of both forward and backward reactions.

89. Catalyst is involved in the reaction.

90. A catalyst lowers the energy of activation of both forward and backward reactions.

91. The equilibrium constant does not change with the use of a catalyst.

92. A catalyst may be activated (and not deactivated) by heating it to a high temperature.

93. The increase in the rate of a reaction primarily increases due to increase in the number of molecules having threshold energy.

94. We have $\ln\left(\dfrac{k'}{k}\right) = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) = \dfrac{E_a}{R}\dfrac{\Delta T}{T_1T_2}$
For ΔT positive, k'/k increases faster with larger value of activation energy. Hence, $(k'_1/k_1) > (k'_2/k_2)$

Multiple Correct Choice Type

1. A catalyst decreases the activation energy. It also alters the reaction mechanism.

2. The rate of reaction will be halved on reducing the concentration of alkyl halide to half. The rate constant will also increase on increasing temperature.

3. For a first-order reaction, $\dfrac{[\text{A}]_0 - x}{[\text{A}]_0} = e^{-kt}$. This gives $\dfrac{x}{[\text{A}]_0} = 1 - e^{-kt}$. In the equation $k = Ae^{-kt}$, A has the same dimension as that of k, i.e. T^{-1}.

6. (a) $\underset{a_0(1-\alpha)}{A} \rightarrow \underset{a_0\alpha}{B}$; $\quad \dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt \;\Rightarrow\; \dfrac{1}{a_0(1-\alpha)} - \dfrac{1}{a_0} = kt$

$$\Rightarrow \frac{1}{1-\alpha} - 1 = a_0kt \;\Rightarrow\; 1 - \alpha = \frac{1}{a_0\,kT} \;\Rightarrow\; \alpha = 1 - 1/a_0kT$$

(b) Plot of $1/[A]_t$ versus t is linear

(c) $\dfrac{1}{0.25a_0} - \dfrac{1}{a_0} = kt$; $\quad \dfrac{1}{0.5a_0} - \dfrac{1}{a_0} = kt_{1/2}$; $\quad t/t_{1/2} = 3$

13. (a) $t_{0.5} = 0.693/k$. Since k varies with temperature, $t_{0.5}$ also varies with temperature.

(c) It is inversely proportional to the initial concentration of reacting species.

(b) Truly speaking it is a third order reaction. Its rate expression is rate = k [ester] [H^+] [H_2O] Now since [H_3O] and [H^+] (which is being used as a catalyst), remain constant, we can write the rate expression as rate = k'[ester] which is first order rate expression.

14. (a) It is a second order reaction. Its rate expression is rate = k [ester] [OH^-]

(d) A few reactions of order three are also known.

15. (b) A catalyst does not affect the enthalpy change of a chemical reaction.

(c) The concentration of reacting species decreases in the exponential manner. $[A] = [A]_0 \exp(-k\,t)$. The concentration of A will be zero only when t is infinite.

(d) It is due to the increase in the number of reacting species having energy E_a or more with increase in temperature.

16. (a) An autocatalyst is one of the products and not reactants.

(b) It enters into the elementary chemical reaction and is regenerated in another elementary reaction.

(c) By definition, activation energy is the difference between the energy of intermediate complex and the average energy of reactants. The energy of the former is greater than the average energy of either reactants or products.

(d) Reaction involving free radicals may have zero activation energy.

17. (c) A catalyst increases the rates of forward and backward reactions and not the relative amounts of reactants and products.

(d) It is given as $[A]_0(1/2)^n$.

18. (c) It is written as $2\mathrm{d}[O_2]/\mathrm{d}t$.

19. (a) It is $-k/2.203$. (d) It is of zero order.

26. (a) It decrease with time (i.e. with the progress of the reaction).

(b) The rate of reaction is one half of the rate of appearance of concentration of B, i.e., $r = \dfrac{1}{2}\dfrac{\mathrm{d}[B]}{\mathrm{d}t}$.

Linked Comprehension Type

1. **(i)** In experiments 1 and 2, $(p_{NO})_0 > (p_{H2})_0$ and thus the rate law may be written as

$$\frac{\mathrm{d}p(N_2O)}{\mathrm{d}t} = k'\,p_{H_2}$$

Since the reaction is of first order, its half-life time will be independent of partial pressure of H_2. Hence its $t_{0.5} = 19.2$ s.

In experiments 3 and 4, $(p_{H_2})_0 > (p_{NO})_0$ and thus the rate law may be written as

$$\frac{\mathrm{d}p(N_2O)}{\mathrm{d}t} = k''(p_{NO})^2$$

Since the reaction is of second order, its half-life time is inversely proportional to p_{NO}. Since in experiment 4, p_{NO} is twice of p_{NO} in experiment 3, the half life with respect to p_{NO} will be 830 s/2 = 415 s.

(ii) From experiment 1 (for which reaction is first order), we get $k' = \dfrac{0.693}{t_{0.5}} = \dfrac{0.693}{19.2\text{ s}} = 0.036\text{ s}^{-1}$

Since $k' = k(p_{NO})^2$, we get $k = \dfrac{k'}{(p_{NO})_0^2} = \dfrac{0.036\text{ s}^{-1}}{(600\text{ mmHg})^2} = 1 \times 10^{-7}\text{ mmHg}^{-2}\text{ s}^{-1}$

(iii) For experiment 5, we have $k_1 = \dfrac{0.693/t_{0.5}}{(p_{NO})^2} = \dfrac{0.693/9.6\text{ s}}{(600\text{ mmHg})^2} = 2.0 \times 10^{-7}\text{ mmHg}^{-2}\text{ s}^{-1}$

Now using Arrhenius equation ($k = A\exp(-E_a/RT)$), we get

$$\ln k_2 = \ln A - E_a/RT_2 \quad\text{and}\quad \ln k_1 = \ln A - E_a/RT_1$$

Hence $\ln k_2 - \ln k_1 = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

or $E_a = \dfrac{2.303\,R\{\log(k_2/k_1)\}T_1T_2}{T_2 - T_1} = \dfrac{(2.303)(8.314\text{ J K}^{-1}\text{ mol}^{-1})\log(2/1)(1100\text{ K})(1120\text{ K})}{(1120\text{ K} - 1100\text{ K})}$

$= 355 \times 10^3\text{ J mol}^{-1} = 355\text{ kJ mol}^{-1}$

2. **(i)** For the reaction

$$\begin{array}{lcccc} & CH_3COCH_3(g) & \rightarrow CH_4(g) & + CO(g) & + H_2(g) \\ t = 0 & p_0 & 0 & 0 & 0 \\ t & p_0 - p & p & p & p \end{array}$$

Total pressure at time $t = (p_0 - p) + p + p + p = p_0 + 2p$

At 1600 s, $p_{total} = 600$ Torr. Hence 600 Torr = 300 Torr + $2p$. This gives $p = 150$ Torr

At 3200 s, $p_{total} = 750$ Torr. Hence 750 Torr = 300 Torr + $2p$. This gives $p = 225$ Torr

The partial pressures of CH_3COCH_3 at these times are 300 Torr – 150 Torr = 150 Torr and 300 Torr – 225 Torr = 75 Torr, respectively.

Hence, the partial pressures of $(CH_3)_2O$ changes as $300\text{ Torr} \xrightarrow{1600\text{ s}} 150\text{ Torr} \xrightarrow{1600\text{ s}} 75\text{ Torr}$

Since the time required to reduce the partial pressures to a half value is independent of partial pressure of CH_3COCH_3, it follows that is the order of the reaction is one.

(ii) The rate constant is $k = \dfrac{0\cdot693}{t_{0.5}} = \dfrac{0\cdot693}{1600\text{ s}} = 4.33 \times 10^{-4}\text{ s}^{-1}$

(iii) To reduce the concentration to one eighth, time required will be three half-life, i.e. 3 × 1600 = 4800 s.

3. **(i)** Since the half-life is not independent of p_0, the reaction is not of first order. Since it depends inversely on p_0, the reaction may be second order, for which, we must have $t_{0.5} \propto 1/p_0$, i.e. $t_{0.5}\,p_0$ = constant. From the given data, we find

$$(425\text{ s})(350\text{ mmHg}) = 148750\text{ mmHg s} \quad\text{and}\quad (275\text{ s})(540\text{ mmHg}) = 148500\text{ mmHg s}$$

Since the two values are more or less identical, the reaction follows second-order kinetics.

(ii) The rate constant of the reaction is

$$k = \frac{1}{t_{0.5}\,a_0} = \frac{1}{(425\text{ s})(350\text{ mmHg})} = 6.72 \times 10^{-6}\text{ mmHg}^{-1}\text{ s}^{-1}$$

(iii) The integrated rate expression is

$$\frac{1}{p_t} - \frac{1}{p_0} = kt \quad\text{i.e.}\quad \frac{1}{300\text{ mmHg}} - \frac{1}{400\text{ mmHg}} = (6.72 \times 10^{-6}\text{ mmHg}^{-1}\text{ s}^{-1})t$$

or $$t = \frac{100}{300 \times 400 \times 6.72 \times 10^{-6}}\text{ s} = 124.0\text{ s}$$

4. **(i)** The Arrhenius equation is $k = A\ \mathrm{e}^{-E_\mathrm{a}/RT}$. This gives $\log k = \log A - \dfrac{E_\mathrm{a}}{2.303\mathrm{R}}\dfrac{1}{T}$

$$\text{Thus } E_{\mathrm{a(f)}} = (2.303\ \mathrm{R})\left(\frac{26000\mathrm{K}}{4.58}\right) = (2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\left(\frac{26000\ \mathrm{K}}{4.157}\right)$$

$$= 119756\ \mathrm{J\ mol^{-1}} \simeq 120\ \mathrm{kJ\ mol^{-1}}$$

$$E_{\mathrm{a(b)}} = (2.303\ \mathrm{R})\left(\frac{52400\mathrm{K}}{4.375}\right) = (2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\left(\frac{52500\mathrm{K}}{4.375}\right)$$

$$= 229766\ \mathrm{J\ mol^{-1}} \simeq 230\ \mathrm{kJ\ mol^{-1}}$$

(ii) The value of $\Delta_\mathrm{r}H$ is $\Delta_\mathrm{r}H = E_{\mathrm{a(f)}} - E_{\mathrm{a\,(b)}} = (120 - 230)\ \mathrm{kJ\ mol^{-1}} = -\ 110\ \mathrm{kJ\ mol^{-1}}$

(iii) The standard equilibrium constant of the reaction is

$$K^\circ_\mathrm{eq} = \frac{k_\mathrm{b}/\mathrm{s^{-1}}}{k_\mathrm{f}/\mathrm{M^{-1}\ s^{-1}}} = \frac{\text{antilog}\,[30.0 - 52500/(4.375\times300)]}{\text{antilog}\,[8.848 - (26000)/(4.157\times300)]} = \frac{1\times10^{-10}}{1\times10^{-12}} = 10^2$$

5. **(i)** In experiments 1 and 2, the $[\mathrm{OCl^-}]$ is changed while those of $\mathrm{I^-}$ and $\mathrm{OH^-}$ are constant. Since the $[\mathrm{OCl^-}]$ and $\mathrm{d}[\mathrm{IO_3^-}]/\mathrm{d}t$ are doubled in experiment 2 as compared to experiment 1, it is concluded that the order of $\mathrm{OCl^-}$ is reaction with respect to 1. The same conclusion is drawn from experiments 1 and 3 where the concentration of $\mathrm{I^-}$ is changed, i.e. the order of reaction with respect to $\mathrm{I^-}$ is 1.

From experiments 1 and 4, it is obvious that on decreasing the concentration of $\mathrm{OH^-}$ to a half value, the rate of reaction is doubled. Hence, it may be concluded that the order of the reaction with respect to $\mathrm{OH^-}$ is $-$ 1.

Hence, the rate law is $\dfrac{\mathrm{d}\left[\mathrm{IO_3^-}\right]}{\mathrm{dt}} = k\dfrac{\left[\mathrm{OCl^-}\right]\left[\mathrm{I^-}\right]}{\left[\mathrm{OH^-}\right]}$

(ii) Taking data from experiment 1, we get

$$1.75\times10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}} = k\frac{(0.0017\mathrm{M})\,(0.0017\mathrm{M})}{(1\,\mathrm{M})} \quad\Rightarrow\quad k = \frac{1.75\times10^{-4}}{(0.0017)^2}\ \mathrm{s^{-1}} = 60.55\ \mathrm{s^{-1}}$$

(iii) $\dfrac{\mathrm{d}\left[\mathrm{IO_3^-}\right]}{\mathrm{d}t} = (60.55\ \mathrm{s^{-1}})\ \dfrac{(0.004\ \mathrm{M})(0.002\ \mathrm{M})}{(0.5\,\mathrm{M})} = 9.7\times10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$

6. **(i)** From the chemical equation $\mathrm{A(g)} \rightarrow \mathrm{2B(g)} + \mathrm{C(g)}$ we find that the decomposition of one gaseous molecule gives three molecules of gaseous products. Therefore, the initial pressure of A will be one third of the pressure obtained after very long time from the initiation of reaction. Hence

$$p_\mathrm{A} = 270\ \mathrm{mmHg}/3 = 90\ \mathrm{mmHg}.$$

(ii) If p is the partial pressure of A that has decomposed after 10 min, we will have

i.e. $p_\mathrm{A} + p_\mathrm{B} + p_\mathrm{C} = 176\ \mathrm{mmHg}$ i.e. $(p_\mathrm{A})_0 - p + 2p + p = (p_\mathrm{A})_0 + 2p = 176\ \mathrm{mmHg}$

$$\text{Hence}\quad p = \frac{176\ \mathrm{mmHg} - (p_\mathrm{A})_0}{2} = \frac{176\ \mathrm{mmHg} - 90\ \mathrm{mmHg}}{2} = 43\ \mathrm{mmHg}$$

The partial pressure of A at this stage will be

$$p_\mathrm{A} = (p_\mathrm{A})_0 - p = 90\ \mathrm{mmHg} - 43\ \mathrm{mmHg} = 47\ \mathrm{mmHg}$$

(iii) The rate constant of the reaction will be

$$k = \frac{2.303\log\left[p_\mathrm{A}/(p_\mathrm{A})_0\right]}{t} = \frac{2.303\log\,[47/90]}{(10\times60\ \mathrm{s})} \simeq 1.1\times10^{-3}\ \mathrm{s^{-1}}$$

7. **(i)** The variations of k_1 and k_2 are given by the expressions

$$\frac{\mathrm{d}k_1}{\mathrm{d}T} = -\frac{E_1}{R}\,(A_1\,\mathrm{e}^{-E_1/RT}) = -\frac{E_1}{R}\,k_1 \quad \text{and} \quad \frac{\mathrm{d}k_2}{\mathrm{d}T} = -\frac{E_2}{R}\,(A_1\,\mathrm{e}^{-E_2/RT}) = -\frac{E_2}{R}\,k_2$$

If k is the rate constant for the disappearance of A with pre-exponential factor A and the activation energy E, then

$$\frac{\mathrm{d}k}{\mathrm{d}T} = -\frac{E}{R}\,(A\ \mathrm{e}^{-E/RT}) = -\frac{E}{R}\,k.$$

Since $k = k_1 + k_2$, we will have

Thus $$\frac{\mathrm{d}k}{\mathrm{d}T} = \frac{\mathrm{d}k_1}{\mathrm{d}T} + \frac{\mathrm{d}k_2}{\mathrm{d}T} = -\frac{E}{R}(k_1 + k_2) = -\frac{E_1}{R}k_1 - \frac{E_2}{R}k_2 \quad \text{or} \quad E = \frac{E_1\,k_1 + E_2\,k_2}{(k_2 + k_2)}$$

(ii) When the rates of formation B and C are identical, then

i.e. $$k_1 = k_2 \quad \text{i.e.} \quad A_1\mathrm{e}^{-E_1/RT} = A_2\mathrm{e}^{-E_2/RT}$$

or $$\frac{\mathrm{e}^{-E_2/RT}}{\mathrm{e}^{-E_1/RT}} = \frac{A_1}{A_2} \quad \text{or} \quad \mathrm{e}^{-(E_2-E_1)/RT} = \frac{A_1}{A_2} \quad \text{or} \quad \frac{-(E_2 - E_1)}{RT} = \ln\frac{A_1}{A_2} \quad \text{or} \quad T = \frac{(E_1 - E_2)}{R\ln(A_1/A_2)}$$

Substituting the values, we get

$$T = \frac{(126000 - 48830)\,\mathrm{J\ mol^{-1}}}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(2.303)\log(10^{15}/10^{13})} = \frac{41570\ \mathrm{K}}{(8.314)(2.303)(2)} = 1086\ \mathrm{K}$$

(iii) We have $-\dfrac{\mathrm{d[X]}}{\mathrm{d}t} = k_1[\mathrm{X}] + k_2[\mathrm{X}] = (k_1 + k_2)\,[\mathrm{X}]$

This gives $$\ln\frac{[\mathrm{X}]}{[\mathrm{X}]_0} = -\,(k_1 + k_2)\,t \quad \text{or} \quad [\mathrm{X}] = [\mathrm{X}]_0\ \mathrm{e}^{-(k_1+k_2)\,t}$$

The rate of formation of A is $$\frac{\mathrm{d[A]}}{\mathrm{d}t} = k_1[\mathrm{X}] = k_1[\mathrm{X}]_0\ \mathrm{e}^{-(k_1+k_2)\,t}$$

which on integration gives $$[\mathrm{A}] = \frac{k_1[\mathrm{X}]_0}{-(k_1 + k_2)}\mathrm{e}^{-(k_1+k_2)t} + \text{constant}$$

Since [A] = 0 at $t = 0$, constant $= k_1[\mathrm{X}]_0/(k_1 + k_2)$

Hence $$[\mathrm{A}] = -\frac{k_1[\mathrm{X}]_0}{k_1 + k_2}\mathrm{e}^{-(k_1+k_2)t} + \frac{k_1[\mathrm{X}]_0}{(k_1 + k_2)} = \frac{k_1[\mathrm{X}]_0}{(k_1 + k_2)}[1 - \mathrm{e}^{-(k_1+k_2)t}]$$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. A first-order reaction is 20% complete in 10 minutes. Calculate (i) the rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion. (1983)

Solution (i) For the first-order reaction, we have

$$k = -\frac{2.303}{t}\log\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\frac{2.303}{(10\ \mathrm{min})}\log\frac{80}{100} = 0.0223\ \mathrm{min^{-1}}$$

(ii) We have $t = -\dfrac{2.303}{k}\log\dfrac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\dfrac{2.303}{(0.0223\ \mathrm{min}^{-1})}\log\dfrac{25}{100} = 62.18\ \mathrm{min}.$

2. While studying the decomposition of gaseous N_2O_5 it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation? (1985)

Solution For a first-order reaction, the integrated rate expression is

$$\log\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -\frac{k}{2.303}t \quad \text{i.e.} \quad \log[\mathrm{A}]_t = \log[\mathrm{A}]_0 - \frac{k}{2.303}t$$

Thus, a plot of log $\{[\mathrm{A}]_t/\mathrm{M}\}$ versus t is linear with slope equal to $-k/2.303$ and intercept equal to log $\{[\mathrm{A}]_0/\mathrm{M}\}$. Hence, from the given plot of log $p_{N_2O_5}$ versus time, we can calculate the rate constant from the slope of the plot. The half-life of the reaction can also be calculated from such a plot.

3. The first-order reaction has $k = 1.5 \times 10^{-6}\ \mathrm{s}^{-1}$ at 200 °C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed into the product? What is the half-life of this reaction? (1987)

Solution For the first-order reaction, we have $\log\dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -\dfrac{k}{2.303}t$

Substituting the given data, we get $\log\dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -\dfrac{1.5\times10^{-6}\mathrm{s}^{-1}}{2.303}(10\times60\times60\ \mathrm{s}) = -0.023\,45$

This gives $[\mathrm{A}]_t/[\mathrm{A}]_0 = 0.947\,4$

Percentage conversion of reactant into product = (1 – 0.947 4) × 100 = 5.26

The half-life of the reaction is $t_{0.5} = \dfrac{0.693}{k} = \dfrac{0.693}{1.5\times10^{-6}\,\mathrm{s}^{-1}} = 4.62\times10^5\ \mathrm{s}.$

4. A first-order reaction is 50 per cent completed in 30 min at 27 °C and in 10 min at 47 °C. Calculate the reaction rate constant at 27 °C and the energy of activation of the reaction. (1988)

Solution Rate constant at 27 °C $= \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{30\,\mathrm{min}} = 0.0231\ \mathrm{min}^{-1}$

Rate constant at 47 °C $= \dfrac{0.693}{10\,\mathrm{min}} = 0.0693\ \mathrm{min}^{-1}$

Now since $k = A\exp(-E_a/RT)$, we get $\log\dfrac{k_1}{k_2} = -\dfrac{E_a}{2.303R}\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)$

Hence, $E_a = -\dfrac{(2.303)R\ T_1T_2}{(T_2-T_1)}\log\dfrac{k_1}{k_2} = -\dfrac{(2.303)(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\,\mathrm{K})(320\ \mathrm{K})}{(320\,\mathrm{K}-300\,\mathrm{K})}\log\dfrac{0.0231}{0.0693}$

$= 43\,850\ \mathrm{J\ mol^{-1}} = 43.85\ \mathrm{kJ\ mol^{-1}}$

5. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4\times10^{13}\ \mathrm{s}^{-1}$ and 98.6 kJ mol^{-1}, respectively. If the reaction is of first-order, at what temperature will its half-life period be ten minutes? (1990)

Solution We have $t_{1/2} = 10$ min. Hence $k = 0.693/10\ \mathrm{min} = 0.0693\ \mathrm{min}^{-1} \simeq 0.001\,155\ \mathrm{s}^{-1}$

Now using the Arrhenius equation $k = A\,\mathrm{e}^{-E_a/RT}$ we get

$$\ln(k/\mathrm{s}^{-1}) = \ln(A/\mathrm{s}^{-1}) - \frac{E_a}{RT} \quad \text{or} \quad \log(k/\mathrm{s}^{-1}) = \log(A/\mathrm{s}^{-1}) - \frac{E_a}{2.303RT}$$

Substituting the given data, we get

$$\log 0.001\,155 = \log 4\times10^{13} - \frac{98.6\times10^3\ \mathrm{J\ mol^{-1}}}{(2.303)(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\,T}$$

or $-2.937\,4 = 13.602\,1 - \dfrac{5149.6}{(T/\mathrm{K})}$. Hence, $T = \dfrac{5149.6}{(13.6021+2.9374)}\ \mathrm{K} = 311.35\ \mathrm{K}.$

6. The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$ is a first-order reaction. After 30 min from the start of decomposition in a closed vessel, the total pressure developed is found to be 284.5 mmHg and on complete decomposition, the total pressure is 584.5 mmHg. Calculate the rate constant of the reaction. (1991)

Solution From the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ we find that 2 mol of $N_2O_5(g)$ on decomposition gives a total of 5 mol of gaseous species (4 mol NO_2 and 1 mol O_2). Hence, pressure of N_2O_5 to start with is given as

$$p_0 = (584.5\ \text{mmHg})\left(\frac{2}{5}\right) = 233.8\ \text{mmHg}$$

Now, the partial pressure of N_2O_5 after 30 min would be given as

$$p_t + (233.8\ \text{mmHg} - p_t)\left(\frac{5}{2}\right) = 284.5\ \text{mmHg} \quad \text{which gives} \quad p_t = 200\ \text{mmHg}$$

Now using the expression

$$\log\frac{p_t}{p_0} = -\frac{k}{2.303}\,t, \quad \text{we get} \quad \log\left(\frac{200}{233.8}\right) = -\left(\frac{k}{2.303}\right)(30\ \text{min})$$

$$\text{or} \qquad k = -\frac{(2.303)}{(30\ \text{min})}\log\frac{(200)}{(233.8)} = 5.21 \times 10^{-3}\ \text{min}^{-1}.$$

7. Two reactions (i) A → products and (ii) B → products follow first-order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K. (1992)

Solution Let us represent $T_1 = 300$ K and $T_2 = 310$ K.

Let the corresponding rate constants be represented as k_1 and k_2, respectively. Now for the reaction

$$\text{A} \rightarrow \text{product}$$

it is given that $k_2 = 2\,k_1$ and $k_2 = 0.693/30\ \text{min} = 0.0231\ \text{min}^{-1}$

Now using Arrhenius equation, we get

$$k_1 = A\exp(-\Delta E_A/RT_1) \qquad \text{and} \qquad k_2 = A\exp(-\Delta E_A/R\,T_2)$$

Therefore, $\dfrac{k_2}{k_1} = \exp\left\{\dfrac{\Delta E_A}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)\right\}$. Substituting $k_2/k_1 = 2$ and taking logarithm, we get

$$\ln 2 = \frac{\Delta E_A}{R}\left(\frac{T_2 - T_1}{T_1\,T_2}\right) \qquad \text{i.e.} \qquad \Delta E_A = \frac{R\,(\ln 2)\,T_2T_1}{(T_2 - T_1)}$$

Now for the reaction B → product we have

$$k_2' = 2\,k_2 = 2 \times 0.0231\ \text{min}^{-1} = 0.0462\ \text{min}^{-1} \quad \text{and} \quad \Delta E_B = \frac{1}{2}\,\Delta E_A = \frac{1}{2}\,\frac{R\,(\ln 2)\,T_2\,T_1}{(T_2 - T_1)}$$

The use of Arrhenius equation in this case gives

$$\frac{k_1'}{k_2'} = \exp\left\{\frac{\Delta E_B}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} = \exp\left\{\frac{1}{R}\left(\frac{1}{2}\,\frac{R\,(\ln 2)\,T_1\,T_2}{(T_2 - T_1)}\right)\left(\frac{T_1 - T_2}{T_1\,T_2}\right)\right\} = \exp\left(-\frac{\ln 2}{2}\right)$$

$$= \exp(\ln 2^{-1/2}) = 2^{-1/2}$$

$$\text{Hence,} \quad k_1' = \frac{1}{\sqrt{2}}\,k_2' = \frac{0.0462\ \text{min}^{-1}}{\sqrt{2}} = 0.0327\ \text{min}^{-1}.$$

8. A first-order reaction, A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25 °C for 20 minutes, 25% decomposition took place. What will be per cent decomposition in the same time in a 30% solution maintained at 40 °C? Assume that activation energy remains constant in this range of temperature. (1993)

Solution For a first-order reaction, the fraction of reactants reacted is independent of initial concentration. Hence, we ignore the terms 20% solution and 30% solution. Now it is given that 25% of A is decomposed in 20 min at 25 °C. Hence, at this temperature, the rate constant is given as

$$k = \left(\frac{1}{t}\right)\left(2.303 \log \frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right) = \left(\frac{1}{20\,\mathrm{min}}\right)\left(2.303 \log \frac{100}{75}\right) = 1.439 \times 10^{-2}\ \mathrm{min}^{-1}$$

Now using Arrhenius equation, we calculate the rate constant at 40 °C.

We have $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

or $$\log k_2 - \log (1.439 \times 10^{-2}) = -\frac{(70 \times 10^3\ \mathrm{J\ mol^{-1}})}{(2.303)\,(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})}\left(\frac{1}{313.15\,\mathrm{K}} - \frac{1}{298.15\,\mathrm{K}}\right)$$

or $$\log k_2 + 1.842 = \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 313.15 \times 298.15} = 0.587$$

or $\log k_2 = 0.587 - 1.842 = -1.255$

or $k_2 = 5.56 \times 10^{-2}\ \mathrm{min}^{-1}$

Finally $$\log \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\left(\frac{k_2}{2.303}\right) t = -\left(\frac{5.56 \times 10^{-2}\ \mathrm{min}^{-1}}{2.303}\right)(20\ \mathrm{min}) = -0.482\,8 \quad \text{or} \quad \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = 0.33$$

Per cent of A remaining = 33% and Per cent of A decomposed = 67%.

9. The gas phase decomposition of dimethyl ether follows first-order kinetics

$$\mathrm{CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)}$$

The reaction is carried out at constant volume container at 500 °C and has a half-life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. (1993)

Solution We have

$$\begin{array}{llllll} & \mathrm{CH_3OCH_3(g)} & \rightarrow & \mathrm{CH_4(g)} + & \mathrm{H_2(g)} + & \mathrm{CO(g)} \\ t = 0 & p_0 & & 0 & 0 & 0 \\ t & p_0 - p & & p & p & p \end{array}$$

Total pressure of the system at time $t = p_0 + 2p$

The rate expression for first order kinetics is

$$\log \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\left(\frac{k}{2.303}\right) t$$

In the present case, we get

$$\log \frac{p_0 - p}{p_0} = -\frac{(0.693/t_{0.5})}{2.303}\, t = \frac{(-0.693/14.5\ \mathrm{min})}{2.303}\,(12\ \mathrm{min}) = -0.249 \quad \text{or} \quad \frac{p_0 - p}{p_0} = 0.564$$

$$p = p_0 - 0.564\,p_0 = p_0\,(1 - 0.564) = (0.40\ \mathrm{atm})\,(0.436) = 0.174\,4\ \mathrm{atm}$$

Hence, Total pressure of the system is $p_0 + 2p = (0.40 + 2 \times 0.174\,4)\ \mathrm{atm} = 0.748\,8\ \mathrm{atm}$.

10. From the following data for the reaction between A and B, calculate (i) the order of the reaction with respect to A and with respect to B, (ii) the rate constant at 300 K, (iii) the energy of activation, and (iv) the pre-exponential factor.

$[\mathrm{A}]/\mathrm{mol\ L^{-1}}$	$[\mathrm{B}]/\mathrm{mol\ L^{-1}}$	Initial rate/$\mathrm{mol\ L^{-1}\ s^{-1}}$ at	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-2}	1.6×10^{-2}	–

(1994)

Solution (i) Let a and b be the orders of the reaction with respect to A and B, respectively. We will have

$$r_0 = k\,[\mathrm{A}]_0^a\,[\mathrm{B}]_0^b$$

Making use of the second and third data in the given table, we get

$$4.0 \times 10^{-3}\ \mathrm{M\ s^{-1}} = k\,[5.0 \times 10^{-4}\ \mathrm{M}]^a\ \ [6.0 \times 10^{-5}\ \mathrm{M}]^b$$

$$1.6 \times 10^{-2}\ \mathrm{M\ s^{-1}} = k\,[1.0 \times 10^{-3}\ \mathrm{M}]^a\ [6.0 \times 10^{-5}\ \mathrm{M}]^b$$

Dividing the two expressions, we get

$$\frac{1.6\times10^{-2}}{4.0\times10^{-3}} = \left[\frac{1.0\times10^{-3}}{5.0\times10^{-4}}\right]^a \qquad \text{i.e.} \qquad 4 = 2^a. \qquad \text{Hence,} \qquad a = 2$$

From the first and second data, we write

$$5.0 \times 10^{-4}\ \mathrm{M\ s^{-1}} = k\,(2.5 \times 10^{-4}\ \mathrm{M})^2(3.0 \times 10^{-5}\ \mathrm{M})^b$$

$$4.0 \times 10^{-3}\ \mathrm{M\ s^{-1}} = k\,(5.0 \times 10^{-4}\ \mathrm{M})^2\ (6.0 \times 10^{-5}\ \mathrm{M})^b$$

Dividing these two expressions, we get

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}} = \left(\frac{5.0\times10^{-4}}{2.5\times10^{-4}}\right)^2\left(\frac{6.0\times10^{-5}}{3.0\times10^{-5}}\right)^b \qquad \text{i.e.} \qquad 8 = 2^2\,2^b. \qquad \text{Hence,} \qquad b = 1.$$

Thus, the order of reaction with respect to A and B are 2 and 1, respectively.

(ii) The rate constant is $\quad k = \dfrac{r_0}{[\mathrm{A}]_0^2\ [\mathrm{B}]_0}$

From the first data at 300 K, we get

$$k = \frac{5.0\times10^{-4}\ \mathrm{M\ s^{-1}}}{(2.5\times10^{-4}\ \mathrm{M})^2\ (3.0\times10^{-5}\ \mathrm{M})} = 2.67 \times 10^8\ \mathrm{M^{-2}\ s^{-1}}$$

(iii) To calculate the energy of activation, we make use of Arrhenius equation $\quad k = A\exp(-E_a/RT)$
For two temperatures, we get

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad \text{or} \quad \log\frac{r_2}{r_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad (\text{since } r \propto k)$$

where r_2 and r_1 refer to the two rates at two temperatures for the same initial concentrations of A and B. Making use of the first data, we get

$$\log\left(\frac{2.0\times10^{-3}}{5.0\times10^{-4}}\right) = \frac{E_a}{(2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})}\left(\frac{1}{300\,\mathrm{K}}-\frac{1}{320\,\mathrm{K}}\right)$$

Hence, $\quad E_a = \dfrac{(2.303)\ (8.314)\ (300)\ (320)\ (\log 4.0)}{(320-300)}\ \mathrm{J\ mol^{-1}} = 5.533 \times 10^4\ \mathrm{J\ mol^{-1}} = 55.33\ \mathrm{kJ\ mol^{-1}}$

(iv) Taking logarithm of Arrhenius equation, we get

$$\ln\,(k/\mathrm{M^{-2}s^{-1}}) = \ln\,(A/\mathrm{M^{-2}s^{-1}}) - \frac{E_a}{RT} \qquad \text{or} \qquad \log\,(A/\mathrm{M^{-2}\ s^{-1}}) = \log\,(k/\mathrm{M^{-2}\ s^{-1}}) + \frac{E_a}{2.303\,RT}$$

Substituting the first data, we get

$$\log\frac{A}{\mathrm{M^{-2}\ s^{-1}}} = \log\,(2.67 \times 10^8) + \frac{5.533\times10^4\ \mathrm{J\ mol^{-1}}}{(2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ (300\ \mathrm{K})}$$

$$= 8.426\,5 + 9.632\,4 = 18.058\,9$$

or $$A = 1.145 \times 10^8\ \mathrm{M^{-2}\ s^{-1}}.$$

11. At 380 °C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450 °C. (1995)

Solution The rate constant at 380 °C is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{360\,\text{min}} = 1.925 \times 10^{-3}\ \text{min}^{-1}$$

Substituting the data

$T_1 = (380 + 273)\ \text{K} = 653\ \text{K}$ $\quad k_1 = 1.925 \times 10^{-3}\ \text{min}^{-1}$

$T_2 = (450 + 273)\ \text{K} = 723\ \text{K}$ $\quad k_2 = ?$

$E_a = 200 \times 10^3\ \text{J mol}^{-1}$

in the expression

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a\,(T_2 - T_1)}{2.303\,R\,(T_1T_2)}$$

we get $\log\left(\dfrac{k_2}{1.925 \times 10^{-3}\ \text{min}^{-1}}\right) = \dfrac{(200 \times 10^3\ \text{J mol}^{-1})\,(723\ \text{K} - 653\ \text{K})}{(2.303)\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(653\ \text{K})\,(723\ \text{K})}$

or $\log\,(k_2/\text{min}^{-1}) = \log\,(1.925 \times 10^{-3}) + 1.548\,7 = -2.715\,6 + 1.548\,7 = -1.166\,9 = \bar{2}.833\,1$

$k_2 = 6.81 \times 10^{-2}\ \text{min}^{-1}$

Now for the first order kinetics, we have $\log \dfrac{[A]}{[A]_0} = -\dfrac{k}{2.303}\,t$. Substituting the data, we get

$$t = -\frac{2.303}{k}\log\frac{[A]}{[A]_0} = -\frac{2.303}{(6.81 \times 10^{-2}\ \text{min}^{-1})}\log\left(\frac{25}{100}\right) = 20.36\ \text{min.}$$

12. The gaseous reaction $A(g) \rightarrow 2B(g) + C(g)$ is observed to be of the first order. On starting with pure A, it is found that at the end of 10 min, the total pressure of the system is 176 mmHg and after a long time it is 270 mmHg. Calculate (a) the initial pressure of A, (b) the partial pressure of A after 10 min, and (c) the rate constant of the reaction.

Solution (a) From the chemical equation $A(g) \rightarrow 2B(g) + C(g)$
we find that a single gaseous molecule produces three gaseous molecules. After a long time, the pressure of the system is 270 mmHg. At this stage, it can be assumed that the whole of A has decomposed to give B and C. Hence, the initial pressure of A would be

$$p_A = \frac{270\ \text{mmHg}}{3} = 90\ \text{mmHg}$$

(b) If p is the decrease in partial pressure of A due to the decomposition of A, the partial pressures of B and C at this stage would be $2p$ and p, respectively. The total pressure at this stage would be

$$p_A + p_B + p_C = 176\ \text{mmHg} \quad \text{i.e.} \quad (90\ \text{mmHg} - p) + 2p + p = 176\ \text{mmHg}$$

or $p = \dfrac{(176 - 90)\ \text{mmHg}}{2} = 43\ \text{mmHg}$

Hence, partial pressure of A at this stage is $p_A = (90 - 43)\ \text{mmHg} = 47\ \text{mmHg}$

(c) Using the expression $\ln \dfrac{p_A}{(p_A)_0} = -kt$ we get $\ln \dfrac{47}{90} = -k\,(10 \times 60\ \text{s})$

Hence, $k = -\dfrac{2.303 \log (47/90)}{(10 \times 60\,\text{s})} = 1.08 \times 10^{-3}\ \text{s}^{-1}$.

13. The rate constant for the first-order decomposition of $N_2O_5(g)$ to $NO_2(g)$ and $O_2(g)$ is $7.48 \times 10^{-3}\ \text{s}^{-1}$ at a given temperature. (a) Determine the length of time required for the total pressure in a system containing N_2O_5 at an initial pressure of 0.1 atm to rise to 0.145 atm. (b) Find the total pressure after 100 s of the reaction.

Solution The required equation is

$$\begin{array}{cccc} & 2N_2O_5(g) \rightarrow & 4NO_2(g) & + \ O_2(g) \\ t = 0 & p_0 & 0 & 0 \\ t & p_0 - 2p & 4p & p \end{array}$$

Total pressure of the system is $p_{\text{total}} = p_{N_2O_5} + p_{NO_2} + p_{O_2} = (p_0 - 2p) + 4p + p = p_0 + 3p$

The partial pressure of $p_{N_2O_5}$ is given by the expression

$$p_{N_2O_5} = p_0 - 2p = p_0 - \tfrac{2}{3}(p_{\text{total}} - p_0) = \tfrac{5}{3}\,p_0 - \tfrac{2}{3}\,p_{\text{total}} \tag{1}$$

(a) When $p_{\text{total}} = 0.145$ atm, the partial pressure of N_2O_5 is

$$p_{N_2O_5} = \tfrac{5}{3}(0.1 \text{ atm}) - \tfrac{2}{3}(0.145 \text{ atm}) = 0.07 \text{ atm}$$

Now, using the expression $\log \dfrac{p_0}{p} = \dfrac{k}{2.303}\,t$, we get

$$t = \frac{2.303}{k}\log\frac{p_0}{p} = \frac{2.303}{(7.48\times10^{-3}\text{ s})}\log\frac{0.1}{0.07} = 47.7 \text{ s}$$

(b) After 100 s, $p_{N_2O_5}$ will be given by the expression

$$\log\frac{p_0}{p} = \frac{k}{2.303}\,t \quad \text{i.e.} \quad \log\frac{0.1\,\text{atm}}{p} = \left(\frac{7.48\times10^{-3}\text{ s}^{-1}}{2.303}\right) = (100\text{ s})$$

or $\log(p/\text{atm}) = -1.0 - 0.325 = -1.325$ or $p = 0.047$ atm

Finally from Eq. (1), we get $p_{\text{total}} = \dfrac{3}{2}\left(\dfrac{5}{3}p_0 - p\right) = \dfrac{3}{2}\left(\dfrac{5}{3}\times 0.1\,\text{atm} - 0.047\,\text{atm}\right) = 0.180$ atm.

14. The half-life for the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ is 2.4 h at 30 °C. (a) Starting with 10 g, what is the mass of N_2O_5 left after 9.6 h? (b) How much time is required to reduce 5.0×10^{10} molecules of N_2O_5 to 1.0×10^8 molecules?

Solution We have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4\times60\times60\,\text{s}} = 8.02\times10^{-5}\text{ s}^{-1}$$

(a) Now using the expression $\log\dfrac{m}{m_0} = -\dfrac{k}{2.303}\,t$, we get

$$\log\frac{m}{10\,\text{g}} = -\left(\frac{8.02\times10^{-3}\text{ s}^{-1}}{2.303}\right)(9.6\times60\times60\text{ s}) = -1.2035$$

or $\dfrac{m}{10\,\text{g}} = 0.0625$ or $m = 0.625$ g

(Note that 9.6 h is four half life, hence, $m = m_0/2^4 = 10\text{ g}/16 = 0.625$ g.)

(b) Using the expression $\log\dfrac{N}{N_0} = -\dfrac{k}{2.303}\,t$, we get

$$t = -\frac{2.303}{k}\log\frac{N}{N_0} = -\frac{2.303}{(8.02\times10^{-5}\text{ s}^{-1})}\log\left(\frac{1.0\times10^8}{5.0\times10^{10}}\right) = 77\,503\text{ s} \equiv 21.52\text{ h.}$$

15. Show that for a first-order reaction, A → products, the time required for the successive reduction in the concentration of A by a constant factor is independent of the initial concentration of A.

Solution Let the concentration of A be reduced by a factor of m, i.e. $[A]_t = [A]_0/m$

For successive reduction by the same factor, we express the above equation as $[A]_t = [A]_0/m^n$ where n is the number of successive stages of reduction. Substitution of the above expression in the rate expression for the first order reaction

$$\log \frac{[A]_t}{[A]_0} = -\left(\frac{k}{2.303}\right) t \quad \text{gives} \quad \log \frac{1}{m^n} = -\left(\frac{k}{2.303}\right) t$$

or $t = \dfrac{2.303\, n \log m}{k}$ which is independent of the initial concentration of A.

16. For the first-order decomposition reaction $(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$ in the gaseous phase, the pressures of the system at $t = 0$ and $t = 15$ min were found to be 169.3 Torr and 256.0 Torr, respectively. Calculate (a) the rate constant of the reaction, (b) half-life period and (c) the pressure of the system at 9 min.

Solution For the given reaction, we have

$$\begin{array}{llll} & (CH_3)_3COOC(CH_3)_3 & \rightarrow 2CH_3COCH_3 & + \; C_2H_6 \\ t = 0 & p_0 & 0 & 0 \\ t & p_0 - p & 2p & p \end{array}$$

Total pressure at time t, $p_t = p_0 + 2p$

Thus from the given data at $t = 0$ and $t = 15$ min, we get 256.0 Torr = 169.3 Torr + $2p$

or $p = \dfrac{(256 - 169.3)\text{ Torr}}{2} = 43.35$ Torr. Hence, $p_0 - p = (169.3 - 43.35)$ Torr = 125.95 Torr

(a) Now using the integrated expression, $\log \dfrac{p_0 - p}{p_0} = -\dfrac{k}{2.303}\, t$, we get (1)

$$k = -\frac{2.303}{(15\text{ min})} \log \left(\frac{125.95}{169.3}\right) = -\frac{2.303}{(15\text{ min})}(-0.1285) = 0.019\,7\text{ min}^{-1}$$

(b) The half-life period is $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{(0.0197\text{ min}^{-1})} = 35.18$ min

(c) Substituting the data in Eq. (1), we get

$$\log \left(\frac{169.3\text{ Torr} - p}{169.3\text{ Torr}}\right) = -\frac{(0.019\,7\text{ min}^{-1})}{(2.303)}(9\text{ min}) = -0.076 \quad \text{or} \quad \frac{169.3\text{ Torr} - p}{169.3\text{ Torr}} = 0.837$$

This gives $p = 27.50$ Torr. Hence, $p_{\text{total}} = p_0 + 2p = (169.3 + 2 \times 27.50)$ Torr = 224.3 Torr.

17. Azomethane decomposes according to the equation $(CH_3)_2N_2(g) \rightarrow C_2H_6(g) + N_2(g)$ The reaction was studied in a 200-mL flask at 300 °C. The data obtained were as follows.

t/min	0	15	30	48	75
p_{total}/Torr	36.2	42.4	46.5	53.1	59.3

Calculate the rate constant and the half-life for this reaction

Solution we have

$$\begin{array}{llll} & (CH_3)_2N_2(g) & \rightarrow C_2H_6(g) & + \; N_2(g) \\ t = 0 & p_0 & 0 & 0 \\ t & p_0 - p & p & p \end{array}$$

Total pressure at time t, $p_{\text{total}} = p_0 + p$

The partial pressure of $(CH_3)_2N_2(g)$ at any time will be given as

$$p_{(CH_3)_2N_2} = p_0 - p = p_0 - (p_{\text{total}} - p_0) = 2p_0 - p_{\text{total}}$$

Hence, we have

t/min	0	15	30	48	75
$p_{(CH_3)_2N_2}$/Torr	36.2	30.0	25.9	19.3	13.1

Table 1 records the calculations for the evaluation of rate constant

$$\text{Average value of } k = 1.26 \times 10^{-2}\ \text{min}^{-1}$$

$$\text{Half-life} = \frac{0.693}{k} = \frac{0.693}{1.26 \times 10^{-2}\ \text{min}^{-1}} = 55\ \text{min}$$

(Alternatively, the value of k may be determined from the slope of straight-line plot of log $p_{(CH_3)_2N_2}$ versus t, slope = – k/2.303.)

Table 1 Evaluation of rate constant

t/min	$k = -\dfrac{2.303}{t} \log \dfrac{p_{(CH_3)_2N_2}}{p_0}$	t/min	$k = -\dfrac{2.303}{t} \log \dfrac{p_{(CH_3)_2N_2}}{p_0}$
15	$k = -\dfrac{2.303}{15\,\text{min}} \log \dfrac{25.9}{36.2} = 1.25 \times 10^{-2}\ \text{min}^{-1}$	30	$k = -\dfrac{2.303}{30\,\text{min}} \log \dfrac{25.9}{36.2} = 1.11 \times 10^{-2}\ \text{min}^{-1}$
48	$k = -\dfrac{2.303}{48\,\text{min}} \log \dfrac{19.3}{36.2} = 1.31 \times 10^{-2}\ \text{min}^{-1}$	75	$k = -\dfrac{2.303}{75\,\text{min}} \log \dfrac{13.1}{36.2} = 1.36 \times 10^{-2}\ \text{min}^{-1}$

18. For the reaction $2NO + H_2 \rightarrow N_2O + H_2O$ the value of $-\mathrm{d}p/\mathrm{d}t$ was found to be 1.50 Torr s^{-1} for a pressure of 359 Torr of NO and 0.25 Torr s^{-1} for a pressure of 152 Torr, the pressure of H_2 being constant. On the other hand, when the pressure of NO was kept constant, $-\mathrm{d}p/\mathrm{d}t$ was 1.60 Torr s^{-1} for a hydrogen pressure of 289 Torr and 0.79 Torr s^{-1} for a pressure of 147 Torr. Determine the the order of the reaction.

Solution For the given reaction, we write $\dfrac{\mathrm{d}p}{\mathrm{d}t} = k\, p_{NO}^{m}\ p_{H_2}^{n}$

For the constant hydrogen pressure, we may write $\dfrac{\mathrm{d}p}{\mathrm{d}t} = k'\, p_{NO}^{m}$

Substituting the given data, we get

$$1.50\ \text{Torr s}^{-1} = k'\,(359\ \text{Torr})^m \quad \text{and} \quad 0.25\ \text{Torr s}^{-1} = k'\,(152\ \text{Torr})^m$$

On dividing, we get

$$\frac{1.50}{0.25} = \left(\frac{359}{152}\right)^m \quad \text{or} \quad m = \frac{\log(1.50/0.25)}{\log(359/152)} = \frac{0.7782}{0.3773} \simeq 2$$

Similarly for the constant nitric oxide pressure, we get

$$n = \frac{\log(1.60/0.79)}{\log(289/147)} = \frac{0.3065}{0.2935} \simeq 1$$

Thus, the overall order of the reaction = $m + n = 3$.

19. For the bromination of acetone $CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^-$ the following data were obtained.

Expt No.	$[CH_3COCH_3]$ / mol dm^{-3}	$[Br]_2$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$(-[Br_2]/\mathrm{d}t)_0$ / mol dm^{-3} s^{-1}
1.	0.30	0.05	0.05	5.7×10^{-5}
2.	0.30	0.10	0.05	5.7×10^{-5}
3.	0.30	0.05	0.10	1.14×10^{-4}
4.	0.40	0.05	0.05	7.6×10^{-5}

Establish the rate law.

Solution In experiments 1 and 2, only the concentration of Br_2 is doubled, but the rate of reaction remains unaffected. It indicates that the reaction is zero-order with respect to Br_2.

In experiments 1 and 3, only the concentration of H^+ is doubled, its effect is to make the rate of reaction twice as fast. This indicates that the reaction is first-order with respect to H^+.

In experiments 1 and 4, only the concentration of CH_3COCH_3 is changed by a factor of 4/3. We find that the rate of reaction is also increased 4/3 times. Hence, the reaction is first-order with respect to CH_3COCH_3. Thus, the rate expression can be written as rate = k $[CH_3COCH_3]$ $[H^+]$.
The value of rate constant is

$$k = \frac{\text{rate}}{[CH_3COCH_3][H^+]} = \frac{5.7 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{(0.30\ \text{M})\ (0.05\ \text{M})} = 3.8 \times 10^{-3}\ \text{mol}^{-3}\ \text{dm3 s}^{-1}$$

20. For the reaction $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ the rate constant is 2.8×10^{-5} mol^{-1} dm^3 s^{-1} at 300 K and 7.0×10^{-1} mol^{-1} dm^3 s^{-1} at 400 K. Calculate (a) the energy of activation, (b) the pre-exponential factor, and (c) rate constant at 350 K.

Solution (a) The Arrhenius equation is

$$k = A\ \exp(-E_a/RT) \quad \text{or} \quad \log\ (k/k°) = \log\ (A/k°) - \frac{E_a}{2.303\,RT};\ \text{where } k° = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Hence, $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ or $E_a = \dfrac{2.303\,R\,T_1\,T_2}{(T_2 - T_1)} \log \dfrac{k_2}{k_1}$

Substituting the given data, we get

$$E_a = \left(\frac{2.303 \times 8.314 \times 300 \times 400}{100} \log \frac{7.0 \times 10^{-1}}{2.8 \times 10^{-5}}\right) \text{J mol}^{-1} = 101\,048\ \text{J mol}^{-1}$$

(b) The pre-exponential factor is

$$A = k\ \exp(E_a/RT) \quad \text{or} \quad \log\ (A/k°) = \log\ (k/k°) + E_a/2.303RT;\ \text{where } k° = 1\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Substituting the given data, we get

$$\log\ (A/k°) = \log\ (2.8 \times 10^{-5}) + \frac{101048}{2.303 \times 8.314 \times 300} = -\ 4.553 + 17.591 = 13.038$$

$$A = 1.091 \times 10^{13}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

(c) We have from Eq. (1)

$$\log\ (k/k°) = \log\ (1.091 \times 10^{13}) - \frac{101048}{2.303 \times 8.314 \times 350} = 13.038 - 15.076 = -\,2.038$$

Hence, $k = 9.16 \times 10^{-3}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$.

21. Rate of a reaction, A + B → product is given as a function of different initial concentrations of A and B.

$[A]/\text{mol L}^{-1}$	$[B]/\text{mol L}^{-1}$	$r_0/\text{mol L}^{-1}\ \text{min}^{-1}$
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. What is the half-life of A in the reaction? (1982)

Solution Inspection of the given data indicates that on doubling the concentration of A keeping that of B constant increases the initial rate of reaction to two fold. This implies that the reaction is first-order with respect to A. On the other hand, doubling the concentration of B keeping that of A constant has no affect on the initial rate of reaction. This implies that the reaction is zero-order with respect to B. Hence, the expression of rate of reaction is

$$\text{rate} = k\ [A]^1\ [B]^0 = k\ [A]$$

that is, the reaction is first-order with respect to A only.
To determine the half-life of A, we determine the rate constant using the above expression. Hence,

$$k = \frac{(\text{rate})_0}{[A]_0} = \frac{0.005\ \text{mol L}^{-1}\ \text{min}^{-1}}{0.01\ \text{mol L}^{-1}} = 0.5\ \text{min}^{-1}. \quad \text{Hence,} \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5\ \text{min}^{-1}} = 1.386\ \text{min.}$$

22. A catalyst lowers the activation energy for a certain reaction from 75 to 20 kJ mol^{-1}. What will be the effect on the rate of the reaction at 20 °C, other things being equal?

Solution According to the Arrhenius equation, we have

$$k = A \exp(-E_a/RT)$$

Hence, $k_1 = A \exp(-75 \text{ kJ mol}^{-1}/RT)$ and $k_2 = A \exp(-20 \text{ kJ mol}^{-1}/RT)$

Thus, $$\frac{k_2}{k_1} = \exp(55 \text{ kJ mol}^{-1}/RT) = \exp\left\{\frac{55 \text{ kJ mol}^{-1}}{(8.314\times10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(293 \text{ K})}\right\} = 6.39 \times 10^9.$$

23. The ionization constant of NH_4^+ in water is 5.6×10^{-10} at 25 °C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25 °C is 3.4×10^{10} L mol^{-1} s^{-1}. Calculate the rate constant for proton transfer from water of NH_3. (1996)

Solution We are given that

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = 5.6 \times 10^{-10}$$

$$NH_4^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_3 + H_2O \qquad k_f = 3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$$

The second equation can be generated as follows.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a$$

$$\text{Subtraction} \quad \underline{2\,H_2O \rightleftharpoons H_3O^+ + OH^-} \qquad K_w$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad K_{eq} = K_a/K_w$$

Also $K_{eq} = k_f/k_b$. Hence $\dfrac{k_f}{k_b} = \dfrac{K_a}{K_w}$

or $$k_b = k_f\left(\frac{K_w}{K_a}\right) = (3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1})\left(\frac{1.0\times10^{-14} \text{ mol}^2 \text{ L}^{-2}}{5.6\times10^{-10} \text{ mol L}^{-1}}\right) = 6.07 \times 10^5 \text{ s}^{-1}$$

24. 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 pre-exponential factor for the reaction is 3.56×10^9 s^{-1}, calculate its rate constant at 318 K and also the energy of activation. (1997)

Solution For a first-order reaction $\log \dfrac{[A]}{[A]_0} = -\dfrac{k}{2.303}t$

From the given data at two temperatures, we get

For $T_2 = 308$ K $\quad \log \dfrac{75}{100} = -\dfrac{k_2}{2.303}t$; For $T_1 = 298$ K $\quad \log \dfrac{90}{100} = -\dfrac{k_1}{2.303}t$

Dividing the two expressions, we get

$$\frac{\log(0.90)}{\log(0.75)} = \frac{k_1}{k_2} \quad \text{i.e.} \quad \frac{k_1}{k_2} = \frac{-0.0458}{-0.1249} = 0.3667$$

Now using the expression $\log \dfrac{k_1}{k_2} = -\dfrac{E_a}{2.303\,R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

we get $$\log(0.3667) = -\frac{E_a}{(2.303)(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}}\right]$$

or $$E_a = \frac{(2.303)(8.314)(298)(308)\log(0.3667)}{(308-298)} \text{ J mol}^{-1} = 76568 \text{ J mol}^{-1} \equiv 76.57 \text{ kJ mol}^{-1}$$

The Arrhenius equation becomes $\quad k = (3.56 \times 10^9 \text{ s}^{-1}) \exp(-76.57 \text{ kJ mol}^{-1}/RT)$

Hence, at 318 K we get

$$k = (3.56 \times 10^9\ \mathrm{s^{-1}})\ \exp\left[\frac{-76.57 \times 10^3\ \mathrm{J\ mol^{-1}}}{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})(318\ \mathrm{K})}\right] = (3.56 \times 10^9\ \mathrm{s^{-1}})\ \exp(-\ 28.96)$$

$$= (3.56 \times 10^9\ \mathrm{s^{-1}})\ (2.65 \times 10^{-13}) = 9.43 \times 10^{-4}\ \mathrm{s^{-1}}$$

25. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log\ (k/\mathrm{s^{-1}}) = 14.34 - (1.25 \times 10^4\ \mathrm{K})/T$$

(i) What is the energy of activation of this reaction?

(ii) At what temperature will its half-life be 256 minutes? (1997)

Solution The Arrehenius equation is

$$k = A\ \exp(-\ E_a/RT) \quad \text{or} \quad \log\ (k/\mathrm{s^{-1}}) = \log\ (A/\mathrm{s^{-1}}) - \frac{E_a}{2.303\ R}\frac{1}{T}$$

Comparing this expression with the given one, we get

$$\frac{E_a}{2.303\ R} = 1.25 \times 10^4\ \mathrm{K}$$

Hence, $E_a = (1.25 \times 10^4\ \mathrm{K})\ (2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) = 2.39 \times 10^5\ \mathrm{J\ mol^{-1}} = 239\ \mathrm{kJ\ mol^{-1}}$

(ii) The reaction is first order as the unit of rate constant is $\mathrm{s^{-1}}$. For a first-order reaction

$$t_{1/2} = 0.693/k$$

Hence, $$k = \frac{0.693}{256 \times 60\,\mathrm{s}} = 4.51 \times 10^{-5}\ \mathrm{s}$$

Substituting this in the given expression, we get

$$\log\ (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^{-5}\,\mathrm{K}}{T}$$

Solving for T, we get $T = 669$ K.

26. The rate constant of a reaction is $1.5 \times 10^7\ \mathrm{s^{-1}}$ at 50 °C and $4.5 \times 10^7\ \mathrm{s^{-1}}$ at 100 °C. Evaluate the Arrhenius parameters A and E_a. (1998)

Solution The Arrhenius equation is $k = A\ \exp(-\ E_a/RT)$

For the two temperatures, we get

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting the given data, we get

$$\log\frac{4.5 \times 10^7}{1.5 \times 10^7} = -\ \frac{E_a}{(2.303)(8.314\ \mathrm{J\ K^{-1}mol^{-1}})}\left[\frac{1}{373\ \mathrm{K}} - \frac{1}{323\ \mathrm{K}}\right]$$

or $$E_a = \frac{(2.303)\,(8.314)\,(373)\,(323)}{50}\ \log\ (3.0) = 22012.7\ \mathrm{J\ mol^{-1}}$$

The value of A would be

$$A = k\ \exp(E_a/RT) = (1.5 \times 10^7\ \mathrm{s^{-1}})\ \exp\left[\frac{22012.7\ \mathrm{J\ mol^{-1}}}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(323\ \mathrm{K})}\right]$$

$$= (1.5 \times 10^7\ \mathrm{s^{-1}})\ (3630.44) = 5.45 \times 10^{10}\ \mathrm{s^{-1}}$$

27. The rate constant for an isomerization reaction A → B is $4.5 \times 10^{-3}\ \mathrm{min^{-1}}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. (1999)

Solution From the unit of rate constant, it follows that the given isomerisation reaction is a first order reaction.

The concentration of A after 1 h as determined from the expression

$$\log \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\frac{k}{2.303}t$$

is $$\log([\mathrm{A}]/\mathrm{mol\ L^{-1}}) = -\frac{4.5 \times 10^{-3}\ \mathrm{min^{-1}}}{2.303}(60\ \mathrm{min}) = -0.1172 \qquad (\text{as } [\mathrm{A}]_0 = 1\mathrm{M})$$

$[\mathrm{A}] = 0.7634$ M.

28. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ $\mathrm{mol^{-1}}$. (2000)

Solution Using Arrhenius equation, we can write

$$k = A\ \mathrm{e}^{-E_1/RT_1} \quad \text{Also} \quad k = A\ \mathrm{e}^{-E_2/RT_2}$$

From these, it follows that

$$\mathrm{e}^{-E_1/RT_1} = \mathrm{e}^{-E_2/RT_2} \text{ or } \frac{E_1}{RT_1} = \frac{E_2}{RT_2} \Rightarrow \frac{E_1}{T_1} = \frac{E_2}{T_2}$$

Since $E_2 = E_1 - 20\ \mathrm{kJ\ mol^{-1}}$, we get

$$\frac{E_1}{T_1} = \frac{E_1 - 20\ \mathrm{kJ\ mol^{-1}}}{T_2} \qquad \text{or} \qquad E_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{20\ \mathrm{kJ\ mol^{-1}}}{T_2}$$

or $$E_1 = \frac{(20\ \mathrm{kJ\ mol^{-1}})(T_1)}{(T_1 - T_2)} = \frac{(20\ \mathrm{kJ\ mol^{-1}})(500\ \mathrm{K})}{(500-400)\ \mathrm{K}} = 100\ \mathrm{kJ\ mol^{-1}}$$

29. The progress of reaction $\mathrm{A} \rightleftharpoons n\mathrm{B}$, with time is presented in the Fig. 10.1. Determine (i) the value of *n*. (ii) the equilibrium constant, *K*, and (iii) the initial rate of conversion of A. (1994)

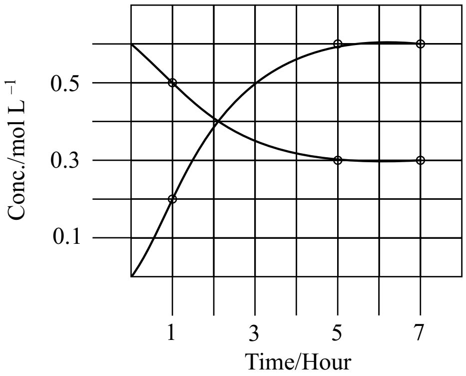


Fig. 10.1

Solution (i) From the given graph, we find that over the time interval 1 to 5 h,

$$\Delta[\mathrm{A}] = (0.3 - 0.5)\ \mathrm{M} = -0.2\ \mathrm{M} \quad \text{and} \quad \Delta[\mathrm{B}] = (0.6 - 0.2)\ \mathrm{M} = 0.4\ \mathrm{M}$$

that is, the obtained amount of B is twice as large as the consumption of A. Hence, *n* in the equation $\mathrm{A} \rightleftharpoons n\mathrm{B}$ is 2.

(ii) From the given graph, we find that $[\mathrm{A}]_{\mathrm{eq}} = 0.3$ M and $[\mathrm{B}]_{\mathrm{eq}} = 0.6$ M

Hence, $$K_{\mathrm{eq}} = \frac{[\mathrm{B}]^2}{[\mathrm{A}]} = \frac{(0.6\ \mathrm{M})^2}{0.3\ \mathrm{M}} = 1.2\ \mathrm{M}$$

(iii) In the time interval 0 to 1 h, the plot of [A] and [B] are almost linear. Hence, the initial rate of conversion of A may be evaluated over this time interval.

$$-\Delta[\mathrm{A}] = (0.6 - 0.5)\ \mathrm{M} = 0.1\ \mathrm{M}$$

Initial rate, $$-\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{0.1\ \mathrm{M}}{1\ \mathrm{h}} = 0.1\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

30. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 minutes and 0.03 mol L^{-1} s^{-1} at 20 minutes after initiation. Find the half life of the reaction. (2001)

Solution For a first-order reaction $A \rightarrow$ product, we can write

$$\text{rate} = -\frac{d[A]}{dt} = k[A]. \quad \text{Hence,} \int_{[A]_1}^{A} \frac{d[A]}{[A]} = k\int_{t_1}^{t_2} dt \quad \text{i.e.} \quad \ln\frac{[A]_1}{[A]_2} = k(t_2 - t_1)$$

$$\text{Also} \quad \frac{(\text{rate})_1}{(\text{rate})_2} = \frac{[A]_1}{[A]_2} \qquad \text{Hence} \quad \ln\frac{(\text{rate})_1}{(\text{rate})_2} = k(t_2 - t_1)$$

$$\text{This gives} \quad k = \frac{\ln\{(\text{rate})_1/(\text{rate})_2\}}{(t_2 - t_1)} = \frac{\ln(0.04/0.3)}{(20-10)\,\text{min}} = 2.88 \times 10^{-2}\ \text{min}^{-1}$$

$$\text{Finally} \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.88\times10^{-2}\ \text{min}^{-1}} = 24.09\ \text{min} \equiv 1445.3\ \text{s}.$$

31. The vapour pressure of two miscible liquids **A** and **B** are 300 and 500 mmHg respectively. In a flask 10 mol of **A** is mixed with 12 mol of **B**. However, as soon as **B** is added, B starts polymerizing into a completely insoluble solid. This polymerization follows first-order kinetics. After 100 minutes, 0.525 mol of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mmHg. Estimate the rate constant of the polymerization reaction. **Assume** negligible volume change on mixing and polymerization, and ideal behaviour for the final solution. (2001)

Solution We have

$$p_A^* = 300\ \text{mmHg} \quad \text{and} \quad p_B^* = 500\ \text{mmHg}$$

$$(n_A)_0 = 10\ \text{mol} \quad \text{and} \quad (n_B)_0 = 12\ \text{mol}$$

Let the amount of A after 100 min is reduced to n_A. At this stage,

$$n_{\text{total}} = n_A + n_B + n_{\text{solute}} = n_A + 12\ \text{mol} + 0.525\ \text{mol} = n_A + 12.525\ \text{mol}$$

The amount fractions of A and B in the solution will be

$$x_A = \frac{n_A}{n_A + 12.525\ \text{mol}} \quad \text{and} \quad x_B = \frac{12\ \text{mol}}{n_A + 12.525\ \text{mol}}$$

Since $p_{\text{total}} = x_A\, p_A^* + x_B\, p_B^*$, we get

$$400\ \text{mmHg} = \left(\frac{n_A}{n_A + 12.525\ \text{mol}}\right)(300\ \text{mmHg}) + \left(\frac{12\ \text{mol}}{n_A + 12.525\ \text{mol}}\right)(500\ \text{mmHg})$$

Solving for n_A, we get $n_A = 9.90$ mol

For the first-order kinetics, we have

$$\ln\frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad k = \frac{\ln[A]_t/[A]_0}{t} = \frac{\ln(9.90/10)}{100\ \text{min}} = 1.00 \times 10^{-4}\ \text{min}^{-1} = 1.68 \times 10^{-6}\ \text{s}^{-1}$$

32. For the reaction $I^- + OCl^- \rightarrow OI^- + Cl^-$ in basic aqueous solution, the following data were obtained.

(a) $[OCl^-]_0 = [OH^-]_0 = 0.1$ M

$[I^-]_0$/M	0.01	0.03	0.05
Initial rate/M s^{-1}	0.6	1.8	3.0

(b) $[I^-]_0 = [OH^-]_0 = 0.1$ M

$[OCl^-]_0$/M	0.01	0.03	0.05
Initial rate/M s^{-1}	0.6	1.8	3.0

(c) $[I^-]_0 = [OCl^-]_0 = 0.1$ M

$[OH^-]$/M	0.01	0.03	0.05
Initial rate/M s^{-1}	60	20	12

Determine (i) the orders of reaction with respect to I^-, OCl^- and OH^-, and (ii) the rate constant of the reaction. (2004)

Solution (i) From the data a, we find that the rate of reaction increases in proportion to the changed concentration of I^- indicating that the reaction is first order with respect to I^-.

From the data b, we find that the rate of reaction increases in proportion to the changed concentration of OCl^- indicating that the reaction is first order with respect to OCl^-.

From the data c, we find that the rate of reaction decreases in proportion to the changed concentration of OH^- indicating that the order of reaction with respect to OH^- is – 1.

Hence, the rate expression is $r = k\,\dfrac{[I^-][OCl^{-1}]}{[OH^-]}$

(ii) Using the data $[OCl^-]_0 = [OH^-]_0 = 0.1$ M and $[I^-]_0 = 0.01$ M, we get

$$k = (\text{rate})\left(\frac{[OH^-]}{[I^-][OCl]}\right) = (0.6\ \text{mol dm}^{-3}\ \text{s}^{-1})\left[\frac{0.1\ \text{mol dm}^{-3}}{(0.01\ \text{mol dm}^{-3})\,(0.1\ \text{mol dm}^{-3})}\right] = 60\ \text{s}^{-1}$$

Unsolved Problems

1. The following measurements of initial rate are made for varying concentrations of OH^- and $H_2PO_2^-$ ions

$[OH^-]$/M	0.21	0.28	0.21
$[H_2PO_2^-]$/M	0.35	0.35	0.52
r_0/mol dm^3	5.23×10^{-5}	9.30×10^{-5}	7.7×10^{-5}

Find the rate law for the reaction.

2. Substance A reacts according to a first-order rate law with $k = 5.0 \times 10^{-5}\ \text{s}^{-1}$. (a) If the initial concentration of A is 1.0 M, what is the initial rate and the rate after 1.0 h?

3. The gas phase decomposition of N_2O_5 to NO_2 and O_2 is monitored by measurement of total pressure. The following data are obtained.

p_{total}/atm	0.154	0.215	0.260	0.315	0.340
t/s	0	52	103	205	309

Determine the value of rate constant.

4. The decomposition of gaseous AsH_3 into solid arsenic and hydrogen gas may be followed by measuring the pressure at constant volume from time to time. In an experiment, the following data were obtained. Show that the decomposition of AsH_3 follows first-order kinetics. Determine its rate constant.

t/h	0	5.5	6.8	8
p/mmHg	733.32	805.78	818.11	835.34

5. Methyl acetate is hydrolysed with 1 N HCl at 25 °C. 5 cm^3 of the reacting mixture is withdrawn at various time intervals and is quickly titrated with 0.185 N NaOH. The volumes of NaOH consumed are as follows.

t/s	339	1 242	2 745	4 546	∞
V_{NaOH}/cm^3	26.34	27.80	29.70	31.81	39.81

Find the order of the reaction and its rate constant.

6. The rate of decomposition of N_2O_3(g) to NO_2(g) and NO(g) is followed by measuring $[NO_2]$ at different times. The following data are obtained.

$[NO_2]$/mol L^{-1}	0	0.193	0.316	0.427	0.78
t/s	0	884	1 610	2 460	50 000

Show that the reaction follows first-order rate law. Determine its rate constant.

7. The first-order decomposition of di-*tert*-butyl peroxide (DTBP) to acetone is given by the equation

$$C_8H_{18}O_2(g) \rightarrow 2CH_3COCH_3(g) + C_2H_6(g)$$

The reaction has a half-life time of 80 min at 147 °C. Starting with pure DTBP in a flask of constant volume at a pressure of 800 Torr, (a) at what time will the partial pressure of DTBP be 100 Torr, (b) at what time will the partial pressure of DTBP be 700 Torr, and (c) what will be the total gas pressure when the partial pressure of DTBP is 700 Torr?

8. For the reaction $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O$ the following data are obtained

$\dfrac{[H_2O_2]}{\text{mol L}^{-1}}$	$\dfrac{[I^-]}{\text{mol L}^{-1}}$	$\dfrac{[H^+]}{\text{mol L}^{-1}}$	$\dfrac{d[I_2]/dt}{\text{mol L}^{-1}\text{ s}^{-1}}$
0.01	0.01	0.10	1.75×10^{-6}
0.03	0.01	0.10	5.25×10^{-6}
0.03	0.02	0.10	1.05×10^{-5}
0.03	0.02	0.20	1.05×10^{-5}

Determine the expression of rate law along with the value of rate constant.

9. At 300 K, a first-order reaction is 50% complete in 20 min. At 350 K, the same reaction is 50% complete in 5.0 min. Calculate the activation energy of the reaction.

10. The half-life of a first-order reaction at 298 K is 21 833 s. If the value of pre-exponential factor in Arrhenius equation is $1.97 \times 10^{12}\ \text{s}^{-1}$, calculate its activation energy.

11. The activation energy of the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is 132.0 kJ mol^{-1} and the rate constant at 500 K is $2.02 \times 10^{-6}\ \text{L mol}^{-1}\ \text{s}^{-1}$. Find the rate constant at 550 K.

12. A substance A was found to undergo two parallel first-order rearrangements A → B and A → C with rate constants $1.26 \times 10^{-4}\ \text{s}^{-1}$ and $3.8 \times 10^{-5}\ \text{s}^{-1}$, respectively. What were the percentage distribution of B and C?

13. The first-order gaseous decomposition of N_2O_4 into NO_2 has a k value of $4.5 \times 10^3\ \text{s}^{-1}$ at 1°C and an energy of activation of 58 kJ mol^{-1}. At what temperature its half-life would be 6.93×10^{-5} s?

14. H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ mol^{-1} at 500 K and energy of activation equal to 77 kJ mol^{-1}. Estimate energy of activation for the bimolecular combination of two OH radicals to form H_2O and O.

15. The rate constant for the forward reaction is $1.2 \times 10^{-3}\ \text{mm}^{-1}$ at 30 °C. The enthalpies of activation and reaction are 85.48 kJ mol^{-1} and -107.1 kJ mol^{-1}, respectively. The rate constant for the reverse reaction is $1.2 \times 10^{-4}\ \text{min}^{-1}$ at 50 °C. What is its value at 40 °C?

16. The total pressure of the system for the equation $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ was observed as a function of time :

t/s	204	942	1686	2466	4944	7500	∞
p_{total}/Torr	325	335	345	355	385	415	594.2

Determine the order of the reaction and its rate constant.

17. The optical rotation of sucrose in 0.9 M HCl at 300 K at various times were found to be as follows.

t/min	0	15	30	45	60	∞
θ	+32.4°	+28.8°	+25.5°	+22.4°	+9.4°	−11.0°

Determine the order of reaction and its rate constant.

18. From the following data at a certain temperature show that the decomposition of H_2O_2 in aqueous solution is first-order reaction.

t/s	0	300	600	900	1200
V_{KMnO_4}/mL	22.8	17.7	13.8	10.6	8.2

Determine its rate constant.

19. The following data are obtained for the hydrolysis of ethyl acetate in the presence of HCl.

t/min	0	25	40	60	∞
V_{NaOH}/mL	19.2	24.2	26.6	29.5	42.1

where V_{NaOH} is the volume of NaOH solution used to neutralize acid present in certain volume of reacting mixture. Find the value of rate constant.

20. Two reactions of same order have equal pre-exponential factors but their activation energies differ by 24.9 kJ mol^{-1}. Calculate the ratio of the rate constants of these reactions at 300 K.

ANSWERS

1. rate = (3.39×10^{-3} mol^{-2} L^{2} s^{-1}) $[OH^-]^2$ $[H_2PO_2^-]$

2. $r_0 = 5.0 \times 10^{-5}$ mol L^{-1} s^{-1},
$r_{1h} = 4.175 \times 10^{-5}$ mol L^{-1} s^{-1}

3. 5.9×10^{-3} s^{-1}

4. 0.040 h^{-1}

5. first order, 1.25×10^{-4} s^{-1}

6. 3.20×10^{-4} s^{-1}

7. (a) 240 min, (b) 15 min, (c) 1000 Torr

8. rate = (1.75×10^{-2} mol^{-1} L s^{-1}) $[H_2O_2]$ $[I^-]$

9. 24.2 kJ mol^{-1}

10. 95.8 kJ mol^{-1}

11. 3.62×10^{-5} L mol^{-1} s^{-1}

12. 76.83% B and 23.17% of C

13. 283 K

14. 5 kJ mol^{-1}

15. 1.21×10^{-5} min^{-1}

16. first order, 5.81×10^{-5} s^{-1}

17. 5.8×10^{-3} min^{-1}

18. 8.5×10^{-4} s^{-1}

19. 9.9×10^{-3} min^{-1}

20. 2.162×10^{4}

CHAPTER 11

SURFACE CHEMISTRY

The term adsorption implies the presence of excess concentration of any particular component (known as adsorbate) at the surface of liquid or solid phase (known as adsorbent) as compared to that present in the bulk of the material. This is due to the presence of residual forces at the surface of the body. The process of adsorption is an exothermic process and is associated with a decrease in entropy of the system, such that $|\Delta H| < T\,\Delta S$ as ΔG of the process is negative.

On the basis of the forces of attraction between adsorbent and adsorbate, two types of adsorption, namely, physisorption (i.e. physical adsorption) and chemisorption, may be identified. Their characteristics are shown in Table 11.1.

Table 11.1 Characteristics of Physisorption and Chemisorption

Physisorption	*Chemisorption*
1. The forces of attractions are of van der Waals type (weak forces)	The forces of attraction are of a chemical nature (strong forces)
2. Predominates at low temperature	Predominates at high temperature
3. All gases show this adsorption at low temperatures	This is highly specific in nature
4. Heat of adsorption is low, about 40 kJ mol^{-1}	Heat of adsorption is large ($\simeq$ 80 to 420 kJ mol^{-1})
5. Reversible in nature	Usually irreversible
6. Low activation energy ($\simeq$ 5 kJ)	Large activation energy
7. Adsorption is multilayer	Adsorption is monolayer

The extent of adsorption of gases increases with increase in the pressure of the gases and it decreases with increase in temperature of the gas. The variation in the mass (x) of gas adsorbed by a given mass (m) of an adsorbent (say, charcoal) with change in the pressure of the gas at a constant temperature may be expressed by the following equations (known as adsorption isotherms).

Freundlich equation $(x/m) = kp^{1/n}$; (k is constant and $n > 1$)[†]

Langmuir equation $(x/m) = k_1p/(1 + k_2p)$; (k_1 and k_2 are constants)

According to Freundich equation, log (x/m) varies linearly with log p. Langmuir equation predicts the linear variation between $p/(x/m)$ and p. The above expressions are also applicable for the adsorption of acetic acid or oxalic acid from its solution by activated charcoal.

Colloids or sols are the substances whose sizes lie in between the solutes present in a true solution (e.g. salt, sugar, urea) and the solutes present in suspension (e.g. sand). The diameters of colloidal particles may range from 1 to 100 nm. The particles in the colloidal state do not settle down on standing, are not visible and can pass through a filter paper but not through perchment paper or animal membrane.

Based on dispersed phase and dispersed medium, eight types of colloidal solutions may be identified (Table 11.2).

A colloidal particle may be classified as lyophobic (solvent hatered) and lyophilic (solvent lovers). In solution, the former is less stable and gets coagulated by adding electrolytes, heating or agitation. They carry charges. On the other hand, lyophilic sols are quite stable and not easily coagulated. They do not carry charges.

[†] $n = 1$ at low pressures; $n = \infty$ at high pressures and $n > 1$ (from 2 to 10) for the intermediate range of pressures.

A colloidal particle may be classified as multimolecular, macromolecular and associated particle depending upon the nature of the particle. A multimolecular colloid consists of an aggregate of small particle held together by van der Waals forces. A macromolecular particle is itself a large molecule (e.g. starch, cellulose and proteins). An associated colloidal system behaves as normal solution at low concentration but becomes colloidal at higher concentrations. Examples include soap and synthetic detergents. The long chain $RCOO^-$ of these molecules associate at higher concentrations and form micelles.

A mixture of colloidal particles and true electrolytes may be separated by using dialysis or electrodialysis method. The mixture is taken in a bag made from parchment paper or a cellophane membrane. This bag is dipped in warm water. Through the parchment paper or cellophane membrane only true particles are able to pass through. The colloidal particles remain within the bag.

The colloidal particles in a solution is a two-phase system. These exhibit Brownian movement (zig-zag motion in all possible directions), Tyndall effect (scattering of light), electrophoresis (preferential movement in the presence of electrical potential), osmotic pressure, diffusion and sedimentation.

Table 11.2 Types of Colloidal Systems

Dispersed phase	*Dispersed medium*	*Colloidal system*	*Examples*
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, minerals
Solid	Liquid	Sol	Starch or proteins in water, paints, gold sol
Solid	Gas	Solid aerosol	Smoke, dust, storm
Liquid	Solid	Gel	Jellies, Cheese, butter, boot polish
Liquid	Liquid	Emulsion	Emulsified oils, milk, cod liver oil, medicines
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays
Gas	Solid	Solid foam	Styrene foam, rubber, occluded gases
Gas	Liquid	Foam or froth	Whipped cream, lemonade froth, soap suds

The colloidal particles in solution acquire charges due to preferential adsorption of ions. For example, ferric hydroxide sol is positively charged due to adsorption of Fe^{3+} ions, and silver iodide in the presence of KI becomes negatively charged due to the adsorption of I^- ions and becomes positively charged in a solution containing silver nitrate due to the adsorption of Ag^+ ions. The colloidal particles get coagulated with the addition of electrolytes due to the neutralization of charges. According to Hardy-Schulze rule, larger the charge on the ion, larger its coagulation ability.

Certain lyophilic sols can protect the lyophobic sols from coagulation by electrolytes. Zsigmondy introduced the term gold number to measure the protective power of different colloids. It is the minimum mass in mg of the dry protective colloid which will check the coagulation of 10 mL of a standard red gold sol on adding 1 mL of 10% sodium chloride solution.

Soap (or detergent) molecules involve a long chain fatty acid terminating in a carboxylate anion (or sulphonate group). In solution, the carboxylate or sulphonate group points towards the surface of water while the long chain fatty acid points outwardly. The hydrocarbon chain is easily miscible with the grease on the clothes and encapsulates it along with the dirt to form a micelle. These micelles are removed by rinsing with water.

Emulsions are sols of liquid in liquid. Two types of emulsions may be distinguished, namely, oil-in-water and water-in-oil. To make emulsions stable, emulsifying agent such as soaps and detergents are added.

Any substance which can decrease the surface tension of water to a large extent is known as surfactant. Examples are soap and detergents. Such substances have larger concentrations at the surface of water as compared to the bulk of the solution.

Straight Objective Type

Adsorption

1. Which of the following statements about physical adsorption is **not** correct?
- (a) It is usually monolayer
- (b) It is reversible in nature
- (c) It involves van der Waals interactions between adsorbent and adsorbate
- (d) It involves small value of heat of adsorption

2. Which of the following statements about chemisorption is **not** applicable?
- (a) It involves chemical forces between adsorbent and adsorbate
- (b) It is irreversible in nature
- (c) It involves high heat of adsorption
- (d) It involves low activation energy

3. Which of the following statements regarding adsorption is **not** correct?
- (a) Extent of adsorption of gases on charcoal increases with increase in pressure of the gas
- (b) Extent of adsorption is independent of temperature
- (c) Extent of adsorption by a given mass of adsorbent has an upper limit
- (d) Extent of adsorption is dependent on the nature of adsorbate and adsorbent

4. Physical adsorption
- (a) involves the weak attractive interactions between the adsorbent and adsorbate
- (b) involves the chemical interactions between the adsorbent and adsorbate
- (c) is irreversible in nature
- (d) increases with increase in temperature

5. Chemisorption
- (a) involves the weak attractive interactions between the adsorbent and adsorbate
- (b) is irreversible in nature
- (c) decreases with increase in temperature
- (d) involves multilayer adsorption

6. Which of the following is **not** correct?
- (a) The extent of adsorption depends on the nature of the adsorbent and adsorbate
- (b) The extent of adsorption depends on the pressure of the gas
- (c) The extent of adsorption depends on the temperature
- (d) The extent of adsorption has no upper limit

7. Which of the following statements regarding adsorption is **not** true?
- (a) The phenomenon of adsorption implies the presence of excess concentration of adsorbate at the surface of adsorbent
- (b) The phenomenon of adsorption is due to the presence of residual forces at the surface of the body
- (c) During adsorption, there occurs a decrease in free energy of the system
- (d) During adsorption, there occurs an increase in entropy of the system

8. Which of the following statements regarding adsorption is **not** correct?
- (a) The process of adsorption is an exothermic process
- (b) The substances being adsorbed is known as adsorbate
- (c) The substance on which adsorption occurs is known as adsorbent
- (d) The activation energy in chemisorption is smaller as compared to that of physisorption

9. Which of the following statements is **not** correct?
- (a) Physical adsorption is monolayer
- (b) Physical adsorption is reversible in nature
- (c) Physical adsorption involves low activation energy
- (d) The extent of physical adsorption decreases with increase in temperature

10. Which of the following statements is **not** correct?
- (a) Chemisorption is monolayer
- (b) Chemisorption is irreversible in nature
- (c) Chemisorption involves larger activation energy
- (d) The extent of chemisorption initially decreases with increase in temperature

11. In the Freundlich adsorption equation $x/m = k\,p^{1/n}$, the value of n is
(a) always greater than one (b)always smaller than one
(c) always equal to one (d) greater than one at low temperature and is smaller than one at high temperature

12. Which of the following graphs would yield a straight line plot?
(a) x/m versus p (b) log x/m versus p (c) log x/m versus log p (d) x/m versus log p

13. Which of the following statements is not correct?
(a) The extent of physical adsorption increases linearly with increase in pressure in the low pressure region
(b) The extent of physical adsorption attains a limiting value at the high pressure region
(c) In the intermediate range of pressure, the increase in adsorption is more than the increase in pressure
(d) Physical adsorption involves the reversible process $\text{G} + \text{S} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \text{GS}$ where G, S and GS represent, respectively, the unabsorbed gaseous molecules, adsorption sites and adsorbed gaseous molecules.

14. According to Langmuir isotherm,
(a) plot of $p/(x/m)$ versus $1/p$ is linear (b) plot of $p/(x/m)$ versus p is linear
(c) plot of $1/(x/m)$ versus p is linear (d) plot of $1/(x/m)$ versus $1/p$ is linear

15. Adsorption of gases on solids is accompanied with
(a) increase in enthalpy (b) increase in entropy
(c) decrease in entropy (d) increase in free energy (2004)

Colloidal Solution

16. Which of the following statements is **not** correct for a lyophobic sol?
(a) It can be easily solvated
(b) It carries charges
(c) The coagulation of this sol is irreversible in nature
(d) It is less stable in a solvent

17. Which of the following statements is correct for a lyophilic sol?
(a) It is not easily solvated
(b) It carries charges
(c) The coagulation of this sol is irreversible in nature
(d) It is quite stable in a solvent

18. Liquid-liquid sol is known as
(a) aerosol (b) foam (c) emulsion (d) gel

19. The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as
(a) aerosol (b) foam (c) emulsion (d) gel

20. Which of the following statements is **not** correct?
(a) A colloidal solution is a heterogeneous two-phase system
(b) Silver sol in water is an example of lyophilic sol
(c) Metal hydroxides in water are examples of lyophobic sol
(d) Liquid-liquid colloidal solution is not stable system

21. Size of colloidal particles may range from
(a) 1 to 100 nm (b) 10 to 100 pm (c) 1 to 100 μm (d) 1 to 10 mm

22. Which of the following represents a associated colloidal particles?
(a) Starch (b) A sol of gold (c) Proteins (d) Soaps

23. Which of the following represents a macromolecular colloidal particles?
(a) Sol of gold (b) Cellulose (c) Soaps (d) Synthetic detergents

24. Which of the following collodial system represents a gel?
(a) Solid in liquid (b) Solid in gas (c) Liquid in solid (d) Liquid in gas

25. Which of the following collodial system represents a sol?
(a) Solid in liquid (b) Solid in gas (c) Liquid in solid (d) Liquid in gas

26. Which of the following represents a multimolecular collodial particles?
(a) Sol of sulphur (b) Starch (c) Soaps (d) Proteins

27. Which of the following does not represent macromolecular collodial particles?
(a) Nylon (b) Plastics (c) Rubber (d) Soaps

28. A sol of sulphur belongs to
(a) lyophilic colloid (b) lyophobic colloid (c) gel (d) emulsion

29. Milk is
(a) fat dispersed in water (b) water dispersed in fat
(c) fat and water dispersed in an oil (d) a homogeneous solution of fat and water

30. Which of the following statements is correct for lyophilic sols?
(a) The coagulation of the sols is irreversible in nature
(b) They are formed by inorganic substances
(c) They are self stabilised
(d) They are readily coagulated by addition of electrolytes. (2005)

Characteristics of Colloidal Solution

31. A colloidal solution can be purified following the method of
(a) dialysis (b) peptization (c) filtration (d) oxidation

32. Which of the following sols is negatively charged?
(a) Arsenious sulphide (b) Aluminium hydroxide
(c) Ferric hydroxide (d) Silver iodide in silver nitrate solution

33. Which of the following statements is **not** correct?
(a) Peptization is the process by which certain substances are converted into the colloidal state
(b) Metal sols of gold, silver and platinum can be prepared by Bredig's arc method
(c) Impurities present in a sol makes it more stable
(d) Dialysis is a process to remove impurities of ions and molecules from a sol

34. Which of the following sols is positively charged?
(a) Silver iodide in potassium iodide solution (b) Ferric hydroxide
(c) Gold (d) Silver

35. The addition of soap in water
(a) increases its surface tension
(b) decreases its surface tension
(c) increases its surface tension at low concentration and decreases at high concentration.
(d) decreases its surface tension at low concentration and increases at high concentration.

36. The presence of electric charge on colloidal particles can be illustrated by the technique of
(a) ultrafiltration (b) dialysis (c) electrophoresis (d) sedimentation

37. At isoelectric point,
(a) a colloidal particle moves towards cathode during electrophoresis
(b) a colloidal particle moves towards anode during electrophoresis
(c) a colloidal particle does not move either towards cathode or towards anode during electrophoresis
(d) pH of medium becomes 7.

38. The Brownian motion is due to the
(a) temperature fluctuation within the liquid phase
(b) electrostatic interactions between charged particles
(c) convection current
(d) impact of solvent molecules on the colloidal particles

39. Tyndall effect is due to
(a) scattering of light by colloidal particles (b) reflection of light by colloidal particles
(c) refraction of light by colloidal particles (d) absorption of light by colloidal particles

40. Which of the following statements is correct?
(a) True particles are able to pass through filter paper and not in semipermeable membrane
(b) Colloidal particles are able to pass through filter paper and not in semipermeable membrane
(c) Both true and colloidal particles are able to pass through filter paper and semipermeable membrane.
(d) Both true and colloidal particles are not able to pass through filter paper and semipermeable membrane

41. Peptization process involves
(a) precipitation of colloidal particles (b) purification of colloidal particles
(c) dispersion of precipitate into colloidal sol (d) movement of colloidal particles in an electric field

Hardy-Schulze Rule

42. Which of the following ions is most effective in the coagulation of an arsenious sulphide sol?
(a) K^+ (b) Mg^{2+} (c) Al^{3+} (d) Ca^{2+}

43. Which of the following ions is most effective in the coagulation of ferric hydroxide sol?
(a) Cl^- (b) Br^- (c) NO_2^- (d) SO_4^{2-}

44. Which of the following anions will have minimum flocculation value for the ferric oxide sol?
(a) Cl^- (b) Br^- (c) SO_4^{2-} (d) $[Fe(CN)_6]^{3-}$

45. Which of the following cations will have maximum flocculation value for the arsenious sulphide sol?
(a) Na^+ (b) Mg^{2+} (c) Ca^{2+} (d) Al^{3+}

46. Which of the following cations will have minimum flocculation value for the arsenious sulphide sol?
(a) Na^+ (b) Mg^{2+} (c) Ca^{2+} (d) Al^{3+}

47. Which of the following anions will have minimum flocculation value for the ferric oxide sol?
(a) Cl^- (b) Br^- (c) SO_4^{2-} (d) $[Fe(CN)_6]^{3-}$

48. The coagulation of 10 mL of a colloidal gold solution is prevented by the addition of 0.024 g of a compound followed by 10 mL of 1% solution of sodium chloride. The gold number of the compound is
(a) 24 (b) 240 (c) 120 (d) 360

49. Which of the following solutions changes the colour from red to blue of a colloidal gold solution?
(a) 10% starch (b) 10% glucose (c) 10% gelatin (d) 10% sodium chloride

50. An As_2S_3 sol carries a negative charge. The maximum precipitating power for this sol is shown by
(a) K_2SO_4 (b) $CaCl_2$ (c) Na_3PO_4 (d) $AlCl_3$

51. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is
(a) $CH_3(CH_2)_{15}\,N^+(CH_3)_3Br^-$ (b) $CH_3(CH_2)_{11}OSO_3^-Na^+$
(c) $CH_3(CH_2)_6COO^-Na^+$ (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$ (2008)

52. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is
(a) Na_2SO_4 (b) $CaCl_2$ (c) $Al_2(SO_4)_3$ (d) NH_4Cl (2009)

Catalysis

53. Which of the following statements is **not** correct?
(a) Catalyst is not involved in the reaction
(b) The concentration of a catalyst remains constant throughout the progress of chemical reaction
(c) The mechanism of catalytic reactions may vary from reaction to reaction
(d) NO acts as a homogeneous catalyst in the oxidation of SO_2 into SO_3

54. Which of the following statements is **not** correct?
(a) The efficiency of a solid catalyst depends upon its surface area
(b) Catalyst operates by providing alternate path for the reaction that involves a lower energy of activation
(c) Catalyst lowers the energy of activation of the forward reaction without affecting the energy of activation of the backward reaction
(d) Catalyst does not affect the overall enthalpy change of the reaction

55. Which of the following statements is **not** correct?
(a) The catalyst changes not only the rate of forward reaction but also that of the backward reaction
(b) The catalyst changes the value of equilibrium constant of the reaction
(c) The mechanism of a catalytic reaction depends on the type of the catalyst, i.e. whether it is homogeneous or heterogeneous
(d) Enzymes are essentially proteins which are responsible for the catalysing reactions occurring in living matter

56. Which of the following enzymes converts starch into maltose?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

57. Which of the following enzymes converts maltose into glucose?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

58. Which of the following enzymes converts glucose into alcohol?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

59. Which of the following statements is **not** correct?
(a) Most heterogeneous catalytic reactions involve the solid surface of the catalyst
(b) Heterogeneous catalysts primarily function by lowering the activation energy of the reaction
(c) A solid catalyst present in the powder form is more effective as it has larger surface area
(d) The catalyst may be deactivated by heating it to a high temperature in vacuum

60. Which of the following statements is **not** correct?
(a) Zeolite contains aluminosilicate framework
(b) The general formula of zeolite is $M^{n+}_{x/n}\,[(AlO_2)_x\,(SiO_2)_y]^{x-} \cdot z\,H_2O$
(c) Zeolites are characterized by their open structures that permit the exchange of anions and water molecules
(d) Sodalite cage is formed by linking 24 SiO_4 tetrahedra

61. Which of the following statements is **not** correct?
(a) Zeolite A is formed by linking sodalite cages through double four-membered rings
(b) Faujasite zeolite is formed by linking the sodalite cages through double six-membered rings
(c) Zeolite structures contain tunnels or systems of interconnected cavaties which have precisely defined dimensions on the atomic scales
(d) Zeolites are anion exchanger

ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (b)	**6.** (d)	**7.** (d)
8. (d)	**9.** (a)	**10.** (d)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (b)
15. (c)	**16.** (a)	**17.** (d)	**18.** (c)	**19.** (d)	**20.** (b)	**21.** (a)
22. (d)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (d)	**28.** (b)
29. (a)	**30.** (c)	**31.** (a)	**32.** (a)	**33.** (c)	**34.** (b)	**35.** (b)
36. (c)	**37.** (c)	**38.** (d)	**39.** (a)	**40.** (b)	**41.** (c)	**42.** (c)
43. (d)	**44.** (d)	**45.** (a)	**46.** (d)	**47.** (d)	**48.** (a)	**49.** (d)
50. (d)	**51.** (a)	**52.** (c)	**53.** (a)	**54.** (c)	**55.** (b)	**56.** (b)
57. (a)	**58.** (c)	**59.** (d)	**60.** (c)	**61.** (d)		

Hints and Solutions

Straight Objective Type

1. Physical adsorption is usually multilayer (and not monolayer).

2. Chemisorption involves high activation energy.

3. Extent of adsorption depends on temperature. It decreases with increase in temperature.

15. Adsorption is accompanied with decrease in entropy as the adsorbed molecules become more ordered.

16. Lyophobic sol is solvent hatered sol. Thus, it is not easily solvated.

17. Lyophilic sol is quite stable in a solvent.

18. Liquid-liquid sol is known as emulsion.

19. Liquid adsorbate dispersed in solid adsorbent is known as gel.

20. Silver sol in water is an example of lyophobic sol.

21. Size of colloidal particles lies in the range of 1 to 100 nm.
22. Soaps are associated colloidal particles.
23. Cellulose is an example of a macromolecular colloidal particles.
30. The lyophilic (solvent lovers) sols are quite stable and are not easily coagulated. The coagulation is reversible in nature.
31. Arsenious sulphide is an example of negatively-charged sol.
32. Impurities persent in a sol makes it less stable (and no more stable)
42. Larger the charge number, the most effective it is for coagulation of sol.
43. Same as Q 42
44. Larger the charge number, minimum the flocculation value
51. Larger the hydrocarbon chain, lesser concentration is required to form micelles.
52. The colloidal particles are coagulated with the addition of electrolytes due to the neutralization of charges. According to Hardy-Schulze rule, larger the charge on the ion, larger its coagulation ability.

Sb_2S_3 being a negative sol, it will be coagulated most effectively by $Al_2(SO_4)_3$ as Al^{3+} ion carries the larger positive charge.

CHAPTER 12

NUCLEAR CHEMISTRY

NUCLEAR CHEMISTRY

The stability of a nucleus depends upon the ratio of neutrons and protons (Fig. 12.1). If this ratio of a nuclide lies away from the corresponding stability ratio (it is one or slightly greater than one for atomic number less than 20 and it increases to about 1.5 with increase in atomic number), it results in an unstable nuclide which tries to attain stability by the spontaneous emission of an α- or a β-particle alongwith the emission of γ-radiations. The spontaneous emission of these particles is known as *radioactivity*. The nuclear changes occurring during the emission of these particles are depicted in the following.

$$^{m}_{n}\mathrm{A} \longrightarrow {}^{m-4}_{n-2}\mathrm{B} + {}^{4}_{2}\mathrm{He}$$

$$^{m}_{n}\mathrm{A} \longrightarrow {}^{\;\;m}_{n+1}\mathrm{B} + {}^{0}_{-1}\mathrm{e}$$

$$^{m}_{n}\mathrm{A}^{*} \longrightarrow {}^{m}_{n}\mathrm{A} + \gamma$$

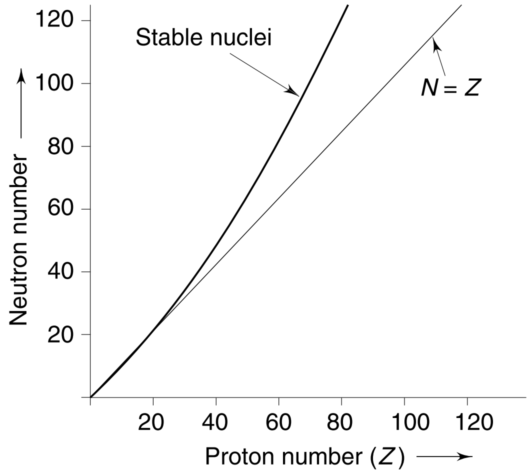


Fig. 12.1 Display of Stable Nuclides

SODDY-FAJAN GROUP DISPLACEMENT LAW

The emission of an α-particle (i.e. $^{4}_{2}\mathrm{He}^{2+}$ particle) results in a daughter element which lies two groups to its left in the periodic table because its atomic number is decreased by two. The emission of a β-particle (i.e. an electron, $^{0}_{-1}\mathrm{e}$) results in an element which lies one group to its right since the atomic number of the daughter element is increased by one.

γ-radiations are electromagnetic radiations (wavelength < 10^{-10} m) and these are emitted when the daughter element in the excited state comes to the lower levels. α- and β-particles being electrically charged species are deflected in the electrical or magnetic field.

The emission of one α-particle followed by two β-particles (or vice versa) results into the daughter element which is the isotope of the parent element. This is depicted below.

$$^{m}_{n}\mathrm{A} \xrightarrow{-\alpha} {}^{m-4}_{n-2}\mathrm{B} \xrightarrow{-\beta} {}^{m-4}_{n-1}\mathrm{C} \xrightarrow{-\beta} {}^{m-4}_{n}\mathrm{A}$$

The emission of a β-particle is due to the conversion of neutron into proton within the nucleus of the atom:

$$\mathrm{n} \rightarrow \mathrm{p} + \mathrm{e}^{-}$$

The emission of β-particle by a radioactive element is also associated with the emission of another particle called antineutrino (symbol: $\bar{\nu}$). Thus, a β-decay shown by $^{14}_{6}\mathrm{C}$ is written as

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} + \bar{\nu}$$

The surplus energy released in β-decay is shared between the emitted electron and antineutrino. The isotopes having too many neutrons compared to the number of protons (that is, lying above the stability range shown in Fig. 12.1) decay by electron emission. There are examples of isotopes which lie below the stability line and decay by the emission of a positron. For example,

$$^{19}_{10}Ne \rightarrow ^{19}_{9}F + ^{0}_{+1}e + \nu$$

where ν represents neutrino which is emitted along with the positron.

Mass Defect The loss of mass when a given nucleus is formed, starting from the appropriate number of neutrons and protons, is known as mass defect. This loss of mass appears in the form of energy in accordance with Einstein equation $E = (\Delta m)c^2$. The energy released, known as *binding energy*, is a measure of the relative stability of the nucleus to dissociate into its constituent particles, namely, protons and neutrons.

The average binding energy per nucleon is defined as the total binding energy of a nucleus divided by its mass number. For ^4_2He it is about 7.1 MeV. Figure 12.2 shows the average binding energy per nucleon as a function of mass number for stable nuclei. The curve rises with increase in mass number and reaches a plateau at about 8 MeV per nucleon above mass number approximately equal to 50. Beyond mass number equal to 60, the curve decreases slowly, indicating that larger nuclei are held together a little less tightly than those in the middle of the periodic table.

This fact is supported by *nuclear fission* reactions. For example, the fission of ^{235}U may be brought about by bombarting with neutron:

$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3^{1}_{0}n$$

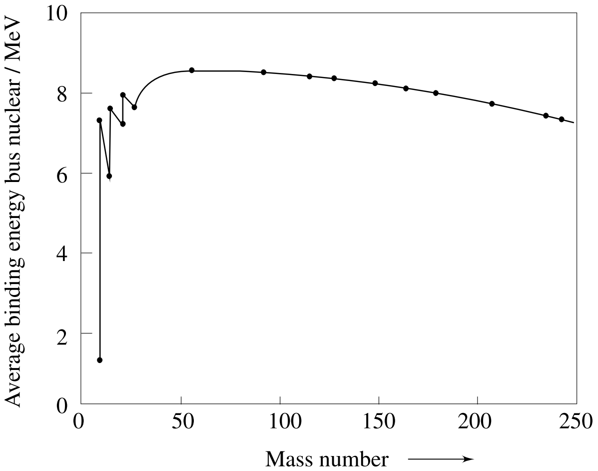


Fig. 12.2 Average binding energy per nucleon versus mass number

The mass of every stable nucleus is less than the sum of the masses of its constituent protons and neutrons. The loss of mass is manifested in the release of a large amount of energy. The process of building up nuclei by bringing together individual protons and neutrons, or building larger nuclei by combining small nuclei, is called *nuclear fusion.* From Fig. 12.2, it is evident that small nuclei can combine to form larger ones with the release of energy; it is because the binding energy per nucleion is smaller for light nuclei than it is for those of intermediate size (mass number ≃ 50 to 100). The energy released in fusion reactions is greater for a given mass of reactants than in fission.

The strength of a radioactivity source can be specified at a given time by stating the activity or how many disintegrations occur per second. A unit of curie (Ci) is defined as 1 Ci = 3.70×10^{10} disintegrations per second

RADIOACTIVE DISINTEGRATION SERIES

A radioactive disintegration series involves the transformation of the parent radioactive element into the nonradioactive end product. There are four such series, known as thorium (4*n*), neptunium (4*n* + 1), uranium (4*n* + 2) and actinium. (4*n* + 3) series. Of these, neptunium or (4*n* + 1) series is man-made while others occur in nature. In elements of 4*n* series, the mass numbers of daughter elements are divisible by 4. In (4*n* + 1), (4*n* + 2), and (4*n* + 3) series, the mass numbers give a remainder of 1, 2 and 3, respectively, when divided by 4. The starting and end members of the four series along with the number of α- and β-particles emitted in each are shown in Table 12.1.

Table 12.1 Four radioactive series

Series		*Numbers of particles emitted*	
		α	β
Thorium or 4*n*	$^{232}_{90}Th \longrightarrow ^{208}_{82}Pb$	6	4
Neptunium or 4*n* + 1	$^{237}_{93}Np \longrightarrow ^{209}_{83}Bi$	7	4
Uranium or 4*n* + 2	$^{238}_{92}U \longrightarrow ^{206}_{82}Pb$	8	6
Actinium or 4*n* + 3	$^{235}_{92}U \longrightarrow ^{207}_{82}Pb$	7	4

KINETICS OF RADIOACTIVE DECAY

The radioactive decays follow the first-order kinetics. The integrated rate expression is

$$\log N = \log N_0 - \frac{\lambda}{2.303}\, t$$

where N and N_0 are the number of radioactive atoms present at time t and 0, respectively, and λ is the decay constant. The time required to reduce the initial number of atoms of a radioactive element to half value is known as *half-life period* and is given by the expression

$$t_{1/2} = \frac{0.693}{\lambda}.$$

Straight Objective Type

General Characteristics

1. The radiations from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are
(a) definitely alpha rays (b) definitely beta rays
(c) both alpha and beta rays (d) either alpha or beta rays (1984)

2. The increasing order for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is
(a) e, p, n, α (b) n, p, e, α (c) n, p, α, e (d) n, α, p, e (1984)

3. Nuclear reaction(s) accompanied with emission of neutron(s) is/are
(a) ${}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{15}\mathrm{P}$ (b) ${}^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{13}_{7}\mathrm{N}$
(c) ${}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{1}\mathrm{e}$ (d) ${}^{241}_{96}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{245}_{97}\mathrm{Bk} + {}^{0}_{1}\mathrm{e}$ (1988)

4. Which of the following is not deflected in an electric field?
(a) Alpha particles (b) Beta particles (c) Gamma rays (d) Positrons

5. The emission of beta particles is from
(a) the valence shell of an atom
(b) the inner shell of an atom
(c) the nucleus due to the nuclear conversion proton → neutron + electron
(d) the nucleus due to the nuclear conversion neutron → proton + electron

6. The instability of a nucleus is due to
(a) high proton : electron ratio (b) high proton : neutron ratio
(c) low proton : electron ratio (d) low proton : neutron ratio

7. Which of the following has a negative charge?
(a) Neutrino (b) Neutron (c) Positron (d) Antiproton

8. Mesons are responsible for
(a) disintegration of the nucleus (b) repulsion between the protons within the nucleus
(c) attraction between nucleus and electrons (d) attraction between nucleons

9. Which of the following isotopes is used in establishing the reaction mechanism of photosynthesis in plants?
(a) ${}^{12}_{6}\mathrm{C}$ (b) ${}^{13}_{6}\mathrm{C}$ (c) ${}^{14}_{6}\mathrm{C}$ (d) ${}^{2}_{1}\mathrm{H}$

10. Which of the following is the man-made radioactive disintegration series ?
(a) Thorium series (b) Neptunium series (c) Uranium series (d) Actinium series

11. The density of a nucleus is of the order of
(a) 10^5 kg m^{-3} (b) 10^{10} kg m^{-3} (c) 10^{17} kg m^{-3} (d) 10^{25} kg m^{-3}

12. One Curie of radioactivity is equal to
(a) 3.7×10^8 disintegrations/s (c) 3.7×10^9 disintegrations/s
(c) 3.7×10^{10} disintegrations/s (d) 3.7×10^{11} disintegrations/s

13. One becquerel of radioactivity is equal to
(a) one disintegration/s (b) two disintegrations/s
(c) 6.023×10^{23} disintegrations/s (d) three disintegrations/s

14. $^{27}_{13}\text{Al}$ is a stable isotope, $^{29}_{13}\text{Al}$ is expected to disintegrate by
(a) α-emission (b) β-emission (c) positron emission (d) proton emission (1996)

15. The number of neutrons accompanying the formation of $^{139}_{54}\text{Xe}$ and $^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by $^{235}_{92}\text{U}$, followed by nuclear fission is
(a) 0 (b) 2 (c) 1 (d) 3 (1999)

16. Which of the following is a man made disintegration series ?
(a) 4*n* series (b) 4*n* + 1 series (c) 4*n* + 2 series (d) 4*n* + 3 series

17. Meson is heavier than electron by
(a) 106 times (b) 207 times (c) 307 times (d) 407 times

18. Positron has a mass
(a) equal to proton (b) equal to electron (c) greater then electron (d) smaller to electron

19. Which of the following is 4*n* series?
(a) Thorium series (b) Neptunium series (c) Uranium series (d) Actinium series

20. Which of the following is 4*n* + 1 series?
(a) Thorium series (b) Neptunium series (c) Uranium series (d) Actinium series

21. Which of the following is 4*n* + 2 series?
(a) Thorium series (b) Neptunium series (c) Actinium series (d) Uranium series

22. Which of the following is 4*n* + 3 series?
(a) Thorium series (b) Neptunium series (c) Actinium series (d) Uranium series

23. The end product of 4*n* + 1 disintegration series is
(a) $^{208}_{82}\text{Pb}$ (b) $^{209}_{83}\text{Bi}$ (c) $^{206}_{82}\text{Pb}$ (d) $^{297}_{82}\text{Pb}$

24. For which radioactive series, lead is not the end product?
(a) 4*n* (b) 4*n* + 1 (c) 4*n* + 2 (d) 4*n* + 3

25. Lead-207 is produced as the end product in
(a) 4*n* series (b) 4*n* + 1 series (c) 4*n* + 2 series (d) 4*n* + 3 series

26. In a β decay, the ratio of p/n of the nucleus is
(a) increased (b) decreased
(c) not changed (d) changed but cannot be predicted

27. The more stable isotope of sodium is ^{23}Na. The atom ^{24}Na can undergo radioactive decay via (2003)
(a) β^- emission (b) α emission (c) β^+ emission (d) K-electron capture

28. A position is emitted from $^{23}_{11}\text{Na}$. The ratio of the mass number and atomic number of the resulting nuclide is
(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12 (2007)

29. Masses of two isobars $^{64}_{29}\text{Cu}$ and $^{64}_{30}\text{Zn}$ are 63.9298 u and 63.9292 u, respectively. It can be concluded from these data that
(a) both the isobars are stable
(b) ^{64}Zn is radioactive, decaying to ^{64}Cu through β-decay
(c) ^{64}Cu is radioactive, decaying to ^{64}Zn through γ–decay
(d) ^{64}Cu is radioactive, decaying to ^{64}Zn through β-decay

30. The electron emitted in beta radiation originates from
(a) inner orbits of atoms (b) free electron existing in nuclei
(b) decay of a neutron in a nucleus (d) photon escaping fron the nucleus

31. In a nuclear reactor, which of the following is used to slow down the fast neutrons released in the fission process?
(a) Moderator (b) Control rods (c) Radiation shielding (d) Heat exchanger

Group Displacement Law

32. If uranium (mass number 238 and atomic number 92) emits an α-particle, the product respectively has mass number and atomic number
(a) 236 and 92 (b) 234 and 90 (c) 238 and 90 (d) 236 and 90 (1981)

33. Group 15 element $^{211}_{83}\text{Bi}$ is transformed to $^{211}_{84}\text{Po}$. To which group does Po belong?
(a) 14 (b) 15 (c) 16 (d) 13

34. An isotope of the parent element is produced with the emission of
(a) one α- and one β-particle (b) one α- and two β-particles
(c) two α- and one β-particles (d) two α- and two β-particles

35. The element $^{210}_{84}$Po emits an alpha particle. The daughter element is
(a) $^{204}_{82}$Pb (b) $^{206}_{82}$Pb (c) $^{208}_{82}$Pb (d) $^{210}_{82}$Pb

36. The element of $^{27}_{12}$Mg emits a beta particle. The daughter element is
(a) $^{23}_{10}$He (b) $^{27}_{12}$Mg (c) $^{27}_{13}$Al (d) $^{23}_{11}$Na

37. In a radioactive decay $^{232}_{90}$Th is transformed into $^{208}_{82}$Pb. The number of alpha and beta particles emitted respectively are
(a) 4, 6 (b) 4, 4 (c) 6, 6 (d) 6, 4

38. After the emission of one α-particle followed by one β-particle from the atom $^{238}_{92}$X, the number of neutrons in the daughter atom will be
(a) 142 (b) 143 (c) 144 (d) 146

39. ^{22}Ne nucleus, after absorbing energy, decays into two α-particles and an unknown nucleus. The unknown nucleus is
(a) nitrogen (b) carbon (c) boron (d) oxygen

40. Thorium series starts from $^{232}_{90}$Th. If there are emission of six α and four β particles, the end products is
(a) $^{209}_{83}$Bi (b) $^{206}_{82}$Pb (c) $^{208}_{82}$Pb (d) $^{208}_{93}$Np

41. $^{234}_{92}$U may be formed from either $^{238}_{92}$U or $^{238}_{93}$Np. The number of α and β particles in these two ways, respectively, are
(a) (1α, 2β) and (1α, 1β) (b) (2α, 1β) and (1α, 2β)
(b) (2α, 2β) and (2α, 1β) (d) (1α, 2β) and (1α, 2β)

42. Which of the following series involves the emission of eight α and five β particles?
(a) 4*n* series (b) 4*n* + 1 series (c) 4*n* + 2 series (d) 4*n* + 3 series

Kinetics of Radioactive Decay

43. The half-life peirod of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
(a) (1/2)g (b) (1/4)g (c) (1/8)g (d) (1/16)g (1986)

44. The half-life of a radioactive decay is given as
(a) $t_{1/2} = 0.693/\lambda$ (b) $t_{1/2} = \log 2/\lambda$ (c) $t_{1/2} = \lambda/0.693$ (d) $t_{1/2} = \lambda/\log 2$

45. If N_0 and N are the number of radioactive particles at $t = 0$ and at time t, then
(a) $\lambda = \frac{1}{t}\log\frac{N_0}{N}$ (b) $\lambda = \frac{2.303}{t}\log\frac{N}{N_0}$ (c) $\lambda = \frac{t}{2.303}\log\frac{N_0}{N}$ (d) $\lambda = \frac{2.303}{t}\log\frac{N_0}{N}$

46. Which of the following isotopes is used in the determination of the age of dead plants and animals?
(a) $^{12}_{6}$C (b) $^{13}_{6}$C (c) $^{14}_{6}$C (d) $^{2}_{1}$H

47. The disintegration rate of a radioactive element changes from an initial value of 10000 disintegrations per minute to 2500 disintegrations per minute in 50 days. The half-life of the element is
(a) 25 days (b) 50 days (c) 75 days (d) 100 days

48. The activity of a sample has 40% as much radioactivity as present originally. If half life period of the radioactivity is 5000 y, the life of the sample undergoing disintegration is
(a) 5000 y (b) 6000 y (c) 6667 y (d) 5667 y

49. The activity of a sample of wood is due to the presence of 50% of ^{14}C as compared to the original sample. If half life of ^{14}C is 5760 y, the life of the sample of wood is
(a) 5760 y (b) 5670 y (c) 6667 y (d) 5000 y

50. The radioactivity due to ^{14}C isotope ($t_{1/2}$ = 5760 y) of a sample of wood from a dead tree was found to be nearly one fourth of fresh wood. The tree died
(a) 5760 y back (b) 9090 y back (c) 11520 y back (d) 2880 y back

51. The reciprocal of radioactive decay constant is called
(a) half-life period (b) average life period
(c) natural life period (d) root mean square life period

52. A radioactive material decays by simultaneous emission of two particles with respective half-lives 1620 and 810 years. The time, in years, after which one–fourth of the material remains is
(a) 1080 (b) 2430 (c) 3240 (d) 4860

53. The half-life of ^{131}I is 8 days. Given a sample of ^{131}I at time $t = 0$, we can assert that
(a) no nucleus will decay before $t = 4$ days

(b) no nucleus will decay before $t = 8$ days
(c) all nuclei will decay before $t = 6$ days
(d) a given nucleus may decay at any time after $t = 0$

54. The half-life period of a radioactive element X is the same as the mean–life time of another radioactive element Y. Initially, both of them have the same number of atoms. Then
(a) X and Y have the same decay rate initially (b) X and Y always decay at the same rate
(c) Y will decay at a faster rate than X (d) X will decay at a faster rate than Y

55. Two radioactive materials X_1 and X_2 have decay constants $10/\lambda$ and λ, respectively. If initially they have the same number of nuclei, then the ratio of the number of nuclei of X_1 to that of X_2 will be λ/e after a time
(a) $1/(10\ \lambda)$ (b) $1/(11\ \lambda)$ (c) $11/(10\ \lambda)$ (d) $11/(9\ \lambda)$

56. The half–life of ^{215}At is 100 μs. The time taken for the radioactivity of a sample of ^{215}At to decay to 1/16th of its initial value is
(a) 400 μs (b) 6.3 μs (c) 40 μs (d) 300 μs

57. If 10% of a radioactive material decays in 5 days, the amount of the original material left after 20 days is about
(a) 80% (b) 75% (c) 70% (d) 65%

58. A freshly prepared radioactive source of half–life 2 h emits radiation of intensity which is 32 times the permissible safe level. The time after which it is safer to work with this source is
(a) 4 h (b) 10 h (c) 16 h (d) 20 h

59. A wodden article found in a cave has only 40% as much C-14 activity as a fresh piece of wood. The age of the article is about (Given: log(40) = 1.60, $t_{0.5}$ of C-14 = 5760 y)
(a) 7.6×10^2y (b) 9.8×10^2y (c) 2.4×10^3y (d) 7.6×10^3y

Mass Defect and Binding Energy

60. The energy equivalent to one atomic mass unit is
(a) 921 MeV (b) 931 MeV (c) 941 MeV (d) 951 MeV

61. The mass defect of the nuclear reaction $^{10}_{4}\text{Be} \rightarrow {}^{10}_{5}\text{B} + {}^{0}_{-1}\text{e}$ is
(a) Δm = atomic mass of $({}^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$
(b) Δm = atomic mass of $({}^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$ + mass of one electron
(c) Δm = atomic mass of $({}^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$ – mass of one electron
(d) Δm = atomic mass of $({}^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$ + mass of two electrons

62. The mass defect of the nuclear reaction $^{8}_{5}\text{B} \rightarrow {}^{8}_{4}\text{Be} + {}^{0}_{+1}\text{e}$ is
(a) Δm = atomic mass of $({}^{8}_{4}\text{Be} - {}^{8}_{5}\text{B})$
(b) Δm = atomic mass of $({}^{8}_{4}\text{Be} - {}^{8}_{5}\text{B})$ + mass of one electron
(c) Δm = atomic mass of $({}^{8}_{4}\text{Be} - {}^{8}_{5}\text{B})$ + mass of one positron
(d) Δm = atomic mass of $({}^{8}_{4}\text{Be} - {}^{8}_{5}\text{B})$ + mass of two electrons

63. For the conversion $^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$ $\Delta m = -7.639 \times 10^{-30}$ kg. The energy released during the process is
(a) 4.14×10^{9} J mol^{-1} (b) 4.14×10^{10} J mol^{-1} (c) 4.14×10^{11} J mol^{-1} (d) 4.14×10^{12} J mol^{-1}

64. The mass defect for the formation of ^{12}C is 0.10242 amu. Its binding energy would be
(a) 95.35 MeV (b) 9.535 MeV (c) 95.35 eV (d) 9.535 eV

65. Energy released during the annihilation of one positron and one electron ($m_e = 9.11 \times 10^{-31}$ kg) is
(a) 8.2×10^{-14} J (b) 1.64×10^{-13} J (c) 2.46×10^{-13} J (d) 4.92×10^{-13} J

66. The binding energy per nucleon of $^{7}_{3}$Li and $^{59}_{27}$Co is 6.44 and 8.57 MeV. Which of the following statements is correct?
(a) Li is more stable than Co
(b) Li is less stable than Co
(c) Both Li and Co are equally stable
(d) The conversion of Co to Li is associated with release of energy

67. If the binding energy per nucleon of ^{7}Li and ^{4}He are 5.60 MeV and 7.06 MeV, respectively, the energy associated with the reaction $^{7}\text{Li} + \text{p} \longrightarrow 2\,{}^{4}_{2}\text{He}$ is
(a) 17.3 MeV (b) – 17.3 MeV (c) 34.6 MeV (d) – 34.6 MeV

68. The binding energy per nucleon of ^{16}O is 7.97 MeV and that of ^{17}O is 7.75 MeV. The energy in MeV required to remove a neutron from ^{17}O is

(a) 3.52 (b) 3.64 (c) 4.23 (d) 7.86

69. When a β^+ particle encounters an electron, they cancel each other and both disappear. This annihilation of matter produces two photons, each having an energy approximately

(a) 0.466 MeV (b) 0.511 MeV (c) 0.869 MeV (d) 1.15 MeV

70. The binding energy per nucleon for ${}_2^4He$ whose mass difference from 2p and 2n is 3.0308×10^{-2}u is approximately

(a) 7.06 MeV (b) 7.59 MeV (c) 8.02 MeV (d) 8.21 MeV

Nuclear Reactions

71. Which one of the following is an (α, n) type nucleus transformation?

(a) ${}_{33}^{75}As + {}_2^4He \rightarrow {}_{35}^{78}Br + {}_0^1n$ (b) ${}_3^7Li + {}_1^1He \rightarrow {}_4^7Be + {}_0^1n$

(c) ${}_{21}^{45}Sc + {}_0^1n \rightarrow {}_{20}^{45}Ca + {}_1^1H$ (d) ${}_7^{14}N + {}_1^1H \rightarrow {}_8^{15}O + \gamma$

72. In the nuclear reaction ${}_7^{14}N + {}_2^4He \longrightarrow {}_8^{17}O + {}_1^1H$ the projectile is

(a) ${}_7^{14}N$ (b) ${}_2^4H$ (c) ${}_8^{17}O$ (d) ${}_1^1H$

73. Atom bombs are based on

(a) natural radioactivity (b) nuclear fission

(c) nuclear fusion (d) spontaneous chemical reaction

74. Hydrogen bomb is based on

(a) natural radioactivity (b) nuclear fission

(c) nuclear fusion (d) spontaneous chemical reaction

75. The material used for absorbing neutrons in a nuclear reactor is

(a) cadmium (b) radium (c) uranium (d) zinc

76. Which of the following is a capture reaction?

(a) ${}_9^{19}F + {}_1^1H \longrightarrow {}_8^{16}O + {}_2^4He$ (b) ${}_3^7Li + {}_2^4He \longrightarrow {}_5^{11}B + \gamma$

(c) ${}_{16}^{32}S + {}_1^3H \longrightarrow {}_{17}^{34}Cl + {}_0^1n$ (d) ${}_4^9Be + \gamma \longrightarrow {}_4^8Be + {}_0^1n$

77. Which of the following is a fission reaction?

(a) ${}_8^{16}O + {}_1^2H \longrightarrow {}_7^{14}N + {}_2^4He$ (b) ${}_{12}^{25}Mg + \gamma \longrightarrow {}_{11}^{24}Na + {}_1^1H$

(c) ${}_{33}^{75}As + {}_2^4He \longrightarrow {}_{35}^{78}Br + {}_0^1n$ (d) ${}_{92}^{235}U + {}_0^1n \longrightarrow {}_{56}^{140}Ba + {}_{36}^{94}Kr + 2{}_0^1n$

78. Which of the following is a spallation reaction?

(a) ${}_8^{16}O + {}_1^2H \longrightarrow {}_7^{14}N + {}_2^4He$ (b) ${}_{29}^{63}Cu + {}_2^4He \longrightarrow {}_{17}^{37}Cl + 16{}_0^1n + 14{}_1^1H$

(c) ${}_1^2H + {}_1^2H \longrightarrow {}_2^4He + \gamma$ (d) ${}_{92}^{238}U + {}_0^1n \longrightarrow {}_{92}^{239}U + \gamma$

79. The expression of mass-energy conversion is

(a) $E = m^2c$ (b) $E = mc^2$ (c) $E^2 = mc$ (d) $E^2 = mc^2$

80. Which of the following reactions represents a fusion reaction?

(a) ${}_{92}^{238}U + {}_0^1n \longrightarrow {}_{92}^{239}U$ (b) ${}_1^3H + {}_1^2H \longrightarrow {}_2^4He + {}_0^1n$

(c) ${}_{33}^{75}As + {}_2^4He \longrightarrow {}_{35}^{78}Br + {}_0^1n$ (d) ${}_{16}^{32}S + {}_1^3H \longrightarrow {}_{17}^{34}Cl + {}_0^1n$

81. In a nuclear reactor, the speed of neutrons is slowed down by

(a) ordinary water (b) heavy water (c) zinc rod (d) mercury

82. The ${}_6^{14}C$ in upper atmosphere is generated by the nuclear reaction

(a) ${}_7^{14}N + {}_1^1H \longrightarrow {}_6^{14}C + {}_1^0e + {}_1^1H$ (b) ${}_7^{14}N \longrightarrow {}_6^{14}C + {}_1^0e$

(c) ${}_7^{14}N + {}_0^1n \longrightarrow {}_6^{14}C + {}_1^1H$ (d) ${}_7^{14}N + {}_1^1H \longrightarrow {}_6^{11}C + {}_2^4He$

83. In nuclear reactors, cadmium is used to

(a) slow down neutron

(b) absorb neutron

(c) activate neutron

(d) absorbed energy released during nuclear reaction.

84. Which of the following isotopes of uranium is a fissionable isotope?

(a) ^{234}U (b) ^{235}U (c) ^{238}U (d) ^{239}U

85. In Breeder reactors, the coolant used is
(a) an alloy of Na and K (b) cadmium
(c) graphite (d) heavy water

86. The energy released in the reaction $^{14}_{7}\text{N}(d, \alpha)^{12}_{6}\text{C}$ (Given: $m(^{14}_{7}\text{N}) = 14.00307\text{u}$, $m(^{2}_{1}\text{H}) = 2.01410\,\text{u}$, $m(^{12}_{6}\text{C}) = 12.0000\,\text{u}$ and $m(^{4}_{2}\text{He}) = 4.002603\,\text{u}$) is
(a) 10.62 MeV (b) 13.6 MeV (c) 15.2 MeV (d) 17.6 MeV

87. If two light nuclei are fused in a nuclear reaction, the average binding energy per nucleon
(a) increases (b) decreases (c) remains the same (d) cannot be determined

88. In the nuclear reaction $^{232}_{92}\text{U} \longrightarrow {}^{228}_{90}\text{Th} + {}^{4}_{2}\text{He}$, (Given: $m(\text{U}) = 232.038$ u, $m(\text{Th}) = 228.029$ u and $m(\text{He}) = 4.003$ u) the ratio of speed of α-particle and speed of light is about
(a) 0.018 (b) 0.036 (c) 0.055 (d) 0.25

89. Naturally occurring uranium contains
(a) 0.7% $^{238}_{92}\text{U}$ and 99.3% $^{235}_{92}\text{U}$ (b) 99.3% $^{238}_{92}\text{U}$ and 0.7% $^{235}_{92}\text{U}$
(c) 50% $^{238}_{92}\text{U}$ and 50% $^{235}_{92}\text{U}$ (d) 80% $^{238}_{92}\text{U}$ and 20% $^{235}_{92}\text{U}$

90. Which of the following elements indicated protons and neutrons is expected to be most stable?
(a) Odd protons and even neutrons (b) Even protons and odd neutrons
(c) Odd protons and odd neutrons (d) Even protons and even neutrons

Multiple Correct Choice Type

1. Which of the following is/are the unit of radioactivity?
(a) Curie (b) Becquerel (c) Tesla (d) Henry

2. Which of the following statements is/are correct?
(a) Most nuclei are approximatlt spherical with a radius directly proportional to the cube root of the mass number.
(b) The value of unfied atomic mass unit is 1.66×10^{-24} kg
(c) The beta radioactive decay is accompanced with the emission of antineutrino.
(d) Electron captured by the nucleus increases the atomic number of atom.

3. Nuclear reaction(s) accompanied by emission of neutron(s) is/are
(a) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P}$ (b) $^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \longrightarrow {}^{13}_{7}\text{N}$
(c) $^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + {}^{0}_{1}\text{e}$ (d) $^{241}_{96}\text{U} + {}^{4}_{1}\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^{0}_{1}\text{e}$

4. Decrease in atomic number is observed during
(a) alpha emission (b) beta emission (c) positron emission (d) electron capture (1998)

5. Which of the following statements for the nuclear reaction $^{1}_{0}\text{e} + {}^{235}_{92}\text{U} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr}$ + neutrons is/are correct?
(a) The number of neutrons emitted in the reaction is three.
(b) The total mass of the product nuclei is greater then of the reactant.
(c) The binding energy per nucleon of each of the two products is larger than that of the reactant.
(d) The bombarding neutron must carry vary large energy so as to break the uranium nucleus.

6. Which of the following statements are **not** correct?
(a) In β-emission from a nucleus the atomic number of the daughter element decreases by one.
(b) The emission of one α-particle from a radioactive atom results in the decrease of atomic number by two and mass number by four.
(c) The successive emission of two β-particles from a radioactive atom results in the decrease of atomic number by one.
(d) Neutrino is a positively charged electron.

7. Which of the following statements are correct?
(a) In the nuclear process $^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + \beta^{+} + \text{X}$, X stands for antineutrino.
(b) In the nuclear reaction, $^{3}_{1}\text{H} \longrightarrow {}^{3}_{2}\text{He} + e^{-} + \text{X}$, X stands for neutrino.

(c) One atomic mass unit is equivalent to 931 MeV energy.

(d) The light radiations with discrete quantities of energy are called photons.

8. Which of the following statements are correct?

(a) ${}^{A}_{Z}\mathrm{M}$ undergoes an α-emission followed by two successive β-emissions. The element is ${}^{A-2}_{Z}\mathrm{M}$.

(b) The group displacement law was established by Soddy–Fajan.

(c) The man made radioactive disintegration series is known as $4n + 1$ series.

(d) The number of α and β-particles emitted in thorium series (${}^{232}_{90}\mathrm{Th} \longrightarrow {}^{208}_{82}\mathrm{Pb}$) are 4 and 6, respectively.

9. Which of the following statements are **not** correct?

(a) The number of α and β-particles emitted in neptunium series (${}^{237}_{93}\mathrm{Np} \longrightarrow {}^{209}_{83}\mathrm{Bi}$) are 7 and 4, respectively.

(b) The number of α and β-particles emitted in uranium series (${}^{238}_{92}\mathrm{U} \longrightarrow {}^{206}_{83}\mathrm{Pb}$) are 6 and 8, respectively.

(c) The number of α and β-particles emitted in actinium series (${}^{235}_{92}\mathrm{U} \longrightarrow {}^{207}_{82}\mathrm{Bi}$) are 4 and 7, respectively.

(d) The half–life of a radioactive decay is given as $t_{1/2} = 0.693/\lambda$, where λ is rate constant.

10. Which of the following statements are correct?

(a) The rest mass of a stable nucleus is lesser than the sum of the rest masses of its separated nucleons.

(b) The rest mass of a stable nucleus is greater than the sum of the rest masses of its separated nucleons.

(c) In nuclear fusion, energy is released by fusing two nuclei of medium mass (approximately 100 amu).

(d) In nuclear fission, energy is released by fragmentation of a very heavy nucleus.

11. The disintegration series involving emission of 8α and 6β particles are

(a) $4n$ series (b) $4n + 1$ series (c) $4n + 2$ series (d) $4n + 3$ series

12. The disintegration series involving emission of a total of eight alpha particles is/are

(a) $4n$ series (b) $4n + 1$ series (c) $4n + 2$ series (d) $4n + 3$ series

13. Which of the following elements have binding energy per nucleon less than 7?

(a) ${}^{6}_{3}\mathrm{Li}$ (b) ${}^{12}_{6}\mathrm{C}$ (c) ${}^{10}_{5}\mathrm{B}$ (d) ${}^{56}_{26}\mathrm{Fe}$

14. Which of the following elements have binding energy per nucleon more than 7?

(a) ${}^{9}_{4}\mathrm{Be}$ (b) ${}^{10}_{5}\mathrm{B}$ (c) ${}^{14}_{7}\mathrm{N}$ (d) ${}^{206}_{82}\mathrm{Pb}$

Linked Comprehension Type

1. In the upper atmosphere, neutrons present in cosmic rays causes the following nuclear reaction

$${}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

The isotope ${}^{14}_{6}\mathrm{C}$, gets circulated in the atmosphere as well as in living species. In a place where nuclear explosion takes place, the concentration of ${}^{14}\mathrm{C}$ increases both in the atmosphere as well as in living species.

The isotope ${}^{14}_{6}\mathrm{C}$ disintegrates according to the reaction

$${}^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}_{-1}^{0}\mathrm{e} + \tilde{\nu}$$

with a half life of 5760 years. When a species dies, the concentration of ${}^{14}\mathrm{C}$ in it decreases due to the above disintegration reaction. The time at which species had died can be estimated from the knowledge of its ${}^{14}\mathrm{C}$ content compared to that existing in atmosphere. Beyond 30000 years, the activity of disintegration is too low to be used for the estimation of time period.

(i) In radiocarbon dating for finding the age of fossils, the correct statement is

(a) During the life time ${}^{14}\mathrm{C}$ assimilated by the human being is in equilibrium with the ${}^{14}\mathrm{C}$ that decomposes by β emission resulting in the constant ratio of ${}^{14}\mathrm{C}/{}^{12}\mathrm{C}$ at a particular instant.

(b) ${}^{14}\mathrm{C}$ dating method is inappropriate for finding the life of a given sample because ${}^{14}\mathrm{C}$ undergoes β emission and the ratio ${}^{14}\mathrm{C}/{}^{12}\mathrm{C}$ is not constant in human beings.

(c) For a dead human being, the decay of ${}^{14}\mathrm{C}$ depends on place to place.

(d) None of the above.

(ii) Two organisms died on the same day. One died at a place where nuclear explosion had taken place while the other died at a place where no such explosion has occurred. The ratio of ^{14}C during life to that present in the fossil at an instant is r_1 for the former and r_2 for the latter. The age of the former was calculated at t_1 and for the latter as t_2. The correct choice for the timings t_1 and t_2 is

(a) $t_1 > t_2$ (b) $t_1 < t_2$ (c) $t_1 = t_2$ (d) none of these

(iii) If both the fossils are brought to a common place where no explosion has occurred then

(a) $t_1 > t_2$ (b) $t_1 < t_2$ (c) $t_1 = t_2$ (d) none of these (2006)

2. In a fission reaction, heavier nucleus splits into two or more lighter nuclei with an enormous release of energy. For example, the fission of $^{235}_{92}$U may be represented as

$$^1_0\text{n} + {}^{235}_{92}\text{U} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow \text{N}_1 + \text{N}_2 + \text{neutrons}$$

Based on this reaction, answer the following three questions

(i) If N_1 and N_2 are ^{90}Sr + ^{143}Xe, then the number of neutron emitted is

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

(ii) The projectile $^1_0$n must have

(a) very high speed (b) low speed

(c) very high temperature (d) their presence in large number near $^{235}_{92}$U

(iii) If the average binding energy per nucleon is 7.6 MeV for ^{235}U and 8.5 MeV for the fission fragments, the total energy released per fission will be about

(a) 100 MeV (b) 150 MeV (c) 210 MeV (d) 260 MeV

3. Carbon dating is the method to determine the time elapsed when a plant was cut or an animal died. This is done on the basis of the measurement of radioactivity of ^{14}C. In an environment the proportion of ^{14}C in carbon di oxide does not change with time because the rate at which ^{14}C nuclei decay is equal to the rate at which these are replenished by the bombardment of cosmic-ray neutron on nitrogen ($^{14}_7\text{N} + {}^1_0\text{n} \longrightarrow {}^{14}_6\text{C} + {}^1_1\text{H}$). In living animals and plants, this ratio is also maintained. But once an animal or a plant die, the replenishment ^{14}C is not carried out resulting into the decrease in ^{14}C content due to its radioactive decay. Based on this information, answer the following three questions

(i) If the half-life period of decay of ^{14}C is 5760 y, the rate constant of the decay is

(a) $1.203 \times 10^{-3}\ y^{-1}$ (b) $1.203 \times 10^{-4}\ y^{-1}$ (c) $5760\ y^{-1}$ (d) $2.406 \times 10^{-3}\ y^{-1}$

(ii) A piece of wood recovered in an exacavation has 30% as much C-14 (half life: 5760 y) as ordinary wood today. The time elapsed when the piece of wood was buried is about

(a) 5760 y (b) 8240 y (c) 10010 y (d) 15240 y

(iii) The analysis of a rock shows that the relative number of ^{206}Pb and ^{238}U is ^{206}Pb/^{238}U = 0.2. If half-life time of $^{238}\text{U} \longrightarrow {}^{206}\text{Pb}$ is 4.0×10^9 y, the age of the rock is about

(a) $1.05 \times 10^9\ y$ (b) $1.05 \times 10^8\ y$ (c) $1.05 \times 10^7\ y$ (d) $1.05 \times 10^6\ y$

Assertion and Reason Type

Given below are questions, each containing two statements. Answer these questions based on the following key.

(a) STATEMENT – 1 is True, STATEMENT – 2 is True; STATEMENT – 2 is a correct explanation for STATEMENT – 1

(b) STATEMENT – 1 is True, STATEMENT – 2 is True; STATEMENT – 2 is Not a correct explanation for STATEMENT – 1

(c) STATEMENT – 1 is True, STATEMENT – 2 is False

(d) STATEMENT – 1 is False, STATEMENT – 2 is True

	Statement–1	Statement–2
1.	Nuclide $^{30}_{13}$Al is less stable than $^{40}_{20}$Ca.	Nuclides having odd number of protons and neutrons are generally unstable.
2.	The plot of atomic number (*y*-axis) versus number of neutrons (*x*-axis) for stable nuclei shows a curvature towards *x*-axis from the line of 45° slope as the atomic number is increased.	Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

3.	Larger the binding energy per nucleon, the greater the stability of nuclide.	Binding energy per nucleon is a measure of strength of nuclear bonding.
4.	The region of greatest stability of nucleus occurs for atomic numbers from 50 to 80.	For low and high atomic number, binding energy per nucleon is lesser than that exists for nuclides from atomic number 50 to 80.
5.	Nuclei containing even numbers of neutrons and protons are more stable than the other nuclei.	Nucleus containing even numbers of neutrons and protons involve complete spin pairing of nucleons.
6.	The proportion of ^{14}C remains constant in the atmosphere.	^{14}C is a non-radioactive nuclide.
7.	The nuclear fusion reactions is accompanied with decrease in binding energy per nucleon.	There occurs a loss of mass in nuclear fusion reactions.
8.	For transmutation experiments, α-particles and protons are accelerated but neutrons have to be slowed down.	α-particles and proton carry positive charge while neutrons are uncharged particles.
9.	The radius of a nucleus is given as $R = R_o A^{1/3}$, where R_o is a constant and A is the mass number of the nucleus.	All neuclei have the same density and thus volume of the nucleus is directly proportional to A.
10.	Alpha decay occurs much more frequently than the release of two neutrons and two protons separately.	Helium ion is an usually stable entity with high binding energy.
11.	The large amount of energy (approximately 200 MeV) is released per fissioning nucleus.	The difference in the masses of the fission fragments is less than the mass of the fission nucleus by an amount corresponding to about 200 MeV.
12.	Lead obtained from uranium series has the same atomic mass as obtained from thorium series.	Uranium and thorium decays belong to different series.
13.	^{238}U decay via α-emission and not via β-emission.	In this case, α-emission is an exothermic process while β-emission is an endothermic process.
14.	Even-even nuclear type nuclides are most stable nuclides while odd-odd nuclear type nuclides are least stable nuclides.	Two nucleons of the same type in a nucleus can interact with each other more strongly than two nucleons of different type.

Matrix Match Type

1. Column I lists the type of artificial transmutation reactions and Column II includes incomplete reactions with target and product elements. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) (p, α)	(p) $^{10}_{5}\text{B} \longrightarrow {}^{7}_{3}\text{Li}$
(b) (α, n)	(q) $^{19}_{9}\text{F} \longrightarrow {}^{16}_{8}\text{O}$
(c) (T, p)	(r) $^{75}_{33}\text{As} \longrightarrow {}^{78}_{35}\text{Br}$
(d) (n, a)	(s) $^{59}_{27}\text{Co} \longrightarrow {}^{61}_{27}\text{Co}$

2. Column I lists the type of artificial transmutation reactions and Column II includes incomplete reactions with target and product elements. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) (p, γ)	(p) $^{31}_{15}\text{P} \longrightarrow {}^{30}_{15}\text{P}$
(b) (D, T)	(q) $^{32}_{16}\text{S} \longrightarrow {}^{34}_{17}\text{Cl}$
(c) (γ, n)	(r) $^{14}_{7}\text{N} \longrightarrow {}^{15}_{8}\text{O}$
(d) (T, n)	(s) $^{9}_{4}\text{Be} \longrightarrow {}^{8}_{4}\text{Be}$

3. Column I lists the four types of radioactive series and Column II includes some of the characteristics of these series. Identify each entry of Column I with those given in Column II.

Column I	**Column II**
(a) 4*n* series	(p) U ⟶ Pb
(b) 4*n* + 1 series	(q) Th ⟶ Pb
(c) 4*n* + 2 series	(r) Pu ⟶ Bi
(d) 4*n* + 3 series	(s) Emission of 8α and 6β particles
	(t) Emission of 8α and 5β particles
	(u) Emission of 6α and 4β particles

4. Column I lists the four radioactive elements and Column II lists their binding energy per nucleon. identify each entry of Column I with those given Column II.

Column I	**Column II**
(a) $^{56}_{26}\mathrm{Fe}$	(p) 2.57
(b) $^{206}_{82}\mathrm{Pb}$	(q) 6.48
(c) $^{3}_{2}\mathrm{He}$	(r) 7.88
(d) $^{10}_{5}\mathrm{B}$	(s) 8.79

5. Given the following sequence of radioactive reactions

$$\mathrm{A} \xrightarrow{-\alpha} \mathrm{B} \xrightarrow{-\beta} \mathrm{C} \xrightarrow{-\beta} \mathrm{D} \xrightarrow{+n} \mathrm{E}$$

Column I lists some of the terms used to describe atoms and Column II lists the elements listed in the above reaction. Match the entry of Column I with those given in Column II.

Column I	**Column II**
(a) Isotopes	(p) A
(b) Isobars	(q) B
(c) Isotones	(r) C
(d) Isoelectronic	(s) D
	(t) E

6. Column I includes a few types of nuclear reactions and Column II lists some of the examples of these reactions. Identify each entry in Column I with those listed in Column II.

Column I	**Column II**
(a) Particle capture reaction	(p) $^{3}_{1}\mathrm{H} + ^{3}_{1}\mathrm{H} \longrightarrow ^{4}_{2}\mathrm{He} + 2^{1}_{0}\mathrm{n}$
(b) Nuclear fission reaction	(q) $^{63}_{29}\mathrm{Cu} + ^{4}_{2}\mathrm{He} \longrightarrow ^{137}_{17}\mathrm{Cl} + ^{16}_{10}\mathrm{n} + ^{14}_{11}\mathrm{H}$
(c) Nuclear fusion reaction	(r) $^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \longrightarrow ^{239}_{92}\mathrm{U} + \gamma$
(d) Spallation reaction	(s) $^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \longrightarrow ^{140}_{56}\mathrm{Ba} + ^{94}_{36}\mathrm{Kr} + 2^{1}_{0}\mathrm{n}$

7. Column I includes four nuclear types and Column II lists their examples and main characteristics. Identify each entry in Column I with those listed in Column II.

Column I	**Column II**
(a) Even-even	(p) $^{23}_{11}\mathrm{Na}$
(b) Even-odd	(q) $^{234}_{91}\mathrm{Pa}$
(c) Odd-even	(r) $^{123}_{50}\mathrm{Sn}$
(d) Odd-odd	(s) $^{234}_{90}\mathrm{Th}$
	(t) most stable nuclides
	(u) least stable nuclides
	(v) largest number of β-stable nuclides

ANSWERS

Straight Objective Type

1. (d) **2.** (d) **3.** (a) **4.** (c) **5.** (d) **6.** (b) **7.** (d)

8. (d) **9.** (c) **10.** (b) **11.** (c) **12.** (c) **13.** (a) **14.** (b)

15. (d) **16.** (b) **17.** (b) **18.** (b) **19.** (a) **20.** (b) **21.** (d)

22. (c) **23.** (b) **24.** (b) **25.** (d) **26.** (a) **27.** (a) **28.** (c)

29. (d) **30.** (c) **31.** (a) **32.** (b) **33.** (c) **34.** (b) **35.** (b)

36. (c) **37.** (d) **38.** (b) **39.** (b) **40.** (c) **41.** (a) **42.** (b)

43. (d) **44.** (a) **45.** (d) **46.** (c) **47.** (a) **48.** (c) **49.** (a)

50. (c) **51.** (b) **52.** (a) **53.** (d) **54.** (c) **55.** (d) **56.** (a)

57. (d) **58.** (b) **59.** (d) **60.** (b) **61.** (a) **62.** (d) **63.** (c)

64. (a) **65.** (b) **66.** (b) **67.** (a) **68.** (c) **69.** (b) **70.** (a)

71. (a) **72.** (b) **73.** (b) **74.** (c) **75.** (a) **76.** (b) **77.** (d)

78. (b) **79.** (b) **80.** (b) **81.** (b) **82.** (c) **83.** (b) **84.** (b)

85. (a) **86.** (b) **87.** (a) **88.** (c) **89.** (b) **90.** (d)

Multiple Correct Choice Type

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

5. (a), (c) **6.** (a), (c), (d) **7.** (c), (d) **8.** (b), (c)

9. (b), (c) **10.** (a), (d) **11.** (c), (d) **12.** (b), (c), (d)

13. (a), (c) **14.** (c), (d)

Linked Comprehension Type

1. **(i)** (a) **(ii)** (a) **(iii)** (c) **2.** **(i)** (c) **(ii)** (b) **(iii)** (c)

3. **(i)** (b) **(ii)** (c) **(iii)** (a)

Assertion and Reason Type

1. (b) **2.** (a) **3.** (a) **4.** (b) **5.** (a) **6.** (c) **7.** (d)

8. (b) **9.** (a) **10.** (a) **11.** (a) **12.** (d) **13.** (a) **14.** (b)

Matrix Match Type

1. (a) – (q); (b) – (r); (c) – (s); (d) – (p)

2. (a) – (r); (b) – (p); (c) – (s); (d) – (q)

3. (a) – (q), (u); (b) – (r), (t); (c) – (p), (s); (d) – (p), (s)

4. (a) – (s); (b) – (r); (c) – (p); (d) – (q)

5. (a) – (p), (s), (t); (b) – (q), (r), (s); (c) – (r), (t); (d) – (p), (s), (t)

6. (a) – (r); (b) – (s); (c) – (p); (d) – (q)

7. (a) – (s), (t), (v); (b) – (r); (c) – (p); (d) – (q), (u)

Hints and Solutions

Straight Objective Type

1. Either alpha or beta rays are deflected in a magnetic field in one direction.
2. Neutron has *e*/*m* value zero. The next higher value is of α-particle. This is followed by proton and finally by electron.
3. In the reaction $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \rightarrow ^{30}_{15}\text{P}$, atomic number is balanced and mass number decreases by one. This reaction will associated with the emission of a neutron.
4. Gamma rays are not deflected by an electric field.
5. The emission of beta particles is from the nucleus due to the nuclear reaction neutron → proton + electron.
6. The instability of a nucleus is due to high proton-neutron ratio.

7. Antiproton has a negative charge.

8. Mesons are responsible for attraction between nucleons.

9. The radioisotope ^{14}C is used to establish reaction mechanism of photosynthesis in plants.

10. Neptunium series is a man-made radioactive disintegration series.

11. The density of a nucleus is of the order of 10^{17} kg m^{-3}.

12. One Curie is equal to 3.7×10^{10} disintegrations per second.

13. One Becquerel of radioactivity is equal to one integration per second.

14. $^{29}_{13}Al$ contains larger neutrons than the stable nucleide. It will undergo the reaction $n \rightarrow p + \bar{e}$.

15. The reaction is $^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{139}_{54}Xe + {}^{94}_{38}Sr + 3\,{}^{1}_{0}n$

The $3\,{}^{1}_{0}n$ is obtained by the balance of charge and mass numbers.

16. $4n + 1$ is a man made disintegration series.

17. Meson is 207 times heavier than an electron.

18. Positron is e^{+}.

19. Thorium series is 4n series.

20. Neptunium series is $4n + 1$ series.

21. Uranium series is $4n + 2$ series.

22. Actinium series is $4n + 3$ series.

23. The end product of $4n + 1$ series is $^{209}_{83}Bi$. In the other three series, Pb is the end product.

24. See Q.23.

25. Lead-207 is the end product of $4n + 3$ series, since 207 when divided by 4 gives 3 as the remainder.

26. In β decay, the reaction occurring is $n \rightarrow p + e^{-}$. This will be accompanied with increase in the value of p/n, as proton is formed and neutron is consumed.

27. ^{24}Na contains one extra neutron as compared to stable ^{23}Na. This is get rid of by converting into proton and electron.

28. The reaction is $^{23}_{11}Na \longrightarrow {}^{23}_{10}Na + {}_{+1}e^{+}$. The balancing of charge number gives +1.

29. The atomic mass of Cu is expected to be smaller than Zn. Since the given mass is larger, it is expected to be unstable.

In β-decay, atomic number is increased by one while mass number remains the same

$$^{64}_{29}Cu \longrightarrow {}^{64}_{30}Zn + {}_{-1}^{0}e$$

30. β radiation is due to reaction $n \longrightarrow p + \beta$.

31. Fast neutrons are slow down with the use of moderator.

32. Mass number = 238 – 4 = 234 and atomic number = 92 – 2 = 90.

33. There is an increase in atomic number one. Thus, the daughter element belongs to the next higher group numbered 16.

34. With the emission of one α-particle and two β-particles, an isotope of parent element is produced.

35. Emission of an alpha particle ($^{4}_{2}He^{2+}$) is accompanied with decrease in charge number and mass number by 2 and 4, respectively.

36. Emission of a beta particle is accompanied with increase in charge number by one with no change in mass number

37. It x and y are the number of alpha and beta particles released, respectively, then

Balancing of charge number: $90 - 2x + y = 82$. Balancing of mass number: $232 - 4x + 0 = 208$

From these, we get $x = 6$ and $y = 2$.

38. Release of one α-particle and one β-particle cause a lose of 2 and 1 neutrons, respectively.

39. The given nuclear reaction is $^{22}_{10}Ne \longrightarrow 2\,{}^{4}_{2}He + {}_{n}X$

The conservation of atomic number gives $2 \times 2 + n = 10 \quad \Rightarrow \quad n = 6$.

Hence, the unknown nucleus is carbon (atomic number 6).

40. Change in charge number = 6(– 2) + 4(+1) = – 8. Change in mass number = 6(– 4) = – 24.

41. Change in mass number indicates the release of one alpha particle. The accompanying decrease in charge number is restored by the release of two beta particles.

42. $4n + 1$ series involves $^{241}_{94}Pu \xrightarrow[\text{5 β particles}]{\text{8 α particles}} {}^{209}_{83}Bi$.

43. 560 days are equivalent to four half-lives. The element left will be $(1/2^{4})$ (1 g), i.e. (1/16) g.

44. The half-life of a radioactive decay is given by $t_{1/2} = 0.693/\lambda$.

45. The expression of decay constant is $\lambda = (2.303/t)\log(N_0/N)$.

46. The radioisotope ${}^{13}_{6}\mathrm{C}$ is used to determine the age of dead plants and animals.

47. 10,000 disintegrations $\xrightarrow[t_{0.5}]{}$ 5000 disintegrations $\xrightarrow[t_{0.5}]{}$ 2500 disintegrations

Obviously, $2t_{0.5} = 50$ days. Hence $t_{0.5} = 25$ days

48. $\lambda = \dfrac{0.693}{5000\ \mathrm{y}}$; $t = -\dfrac{2.303}{\lambda}\log\dfrac{[\mathrm{A}]}{[\mathrm{A}]_0} = -\dfrac{2.303 \times 5000\ \mathrm{y}}{0.693}\log(0.4) = \dfrac{2.303 \times 5000}{0.693} \times 0.401\ \mathrm{y} = 6667\ \mathrm{y}$.

49. 50% of ${}^{14}\mathrm{C}$ means half of ${}^{14}\mathrm{C}$ has disappeared. Therefore, $t = t_{0.5} = 5760$ y.

50. One fourth implies two half lives. Hence, $t = 2t_{0\cdot 5}$.

51. Average life time is reciprocal of decay constant.

52. The rate of decay for the material is

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\lambda_1 N - \lambda_2 N = -N(\lambda_1 + \lambda_2) \quad \text{or} \quad N = N_0 \mathrm{e}^{-(\lambda_1+\lambda_2)t} \quad \text{or} \quad \ln N = \ln N_0 - (\lambda_1 + \lambda_2)t$$

$$\text{or} \qquad \ln\left(\frac{N}{N_0}\right) = -\left[\frac{\ln 2}{(t_{0.5})_1} + \frac{\ln 2}{(t_{0.5})_2}\right]t = -(\ln 2)\left[\frac{(t_{0.5})_1 + (t_{0.5})_2}{(t_{0.5})_1 (t_{0.5})_2}\right]t$$

$$\text{or} \qquad t = \left[\frac{\ln(N_0/N)}{\ln 2}\right]\left[\frac{(t_{0.5})_1 (t_{0.5})_2}{(t_{0.5})_1 + (t_{0.5})_2}\right] = (2)\left[\frac{(1620)\,(810)}{1620 + 810}\right] y = 1080\ y$$

53. The number of radioactive particles at any instant will be given by $N = N_0 \mathrm{e}^{-\lambda t}$ where $\lambda = 0.693/t_{1/2}$
A given nucleus may decay at any time after $t = 0$ but the number of radioactive particles will be given by the above expression.

54. By definition $t_{1/2} = 0.693/\lambda$ and $t_\mathrm{m} = 1/\lambda$
It is given that $(t_{1/2})_\mathrm{X} = (t_\mathrm{m})_\mathrm{Y}$, that is

$$\frac{0.693}{\lambda_\mathrm{X}} = \frac{1}{\lambda_\mathrm{Y}} \Rightarrow \lambda_\mathrm{Y} > \lambda_\mathrm{X}$$

The expression of rate law is

$$-\frac{\mathrm{d}N}{N} = \lambda N.$$

Since $\lambda_\mathrm{Y} > \lambda_\mathrm{X}$, it follows that $\left(-\dfrac{\mathrm{d}N}{N}\right)_\mathrm{Y} > \left(-\dfrac{\mathrm{d}N}{N}\right)_\mathrm{X}$

55. $N_1 = N_0 \mathrm{e}^{-\lambda_1 t}$ and $N_2 = N_0 \mathrm{e}^{-\lambda_2 t}$ Thus $\dfrac{N_1}{N_2} = \dfrac{\mathrm{e}^{-\lambda_1 t}}{\mathrm{e}^{-\lambda_2 t}} = \mathrm{e}^{-(\lambda_1 - \lambda_2)t} = \mathrm{e}^{-9\lambda t}$

It is given that $N_1/N_2 = \mathrm{e}^{-1}$. Hence $-9\lambda t = -1 \Rightarrow t = 1/(9\lambda)$

56. Since $\dfrac{1}{16} = \dfrac{1}{2^4}$, $t = 4t_{1/2} = 4(100\ \mu\mathrm{s}) = 400\ \mu\mathrm{s}$

57. $\ln\left(\dfrac{0.9}{1}\right) = -\lambda\,(5\ \mathrm{d})$ and $\ln\left(\dfrac{N}{N_0}\right) = -\lambda\,(20\ \mathrm{d})$.

Thus $\ln\left(\dfrac{N}{N_0}\right) = \left(\dfrac{1}{5}\ln 0.9\right)(20) = 4\ln(0.9)$

or $\dfrac{N}{N_0} = (0.9)^4 = 0.6561 \quad \Rightarrow$ Per cent of material left = 65.6 %

58. The intensity will decrease 32 times after five half-lives.

59. $t = \dfrac{2.303}{\lambda}\log\dfrac{N_t}{N_0} = -\dfrac{2.303}{0.693/t_{0.5}}\log\dfrac{N_t}{N_0} = -\dfrac{2.303}{(0.693/5760y)}\log\left(\dfrac{40}{100}\right) = \dfrac{2.303\times5760\times0.40}{0.693}y = 7.6\times10^3y$

60. 1 amu $= \dfrac{1}{12}\,m(^{12}\text{C}) = \dfrac{1}{12} = \left[\dfrac{M(^{12}\text{C})}{N_\text{A}}\right] = \dfrac{1}{12}\left[\dfrac{0.012\text{ kg mol}^{-1}}{6.022\times10^{23}\text{ mol}^{-1}}\right] = 1.6606\times10^{-27}$ kg

$$E = mc^2 = (1.6606\times10^{-27}\text{ kg})\,(3\times10^8\text{ m s}^{-1})2 = 1.4945\times10^{-10}\text{ J}$$

$$= (1.4945\times10^{-10}\text{ J})\left(\dfrac{1\text{ eV}}{1.602\times10^{-19}\text{J}}\right) = 9.33\times10^9\text{ eV} = 933\text{ MeV}$$

61. We have Δm = Mass of $(^{10}_{5}\text{B}^+ + {}^{0}_{-1}\text{e})$ – Mass of $^{10}_{4}$Be = Mass of $(^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$

62. We have Δm = Mass of $(^{8}_{4}\text{Be} + {}^{0}_{+1}\text{e})$ – Mass of $^{8}_{5}$B = Mass of ($^{8}_{4}$Be + 2 electrons) – Mass of $^{8}_{5}$B

63. Energy released per mole of reaction is

$E = (\Delta m)c^2 N_\text{A} = (7.64\times10^{-30}\text{ kg})\,(3\times10^8\text{ m s}^{-1})^2\,(6.022\times10^{23}\text{ mol}^{-1}) = 4.14\times10^{11}\text{ J mol}^{-1}$

64. Binding energy = (0.10242 amu) $\left(\dfrac{931\text{ MeV}}{1\text{ amu}}\right)$ = 95.35 MeV

65. $E = (2\,m_\text{e})c^2 = (2\times9.11\times10^{-31}\text{ kg})\,(3\times10^8\text{ m s}^{-1})^2 = 1.64\times10^{-13}$ J

66. The more tightly bound the nucleus is, the more stable the nucleus becomes and larger is its binding energy.

67. $\Delta E = 2[4\times7.06]$ MeV – 7×5.06 MeV = 17.28 MeV.

68. Total binding energy of ^{17}O = (17) (7.75 MeV) = 131.75 MeV

Total binding energy of ^{16}O = (16) (7.97 MeV) = 127.52 MeV

Energy required to remove a neutron from ^{17}O = (131.75 – 127.52) MeV = 4.23 MeV

69. $\Delta E = \dfrac{1}{2}\,[2m_\text{e}c^2] = (9.11\times10^{-31}\text{ kg})\,(3\times10^8\text{ m s}^{-1})^2 = (8.199\times10^{-14}\text{ J})$

$$= (8.199\times10^{-14}\text{ J})\left(\dfrac{1\text{ eV}}{1.602\times10^{-19}\text{J}}\right) = 5.12\times10^5\text{ eV} = 0.512\text{ MeV.}$$

70. Total binding energy = $(3.0308\times10^{-2}$ u) (931.5 MeV) = 28.296 MeV

Binding energy per nucleon = $\dfrac{28.296\text{ M eV}}{4}$ = 7.06 MeV

71. The nuclear transformation (α, n) implies the absorption of α-particles and release of a neutron.

78. In a spallation reaction, a high-speed bombarding particle is absorbed by the target nucleus forming a normal nucleus and a large number of light particles.

86. The nuclear reaction $^{14}_{7}\text{N} + {}^{2}_{1}\text{H} \rightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He}$

$$\Delta m = m(^{12}_{6}\text{C}) + m(^{4}_{2}\text{He}) - m(^{14}_{7}\text{N}) - m(^{2}_{1}\text{H}) = (12.0000 + 4.00307 - 14.002603 - 2.01410)\text{u}$$
$$= -\,0.01457\text{u}$$

$$Q = (\Delta m)\,(931.48\text{ MeV/u}) = (-\,0.01457\text{u})\,(931.48\text{ MeV/u}) = 13.6\text{ MeV}$$

87. During a fusion reaction, energy is released because the binding energy per nucleon of light elements is smaller than those of the intermediate size.

88. $\Delta m = m(\text{Th}) + m(\text{He}) - m(\text{U}) = (228.029 + 4.003 - 232.038)\text{ u} = -\,0.006\text{ u}$

Hence $\frac{1}{2}m(\mathrm{He})u^2 = |(\Delta m)|c^2$ or $(u/c) = \sqrt{\frac{21(\Delta m)}{m}}$

or $(u/c) = (2 \times 0.006/4.003)^{1/2} = 0.055$

Multiple Correct Choice Type

1. Curie and Becquerel are the units of radioactivity.

2. The value of atomic mass unit is 1.66×10^{-27} kg.
Electron capture causes the reaction $\mathrm{p} + \mathrm{e}^- \rightarrow \mathrm{n}$. Thus atomic number is decreased.

3. In reactions a and d, charge number is balanced but not mass number.

4. During alpha emission and positron emission, number of protons in the nucleus decreases.

5. Balancing of mass number requires three neutrons.
For the reaction to occur, total mass of product must be less than those of reactants, larger the binding energy per nucleon, more stable the nuclide.

6. (a) In β-emission, the atomic number of daughter element is increased by one, due to the basic conversion of neutron into proton in the nucleus.

(b) An α-particle is $^4_2\mathrm{He}^{2+}$. Hence, atomic number and mass of daughter element are decreased by 2 and 4, respectively.

(c) There will occur an increase in atomic number by two: $^m_n\mathrm{A} \xrightarrow{-\beta} {}^{\;\;m}_{n+1}\mathrm{B} \xrightarrow{-\beta} {}^{\;\;m}_{n+2}\mathrm{C}$

(d) The neutrino has zero charge and seems to have rest mass equal to zero. It is emitted along with the emission of a positron (positive charge of + 1e and mass equal to electron). For example $^{19}_{10}\mathrm{Ne} \longrightarrow {}^{19}_{9}\mathrm{F} + {}^{0}_{1}\mathrm{e} + v$
Antineutrino is emitted along with the emission of β-particle.

11. $4n$ series $^{232}_{90}\mathrm{Th} \longrightarrow {}^{200}_{882}\mathrm{Pb}$; 6 alpha and four beta
$4n + 1$ series $^{241}_{90}\mathrm{Th} \longrightarrow {}^{209}_{83}\mathrm{Bi}$; 8 alpha and five beta
$4n + 2$ series $^{238}_{92}\mathrm{U} \longrightarrow {}^{206}_{82}\mathrm{Pb}$; 8 alpha and six beta
$4n + 3$ series $^{239}_{92}\mathrm{U} \longrightarrow {}^{207}_{82}\mathrm{Pb}$; 8 alpha and six beta

Linked Comprehension Type

1. (ii) We have

$$r_1 = \frac{[^{14}\mathrm{C}]_{\text{living explosion}}}{[^{14}\mathrm{C}]_{\text{dead}}} \quad \text{and} \quad r_2 = \frac{[^{14}\mathrm{C}]_{\text{living, no explosion}}}{[^{14}\mathrm{C}]_{\text{dead}}}$$

Since $[^{14}\mathrm{C}]_{\text{living, explosion}} > [^{14}\mathrm{C}]_{\text{living, no explosion}}$, we will have $r_1 > r_2$. Moreover, since $\ln r = (1/\lambda)t$, it follows that $t_1 > t_2$.

(iii) Here $r_1 = r_2$. Hence $t_1 = t_2$

2. (i) Balancing of mass numbers gives $90 + 143 + x = 236 \Rightarrow x = 3$
Hence, three neutrons are released in the given fission reaction.

(ii) The projectile $^1_0\mathrm{n}$ must have slow speed, so that the nucleus of $^{235}_{92}\mathrm{U}$ has a high probability of absorbing the projectile to give activated complex.

(iii) The total energy released per fission will be {(8.5 MeV/nucleon) – (7.6 MeV/nucleon)} (236 nucleon) ≅ 212 MeV

3. (i) Rate constant $\lambda = 0.693/t_{0.5} = 0.693/5760\ y = 1.203 \times 10^{-4}\ y^{-1}$

(ii) $$t = -\left(\frac{2.303}{\lambda}\right)\ln\left(\frac{N}{N_0}\right) = -\left(\frac{2.303}{1.203 \times 10^{-4}\ y^{-1}}\right)\log(0.3) = 10010\ y.$$

(iii) $$\frac{\text{Atoms of Pb}}{\text{Atoms of U}} = 0.2 \quad \text{or} \quad \frac{\text{Atoms of (Pb + U)}}{\text{Atoms of U}} = 1.2$$

Since 1 atom of U gives 1 atom of Pb on disintegration, the above expression may be written as

$$\frac{\text{Initial atoms of U}}{\text{Present atoms of U}} = 1.2$$

Now using the expression $t = \dfrac{2.303}{\lambda}\log\dfrac{[\text{U}]_0}{[\text{U}]}$ we get $t = \dfrac{2.303}{(0.693/4.0\times 10^9\,y)}\log(1.2)$

$$= \frac{2.303}{(0.173\times 10^{-9}\,y)}(0.079) = 1.05\times 10^9\,y$$

ANNEXURE

Subjective Problems for Practice

SOLVED NUMERICALS

1. Naturally occurring boron consists of two isotopes whose atomic masses are 10.01 and 11.01 amu. The atomic mass of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. (1982)

Solution Let x be the percentage of isotope of atomic mass 10.01 amu. We will have

$$\frac{x(10.01\,\text{amu}) + (100-x)(11.01\,\text{amu})}{100} = 10.81$$

Solving for x, we get $x = 20$

Hence, Abundance of isotope of atomic mass 10.01 amu = 20%

Abudance of isotope of atomic mass 11.01 amu = 80%.

2. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant for the decay? What fraction would remain after 11540 years? (1984)

Solution We have $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{5770\text{ y}} = 1.201\times 10^{-4}\text{ y}^{-1}$

Since 11540 years is equivalent two half-lives, we would have 25% radioactive carbon left after 11540 years.

3. ${}^{234}_{90}\text{Th}$ disintegrates to give ${}^{206}_{82}\text{Pb}$ as the final product. How many alpha and beta particles are emitted during this process? (1986)

Solution Since the change in mass number is only due to the emission of α-particle, we have

$$\text{Number of } \alpha\text{-particles emitted} = \frac{234-206}{4} = 7$$

Now, the associated decrease in atomic number would be 14 (= 2 × 7) and thus the atomic number of the daughter atom would be 76 (= 90 – 14). But the actual atomic number of lead is 82, i.e. the atomic number is six more than expected. This is because of the emission of β-particles. Since there is an increase of one in atomic number due to the emission of one β-particle, we have

$$\text{Number of } \beta\text{-particles emitted} = \frac{82-76}{1} = 6$$

Hence, Number of α-particles emitted = 7 and Number of β-particles emitted = 6

4. An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of ${}^{99}_{42}\text{Mo}$, which is a beta emitter, is 66.6 hours. Find the minimum amount of ${}^{90}_{42}\text{Mo}$ required to carry out the experiment in 6.909 hours. (1989)

Solution Minimum β-activity required = 346 min^{-1}

Number of β-particle required to carry out the experiment for 6.909 h = (346 min^{-1}) (6.909 × 60 min) = 143 431

$$\text{Amount of } \beta\text{-particles required} = \frac{143431}{6.022\times 10^{23}\text{ mol}^{-1}} = 2.3818\times 10^{-19}\text{ mol}$$

Now, the rate constant of radioactive decay is $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{66.6\ \text{h}} = 0.010404\ \text{h}^{-1}$

Now using the integrated rate expression $\log \dfrac{n_0 - n_{\text{consumed}}}{n_0} = -\dfrac{\lambda t}{2.303}$, we get

$$\log \frac{n_0 - 2.3818 \times 10^{-19}\ \text{mol}}{n_0} = -\frac{(0.010404\ \text{h}^{-1})(6.909\ \text{h})}{2.303} = -0.03121 \quad \text{or} \quad \frac{n_0 - 2.3818 \times 10^{-19}\ \text{mol}}{n_0} = 0.9306$$

Solving for n_0, we get

$$n_0 = \frac{2.3818 \times 10^{-19}\ \text{mol}}{1 - 0.9306} = 3.43 \times 10^{-18}\ \text{mol.}$$

5. One of the hazards of nuclear explosion is the generation of ^{90}Sr and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much ^{90}Sr will remain in his bones after 20 years? (1995)

Solution For the half-life $t_{1/2} = 28.1$ y, the decay constant is $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{28.1\ y}$

Since the radioactivity decay follows the first order kinetics, we have $\log \dfrac{[\text{A}]}{[\text{A}]_0} = -\dfrac{\lambda}{2.303}t$

Thus $$\log \frac{[\text{A}]}{1.0\ \mu\text{g}} = -\frac{0.693}{28.1\ \text{y}} \times \frac{20\ \text{y}}{2.303} \quad \text{or} \quad \log [\text{A}]/\mu\text{g} = -0.2142 \quad \text{or} \quad [\text{A}] = 0.6107\ \mu\text{g}.$$

6. Calculate the mass of ^{14}C (half-life period = 5720 y) atom which gives 3.70×10^7 disintegrations per second.

Solution Since the radioactive decay is first order, we will have

$$-\frac{\mathrm{d}n(^{14}\text{C})}{\mathrm{d}t} = \lambda\, n(^{14}\text{C}) \quad \text{where} \quad -\frac{\mathrm{d}n(^{14}\text{C})}{\mathrm{d}t} = \frac{3.70 \times 10^7\ \text{s}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}} = 6.143 \times 10^{-17}\ \text{mol s}^{-1}$$

Now $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5720 \times 365 \times 24 \times 60 \times 60\ \text{s}} = 3.842 \times 10^{-12}\ \text{s}^{-1}$$

Hence, $$n(^{14}\text{C}) = \left(-\frac{\mathrm{d}n(^{14}\text{C})}{\mathrm{d}t}\right)\left(\frac{1}{\lambda}\right) = \frac{6.143 \times 10^{-17}\ \text{mol s}^{-1}}{3.842 \times 10^{-12}\ \text{s}^{-1}} = 1.599 \times 10^{-5}\ \text{mol}$$

$$m(^{14}\text{C}) = (1.599 \times 10^{-5}\ \text{mol})\ (14\ \text{g mol}^{-1}) = 2.340 \times 10^{-4}\ \text{g.}$$

7. An analysis of the rock shows that the relative number of ^{87}Sr and ^{87}Rb atoms is $^{87}\text{Sr}/^{87}\text{Rb} = 0.052$. Determine age of the rock. Given that the half-life period of β-decay of Rb to Sr is 4.7×10^{10} y.

Solution We have

$$\frac{\text{Atoms of Sr}}{\text{Atoms of Pb}} = 0.052$$

Adding one on both sides, we get

$$\frac{\text{Atoms of (Sr + Pb)}}{\text{Atoms of Pb}} = 1.052 \quad \text{or} \quad \frac{\text{Initial atoms of Pb}}{\text{Present atoms of Pb}} = 1.052$$

Now $$t = \frac{2.303}{k} \log \frac{[\text{Pb}]_0}{[\text{Pb}]} = \frac{2.303}{(0.693/t_{1/2})} \log \frac{[\text{Pb}]_0}{[\text{Pb}]} = \frac{2.303(4.7 \times 10^{10}\ \text{y})}{0.693} \log 1.052 = 3.725 \times 10^{9}\ \text{y}$$

8. Compute the frequency of a gamma ray produced by positron-electron annihilation which results in the production of two photons of identical energy.

Solution The equation to be considered is $^{0}_{+1}\mathrm{e} + ^{0}_{-1}\mathrm{e} \rightarrow$ pair of photons of equal energy

The energy released in the above annihilation process is

$$E = 2m_\mathrm{e}c^2 = 2(9.11 \times 10^{-31}\ \mathrm{kg})(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})^2 = 1.64 \times 10^{-13}\ \mathrm{J}$$

Since two photons are produced, the energy per photon is, $E' = \frac{1}{2}E = \frac{1}{2}(1.64 \times 10^{-13}\ \mathrm{J}) = 8.20 \times 10^{-14}\ \mathrm{J}$

The frequency of γ-radiation having energy E' is $\nu = \frac{E'}{h} = \frac{8.20 \times 10^{-14}\ \mathrm{J}}{6.626 \times 10^{-34}\ \mathrm{J\ s}} = 1.24 \times 10^{20}\ \mathrm{s^{-1}}$

9. The observed mass of $^{56}_{26}\mathrm{Fe}$ is 55.9375 amu. Taking the masses of proton and neutron as 1.00737 amu and 1.00866 amu, respectively, calculate the binding energy per nucleon of Fe atom. Take 1 amu = 931 MeV.

Solution The nuelcus of $^{56}_{26}\mathrm{Fe}$ contains 26 protons and 30 neutrons. Hence,

Mass of 26 protons = 26 × 1.007 37 amu = 26.19162 amu

Mass of 30 neutrons = 30 × 1.00866 amu = 30.2598 amu

Total mass of 26 protons and 30 neutrons = (26.19162 + 30.25980) amu = 56.45142 amu

Mass defect = (56.45142 – 55.9375) amu = 0.51392 amu

Binding energy = 0.51392 × 931 MeV = 478.45952 Mev

Binding energy per nucleon $= \frac{478.45952\ \mathrm{MeV}}{56} = 8.544\ \mathrm{MeV}.$

10. Show that the mass defect of the nuclear reaction $^{10}_{4}\mathrm{Be} \rightarrow ^{10}_{5}\mathrm{B} + ^{0}_{-1}\mathrm{e}$ is given as Δm = atomic mass of ($^{10}_{5}\mathrm{B} - ^{10}_{4}\mathrm{Be}$) whereas for the reaction $^{8}_{5}\mathrm{B} \rightarrow ^{8}_{4}\mathrm{Be} + ^{0}_{+1}\mathrm{e}$ is given as Δm = atomic mass of ($^{8}_{4}\mathrm{Be} - ^{8}_{5}\mathrm{B}$) + mass of 2 electrons

Solution In the nuclear reaction $^{10}_{4}\mathrm{Be} \rightarrow ^{10}_{5}\mathrm{B} + ^{0}_{-1}\mathrm{e}$ the basic conversion is $^{1}_{0}\mathrm{n} \rightarrow ^{1}_{1}\mathrm{p} + ^{0}_{-1}\mathrm{e}$

Hence, the precise reaction is $^{10}_{4}\mathrm{Be(4p,\ 6n,\ 4e)} \rightarrow ^{10}_{5}\mathrm{B(5p,\ 5n,\ 4e)} + ^{0}_{-1}\mathrm{e}$

Thus, the mass defect is

$$\begin{aligned}\Delta m &= m_{\text{products}} - m_{\text{reactant}}\\ &= \{\text{mass of (5p, 5n, 4e)} + \text{mass of an electron}\} - \text{mass of (4p + 6n + 4e)}\\ &= \text{mass of (5p, 5n, 5e)} - \text{mass of (4p, 6n, 4e)}\\ &= \text{Atomic mass of } (^{10}_{5}\mathrm{B} - ^{10}_{4}\mathrm{Be})\end{aligned}$$

Now, in the nuclear reaction $^{8}_{5}\mathrm{B} \rightarrow ^{8}_{4}\mathrm{Be} + ^{0}_{+1}\mathrm{e}$ the basic conversion is $^{1}_{1}\mathrm{p} \rightarrow ^{1}_{0}\mathrm{n} + ^{0}_{+1}\mathrm{e}$

Hence, the precise reaction is $^{8}_{5}\mathrm{B\ (5p,\ 3n,\ 5e)} \rightarrow ^{8}_{4}\mathrm{Be(4p,\ 4n,\ 5e)} + ^{0}_{+1}\mathrm{e}$

Thus, the mass defect is

$$\begin{aligned}\Delta m &= m_{\text{products}} - m_{\text{reactant}}\\ &= \{\text{mass of (4p + 4n + 5e)} + \text{mass of a positron}\} - \text{mass of (5p + 3n + 5e)}\\ &= \text{mass of (4p + 4n + 4e)} + \text{mass of (electron + positron)} - \text{mass of (5p + 3n + 5e)}\\ &= \text{Atomic mass of } (^{8}_{4}\mathrm{Be} - ^{8}_{5}\mathrm{B}) + \text{mass of 2 electrons.}\end{aligned}$$

11. Calculate the energy change for each of the following three types of decay

(a) $^{40}_{19}\mathrm{K} \rightarrow ^{40}_{20}\mathrm{Ca} + ^{0}_{-1}\mathrm{e}$ (b) $^{40}_{19}\mathrm{K} + ^{0}_{-1}\mathrm{e} \rightarrow ^{40}_{18}\mathrm{Ar}$, and (c) $^{40}_{19}\mathrm{K} \rightarrow ^{40}_{18}\mathrm{Ar} + ^{0}_{+1}\mathrm{e}$

Given: Atomic masses of $^{40}\mathrm{K}$, $^{40}\mathrm{Ar}$ and $^{40}\mathrm{Ca}$ are 39.964008, 39.962384, and 39.962589 amu, respectively, and that the mass of an electron is 0.0005486 amu. Take 1 amu = 931 MeV.

Solution

(a) In this nuclear reaction, since the mass of electron is included in Ca atom, we have

$$\Delta m = \text{Atomic mass of (Ca – K)} = (39.962589 - 39.964008)\ \text{amu} = -1.419 \times 10^{-3}\ \text{amu}$$

$$E = -1.419 \times 10^{-3} \times 931\ \text{MeV} = -1.32\ \text{MeV}$$

(b) In this nuclear reaction, since the mass of electron is included in K atom, we have

$$\Delta m = \text{Atomic mass of (Ar – K)} = (39.962384 - 39.964008)\ \text{amu} = -1.624 \times 10^{-3}\ \text{amu}$$

$$E = -1.624 \times 10^{-3} \times 931\ \text{Mev} = -1.51\ \text{MeV}.$$

(c) In this nuclear reaction, there is a loss of 2 electronic masses from K atom. Hence,

$$\Delta m = \text{Atomic mass of (Ar – K)} + \text{mass of 2 electrons}$$

$$= (39.962384 - 39.964008 + 2 \times 0.0005486)\text{amu} = -5.27 \times 10^{-4}\ \text{amu}$$

Hence, $E = -5.27 \times 10^{-4} \times 931\ \text{MeV} = -0.49\ \text{MeV}.$

12. Calculate the energy change in the fusion reaction of deuterium: ${}^2_1\text{H} + {}^2_1\text{H} \rightarrow {}^3_2\text{He} + {}^1_0\text{n}$

Given: Atomic masses of ^{2}H, ^{3}He and n are 2.0141022, 3.0160299 and 1.0086654 amu, respectively. Take 1 amu = 931 Mev.

Solution For the given reaction

$$\Delta m = m_{\text{products}} - m_{\text{reactants}}$$

$$= \text{mass of } ({}^3_2\text{He} + {}^1_0\text{n}) - \text{mass of } ({}^2_1\text{H} + {}^2_1\text{H})$$

$$= [(3.0160299 + 1.0086654) - 2(2.0141022)]\text{amu} = -0.0035091\ \text{amu}$$

Hence, $E = -0.0035091 \times 931\ \text{MeV} = -3.267\ \text{MeV}.$

13. ^{227}Ac has a half-life of 22.0 years with respect to radioactive decay. The decays follows two parallel paths, one leading to ^{227}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths? (1996)

Solution The rate constant of the decay is

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{22.0\ \text{y}}$$

If λ_1 and λ_2 are the rate constants of the reactions leading to ^{227}Th and ^{223}Fr, respectively, we have

$$\lambda_1 + \lambda_2 = \frac{0.693}{22.0\,y} \quad \text{and} \quad \frac{\lambda_1}{\lambda_2} = \frac{2}{98}$$

Solving for λ_1, and λ_2, we get $\lambda_1 = 0.00063\ \text{y}^{-1}$ and $\lambda_2 = 0.03087\ \text{y}^{-1}$

14. With what velocity should an α-particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} m from the nucleus of the Cu atom? (1997)

Solution Potential energy of an α-particle at a distance 10^{-13} m from the nucleus of copper atom is

$$V = -\frac{Z_1Z_2e^2}{(4\pi\varepsilon_0)\,r} = -\frac{(29)(4)(1.6\times10^{-19}\ \text{C})^2}{(4)(3.14)(8.85\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})(10^{-13}\text{m})} = -2.67 \times 10^{-13}\ \text{J}$$

Velocity at which α-particle should move is

$$v = \sqrt{\frac{2|V|}{m}} = \left[\frac{2(2.67\times10^{-13}\ \text{J})}{(4.0\times10^{-3}\ \text{kg mol}^{-1})/(6.023\times10^{23}\ \text{mol}^{-1})}\right]^{1/2} = 8.97 \times 10^{6}\ \text{m s}^{-1}$$

15. ${}^{238}_{92}$U is radioactive and it emits α and β particles to form ${}^{206}_{82}$Pb. Calculate the number of α and β particles emitted in the conversion. An ore of ${}^{238}_{92}$U is found to contain ${}^{238}_{92}$U and ${}^{206}_{82}$Pb in the mass ratio of 1:0.1. The half life period of ${}^{238}_{92}$U is 4.5×10^9 years. Calculate the age of the ore. (2000)

Solution The release of an α-particle causes

Decrease in atomic number = 2 and Decrease in mass number = 4

The release of a β-particle causes

Increase in atomic number = 1 and No change in mass number

Since the mass number changes only due to the emission of α-particles, we will have

$$\text{Number of } \alpha\text{-particles emitted} = \frac{238-206}{4} = \frac{32}{4} = 8$$

The associated decrease in atomic number would be 8 × 2 = 16. But the actual decrease is only 10. The increase in atomic number from 76 (= 92 – 16) to 82 is due to emission of β-particles. Hence

Number of β-particles emitted = 82 – 76 = 6

Assuming atomic mass equal to mass number, we will have

	U		Pb	
Mass ratio	1	:	0.1	
Amount ratio	$\frac{1}{238}$	:	$\frac{0.1}{206}$	i.e. $4.202 \times 10^{-3} : 4.854 \times 10^{-4}$

Original amount of U, $[\mathrm{U}]_0 = [\mathrm{U}] + [\mathrm{Pb}] = (4.202 \times 10^{-3} + 4.854 \times 10^{-4})$ mol $= 4.687 \times 10^{-3}$ mol

Present amount of U, $[\mathrm{U}] = 4.202 \times 10^{-3}$ mol

The rate constant of radioactive decay is given by $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{4.5 \times 10^9\ \mathrm{y}} = 1.54 \times 10^{-10}\ y^{-1}$

Now, using the expression $\ln \dfrac{[\mathrm{U}]}{[\mathrm{U}]_0} = -\lambda t$ we get

$$t = -\frac{1}{\lambda}\left(2.303 \log \frac{[\mathrm{U}]}{[\mathrm{U}]_0}\right) = -\frac{1}{(1.54 \times 10^{-10}\,\mathrm{y}^{-1})}\left[2.303 \log\left(\frac{4.202 \times 10^{-3}}{4.687 \times 10^{-3}}\right)\right] = 7.09 \times 10^{8}\ \mathrm{y}$$

16. The nucleidic ratio, ${}^3_1\mathrm{H}$ to ${}^1_1\mathrm{H}$ in a sample of water is $8.0 \times 10^{-18} : 1$. Tritium undergoes decay with a half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected? (1992)

Solution We have

$$\frac{\text{Number of tritium (T) atoms}}{\text{Number of hydrogen (H) atoms}} = \frac{8.0 \times 10^{-18}}{1} \quad \text{or} \quad \frac{\text{Number of (T}_2\text{O) molecular}}{\text{Number of H}_2\text{O molecular}} = \frac{8.0 \times 10^{-18}/2}{1/2} = \frac{8.0 \times 10^{-18}}{1}$$

or
$$\frac{\text{Amount of (T}_2\text{O) molecular}}{\text{Amount of H}_2\text{O molecular}} = \frac{8.0 \times 10^{-18}/6.023 \times 10^{23}}{1/6.023 \times 10^{23}} = \frac{8.0 \times 10^{-18}}{1}$$

or
$$\frac{\text{Mass of T}_2\text{O molecules}}{\text{Mass of H}_2\text{O molecules}} = \frac{22 \times 8 \times 10^{-18}}{18}$$

Mass of T_2O molecules in 10.0 g of sample of water

$$= \frac{22 \times 8 \times 10^{-18}}{18 + 22 \times 8 \times 10^{-18}} \times 10.0\ \mathrm{g} = \frac{22 \times 8 \times 10^{-18}}{18} \times 10.0\ \mathrm{g} = 9.777 \times 10^{-17}\ \mathrm{g}$$

$$\text{Amount of T}_2\text{O molecules} = \frac{9.777 \times 10^{-17}\ \mathrm{g}}{22\ \mathrm{g\ mol^{-1}}} = 4.444 \times 10^{-16}\ \mathrm{mol}$$

Now using the intergrated rate expression $\log \dfrac{[\mathrm{T_2O}]}{[\mathrm{T_2O}]_0} = -\dfrac{k}{2.303} t$ for the first order reaction, we get

$$\log n(\mathrm{T_2O}) = \log n_0\,(\mathrm{T_2O}) - \frac{1}{2.303}\left(\frac{0.693}{t_{0.5}}\right)t = \log(4.444 \times 10^{-16}) - \frac{1}{2.303}\left(\frac{0.693}{12.3\,y}\right)(40\,y)$$

$= -\ 15.3522 - 0.9786 = -\ 16.3308$

or $n(\mathrm{T_2O}) = 4.6687 \times 10^{-17}$ mol

Number of $\mathrm{T_2O}$ molecules $= (4.6687 \times 10^{-17})\ (6.023 \times 10^{23}) = 2.812 \times 10^{7}$

Number of T atoms $= 2 \times 2.812 \times 10^{7} = 5.624 \times 10^{7}$

17. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-life for each of the decay processes. (2002)

Solution The nuclear reactions are as follows

β^- emission $\quad {}^{64}_{29}\mathrm{Cu} \longrightarrow {}^{64}_{30}\mathrm{Zn} + {}^{\ 0}_{-1}\mathrm{e}$ $\qquad$ β^+ emission $\quad {}^{64}_{29}\mathrm{Cu} \longrightarrow {}^{64}_{28}\mathrm{Ni} + {}^{\ 0}_{+1}\mathrm{e}$

Electron capture $\quad {}^{64}_{29}\mathrm{Cu} + {}^{\ 0}_{-1}\mathrm{e} \longrightarrow {}^{64}_{82}\mathrm{Ni}$

If r_1, r_2 and r_3 are the respective rates of decay of Cu and r is the overall rate of decay of Cu, we will have

$$r = r_1 + r_2 + r_3 \quad \text{i.e.} \quad \lambda[\mathrm{Cu}] = \lambda_1[\mathrm{Cu}] + \lambda_2[\mathrm{Cu}] + \lambda_3[\mathrm{Cu}] \quad \text{i.e.} \quad \lambda = \lambda_1 + \lambda_2 + \lambda_3 \qquad (1)$$

The overall decay constant λ is given by $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{12.8\ \mathrm{h}}\ 5.414 \times 10^{-2}\ \mathrm{h^{-1}}$ $\qquad$ (2)

It is given that $\dfrac{\lambda_1}{\lambda_3} = \dfrac{38}{43} = 0.884$ and $\dfrac{\lambda_2}{\lambda_3} = \dfrac{19}{43} = 0.442$

Substituting these in Eq. (1), we get $\lambda = 0.884\ \lambda_3 + 0.442\ \lambda_3 + \lambda_3 = 2.326\ \lambda_3$

Hence, $\lambda_3 = \dfrac{\lambda}{2.326} = \dfrac{5.414 \times 10^{-2}\,\mathrm{h^{-1}}}{2.326} = 2.328 \times 10^{-2}\ \mathrm{h^{-1}}$; $\quad (t_{1/2})_3 = \dfrac{0.693}{\lambda_3} = \dfrac{0.693}{2.328 \times 10^{-2}\ \mathrm{h^{-1}}} = 29.77$ h

$$\lambda_1 = 0.884\ \lambda_3 = (0.884)\ (2.328 \times 10^{-2}\ \mathrm{h^{-1}}) = 2.058 \times 10^{-2}\ \mathrm{h^{-1}}$$

$$(t_{1/2})_1 = \frac{0.693}{\lambda_1} = \frac{0.693}{2.058 \times 10^{-2}\ \mathrm{h^{-1}}} = 33.67\ \mathrm{h}$$

$$\lambda_2 = 0.442\ \lambda_3 = (0.442)\ (2.328 \times 10^{-2}\ \mathrm{h^{-1}}) = 1.029 \times 10^{-2}\ \mathrm{h^{-1}}$$

$$(t_{1/2})_2 = \frac{0.693}{\lambda_2} = \frac{0.693}{1.029 \times 10^{-2}\ \mathrm{h^{-1}}} = 67.35\ \mathrm{h}$$

UNSOLVED NUMERICALS

1. Calculate the energy released in (α, n) reaction for ${}^{9}_{4}\mathrm{Be}$. The masses of ${}^{9}_{4}\mathrm{Be}$, ${}^{4}_{2}\mathrm{He}$, ${}^{12}_{6}\mathrm{C}$, and ${}^{1}_{0}\mathrm{n}$ are 9.0121833 u, 4.002603 u, 12.000000 u. and 1.008665 u, respectively. Take 1 u = 931 Mev.
2. The half-life of radium is 1620 years. How many radium atoms decay in 1 s in 1-g sample of radium? The molar mass of radium is 226 g mol^{-1}.
3. A laboratory has 1.49 μg of pure ${}^{13}_{7}\mathrm{N}$ which has a half-life of 10.0 min. (a) How many nuclei are present initially? (b) What is the activity initially? (c) What is the activity after 1.00 h? (d) After approximately how long will the activity drop to less than one per cent?
4. Determine the maximum kinetic energy of β^+ particle released when ${}^{11}_{6}\mathrm{C}$ decays to ${}^{11}_{5}\mathrm{B}$. What is the maximum energy the neutrinos can have? What is its minimum energy?
5. The ${}^{3}_{1}\mathrm{H}$ isotope of hydrogen, tritium, has a half-life of 12.33 y. Determine the age of a bottle of wine whose ${}^{3}_{1}\mathrm{H}$ radiation is about 1/10 that present in a new bottle of wine.
6. Calculate the energy released in the fission reaction ${}^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{88}_{38}\mathrm{Sr} + {}^{136}_{54}\mathrm{Xe} + 12\,{}^{1}_{0}\mathrm{n}$

   Assume the initial kinetic energy of the neutron is very small. Take the masses of species involved in the above reaction as given in the following.

neutron	1.008665 u	${}^{88}_{38}\mathrm{Sr}$	87.905625 u
${}^{235}_{92}\mathrm{U}$	235.043925 u	${}^{7136}_{54}\mathrm{Xe}$	135.90722 u

ANSWERS

1. 5.70 MeV

2. 3.6×10^{10}

3. (a) 6.90×10^{16} nuclei;
(b) 8.00×10^{13} decays/s
(c) 1.23×10^{12} s^{-1}
(d) 7.66 h

4. 0.960 MeV; 0.960 MeV; 0

5. 41 y

6. 1.222×10^{13} J mol^{-1}.

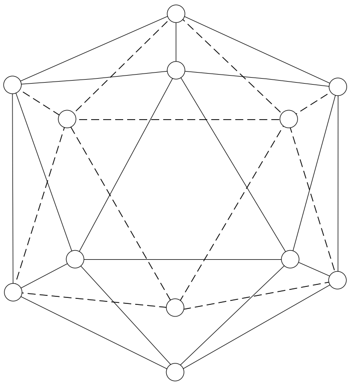
INORGANIC CHEMISTRY

CHAPTER 13

NON-METALS

BORON

Boron belongs to Group 13. It is a nonmetal and has a very high melting point (2453 K). The structure of crystalline boron is icosahedral (20-faced) with boron atoms at all 12 corners.



Icosahedral structure of boron

Boron is extracted from its mineral borax $Na_2B_4O_7$ or colemanite $Ca_2B_6O_{11}$. The latter is converted into borax by boiling with a solution of sodium carbonate in the requisite proportions.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \rightarrow 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

From the above solution, borax is crystallized from the mother liquor.

Borax is firstly converted into boron trioxide by treating it with hot concentrated hydrochloric acid followed by strongly heating the precipitated boric acid.

$$Na_2B_4O_7 + 2HCl \rightarrow 2NaCl + H_2B_4O_7; \qquad H_2B_4O_7 + 5H_2O \rightarrow \underset{\text{Boric acid}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow[\Delta]{} B_2O_3 + 3H_2O$$

The obtained boron trioxide is reduced to boron by heating with Na, K or Mg pieces.

$$B_2O_3 + 6K \rightarrow 2B + 3K_2O; \qquad B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$

The above method results into amorphous form of boron. Its crystalline form is obtained by passing a mixture of boron tribromide vapours and hydrogen over electrically heated filament of tungsten at 1200 °C. It may also be obtained by reducing boron trioxide or boron halide with excess of aluminium

$$B_2O_3 + 2Al \rightarrow Al_2O_3 + 2B; \qquad KBF_4 + Al \rightarrow AlF_3 + KF + B$$

Boron is unaffected by air at room temperature, but when heated to about 700 °C, it forms protective layers of boron trioxide and boron nitride

$$4B + 3O_2 \rightarrow 2B_2O_3; \qquad 2B + N_2 \rightarrow 2BN$$

With hot concentrated HNO_3 and H_2SO_4, amorphous boron reacts to form boric acid.

$$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO; \qquad 2B + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3SO_2$$

With fused caustic alkali, boron forms borates.

$$2B + 6OH^- \rightarrow 2BO_3^{2-} + 3H_2$$

Boron combines with nitrogen, chlorine, bromine and carbon at higher temperatures to form nitride, trichloride, tribromide and carbide, respectively.

Boron is a reducing agent. It can reduce CO_2 and SiO_2 to C and Si, respectively.

$$3CO_2 + 4B \rightarrow 2B_2O_3 + 3C; \qquad 3SiO_2 + 4B \rightarrow 2B_2O_3 + 3Si$$

Boron can also react with metals (except Cu, Ag and Au) to form borides. Magnesium and beryllium borides react with acids to form hydrides of boron.

ALLOTROPES OF CARBON

Carbon exists in two true allotropic forms, namely, diamond and graphite. Besides these, different amorphous varieties of carbon, such as coal, coke, charcoal, animal charcoal, lampblack, carbon black, etc. are known. All these amorphous carbons are microcrystals of graphite.

Diamond Diamond crystallizes in the face-centred cubic system. The diamond crystal is built up of a giant three dimensional structure with tetrahedral arrangement of carbon atoms which are at equal distance of 154 pm from one another (Fig. 13.1) The forces acting between atoms are very strong. The crystal of diamond is a nonconductor of electricity as all the electrons of carbon are held in the bonds between carbon atoms. It is the densest and purest variety of carbon. Also, it is the hardest natural substance known. Diamond has a high refractive index (= 2.45) because of which much of the light falling on it is internally reflected from interior surfaces without escaping. Diamond is not affected by almost all chemical reagents. It burns in air at 900 °C and in oxygen at 700 °C to form carbon dioxide.

Graphite Structurally graphite consists of a two-dimensional sheet-like network in which the carbon atoms are joined together in hexagonal rings (Fig. 13.2).

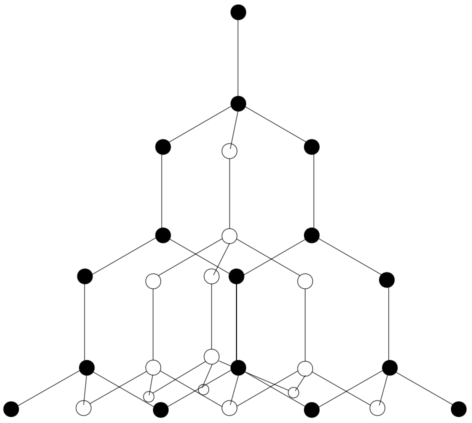


Fig. 13.1 The crystal structure of diamond

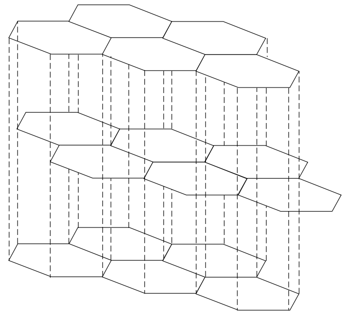


Fig. 13.2 The layer structure of graphite

The two layers of carbon network in graphite are held together by weak van der Waals forces and are about 335 pm apart. Within the layer, each carbon atom is covalently bonded by sp^2 hybrid orbitals to three carbon atoms with C—C distance equal to 142 pm. Thus, three of the four valence electrons are utilized in bonding with other carbons within the layer and the fourth electron is in the p_z atomic orbital which is perpendicular to the layer and is involved in π bonding with such electrons in the same layer. Because of the highly delocalized nature of π electrons, graphite is a good conductor of heat and electricity. It is less dense as compared to diamond. Since the different layers are held by weak van der Waals forces, each layer can slide over the other and this leads to the softness and the lubrication properties of graphite.

Graphite is thermodynamically more stable than diamond.

Besides graphite and diamond, there are several amorphous forms of carbon which resemble graphite in character. These include coal, coke, wood charcoal, carbon black, etc. Coal is believed to have been formed by the slow carbonization of vegetable matter buried underneath the earth centuries ago, in limited supply of air under high temperature and pressure prevailing there. The different varieties of coal available are peat (60% C), lignite (70% C), bituminous (78% C), semibituminous (83% C) and anthracite (90% C). The common variety of coal is bituminous. When coal is subjected to destructive distillation by heating in the absence of air, the residue left is known as coke. Wood charcoal is obtained by heating wood in the absence of air.

SILICON

Silicon belongs to Group 14 and is classified as a metalloid. It exists in two allotropic forms; the amorphous silicon and the crystalline or admantine silicon.

Silicon is second only to oxygen in mass percentage of the earth's crust (about 28%) and is found as silicate minerals.

The amorphous silicon is the common form of the element and may be obtained as follows.

1. Heating finely divided silica with magnesium powder. $SiO_2 + 2Mg \rightarrow Si + 2MgO$

MgO can be removed by washing the residue with dilute HCl and SiO_2 is removed by treating with HF.

2. Heating potassium silicofluoride with potassium metal. $K_2SiF_6 + 4K \rightarrow 6KF + Si$

The crystalline variety of silicon is obtained by crystallizing amorphous silicon from molten aluminium or molten silver. It may be prepared by the following methods.

1. Heating potassium silicofluoride with Al or Zn or red heat in an iron crucible

$$3K_2SiF_6 + 4Al \rightarrow 4AlF_3 + 6KF + 3Si; \qquad K_2SiF_6 + 2Zn \rightarrow 2ZnF_2 + 2KF + Si$$

The resulting mass is treated with dilute HCl to remove the unreacted metal and then with HF to remove silica. The crystallization of the resulting solution gives crystalline variety of silicon.

2. Passing a current of $SiCl_4$ over molten aluminium. $3SiCl_4 + 4Al \rightarrow 4AlCl_3 + 3Si$

$AlCl_3$ being volatile passes over and Si dissolved in molten Al is obtained. The crystallization results in the formation of crystalline silicon.

High purity Si for the semiconductor industry is made by converting Si to $SiCl_4$, purifying this by distillation and reducing the chloride with Mg or Zn. It can be made super pure by zone refining.

Amorphous silicon is a dark brown powder which is insoluble in water. Crystalline silicon forms pale yellow crystals and crystallizes in a diamond-type lattice.

Silicon burns in air or oxygen forming silicon dioxide. With halogens, it forms halides, SiX_4. With fused aqueous caustic alkalis, silicon forms alkali silicates with liberation of hydrogen.

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$

Silicon decomposes steam on red heating liberating hydrogen. Metals like Mg and the element carbon forms silicides with silicon.

Silicon is not attacked by acids except HF, presumably due to the stability of SiF_6^{2-}.

Silicon differs from carbon in that (a) it does not form double bonds such as in CO_2, (b) it does not readily form Si—Si bonds, and (c) it has vacant 3d orbitals in its valence shell to accept electrons from the donor atoms. The Si—O single bond is the strongest of all silicon bonds and accounts for the stability of silica (SiO_2) and silicates. Silicon does not form pπ-pπ bonds, principally because the atomic orbitals are too large and diffuse to obtain effective overlap, but it can use d orbitals in multiple bonding.

Silicon is insulator when pure, but becomes p-type or n-type semiconductors when doped with a Group III or Group V element, respectively.

NITROGEN

Atmosphere contains about 78.1% of nitrogen by volume. In the combined form, it occurs as KNO_3 (Indian saltpeter), $NaNO_3$ (Chile saltpeter) and ammonium salts.

Nitrogen can be conveniently prepared as follows.

1. Heating a solution containing NH_4^+ and NO_2^- ions. $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$
2. Heating ammonium dichromate. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$
3. Heating urea with an acidified solution of nitrite. $NH_2CONH_2 + 2H^+ + 2NO_2^- \rightarrow 2N_2 + CO_2 + 3H_2O$
4. Treating urea or ammonium salt with an alkaline solution of sodium hypobromite

$$2NH_4Cl + 3NaOBr + 2NaOH \rightarrow 3NaBr + 5H_2O + 2NaCl + N_2$$
$$NH_2CONH_2 + 3NaOBr \rightarrow 3NaBr + 2H_2O + CO_2 + N_2$$

5. Heating sodium azide. $2NaN_3 \rightarrow 2Na + 3N_2$
6. Oxidation of ammonia with red hot CuO. $2NH_3 + 3CuO \rightarrow N_2 + 3H_2O + 3Cu$

For industrial purposes, nitrogen is obtained by fractional evaporation of liquid air.

Nitrogen is an inactive element. Its inactiveness is primarily due to the great strength of the $N\equiv N$ bond. It combines with other metals and nonmetals at elevated conditions.

$$N_2 + O_2 \xrightleftharpoons[\text{arc}]{\text{electric}} 2NO \qquad N_2 + 2Al \xrightleftharpoons[\text{temperature}]{\text{high}} AlN$$

$$N_2 + 3H_2 \xrightleftharpoons[\text{725 K}]{\text{Fe, Mo}} 2NH_3 \qquad CaC_2 + N_2 \xrightleftharpoons[\text{heat}]{} CaCN_2 + C$$

$$N_2 + 3Mg \xrightleftharpoons[\text{temperature}]{\text{high}} Mg_3N_2$$

PHOSPHORUS

Phosphorus belongs to Group 15 and its electronic configuration is $[Ne](3s)^2(3p)^3$. It occurs only in the combined form as phosphates. For example, phosphorite, $Ca_3(PO_4)_2$; chlorapatite, $3Ca_3(PO_4)_2 \cdot CaCl_2$ and fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$. It also occurs in all living things. The tooth enamel is nearly pure hydroapatite, $Ca_5(PO_4)_3OH$ and the resistance to dental caries is enhanced by fluoridation of this salt to give $Ca_5(PO_4)_3F$, which is more tough and less soluble.

Phosphorus may be manufactured by the reduction of a mineral phosphate by carbon in the presence of silica in an electrical furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$$
$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

In an old process, the bone ash or phosphorite mineral is heated with the requisite quantity of concentrated sulphuric acid followed by filtration. The filtrate is evaporated and the residue is mixed with coke and distilled.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4\downarrow + \underset{\text{orthophosphoric acid}}{2H_3PO_4}$$

$$H_3PO_4 \rightarrow \underset{\text{metaphosphoric acid}}{HPO_3} + H_2O$$

$$4HPO_3 + 10C \rightarrow P_4 + 10CO + 2H_2O$$

Phosphorus obtained in the above two processes is white phosphorus. Two other allotropic modifications of phosphorus are red phosphorus and black phosphorus.

White Phosphorus When freshly prepared, white phosphorus is nearly colourless but acquires pale lemon-yellow colour on standing due to the formation of a film of red variety on the surface. It is for this reason, it is also known as yellow phosphorus. It has a characteristic garlic smell, poisonous in nature, insoluble in water and soluble in carbon disulphide and oil. It glows in the dark.

Its ignition temperature is low and thus it readily catches fire in air giving P_2O_5. It dissolves in caustic soda on boiling in an inert atmosphere giving phosphine

$$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + \underset{\text{hypophosphite ion}}{3H_2PO_2^-}$$

Phosphorus directly combines with halogens and a number of metals giving halides and phosphides. It is a powerful reducing agent. Concentrated HNO_3 and H_2SO_4 are reduced on heating with P_4. For example

$$P_4 + 20HNO_3 \rightarrow \underset{\text{phosphoric acid}}{4H_3PO_4} + 20NO_2 + 4H_2O$$

Red Phosphorus White phosphorus is changed to red variety when the former is heated for several houres in the absence of air and light to a temperature of 420 K. It is a dark red powder, odourless, nonpoisonous and insoluble in both water and carbon disulphide. It is also chemically less reactive than yellow phosphorus. It does not glow in the dark. Its ignition temperature is high, so it does not catches fire at room temperature. Caustic soda has no action on red variety. Red variety can be converted to white variety by boiling the former in an inert atmosphere and the vapours condensed under water.

Black Phosphorus It is prepared by heating white phosphorus to 473 K under very high pressure. It has a crystalline layer structure and is semiconducting.

The four atoms in white phosphorus are arranged tetrahedrally. Red phosphorus is believed to be polymeric and consists of chains of P_4 tetrahedrally linked together as shown in Fig. 13.3.

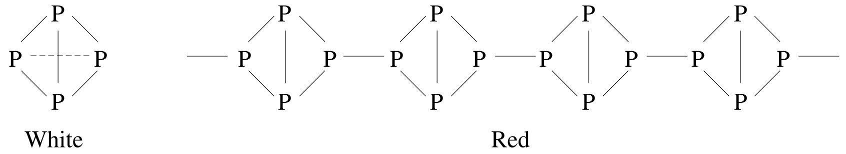


Fig. 13.3 Structures of white and red phosphorus

In the liquid and in solid white phosphorus exists as tetrahedral P_4 molecule with P—P distance 221 pm and bond angle P—P—P equal to 60°. The low angle indicates considerable strain. The total energy of the six P—P bonds in P_4 molecule is much smaller than the total energy expected for six P—P bonds of the same length with normal bond angles. Because of the strain in P_4 molecule, phosphorus is very reactive.

White P_4 is stored under water to protect it from the air, whereas the red and black are stable in air. White P_4 inflames in air and is soluble in organic solvents such as CS_2 and benzene.

Phosphorus does not have a structure like nitrogen ($N \equiv N$). This can be understood from the following bond enthalpy data.

$$\varepsilon(N \equiv N) = 946 \text{ kJ mol}^{-1} \qquad \varepsilon(P \equiv P) = 490 \text{ kJ mol}^{-1}$$
$$\varepsilon(>N - N<) = 160 \text{ kJ mol}^{-1} \qquad \varepsilon(>P - P<) = 200 \text{ kJ mol}^{-1}$$

The species $N \equiv N$ is more stable than three $N - N$ bonds whereas $P \equiv P$ is less stable than three $P - P$ bonds. It is because of this factor, phosphorus atoms are liked through single bonds.

OXYGEN

Atmosphere contains about 20% of oxygen by volume. In the combined form, it is present in water (89% by mass), earth's crust (about 50%), plants and animal tissues (50.7%).

Oxygen can be conveniently prepared as follows.

1. By heating chlorates, nitrates and permanganate. $2KClO_3 \xrightarrow{\text{heat}} 2KCl + 3O_2$
2. By heating metallic oxide such as HgO, PbO, Ag_2O, MnO_2 and BaO_2. $2HgO \xrightarrow{\text{liquid}} 2Hg + O_2$
3. By the action of water on peroxides. $2Na_2O_2 + 2H_2O \rightarrow 2NaOH + O_2$
4. By the decomposition of peroxides or hypochlorites.

$$2H_2O_2 \rightarrow 2H_2O + O_2; \qquad 2CaOCl_2 \xrightarrow{COCl_2} 2CaCl_2 + O_2$$

5. By the action of concentrated H_2SO_4 on $KMnO_4$, $K_2Cr_2O_7$ or MnO_2

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

Commercially, oxygen is obtained by fractional evaporation of liquid air or by electrolysis of acidic or alkaline solution of water.

Oxygen combines with a large number of elements and compounds under different conditions. It is a paramagnetic with two unpaired electrons. This behaviour has been explained on the basis of molecular orbital theory. Its electronic configuration is

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2\ (\pi 2p_x)^2(\pi 2p_y)^2\ (\pi^* 2p_x)^1(\pi^* 2p_y)^1$$

Ozone Ozone is an allotropic modification of oxygen. It is prepared by the passage of silent electric discharge through pure and dry oxygen or air. The silent discharge is carried out by packing insulating materials in the space between electrodes through which discharge passes. This prevents any local rise in temperature, which would lead to the decomposition of ozone. The reaction

$$3O_2 \rightleftharpoons 2O_3$$

is endothermic (ΔH = +284.5 kJ mol^{-1}).

Ozone is a pale-blue gas with a characteristic strong smell. When inhaled in small amount, it causes headache and nausea. In larger quantities, it is poisonous. The main reactions of ozone are the oxidation reactions.

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2; \qquad \underset{\text{(neutral medium)}}{2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2}$$

$$2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2; \qquad 2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$

$$\underset{\text{(moist)}}{2I_2 + 2H_2O + 4O_3 \rightarrow 4HIO_3 + O_2}; \qquad 2K_4Fe(CN)_6 + O_3 + H_2O \rightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$$

Moist sulphur, phosphorus and arsenic are also oxidized to higher acids.

When ozone is passed through mercury, the latter loses its meniscus and sticks to glass due to the formation of Hg_2O which dissolves in mercury.

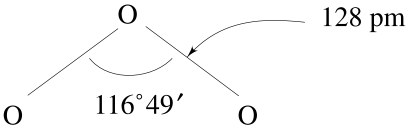
With peroxides, the reactions taking place are

$$BaO_2 + O_3 \rightarrow BaO + 2O_2; \qquad H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

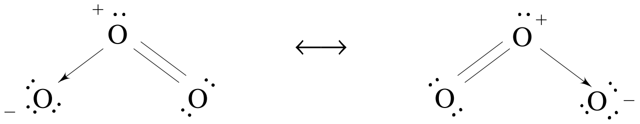
With organic compounds containing double and triple carbon-carbon bonds, ozone forms ozonides which gets decomposed by water or dilute acids.

Ozone is formed at the height of about 20 km from oxygen by the absorption of sunlight. There is a formation of ozone layer which protects the earth's surface from an excessive concentration of ultraviolet radiations. Chlorofluorocarbons (such as CCl_2F_2, which is used as a refrigerant (Freon-12) and as a propellant in aerosol spray) contribute to the decompositon of ozone layer. Sunlight causes the decomposition of these compounds producing active chlorine which catalysed the decomposition of ozone. Emission of nitrogen oxides from supersonic jets also contribute in depleting the ozone layer.

The structure of ozone is



The oxygen-oxygen bond length in ozone is 128 pm which is intermediate between a single bond (148 pm) and a double bond (121 pm). It has been explained on the base of the resonating structures shown below.



The structure of ozone is best described as follows. The oxygen atoms are sp^2 hybridized. Two of these orbitals in the central atom and one each of the terminal oxygens are involved in σ bonds. The remaining sp^2 orbitals contain lone pairs of electrons. There are five such pairs-one at the central atom and two each on the terminal oxygen. The remaining four electrons (= 18 – 4 – 10) occupy molecular orbitals formed from the three p_z atomic orbital from the three oxygen atoms. Two of these electrons are in the bonding molecular orbital and the remaining two in the nonbonding molecular orbital. Thus, double bonds involving three oxygen atom is best described as four-electron three-centre bond. The bond order of each O—O bond is 1.5.

SULPHUR

Sulphur occurs in the native as well as combined form. Large quantities of sulphur are obtained from under ground deposits of the element in USA. It may also be produced by the partial combustion of H_2S or by the reaction of H_2S with SO_2.

$$2H_2S + O_2 \rightarrow 2H_2O + S; \qquad 2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

Sulphur occurs as puckered S_8 ring with a crown conformation. Several allotropic forms of sulphur are known.

The stablest form is the rhombic sulphur (or α-sulphur). It is obtained by evaporation of the solution of sulphur in carbon disulphide. At about 95 °C-96 °C, rhombic sulphur is changed into monoclinic sulphur (also known as prismatic or β-sulphur). Monoclinic sulphur has needle-shaped crystals. This form of sulphur can be prepared by melting sulphur in a dish and cooling till the crust is formed. Liquid is drained off through holes made in the crust and then removing crust, one gets needle-like crystals.

Other allotropic forms are amorphous (or colloidal) and plastic sulphur (or γ-sulphur). This form is obtained by the action of dilute HCl on sodium thiosulphate solution or when H_2S is passed through dilute nitric acid.

$$2HNO_3 + H_2S \rightarrow S + 2NO_2 + 2H_2O; \qquad Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$

Plastic sulphur is obtained by pouring boiling sulphur in cold water. It consists of a completely random arrangement of chains of sulphur atoms. On standing, it passes over to the crystalline rhombic sulphur.

Sulphur is as active as oxygen, it combines with a large number of metals and nonmetals. Sulphur is oxidized by concentrated HNO_3 and H_2SO_4.

$$S + 6HNO_3 \rightarrow 2H_2O + H_2SO_4 + 6NO_2; \qquad S + 2H_2SO_4 \rightarrow 2H_2O + 3SO_2$$

Sulphur also reacts with hot concentrated solution of alkalis. $3S + 6OH^- \rightarrow 2S^{2-} + SO_3^{2-} + 3H_2O$

Sulphide produced reacts with sulphur producing polysulphite (S_n^{2-}). Similarly, sulphite reacts giving thiosulphate ($S_2O_3^{2-}$).

HALOGENS

Fluorine, chlorine, bromine and iodine belong to Group 17 and are collectively known as halogens (which means salt producer).

Fluorine is the most electronegative element and it has oxidation state of –1 only. Other halogens exhibit variable oxidation states due to the availability of vacant d orbitals.

The halogens are very reactive and react with metals and many nonmetals. Fluorine is the most reactive and the reactivity decreases with increase in atomic number. The maximum reactivity of fluorine is due to high electronegativity, small size of its atom, extremely high oxidizing power and low energy of the F—F bond.

The oxidizing power of halogens decreases down the group and the reducing power increases down the group.

The electronic configuration of halogens is $(ns)^2(np)^5$. All halogens form mononegative ions by accepting one electron each into the singly filled p orbital. The halides of metals in low-valence states are mostly ionic, but in high-valence states, metal halides tend to be polar covalent. The halides of all nommetals and some metals are covalent, and the halogen atoms (except fluorine) may have +1 or –1 oxidation state depending on the electronegativity of other element with which it is covalently bonded.

The halogens form diatomic molecules. The bond enthalpy of F_2 is very low (159 kJ mol^{-1}). This is due to repulsion between nonbonding electrons. In Cl_2, Br_2 and I_2 molecules, there is possibility of multiple bonding involving d orbitals, thus they have higher bond enthalpies. For example, ε(Cl—Cl) is 243 kJ mol^{-1}, ε(Br—Br) = 193 kJ mol^{-1}, and ε(I—I) = 151 kJ mol^{-1}. The multiple bonding may be illustrated by taking the example of chlorine.

The electronic configuration of chlorine atom is $(1s)^2(2s)^2(2p)^6(3s)^2(3p_x)^2(3p_y)^2\,(3p_z)^1$. A molecule of chlorine is diatomic which is formed by the overlapping of $3p_z$ orbitals centred on the two atoms. In addition to this σ bond, an additional π bond exists between the two atoms via donor-acceptor mechanism. In this mechanism, the overlapping of a p orbital (containing two electrons) of one atom can overlap with the empty d orbital of the second atom and two electrons are shared between the two atoms resulting in the formation of π bond. This additional bonding strengthens the molecule.

Fluorine Fluorine occurs in the combined form as fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($CaF_2 \cdot 3Ca_3(PO_4)_2$).

Fluorine is manufactured by the electrolysis of a fused mixture of KF with 2 to 3 moles of HF at about 343—373 K in a rectangular steel vessel. The steel vessel serves as the cathode and the anode is graphite.

Fluorine, being most reactive nonmetal, combines with most metals and nonmetals.

Fluorine interacts with the noble gas xenon to form three definite fluorides XeF_2, XeF_4 and XeF_6. The final product depends on the temperature, pressure and mixing ratio of the constituents.

$$\underset{\text{(ratio 2 : 1)}}{Xe + F_2} \xrightarrow{\text{675 K}} XeF_2; \qquad \underset{\text{(ratio 1:5)}}{Xe + 2F_2} \xrightarrow{\text{725 K—775 K}} XeF_4$$

$$\underset{\text{(ratio 1:20)}}{Xe + 3F_2} \xrightarrow[\text{50 atm}]{\text{575 K}} XeF_6$$

Fluorine is a powerful oxidizing agent. It oxidizes water to oxygen. $2H_2O + 2F_2 \rightarrow 4HF + O_2$

It also oxidizes chlorate to perchlorate, iodate to periodate, bisulphate to perbisulphate, Cr(IV) to Cr(VI).

Fluorine liberates Cl_2, Br_2 and I_2 from the respective salts.

Fluorine reacts with alkalis as follows.

$$2F_2 + 2(\text{dil NaOH}) \rightarrow F_2O + 2NaF + H_2O$$
$$2F_2 + 4(\text{conc. NaOH}) \rightarrow 4NaF + O_2 + 2H_2O$$

Chlorine Chlorine (from Greek chloros meaning green) occurs in the combined form as NaCl, KCl, $MgCl_2$ and $CaCl_2$ in salt water and salt beds. It is commercially produced by the electrolysis of concentrated aqueous solution of sodium chloride.

In laboratory, the oxidation of HCl (or Cl^- + acid) by MnO_2, $Cr_2O_7^{2-}$, bleaching powder and red lead produces chlorine.

$MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + 2H_2O$; $2MnO_4^- + 16H^+ + 10\ Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$; $CaOCl_2 + 2HCl \rightarrow CaCl_2 + Cl_2 + H_2O$

$PbO_2 + 4H^+ + 2Cl^- \rightarrow Pb^{2+} + Cl_2 + 4H_2O$; $Pb_3O_4 + 8H^+ + 2Cl^- \rightarrow 3Pb^{2+} + Cl_2 + 4H_2O$

Chlorine directly combines with a number of other elements. If an element exhibits more than one oxidation state, chlorine forms chloride with that element in the higher oxidation state. For example, iron and copper give ferric and cupric chlorides and not ferrous and cuprous chlorides.

Chlorine is an oxidizing agent. It oxidizes Fe^{2+} to Fe^{3+}, H_2S to S, SO_3^{2-} and $S_2O_3^{2-}$ to SO_4^{2-}, etc.

$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$; $SO_3^{2-} + H_2O + Cl_2 \rightarrow SO_4^{2-} + 2H^+ + 2Cl^-$;

$H_2S + Cl_2 \rightarrow 2HCl + S$; $S_2O_3^{2-} + H_2O + Cl_2 \rightarrow SO_4^{2-} + S + 2H^+ + 2Cl^-$

In the moisture, chlorine acts as a bleaching agent and its bleaching effect is permanent. Delicate articles like straw, silk, wool, etc. cannot be bleached as they are damaged by chlorine.

With cold NaOH (or milk of lime), Cl_2 forms chloride and hypochlorite while with hot solution, chloride and chlorate are formed.

$\underset{\text{cold}}{2OH^-} + Cl_2 \rightarrow Cl^- + ClO^- + H_2O$; $\underset{\text{hot}}{6OH^-} + 3Cl_2 \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

With slaked lime, however, bleaching powder ($CaOCl_2$) is formed.

With NH_3, nitrogen is evolved provided NH_3 is present in excess. If Cl_2 is present in excess, an explosive nitrogen trichloride is formed.

$\underset{\text{(excess)}}{2NH_3} + 3Cl_2 \rightarrow N_2 + 6HCl$; $NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$

Chlorine liberates bromine and iodine with their respective salts.

Chlorine decomposes water giving HCl and O_2.

Bromine Bromine occurs only in the combined state as bromides of sodium, potassium and manganese in seawater, certain mineral springs and Stassfurt deposits.

Bromine can be prepared by heating a mixture of concentrated sulphuric acid, manganese dioxide and bromide.

$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

Passing chlorine gas through KBr solution generates bromine. $2KBr + Cl_2 \rightarrow 2KCl + Br_2$

Commercially, bromine is also manufactured based on the above equation.

Bromine is reddish-brown liquid. It combines with a number of elements.

Bromine decomposes water in the presence of sunlight, but the reaction is slow in comparison to chlorine.

Bromine is an oxidizing agent. It can oxidize S^{2-} to S, SO_2 to H_2SO_4, SO_3^{2-} and $S_2O_3^{2-}$ to SO_4^{2-} and AsO_3^{3-} to AsO_4^{3-}.

With cold NaOH, bromine forms bromide and hypobromite while with hot NaOH, bromide and bromate are formed.

$\underset{\text{(cold)}}{2OH^-} + Br_2 \rightarrow Br^- + BrO^- + H_2O$; $\underset{\text{(hot)}}{6OH^-} + 3Br_2 \rightarrow 5Br^- + BrO_3^- + 3H_2O$

Ammonia is oxidized to N_2 with bromine $8NH_3 + 3Br_2 \rightarrow N_2 + 6NH_4Br$

Bromine liberates iodine from iodides.

Iodine Iodine occurs only in the combined state as iodides in California oil-well brines, in seawater, in sea weeds and sponges. Large amounts of iodine are present in Caliche (crude chile saltpetre) as sodium iodate.

Iodine can be prepared by treating iodide with concentrated sulphuric acid in the presence of MnO_2.

$$2NaI + MnO_2 + 3H_2SO_4 \rightarrow I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$$

Chlorine or bromine generates iodine from sodium iodide solution.

Commercially, iodine is obtained from sea weeds and Caliche.

Sea weeds are burnt in shallow pits and then treated with water to extract the dissolved iodide, sulphates and chlorides. It is concentrated and the mother liquor is treated with concentrated sulphuric acid in the presence of MnO_2. Iodine sublimes on heating and is condensed.

The mother liquor obtained after the crystallization of nitre from crude Chile saltpetre is treated with calculated quantity of sodium bisulphite.

$$2NaIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + I_2 + H_2O$$

Iodine is steel-grey solid which sublimes on heating. On condensing rhombic crystalline plates of iodine are obtained.

It is slightly soluble in water, but in the presence of I^- ions, its solubility is very much enhanced. This is due to the reaction

$$I^- + I_2 \rightleftharpoons I_3^-$$

Iodine is less reactive than chlorine and bromine.

Iodine combines with a number of elements. It does not decompose water. Iodine is an oxidizing agent, but less powerful than chlorine and bromine. A few reactions exhibiting oxidizing nature of iodine are as follows.

$$S^{2-} + I_2 \rightarrow S + 2I^-; \qquad SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^-$$

$$SO_2 + 2H_2O + I_2 \rightarrow SO_4^{2-} + 2I^- + 4H^+; \qquad AsO_3^{3-} + I_2 + H_2O \rightarrow AsO_4^{3-} + 2H^+ + 2I^-$$

$$NO_2^- + I_2 + H_2O \rightarrow NO_3^- + 2H^+ + 2I^-$$

With sodium thiosulphate, iodine reacts quantitatively giving sodium tetrathionate

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

With cold dilute NaOH, iodine forms hypoiodite which is hydrolysed further yielding hypoiodous acid.

$$\begin{array}{l} 2OH^- + I_2 \rightarrow IO^- + I^- + H_2O \\ IO^- + H_2O \rightarrow HIO + OH^- \\ \hline OH^- + I_2 \rightarrow HIO + I^- \end{array}$$

With hot or in cold on standing, iodine produces iodate with alkalis.

$$6OH^- + 3I_2 \rightarrow 5I^- + IO_3^- + 3H_2O$$

$$\begin{array}{l} 2NaOH + I_2 \rightarrow NaI + NaIO + H_2O] \times 3 \\ 3NaIO \rightarrow NaIO_3 + 2NaI \\ \hline 6NaOH + 3I_2 \rightarrow 5NaI + NaIO_3 + 3H_2O \end{array}$$

With liquor ammonia, iodine reacts to give nitrogen triiodide. $2NH_3 + 3I_2 \rightarrow NI_3 \cdot NH_3 + 3HI$

Iodine does not decompose any halide, but potassium chlorate in the presence of little nitric acid reacts with iodine producing potassium iodate

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$$

Iodine is used as an antiseptic and germicide in the form of tincture of iodine, a solution in alcohol. It is contained in the growth regulating hormone thyroxine produced by thyroid gland.

Straight Objective Type

Boron

1. Boron is a nonmetal it's very high melting point is due to its

(a) electronic configuration $(1s)^2$ $(2s)^2$ (2p)

(b) first position in Group 13 of the periodic table.

(c) polymeric form

(d) icosahedral structure

2. Heating of boron trioxide with K yields

(a) amorphous form of boron

(b) crystalline form of boron

(c) amorphous or crystalline depending upon temperature

(d) polymeric form

3. Which of the following statements regarding boron is correct?
(a) Boron is an oxidizing agent.
(b) Boron acts as a reducing agent in its reaction with CO_2 or SiO_2.
(c) Boron is a metal.
(d) Boron has a low melting point.

4. Which of the following statements related to boron is **not** correct?
(a) Boron has a very high cross-section for capturing neutrons.
(b) Boron is used to make impact resistant steel
(c) Boron shows valency of +1 and +3
(d) Boron compounds are electron deficient

Carbon and Silicon

5. The material used in solar cells contains
(a) Cs (b) Si (c) Sn (d) Ti (1993)

6. Electrical conductivity is shown by
(a) diamond (b) silica (c) carborundum (d) graphite

7. The variety of coal containing the least percentage of carbon is
(a) lignite (b) bituminous (c) anthracite (d) peat

8. The variety of coal containing the maximum percentage of carbon is
(a) lignite (b) bituminous (c) anthracite (d) peat

9. Which of the following statements regarding diamond is **not** correct?
(a) Diamond is a bad conductor of heat and electricity
(b) Diamond crystallizes in the body-centred cubic lattice
(c) The carbon-carbon bond length in diamond is 154 pm
(d) Diamond is more dense than graphite

10. Which of the following statements regarding graphite is **not** correct?
(a) Graphite is a good conductor of electricity
(b) Graphite is lense dense than diamond
(c) The bond length of σ bonded carbon-carbon bond is 154 pm
(d) Graphite is thermodynamically more stable than diamond

11. Which of the following statements regarding silicon is **not** correct?
(a) Silicon is a metalloid
(b) Crystalline silicon crystallizes in a diamond-type lattice
(c) Because of larger radius of silicon atom, the latter does not form double and triple silicon-silicon bond
(d) Silicon occurs in the native form

12. Lead pencil contains
(a) Pb (b) FeS (c) Graphite (d) PbS

13. The hybridization in diamond and graphite, respectively, are
(a) sp^2, sp^2 (b) sp^2, sp^3 (c) sp^3, sp^2 (d) sp^3, sp^3

14. Graphite has a layer type structure. The C—C distance along the layer and perpendicular to the layer respectively, are
(a) 142 pm, 142 pm (b) 154 pm, 335 pm
(c) 154 pm, 154 pm (d) 142 pm, 335 pm

15. Silicon is attacked by acid such as
(a) HF (b) HCl (c) HNO_3 (d) H_2SO_4

16. Crystalline silicon is obtained when K_2SiF_6 reacts with
(a) Na (b) K (c) Mg (d) Al

17. The super pure form of silicon can be obtained by
(a) fractional crystallization (b) fractional distillation
(c) the technique of zone refining (d) solvent extraction

18. Which one of the bonds in elemental form has the maximum bond energy?
(a) C—C (b) Si—Si (c) Ge—Ge (d) Sn—Sn

19. Which of the following elements exhibits the phenomenon of catenation?
(a) C (b) Si (c) Ge (d) Sn

20. Which of the following statements is correct?
(a) The electronegativity of Si is more than that of C.
(b) Si—C bonds are as strong as C—C bonds
(c) Both C and Si can form pπ-pπ bond
(d) Both CO_2 and SiO_2 has linear structures.

Nitrogen and Phosphorus

21. Which of the following statements regarding nitrogen molecule is not correct?
(a) Amongst the homonuclear diatomic molecules of second period, the bond dissociation enthalpy is maximum for nitrogen molecule.
(b) Amongst the homonuclear diatomic molecules of second period, the bond length is minimum for nitrogen molecule.
(c) Nitrogen molecule is paramagnetic in nature.
(d) Nitrogen reacts with metals and nonmetals at high temperatures forming ionic and covalent nitrides.

22. Heating of ammonium dichromate produces
(a) $NH_3 + Cr_2O_3 + H_2O$ (b) $N_2 + Cr_2O_3 + H_2O$
(c) $H_2O + CrO_3 + H_2O$ (d) $NO_2 + CrO_3 + H_2O$

23. Which of the following statements regarding phosphorus is **not** ture?
(a) Phosphorus belongs to Group 15 of the periodic table.
(b) The element phosphorus is obtained by heating the rock phosphate with coke and sand in an electric furnace at about 1700–1800 K.
(c) The formula of phosphorus is P_4.
(d) Black phosphorus is the least stable form of the allotropes of phosphorus.

24. The white phosphorus is stored
(a) in air (b) under water (c) under kerosene (d) under CS_2

25. Which of the following statements regarding phosphorus is true?
(a) Both white and red phosphorus are soluble in water.
(b) Both white and red phosphorus are soluble in carbon disulphide.
(c) White phosphorus is soluble in carbon disulphide whereas red phosphorus is insoluble.
(d) White phosphorus is insoluble in carbon disulphide whereas red phosphorus is soluble.

26. Which of the following characteristics about phosphorus is correct?
(a) Both white and red phosphorus are reactive.
(b) Both white and red phsophorus are inactive.
(c) White phosphorus is reactive whereas red phosphorus is inactive.
(d) White phosphorus is inactive whereas red phosphorus is reactive.

27. Which of the following statements regarding phosphorus is **not** correct?
(a) Phosphorus does not occur in native state.
(b) Phosphorus is present in bones and teeth.
(c) Phosphorus exists in several allotropic forms.
(d) White phosphorus is much less reactive than red variety.

28. When phosphorus is heated with concentrated HNO_3, it reduces the acid to
(a) NO (b) NO_2 (c) N_2O_3 (d) N_2O_5

29. When phosphorus is heated with concentrated HNO_3, it is oxidized to
(a) H_3PO_2 (b) H_3PO_3 (c) H_3PO_4 (d) $H_4P_2O_7$

30. The semiconducting form of phosphorus is
(a) white (b) red (c) black (d) yellow

31. In white phosphorus, the arrangement of phosphorus atoms is
(a) linear (b) square planar (c) tetrahedral (d) octahedral

32. Which of the following statements regarding white phosphorus is not correct?
(a) It is nonpoisonous. (b) It glows in dark.
(c) It has low ignition temperature. (d) It is a powerful reducing agent.

33. Which of the following statements regarding red phosphorus is not correct?
(a) It is nonpoisonous. (b) It is leas reactive than white variety.
(c) It glows in dark. (d) It is not attack by caustic soda.

34. The element with the highest first ionization potential is
(a) boron (b) carbon (c) nitrogen (d) oxygen

35. Which of the following isomers of phosphorus are thermodynamically least and most stable?
(a) White (least), Red (most) (b) Yellow (least), Red (most)
(c) Red (least), White (most) (d) White (least), Black (most) (2005)

Oxygen and Sulphur

36. A gas that cannot be collected over water is
(a) N_2 (b) O_2 (c) SO_2 (d) PH_3 (1985)

37. The compound which gives off oxygen on moderate heating is
(a) cupric oxide (b) mercuric oxide (c) zinc oxide (d) aluminium oxide (1986)

38. Oxygen molecule contains
(a) no unpaired electrons (b) one unpaired electrons
(c) two unpaired electrons (d) four unpaired electrons

39. Which of the following statements regarding ozone is **not** correct?
(a) Ozone is an allotrope of oxygen.
(b) The ozone layer protects the earth's surface from an excessive concentration of harmful ultraviolet radiation.
(c) The conversion of oxygen to ozone is an exothermic process.
(d) Ozone is much more powerful oxidizing agent than molecular oxygen.

40. Which of the following statements regarding ozone is not correct?
(a) The ozone molecule is angular in shape.
(b) The ozone molecule is a resonance hybrid of the two structures
(c) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen.
(d) Ozone is used as germicide and disinfectant for the purification of air.

41. Ozone is **not**
(a) a fast oxidizing agent (b) a powerful oxidizing agent
(c) a bent molecule (d) a stable allotrope

42. On heating, the volume of ozone will
(a) decrease (b) increase (c) remain unchanged (d) become double

43. Which of the following is **not** the mineral of sulphur?
(a) Floroapatite (b) Fool's gold (c) Sphaelerite (d) Chalcopyrite

44. Which of the following characteristics regarding sulphur is **not** correct?
(a) Rhombic sulphur is stable at room temperature.
(b) Monoclinic sulphur is stable at room temperature.
(c) Both rhombic and monoclinic sulphur are soluble in CS_2.
(d) Both rhombic and monoclinic sulphur has the molecular formula S_8.

45. Which of the following statements regarding sulphur is true?
(a) Both rhombic and monoclinic sulphur are soluble in water.
(b) Both rhombic and monoclinic sulphur are soluble in CS_2.
(c) Both rhombic and monoclinic sulphur are insoluble in CS_2.
(d) Rhombic sulphur can be converted into monoclinic sulphur but the reverse is not possible.

46. Passing H_2S gas through nitric acid produces
(a) rhombic sulphur (b) monoclinic sulphur (c) amorphous sulphur (d) plastic sulphur

47. The treatment of S with concentrated HNO_3 produces
(a) $SO_2 + NO_2 + H_2O$ (b) $SO_2 + NO + H_2O$
(c) $H_2SO_4 + NO + H_2O$ (d) $H_2SO_4 + NO_2 + H_2O$

48. Oxygen and sulphur belong to
(a) alkaline earth metals (b) s block element
(c) chalcogens (d) halogens

49. Common allotropic forms of sulphur are represented as
(a) S_2 (b) S_4 (c) S_6 (d) S_8

50. The bond angle O—O—O in ozone is about
(a) 180° (b) 90° (c) 116° 5′ (d) 135°

51. The bond order of O—O bonds in ozone is
(a) 1 (b) 1.5 (c) 2 (d) 2.5

Halogens

52. Chlorine acts as a bleaching agent only in presence of
(a) dry air (b) moisture (c) sunlight (d) pure oxygen (1983)

53. Bromine can be liberated from potassium bromide solution by action of
(a) iodine solution (b) chlorine solution (c) sodium chloride (d) potassium iodide (1987)

54. Concentrated HNO_3 reacts with iodine to give
(a) HI (b) HOI (c) $HOIO_2$ (d) $HOIO_3$ (1989)

55. The gaseous flourine is pale yellow in colour. The light absorbed by fluorine in the visible region would be
(a) violet light (b) red light (c) green light (d) orange light

56. The gaseous iodine molecules absorb yellow light from the visible region. Its colour would be
(a) yellow (b) red (c) green (d) violet

57. Which of the following sequences of electron affinity regarding halogens is correct?
(a) $F < Cl < Br$ (b) $F > Cl > Br$ (c) $F < Cl > Br$ (d) $F > Cl < Br$

58. Which of the following characteristics regarding halogens is not correct?
(a) Ionization energy decreases with increase of atomic number.
(b) Electronegativity decreases with increase of atomic number.
(c) Electron affinity decreases with increase of atomic number.
(d) Enthalpy of fusion increases with increase of atomic number.

59. The halogen exhibiting no positive oxidation state is
(a) fluorine (b) chlorine (c) bromine (d) iodine

60. Which of the following reactions is not observed?
(a) $2F_2 + \underset{\text{(dilute)}}{2OH^-} \rightarrow 2F^- + H_2O + OF_2$ (b) $2F_2 + \underset{\text{(conc.)}}{4OH^-} \xrightarrow[\text{hot}]{} 4F^- + 2H_2O + O_2$
(c) $\underset{(F_2,\ Cl_2,\ I_2)}{X_2} + \underset{\text{(conc.)}}{2OH^-} \xrightarrow[\text{hot}]{} H_2O + X^- + XO^-$ (d) $Xe + F_2 \xrightarrow{\text{(light)}} XeF_2$

61. Which of the following reactions would not proceed to right hand side?
(a) $F_2 + Cl^- \rightarrow$ (b) $Cl_2 + Br^- \rightarrow$ (c) $Br_2 + I^- \rightarrow$ (d) $I_2 + Cl^- \rightarrow$

62. Amongst the halogens, the strongest oxidizing agent is
(a) fluorine (b) chlorine (c) bromine (d) iodine

63. The products obtained when chlorine reacts with cold and dilute solution of sodium hydroxide are
(a) $Cl^- + ClO^-$ (b) $Cl^- + ClO_2^-$ (c) $Cl^- + ClO_3^-$ (d) $Cl^- + ClO_4^-$

64. The products obtained when iodine reacts with hot and concentrated solution of sodium hydroxide are
(a) $I^- + IO^-$ (b) $I^- + IO_3^-$ (c) $I^- + IO_4^-$ (d) $I^- + I_2O_9^{4-}$

65. With excess of Cl_2, ammonia forms
(a) NH_4Cl (b) N_2 (c) NCl_3 (d) $NCl_3 \cdot NH_3$

66. Which of the following compounds undergoes hydrolysis?
(a) SF_6 (b) NF_3 (c) SF_4 (d) CCl_4

67. The highest bond enthalpy is shown by the halogen
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

68. I_2 reacts with NH_3 giving
(a) NI_3 (b) $NI_3 \cdot NH_3$ (c) N_2 (d) NH_4I

69. Which of the fluoride of xenon is not formed?
(a) XeF (b) XeF_2 (c) XeF_4 (d) XeF_6

70. Iodine reacts with cold dilute sodium hydroxide producing
(a) NaI + NaOI (b) NaI + IO_3Na (c) HIO + NaI (d) HIO_3 + Na

71. A gas "X" is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of colourless gas 'Y'. The X and Y, respectively, are
(a) CO_2, Cl_2 (b) Cl_2, CO_2 (c) Cl_2, H_2 (d) H_2, Cl_2 (2002)

72. Which of the following statements regarding halogens is **not** correct?
(a) The energy difference between ground state and the first excited state increases on descending the Group 17.
(b) I_2 conducts electricity to a small extent due to its self ionization $3I_2 \rightleftharpoons I_3^+ + I^-$
(c) Conductivity of I_2 increases on increasing temperature
(d) The compounds C_nF_{2n+2} are known as perfluoro compounds.

73. Which of the following statements regarding halogens is **not** correct?
(a) The high reactivity of fluorine may be attributed to its low bond energy.
(b) Chlorine amongst halogens is the strongest oxidizing agent in solution due to its highest electron affinity.
(c) Amongst halide ions in solution, hydration free energy is maximum in case of F^- ions.
(d) Chlorofluorocarbons damage the ozone layer in the upper atmosphere.

74. Teflon is
(a) polytetrafluoroethylene (b) polytetrachloroethylene
(c) polytetrabromoethylene (d) polytetraiodoethylene

Multiple Correct Choice Type

1. Which of the following statements regarding ozone is/are correct?
(a) Ozone is an allotrope of oxygen.
(b) Ozone layer protects the earth's surface from excess concentration of the harmful ultra violet high from the sun.
(c) The conversion of oxygen into ozone is an exothermic process.
(d) Ozone is a more powerful oxidising agent than molecular oxygen.

2. Which of the following statements regarding sulphur is/are correct?
(a) Rhombic sulphur is less stable than monoclinic sulphur at room temperature.
(b) Both rhombic and monoclinic sulphur are soluble in CS_2.
(c) Rhombic sulphur can be converted into monoclinic sulphur but the reverse is not possible.
(d) Colloidal sulphur is obtained when H_2S is passed through water containing HNO_3.

3. Ozone is
(a) a germicide and disinfectant. (b) an allotrope of oxygen.
(c) isomer of oxygen. (d) isotope of oxygen.

4. Fluorine is the most reactive among halogens because of
(a) its gaseous nature. (b) its high electronegativity.
(c) its small size. (d) low dissociation of the F—F bond.

5. The variable oxidation state is shown by
(a) fluorine (b) chlorine (c) bromine (d) iodine

6. Which of the following statements regarding halogens is/are correct?
(a) Ionization energy decreases with increasing atomic number.
(b) Electronegativity decreases with increasing atomic number.
(c) Electron affinity decreases with increasing atomic number.
(d) Enthalpy of fusion increases with increasing atomic number.

7. Which of the following statements is/are correct?
(a) The bond enthalpy $\varepsilon(N = N)$ is more that twice of the bond enthalpy $\varepsilon(N - N)$.
(b) The bond enthalpy $\varepsilon(N = N)$ is lesser than twice of the bond enthalpy $\varepsilon(N - N)$.

(c) The bond enthalpy $\varepsilon(P = P)$ is more than twice of the bond enthalpy $\varepsilon(P - P)$.
(d) The bond enthalpy $\varepsilon(P = P)$ is lesser than twice of the bond enthalpy $\varepsilon(P - P)$.

8. Which of the following statement is/are correct?
(a) The first ionization energy of magnesium is lesser than that of aluminium.
(b) The first ionization energy of phosphorus is greater than that of sulphur.
(c) The second ionization energy of sodium is greater than that of magnesium.
(d) The first ionization of zinc is much greater than that of copper.

9. Which of the following statement(s) is/are correct?
(a) All alkaline earth and noble gas elements have positive values of electron attachment enthalpies.
(b) The electron attachment enthalpy of chlorine is more negative than that of fluorine.
(c) The electron attachment enthalpy of nitrogen is more negative than that of oxygen.
(d) The electron attachment enthalpy of sulphur is less negative than that of oxygen.

10. Which of the following statements regarding elements of Group 14 is/are correct?
(a) Dry graphite in a vacuum is not slippery.
(b) Graphite is thermodynamically more stable than diamond.
(c) The liquid germanium contract on converting to the solid form.
(d) Both $N(CH_3)_3$ and $N(SiH_3)_3$ have pyramidal geometry.

11. Which of the following facts regarding elements of Group 17 is/are correct?
(a) Electron affinity follows the order : $F < Cl > Br$
(b) Electronegativity follows the order : $F > Cl > Br$
(c) Bond enthalpy follows the order : $\varepsilon(F–F) < \varepsilon(Cl–Cl) > \varepsilon(Br–Br)$
(d) The reaction $I_2 + 2H_2O \rightarrow 2H^+ + 2I^- + O_2$ is thermodynamically feasible.

12. White phosphorus (P_4) has
(a) six P—P single bonds. (b) four P—P single bonds.
(c) four lone pairs of electrons. (d) PPP angle of 60°. (1998)

13. Which of the following statements are **not** correct?
(a) Red phosphorus is less volatile than white phosphorus because the former has a tetrahedral structure.
(b) In an aqueous solution chlorine is a stronger oxidizing agent than fluorine.
(c) Graphite is a better lubricant on the moon than on the earth.
(d) The decreasing order of electron affinity of F, Cl, Br is $F > Cl > Br$.

14. Which of the following statements are correct?
(a) Diamond is harder than graphite.
(b) The tendency for catenation is much higher for C than for Si.
(c) The amorphous varieties of carbon contain microcrystals of graphite.
(d) Diamond is a good conductor of electricity.

15. Which of the following statements are **not** correct?
(a) Diamond has a high value of refractive index.
(b) Each carbon atom in diamond is sp^2 hybridized.
(c) Bituminous contains maximum carbon content.
(d) Coal and coke represent one and the same type of carbon.

16. Which of the following statements are correct?
(a) Heating of finely divided silica with magnesium produces crystalline variety of silicon.
(b) Silicon is a nonmetal.
(c) Silicon does not form Si=O double bonds.
(d) Silicon does not form Si—Si bond readily.

17. Which of the following statements are **not** correct?
(a) Silicon-oxygen bond is less stable as compared to silicon-halogen bond.
(b) Heating of ammonium nitrate produces nitric oxide gas.
(c) White phosphorus is nonpoisonous whereas red phosphorus is poisonous.
(d) White phosphorus is insoluble in water and soluble in CS_2.

18. Which of the following statements are correct?
(a) White phosphorus reacts with concentrated nitric acid producing P_2O_5 and nitric oxide gas.
(b) Red phosphorus is soluble both in water and carbon disulphide.
(c) Red phosphorus is chemically more reactive than white phosphorus.
(d) Caustic soda has no action on red phosphorus.

19. Which of the following statements are correct?
(a) Red phosphorus glows in dark.
(b) Black phosphorus is semiconducting.
(c) Red phosphorus is a polymeric substance.
(d) The species (N ≡ N) is more stable than three N—N bonds.

20. Which of the following statements are **not** correct?
(a) The species (P ≡ P) is more stable than three P—P bonds.
(b) Oxygen is diamagnetic in nature.
(c) Ozone is an allotropic modification of oxygen.
(d) The conversion of O_2 into O_3 is an exothermic reaction.

21. Which of the following statements are not correct?
(a) Ozone is not poisonous in nature.
(b) Ozone is a linear molecule.
(c) Of the halogens, Cl_2 has the maximum bond enthalpy.
(d) Fluorine forms six salts with xenon. These are XeF_2, XeF_3, XeF_4, X_3F_5, XeF_6, XeF_7.

22. Which of the following statements are correct?
(a) Iron combines with Cl_2 forming ferrous chloride.
(b) The bleaching effect of chlorine is permanent in nature.
(c) Delicate articles such as straw, silk and wool are not bleached by chlorine as it damages these articles.
(d) Iodine is as powerful oxidizing agent as chlorine and bromine.

23. Which of the following statements are correct?
(a) Iodine reacts with cold dilute sodium hydroxide solution forming NaI and NaOI.
(b) Iodine reacts with hot sodium hydroxide solution forming NaI and $NaIO_3$.
(c) Interhalogen compounds involve ionic bonding.
(d) Iodine can be obtained by oxidizing I^- with Cl_2.

24. Which of the following statements are correct?
(a) Bromine is the only liquid nonmetallic element at room temperature.
(b) The structure of $N(SiH_3)_3$ is planar whereas that of $N(CH_3)_3$ is pyramidal.
(c) The bond enthalpy of C—C bond is greater than that of Si—Si bond.
(d) One recently discovered allotrope of carbon (e.g. C_{60}) is commonly known as fullerene.

25. Which of the following statements are correct?
(a) There are two π bonds in a nitrogen molecule.
(b)The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of KI_3.
(c) White phosphorus is reactive because of its highly strained tetrahedral structure.
(d) Sulphur acts as polymerizing agent in vulcanization of rubber.

26. Which of the following statements are **not** correct?
(a) The hydrolysis of alkyl substituted chlorosilane gives silicon dioxide.
(b) The unit cell of diamond is primitive cube.
(c) In diamond, the arrangement of carbon atom is tetrahedral.
(d) Diamond is more dense then graphite.

27. Which of the following statements are correct?
(a) The distance between the two hexagonal net work in graphite is 335 pm.
(b) Each carbon atom in graphite is sp^2 hybridized.
(c) The carbon-carbon distance in hexagonal network in graphite of coal is 335 pm
(d) The common variety of coal is bituminous.

28. Which of the following statements are **not** correct?
(a) The coal containing maximum carbon content is bituminous.
(b) The coal containing minimum carbon content is anthracite.
(c) Silicon exists in the two allotropic forms.
(d) Silicon crystallizes in face-centred cubic lattice.

29. Which of the following statements are **not** correct?
(a) Treatment of urea or ammonium salt with an alkaline solution of sodium hypobromite produces N_2 gas.
(b) The mineral phosphorite is $Ca_3(PO_4)_2$.
(c) Phosphorus is manufactured by reducing calcium phosphate by Al in the presence of SiO_2.
(d) Phosphorus has five allotropic modifications.

30. Which of the following statements are not correct?
(a) White phosphorus on boiling with caustic soda produces PH_3 gas.
(b) Four phosphorus atoms in white variety are arranged tetrahedrally.
(c) The meniscus of mercury disappears when it comes in contact with ozone. This is due to the formation of HgO.
(d) The central oxygen atom in ozone is sp hybridized.

31. Which of the following statements are correct?
(a) In elemental form, sulphur exists as S_8 molecule.
(b) The stablest variety of sulphur is rhombic sulphur.
(c) The transition temperature of rhomic sulphur into monoclinic sulphur is 95°C – 96°C at 1 atm pressure.
(d) Passing H_2S through dilute nitric acid produces colloidal form of sulphur.

32. Which of the following statements are **not** correct?
(a) The reactivity of halogens towards metals increases on descending the group.
(b) Of halogens, the halogen having low enthalpy of dissociation is iodine.
(c) Fluorspar is CaF_2
(d) Cryolite is Na_3AlF_6

33. Which of the following statements are **not** correct?
(a) Fluorapatite is $CaF_2 \cdot 3Ca_3(PO_4)_2$.
(b) Fluorine reacts with water forming HF and O_2.
(c) With slaked lime, chlorine forms $CaCl_2$.
(d) With excess of ammonia, chlorine forms N_2 and HCl.

34. Which of the following statements are correct?
(a) With excess of chlorine, ammonia forms NCl_3 which is explosive in nature.
(b) The ultimate product of the hydrolysis of NCl_3 are NH_3 and HOCl.
(c) Iodine oxidizes thiosulphate to tetrathionate.
(d) The equivalent mass of sodium thiosulphate in its reaction with iodine is equal to its molar mass divided by two.

35. Which of the following statements are **not** correct?
(a) *Ortho* hydrogen molecule have antiparallel spins of nuclei.
(b) *Para* hydrogen molecule has parallel spins of nuclei.
(c) The *para* hydrogen molecule has energy higher than *ortho* isomer.
(d) At low temperatures, the predominant isomer of hydrogen molecule is *para*.
(e) At higher temperatures, the predominant isomer of hydrogen molecule is *ortho*.

36. The crystalline form of boron may be obtained by
(a) heating B_2O_3 with Mg.
(b) reducing B_2O_3 with excess of Al
(c) passing a mixture of boron tribmode vapours and hydrogen over electrically heated filament of tungsten at about 1500 K
(d) strong heating of B_2O_3.

Linked Comprehension Type

1. The halogens act as oxidizing agents. The strength of an oxidizing agent (which itself is reduced) is measured by its reduction potential which represents the tendency of the reaction $X_2 + 2e^- \rightarrow 2X^-(aq)$ to occur in the solution. The reduction potential may be determined from the free energy changes shown in the following Fig. 13.4.

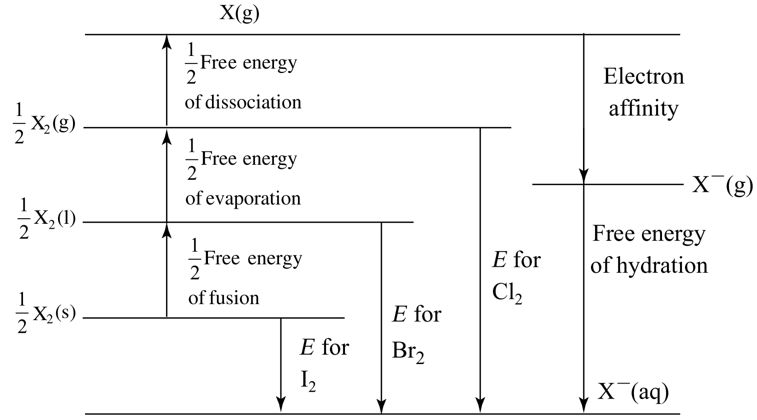


Fig. 13.4

Based on the above diagram, answer the following four questions.

(i) Which halogen is expected to have the largest free energy of dissociation?

(a) $F_2(g)$ (b) $Cl_2(g)$ (c) $Br_2(g)$ (d) $I_2(g)$

(ii) Which halogen is expected to have the largest negative value of electron affinity?

(a) F(g) (b) Cl(g) (c) Br(g) (d) I(g)

(iii) Which halogen is expected to have largest negative value of free energy of hydration?

(a) $F^-(g)$ (b) $Cl^-(g)$ (c) $Br^-(g)$ (d) $I^-(g)$

(iv) Which halogen is expected to have largest value of reduction potential?

(a) $F_2(g)$ (b) $Cl_2(g)$ (c) $Br_2(l)$ (d) $I_2(s)$

2. Based on the structure of O_3 (which is a triatomic allotrope of O_2 and is responsible for protecting people from the harmful UV radiation from the sun) answer the following three questions.

(i) The shape and total number of valence electrons are

(a) linear molecule and 18 electrons (b) nonlinear molecule and 18 electrons
(c) linear molecule and 24 electrons (d) nonlinear molecule and 24 electrons

(ii) The number of lone pairs of electrons are

(a) one each in the terminal oxygens and two in the central oxygen
(b) one each in each of oxygens
(c) two each in the terminal oxygens and one in the central oxygen
(d) two each in each of oxygens

(iii) The bond order of O—O in O_3 is

(a) 2.0 (b) 1.5 (c) 2.5 (d) 3

3. Xenon is a noble gas. Unlike other noble gases, such as helium, neon and argon, the noble gas xenon combines with fluorine to give xenon fluorides. Based on this information, answer the following questions.

(i) The ionization energy of xenon is very close to the ionization energy of

(a) $N_2 \rightarrow N_2^+$ (b) $O_2 \rightarrow O_2^+$ (c) $F \rightarrow F^+$ (d) $C \rightarrow C^+$

(ii) Xenon fluorides are formed when the xenon gas is heated with fluorine at 400 °C in a sealed nickel vessel. The product depends on the F_2/Xe ratio. If the ratio is 1 : 5, the product is

(a) XeF_2 (b) XeF_3 (c) XeF_4 (d) XeF_6

(iii) Which of the following compounds involves trigonal bipyramidal arrangement of electron pairs around xenon?

(a) XeF_2 (b) XeF_4 (c) XeO_3 (d) $XeOF_4$

Assertion and Reason Type

The following questions contain two statements. Based on the following keys, answer correctly each question.

(a) Statement–1 is correct, Statement–2 is correct and is also a correct explanation for Statement–1.
(b) Statement–1 is correct, Statement–2 is correct and is **not** a correct explanation for Statement–1.
(c) Statement–1 is correct and Statement–2 is not correct.
(d) Statement–1 is not correct and Statement–2 is correct.

	Statement–1	**Statement–2**
1.	Boron always forms covalent bond.	The small size of B^{3+} favours the formation of covalent bond.
2.	Amongst elements of Group 13, boron has the highest melting point.	Boron exists as a polymeric form.
3.	Diamond is a nonconductor while graphite is a good conductor of electricity.	Diamond does not contain mobile electrons while graphite has mobile π electrons.
4.	Graphite is thermodynamically less stable than diamond.	The free energy of formation of graphite is zero while that of diamond has a negative value.
5.	Silicon is insulator when pure, but becomes p-type or n-type semi-conductor when doped with a Group III or Group V element respectively.	The conduction in p-type semiconductor is due to the presence of holes while in n-type semiconductor, it is due to the movement of free electron.
6.	The conductivity of semiconductors, unlike metals, increases with increase in temperature.	The mechanism of conduction is different in semiconductors and metallic conductors.
7.	The compounds N_2O_3 and N_2O_5 are monomeric whereas P_2O_3 and P_2O_5 exist as diamer.	Nitrogen can form strong pπ-pπ multiple bond whereas no such tendency exists for phosphorus.
8.	The viscosity of liquid sulphur increases upto 200°C followed by a decrease upto its boiling point of 444°C.	The S_8 rings break and diradical produced are polymerize to different extent up to 200°C beyond which the fragmentation of polymerized molecules proceeds resulting into increase of viscosity.
9.	Ozone is dark blue coloured gas.	The blue colour is due to absorption of blue light.
10.	Fluorine can be obtained by carrying out the electrolysis of aqueous solution of HF containing KHF_2.	Fluorine oxidizes water to O_2.

ANSWERS

Straight Objective Type

1. (d)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (d)
8. (c)	**9.** (b)	**10.** (c)	**11.** (d)	**12.** (c)	**13.** (c)	**14.** (d)
15. (a)	**16.** (d)	**17.** (c)	**18.** (a)	**19.** (a)	**20.** (b)	**21.** (c)
22. (b)	**23.** (d)	**24.** (b)	**25.** (c)	**26.** (c)	**27.** (d)	**28.** (b)
29. (c)	**30.** (c)	**31.** (c)	**32.** (a)	**33.** (c)	**34.** (c)	**35.** (d)
36. (c)	**37.** (b)	**38.** (c)	**39.** (c)	**40.** (c)	**41.** (d)	**42.** (b)
43. (a)	**44.** (b)	**45.** (b)	**46.** (c)	**47.** (d)	**48.** (c)	**49.** (d)

50. (c) **51.** (b) **52.** (b) **53.** (b) **54.** (c) **55.** (a) **56.** (d)
57. (c) **58.** (c) **59.** (a) **60.** (c) **61.** (d) **62.** (a) **63.** (a)
64. (b) **65.** (c) **66.** (c) **67.** (b) **68.** (b) **69.** (a) **70.** (c)
71. (c) **72.** (a) **73.** (b) **74.** (a)

Multiple Correct Choice Type

1. (a), (b), (d) **2.** (b), (d) **3.** (a), (b) **4.** (b), (c), (d)
5. (b), (c), (d) **6.** (a), (b), (d) **7.** (a), (d) **8.** (b), (c), (d)
9. (a), (b) **10.** (a), (b) **11.** (a), (b), (c) **12.** (a), (c), (d)
13. (a), (b), (c), (d) **14.** (a), (b), (c) **15.** (b), (c), (d) **16.** (c), (d)
17. (a), (b), (c) **18.** (b), (d) **19.** (b), (c), (d) **20.** (a), (b), (d)
21. (a), (b, (d) **22.** (b), (c) **23.** (a), (d) **24.** (a), (b), (c), (d)
25. (a), (b), (c), (d) **26.** (a), (b) **27.** (a), (b), (d) **28.** (a), (b)
29. (c), (d) **30.** (c), (d) **31.** (a), (b), (c), (d) **32.** (a), (b)
33. (c), (d) **34.** (a), (b), (c) **35.** (a), (b), (c) **36.** (b), (c)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (b) **(iii)** (a)
2. **(i)** (b) **(ii)** (c) **(iii)** (b)
3. **(i)** (b) **(ii)** (c) **(iii)** (a)

Assertion and Reason Type

1. (a) **2.** (c) **3.** (a) **4.** (d) **5.** (a) **6.** (b) **7.** (a)
8. (a) **9.** (c) **10.** (d)

Hints and Solutions

Straight Objective Type

9. Diamond crystallizes in the face-centred cubic lattice.
10. The bond length of σ bonded carbon-carbon bond in graphite is 142 pm.
11. Silicon occurs mostly as silicon dioxide.
18. C—C bond has maximum energy. The phenomenon of catenation is due to the ability of carbon to bond carbon with maximum bond energy as compared to the other elements of Group 14.
19. See, Q.18.
20. Si—C bond is also strong. Si does not form pπ-pπ bond due to its larger size. Carbon dioxide molecule is linear while SiO_2 is a network of Si and O atoms bonded by a single bond.
21. Nitrogen is diamagnetic as there are no unpaired electrons in it.
22. The reaction is $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$
23. Black phosphorus is the most stable allotrope.
24. White phosphorus being most reactive is stored under water.
28. The reaction is $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$.
29. See, Q.28.
30. Black phosphorus is semiconducting because of its layer structure.
34. N_2 has the highest bond energy due to triple bond between the two nitrogen atoms.
35. White phosphorus is most reactive while black phosphus is least reactive.
36. SO_2 is soluble in water. **37.** The reaction is $2HgO \rightarrow 2Hg + O_2$.
38. The electronic configuration of O_2 is KK $(\sigma\, 2s)^2\, (\sigma^*2s)^2\, (\pi 2p_x)^2\, (\pi 2p_y)^2\, (\sigma 2p_z)^2\, (\pi^*2p_x)^1\, (\pi^*2p_y)^1$
39. The conversion of O_2 to O_3 is endothermic.
40. The bond length O—O in ozone is about 128 pm which is intermediate between a single bond (148 pm in H_2O_2) and a double bond (121 pm) in O_2.
41. O_3 is unstable, and decomposes to O_2.

42. The reaction is $2O_3 \rightarrow 3O_2$. This reaction is accompanied with $\Delta \nu_g = +1$, hence, increase in volume at constant temperature and pressure.
43. Floropatite is $[Ca_3(PO_4)_2 \,.\, CaF_2]$; Fool's gold is FeS_2; Sphaelerite is ZnS; Chalcopyrite is $CuFeS_2$
44. Rhombic sulphur is stable at room temperature.
47. The reaction is $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$
50. The bond angle is near to 120° as oxygens are sp^2 hybridized.
51. The bond order is 1.5; one from sigma bond and 0.5 from four-electron three-centred π bond.
54. The reaction is $I_2 + 2HNO_3 \rightarrow 2HIO_3 + N_2$
55. Light absorbed is of complimentary colour of yellow which is violet light. **56.** See, Q.55.
57. Chlorine has larger electron affinity as compared to fluorine and bromine. **58.** See Q.57.
59. Fluorine being most electronegative, it does not show positive oxidation state. It has only 0 and – 1 oxidation states.
60. The reaction is $6OH^- + 3X_2 \rightarrow 5X^- + XO_3^- + 3H_2O$.
61. I_2 is least reactive.
62. Fluorine is the strongest oxidation agent.
63. The reaction is $2OH^- + Cl_2 \rightarrow Cl^- + ClO^- + H_2O$ **64.** See, Q.60.
65. The reaction is $NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$
66. SF_4 undergoes hydrolysis due to d orbitals in S.
67. Cl–Cl bond energy is maximum due to double bond-one σ bond and one π bond due to back bonding.
68. The reaction is $2NH_3 + I_2 \rightarrow NI_3 \cdot NH_3 + 3HI$
70. The reaction is $I_2 + \underset{\text{cold}}{OH^-} \rightarrow HIO + I^-$
72. The energy levels become closer. The promotion energy from ground state to the first excited state decreases and thus wavelength of energy becomes larger. This is supported by the colour of halogens. Gaseous F_2 is light yellow, Cl_2 gas is yellow-green, Br_2 gas and liquid are dark red-brown and I_2 gas is violet.

Multiple Correct Choice Type

13. (a) Red phosphorus has polymeric structure and not a tetrahedral, due to which red phosphorus is less volatile than white phosphorus.
(c) The lubricating properties of graphite depend not only on the slippage between the planes, but also on a film of moisture or gas molecules adsorbed on the surface of the graphite layers. The adsorbed substance decreases the friction as the layers in graphite slide past each other. Dry graphite in vacuum is not slippery.
(d) The correct order is F < Cl > Br. The larger electronic repulsion in F due to smaller size makes its electron affinity less than that of Cl.
14. (a) In diamond, all the four valencies of carbon are involved in stronger σ bonding whereas in graphite, three are involved in σ bonding whereas the fourth one is involved in weak π bonding.
(b) The tendency for catenation is related to the strength of C—C bond. The C—C bond is much stronger than Si—Si.
(d) It is a bad conductor of electricity. Graphite is a conductor of electricity.
15. (b) Each carbon in diamond is sp^3 hybridized.
(c) It is anthracite which contains maximum carbon content.
(d) Coke is obtained when coal is subjected to destructive distillation in the absence of air.
16. (a) The amorphous carbon is obtained by this method.
(b) It is a metalloid.
17. (a) The Si—O single bond is the strongest of all silicon bonds.
(b) Heating of ammonium dichromate produces nitrogen gas according to the reaction

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3.$$

(c) White phosphorus is poisonous in nature, while red phosphorus is nonpoisonous.
18. (a) The products are phosphoric acid and nitrogen dioxide:

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(c) The reverse is correct.

19. (a) White phosphorus glows in dark.

20. (a) $\varepsilon(P \equiv P) > 3\varepsilon(P—P)$. It is because of this phosphorus does not have the structure of the type $P \equiv P$.

(b) Oxygen contains two unpaired electrons, hence it is paramagnetic.

(d) It is an endothermic reaction.

21. (b) It is a bent molecule with bond angle of 116°49′.

(d) Only three halides XeF_2, XeF_4 and XeF_6 are known.

22. (a) Chlorine combines with iron forming ferric chloride. The metal is in the higher oxidation state.

(d) The oxidizing nature decreases on descending the group.

23. (a) The products are HOI and I^-.

24. (b) Because of an empty d orbital on silicon, $N(SiH_3)_3$ involves pπ-dπ bonding causing it to be planar. No such bond is possible in $N(CH_3)_3$ making it to be pyramidal.

CHAPTER 14

COMPOUNDS OF METALS

SODIUM AND POTASSIUM

Oxides Burning of sodium in air produces both monoxide (Na_2O) and peroxide (Na_2O_2). Because of difficulty in separating the two, monoxide can be prepared by either of the following two ways.

(a) Heating sodium nitrate or nitrite with sodium. $2NaNO_3 + 10\ Na \xrightarrow{\text{fusion}} 6Na_2O + N_2$
(b) Heating sodium azide with sodium nitrite. $3NaN_3 + NaNO_2 \longrightarrow 2Na_2O + 5N_2$

Potassium monoxide can also be prepared in a similar manner.

Monoxides of sodium and potassium react with water forming hydroxides.The reactivity increases in going from sodium to potassium.

$$M_2O + H_2O \rightarrow 2MOH$$

Both oxides disproportionate on heating at 670 K. $2M_2O \xrightarrow[\text{peroxide}]{670\ K} M_2O_2 + 2M$

Both react with liquid ammonia to form amides. $M_2O + NH_3 \rightarrow MNH_2 + MOH$

Peroxides Heating of sodium or potassium in excess of air, free from moisture and carbon dioxide produces peroxide (M_2O_2). Sodium peroxide is pale blue whereas potassium peroxide is orange.

At low temperatures, the treatment of peroxides of sodium and potassium with water liberates H_2O_2

$$M_2O_2 + 2H_2O \rightarrow 2MOH + H_2O_2$$

At higher temperatures, oxygen is liberated $2M_2O_2 + 2H_2O \rightarrow 4MOH + O_2$

Dilute acid also generates H_2O_2 in cold and O_2 when they are hot.

$$M_2O_2 + H_2SO_4 \rightarrow M_2SO_4 + H_2O_2$$
$$2M_2O_2 + 2H_2SO_4 \rightarrow 2M_2SO_4 + 2H_2O + O_2$$

Peroxides are powerful oxidizing agent. They can oxidize chromic hydroxide to chromate, manganous salts to manganate and sulphides to sulphates. The reactions may be formulated as follows.

Reduction $O_2^{2-} + 2H_2O + 2e^- \rightarrow 4OH^-$

Oxidations $Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$; $Mn^{2+} + 8OH^- \rightarrow MnO_4^- + 4H_2O + 5e^-$

$S^{2-} + 8OH^- \rightarrow SO_4^{2-} + 4H_2O + 8e^-$

With carbon monoxide, peroxides form carbonates. $M_2O_2 + CO \rightarrow M_2CO_3$

Potassium when burned in excess of moisture free oxygen forms superoxide. $K + O_2 \rightarrow KO_2$

It reacts with water at low temperatures forming hydroxide, hydrogen peroxide and oxygen.

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

With carbon monoxide, potassium superoxide gives potassium carbonate and oxygen :

$$2KO_2 + CO \rightarrow K_2CO_3 + O_2$$

The superoxide, O_2^-, contains a three electron bond and thus the molecule containing superoxide is paramagnetic and coloured. From the molecular orbital viewpoint, O_2^- contains one unpaired electron.

Hydroxides The hydroxides may be prepared by dissolving the metals or their oxides in water. Commercially, these are prepared by the electrolysis of solution of alkali chlorides. During electrolysis, water is reduced at the cathode (because of its lower discharge potential than Na^+ or K^+) and chloride is oxidized to chlorine.

Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ *Anode* $2Cl^- \rightarrow Cl_2 + 2e^-$

Thus, NaOH (or KOH) is formed at cathode. This is not allowed to come in contact with Cl_2 as otherwise the following reaction would take place.

$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

KOH is stronger alkali than NaOH and is also more soluble in alcohol. They are soapy to touch and are very corrosive. NaOH (or KOH) reacts with a large number of metals and nonmetals. A few examples are given below.

$2NaOH + Zn \rightarrow Na_2ZnO_2 + H_2$

$2NaOH + 2Al + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

$2NaOH + Sn + H_2O \rightarrow Na_2SnO_3 + 2H_2$

$2NaOH + Si + H_2O \rightarrow Na_2SiO_3 + 2H_2$

$6NaOH\ (hot) + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$

$6NaOH + 4S \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

$3NaOH + P_4 + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

In general, basic nature of the hydroxides of Group 1 elements increases on moving down the group from LiOH to CsOH. Similarly, their thermal stability also increases.

Carbonates and Bicarbonates Sodium carbonate is prepared industrially by Solvay (or ammonia-soda) process. In this process, brine solution is saturated with ammonia and the resultant solution is treated with carbon dioxide gas when less soluble $NaHCO_3$ precipitates out which on heating yields Na_2CO_3.

$$NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3(s) + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2$$

The remaining solution contains NH_4HCO_3 and a little NH_4Cl. From this, NH_3 is recovered by adding milk of lime.

$$NH_4HCO_3 \xrightarrow{\text{heat}} NH_3 + CO_2 + H_2O$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Potassium carbonate cannot be obtained by this method as $KHCO_3$ is highly soluble in water. This is obtained by Engel-Percht process in which CO_2 is passed into a solution of KCl at 290 K in the presence of hydrated magnesium carbonate ($MgCO_3 \cdot 3H_2O$). This results into the precipitation of $KHCO_3 \cdot MgCO_3 \cdot 4H_2O$.

$$2KCl + 3MgCO_3 + 9H_2O + CO_2 \rightarrow 2(KHCO_3 \cdot MgCO_3 \cdot 4H_2O) \downarrow + MgCl_2$$

This is filtered. The residue is heated under pressure which decomposes to give K_2CO_3 (soluble) and $MgCO_3$ (insoluble) with the evolution of carbon dioxide.

$$2(KHCO_3 \cdot MgCO_3 \cdot 4H_2O) \xrightarrow[410\ K]{} K_2CO_3 + 2MgCO_3 + CO_2 + 9H_2O$$

Alternatively, the residue may be treated with a suspension of magnesium oxide in water below 290 K.

$$2(KHCO_3 \cdot MgCO_3 \cdot 4H_2O) + MgO \rightarrow 3(MgCO_3 \cdot 3H_2O) + K_2CO_3$$

Potassium carbonate is extracted from the residue with water, concentrated and crystallized. Potassium bicarbonate can be obtained by passing CO_2 in a cold saturated solution of K_2CO_3, when it being less soluble than carbonate is precipitated out.

$$K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3$$

Sodium carbonate crystallizes as $Na_2CO_3 \cdot 10H_2O$. The crystals effloresce on standing in air and becomes powder, probably due to the formation of $Na_2CO_3 \cdot H_2O$.

On heating, water of crystallization is lost and anhydrous sodium carbonate is formed. It also forms heptahydrate, $Na_2CO_3 \cdot 7H_2O$.

Potassium carbonate crystallizes as $K_2CO_3 \cdot 3H_2O$ at temperatures between 280 K-300 K. At 370 K, it is converted to $K_2CO_3 \cdot H_2O$ and finally at 400 K, anhydrous K_2CO_3 is obtained.

Sodium carbonate is known as *washing soda* and is used in the manufacture of soap, glass, caustic soda and borax. Sodium bicarbonate is known as *baking soda* and is used as leavening agent in cooking. It is also used as antacid to neutralize acidity in the stomach.

In general, carbonates of alkali metals are soluble in water except Li_2CO_3 which is sparingly soluble. Bicarbonates are very much less soluble than the corresponding carbonates.

Chlorides Sodium chloride is known as *common salt* and is manufactured from seawater and water of certain lakes by evaporation. The salt obtained is slightly hygroscopic due to traces of $MgCl_2$ and $CaCl_2$ present in it. Potassium chloride is extracted from the mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). It is a good substituent for NaCl for patients with high blood pressure.

Sulphates The hydrated salt $Na_2SO_4 \cdot 10H_2O$ is known as *Glauber's salt*. Sodium sulphate is manufactured by heating sodium chloride with sodium bisulphate.

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

Cooling of the saturated solution of decahydrate below 285 K results into the formation of heptahydrate, $Na_2SO_4 \cdot 7H_2O$.

Potassium sulphate is manufactured from the mineral schonite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ by a process of crystallization after treating with sylvine (KCl).

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2KCl \rightarrow 2K_2SO_4 + MgCl_2 + 6H_2O$$

MAGNESIUM AND CALCIUM

Oxides These can be obtained by heating either carbonate or hydroxide of the metal. Magnesium oxide is a white powder and is very resistant to change at high temperatures. It is used as a refractory material for lining electric furnaces. Calcium oxide is also known as *quicklime*. On adding water it gives a hissing sound and becomes very hot. The product obtained is $Ca(OH)_2$ and is known as *slaked lime*. This process is known as slaking of lime. The paste of lime in water is known as *milk of lime* whereas the filtered and clear solution is known as *lime water*. Moist Cl_2, CO_2, SO_2 and HCl gives $CaOCl_2 \cdot H_2O$ (bleaching powder), $CaCO_3$, $CaSO_3$ and $CaCl_2$ respectively when reacted with CaO.

Both the oxides are basic. These are less basic than the oxides of alkali metals. The basic properties increase with descent of the group.

Moistening of MgO with a saturated solution of magnesium chloride results in the formation of a firm hard cement known as *Sorel's cement*. It is used as a stopping for teeth.

Peroxides The addition of hydrogen peroxide (or sodium peroxide) to cold alkaline solutions of magnesium and calcium salt results into the formation of peroxides. For example

$$Ca^{2+} + H_2O_2 + 8H_2O \rightarrow \underset{\text{crystallizes out}}{CaO_2 \cdot 8H_2O} + 2H^+$$

CaO_2 is less stable than MgO_2. Both react with acid producing H_2O_2 and O_2.

In general, Be forms only the monoxide, all other elements of Group 2 form monoxides and peroxides. BeO is predominantly covalent. All oxides are thermally very stable. BeO and MgO are insoluble in water, rest react with water giving hydroxides. BeO is amphoteric while others are basic in nature. The thermal stability of peroxides increases with increasing cation size on descending the group.

Hydroxides The addition of alkali to magnesium salts solution precipitates out magnesium hydroxides. In qualitative analysis, magnesium is not percipitated out by adding ammonium hydroxide in the presence of ammonium chloride. An aqueous suspension of $Mg(OH)_2$ is known as *milk of magnesia* and is used as a digestive antacid.

In general, the hydroxides of Group 2 are less basic than alkali metal hydroxides. The basic character increases on moving down the group. Their solubility also increases on moving down the group, $Be(OH)_2$ is least soluble while $Ba(OH)_2$ is most soluble.

Carbonates and Bicarbonates Carbonates of magnesium and calcium can be obtained by adding sodium carbonate in the aqueous solution of respective salt. When carbon dioxide is passed through the suspension of carbonates, the latter dissolve forming bicarbonate.

$$\underset{\text{(insoluble)}}{MgCO_3} + H_2O + CO_2 \rightarrow \underset{\text{(soluble)}}{Mg(HCO_3)_2}$$

The carbonates of magnesium and calcium are thermally unstable and decompose below their melting points. Thermal stability increases from $MgCO_3$ to $BaCO_3$ due to the increase in the size of cation. The smaller size cation distorts or polarizes the larger carbonate anion and thus decreases its stability.

The bicarbonates of magnesium and calcium are stable only in solution because the close approach of a cation and anion in the crystalline salt causes the decomposition of bicarbonate ion.

Chlorides Both magnesium and calcium chlorides occur as hexahydrate, i.e. $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$. In laboratory, these can be prepared by the action of hydrochloric acid on oxide or carbonate.

Magnesium chloride can be obtained from the mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) by fusing, then cooling to 448 K when whole of potassium chloride separates out. On further cooling, the remaining potassium chloride separaters as carnallite leaving behind fused magnesium chloride.

Calcium chloride is obtained as a byproduct in ammonia soda process for the manufacture of washing soda.

Anhydrous magnesium chloride cannot be prepared by heating $MgCl_2 \cdot 6H_2O$ as the latter undergoes partial hydrolysis:

$$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$$

However, it can be prepared by heating in a current of dry hydrogen chloride or by direct combination of metal and chlorine.

Anhydrous calcium chloride can be obtained by heating:

$$CaCl_2 \cdot 6H_2O \xrightarrow[473\ K]{} CaCl_2 \cdot 2H_2O \xrightarrow[fusion]{} CaCl_2$$

Both magnesium and calcium chlorides are deliquescent. Calcium chloride is used as dehydrating agent.

Anhydrous calcium chloride melts at a temperature higher than that of anhydrous magnesium chloride. This is because of higher charge: radius ratio for Mg^{2+} ions in comparison to Ca^{2+} ions. In general, beryllium halides are covalent and those of other elements of Group 2 are ionic. Their solubility in water decreases on descending the group.

Sulphates Heptahyadrate of magnesium sulphate ($MgSO_4 \cdot 7H_2O$) is known as *epsom salt* and dihydrate of calcium sulphate ($CaSO_4 \cdot 2H_2O$) is known as *gypsum*. Magnesium sulphate is soluble in water whereas calcium sulphate is sparingly soluble. Soluble magnesium sulphate can be obtained by adding dilute sulphuric acid to an aqueous solution of magnesium salt followed by evaporation.

Epsom salt is used as a puragative. Gypsum gives *plaster of paris* ($CaSO_4 \cdot \frac{1}{2}H_2O$ or $2CaSO_4 \cdot H_2O$) on heating at 325K. The latter finds use as dehydrant and making plaster casts in orthopaedic surgery. Gypsum finds use in the preparation of cement.

Factors determining the solubility of an ionic solid in water The following two opposite factors play key role in the solubility of ionic solids in water.

1. *Lattice energy* It is the energy released when the requisite number of gaseous ions are converted into 1 mol of crystalline lattice. Higher the lattice energy more tightly the ions are held together in the crystal, lesser will be its tendency to split into ions to pass over in the solution, i.e. lesser will be its solubility.
2. *Hydration energy* It is the heat released when the dissolved ions get hydrated in the solution. Higher the hydration energy, the more heat is released and thus higher is the solubility.

Thus, we have

Higher the lattice energy, lesser the solubility and higher the hydration energy, more the solubility.

In case of sulphates of alkaline earth metals, the SO_4^{2-} ion itself being large, the changes in the size of metallic ion from Be^{2+} to Ba^{2+} do not make much difference in the lattice energy. However, the change in the hydration energy is more predominant which decrease regularly from Be^{2+} to Ba^{2+} causing the decrease in the solubility from $BeSO_4$ to $BaSO_4$.

In case of salts such as chlorides and hydroxides, the size of anion is not large, the change in the size of cation causes significant change in lattice energy which decrease from Be^{2+} to Ba^{2+} ions. This factor is predominant as compared to the decrease in the hydration energy, thus causing the solubility of such salts to increase as we go from Be to Ba salts.

Hardness of Water

Hardness of water is due to the presence of dissolved salts such as carbonates, bicarbonates or sulphates of magnesium and calcium. Such a solution does not form lather with soap but only insoluble scum of sterate is formed.

Hardness of water may be classified as temporary and permanent. Temporary hardness is due to the presence of bicarbonates of magnesium and calcium. These can be removed by merely boiling the water which causes the precipitation of carbonates:

$$2HCO_3^- \rightleftharpoons CO_3^{2-} + CO_2 + H_2O$$

Carbon dioxide is driven off causing the equilibrium to the right side. The addition of lime also helps removing temporary hardness.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2H_2O$$

Permanent hardness is due to sulphates of Mg or Ca in solution. Its hardness can be removed by distilling the water or passing through ion-exchange resin when Ca^{2+} and Mg^{2+} ions are replaced by Na^+ ions or by adding salts such as trisodium phosphate (Na_3PO_4), sodium pyrophosphate ($Na_4P_2O_7$), tripolyphosphate ($Na_5P_3O_{10}$) or Grahams salt ($(NaPO_3)_n$). These salts form complex with Ca^{2+} and Mg^{2+} ion and thus do not react with soap. The addition of Na_2CO_3 causes the precipitation of $CaCO_3$.

ALUMINIUM

Alumina Aluminium oxide is known as alumina. It can be prepared by igniting aluminium hydroxide, aluminium sulphate or ammonium alum.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O; \qquad Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$$

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow 2NH_3 + Al_2O_3 + 4SO_3 + 25H_2O$$

Alumina exists in two polymorphic forms, namely, α-Al_2O_3 and γ-Al_2O_3.

Because of its great hardness, high melting point, chemical inertness and good electrical insulating properties, α-Al_2O_3 is used as abrasives, refractories and ceramics. It is also used as gemstones, the colour of these is due to the traces of metallic oxides. A few synthetic precious gemstones are ruby (Cr^{3+}, red), sapphire (Fe^{2+}, Ti^{4+}, blue), emerald (V^{3+}, green) and topaz (Fe^{3+}, yellow).

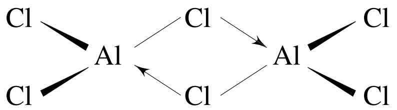
Chloride Aluminium chloride is prepared by dissolving aluminium, its oxide or hydroxide in hydrochloric acid. On crystallizing, $AlCl_3 \cdot 6H_2O$ is obtained. On heating, this decomposes as follows.

$$2AlCl_3 \cdot 6H_2O \rightarrow Al_2O_3 + 6HCl + 3H_2O$$

Thus, anhydrous aluminium chloride cannot be prepared by heating hydrated salt. Instead, heating aluminium in the atmosphere of Cl_2 or HCl gives anhydrous chloride. The anhydrous salt may also be obtained by heating a mixture of alumina and coke in a current of Cl_2 (MacAffe Process):

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$$

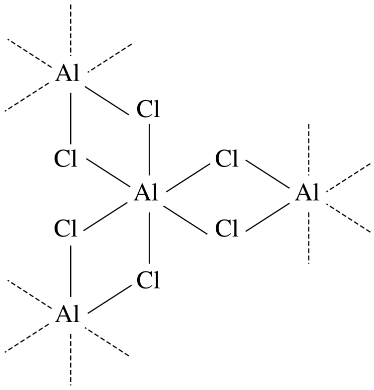
Aluminium chloride exists as a dimer:



Each atom in the above structure attains an octet of electrons. It is covalent compound and is soluble in alcohol, ether and benzene. It acts as a Lewis acid.

In aqueous solution, aluminium chloride is present in the form of ions, $Al(H_2O)_6^{3+}$ and Cl^-. An aqueous solution of this salt is acidic due to hydrolysis. When its aqueous solution is concentrated, the crystals of $Al_2Cl_6 \cdot 12H_2O$ are deposited.

The structure of $AlCl_3$ in solid phase is



The coordination number of aluminium is six in solid aluminium chloride.

Alums Alums are double salts with formula $M_2SO_4, M'_2(SO_4)_3 \cdot 24H_2O$ where M is monopositive ion (Na^+, K^+ or NH_4^+) and M′ is tripositive ion (Al^{3+}, Cr^{3+} or Fe^{3+}). Ordinary alum is potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$. This can be prepared by mixing equimolar solutions of K_2SO_4 and $Al_2(SO_4)_3$ followed by concentration.

Alums may be equally represented as $M(H_2O)_6 \cdot M'(H_2O)_6 \cdot (SO_4)_2$. The crystals of alum are octahedrally shaped and are isomorphous with one another. These are double salts. Some common alums are

Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12H_2O$	Chrome alum	$KCr(SO_4)_2 \cdot 12H_2O$
Sodium alum	$NaAl(SO_4)_2 \cdot 12H_2O$	Alum	$KAl(SO_4)_2 \cdot 12H_2O$
Ferric alum	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	Manganic alum	$KMn(SO_4)_2 \cdot 12H_2O$

Potash alum is used in purification of water, as a modant in dyeing and for tanning of leather.

TIN AND LEAD

Tin and lead give two series of compounds with valencies 2 and 4. Tin(IV) salts are more stable than tin(II) salts. Thus, tin(II) salts are readily oxidized and are good reducing agents. On the contrary, Pb(II) salts are more stable than Pb(IV) salts. Thus, Pb(IV) salts are readily reduced and are good oxidizing agents. This contrast behaviour is due to the *inert-pair effect*. Divalent tin or lead compounds are essentially ionic in nature whereas tetravalent are generally covalent.

Oxides Tin forms two oxides—stannous oxide (SnO) and stannic oxide (SnO_2).

Stannous oxide is obtained by heating stannous oxalate or hydroxide in a current of carbon dioxide.

$$(COO)_2Sn \rightarrow SnO + CO + CO_2; \qquad Sn(OH)_2 \rightarrow SnO + H_2O$$

It is a dark-grey or black powder. It is an amphoteric oxide and dissolves in both acids and alkalis.

$$SnO + 2HCl \rightarrow SnCl_2 + H_2O; \qquad SnO + 2NaOH \rightarrow \underset{\text{Sodium}}{Na_2SnO_2} + \underset{\text{stannite}}{H_2O}$$

The stannites are known only in aqueous solutions which is oxidized by atmospheric oxygen.

$$\underset{\text{Sodium}}{2Na_2SnO_2} + \underset{\text{stannate}}{O_2} \rightarrow 2Na_2SnO_3$$

Stannite ion acts as a powerful reducing agent. For example, MnO_4^- is reduced to MnO_2.

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-\ ] \times 2 \\ SnO_2^{2-} + 2OH^- \rightarrow SnO_3^{2-} + H_2O + 2e^-\ ] \times 3 \\ \hline 2MnO_4^- + 3SnO_2^{2-} + H_2O \rightarrow 2MnO_2 + 3SnO_3^{2-} + 2OH^- \end{array}$$

and Bi^{3+} ions is reduced to Bi

$$2Bi^{3+} + 6OH^- + 3\ SnO_2^{2-} \rightarrow 2\ Bi + 3\ SnO_3^{2-} + 3H_2O$$

Stannic oxide is obtained when tin is burnt in air or when metastannic acid, which is formed by the action of nitric acid on tin, is calcined.

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O; \qquad H_2SnO_3 \xrightarrow[\text{heat}]{} SnO_2 + H_2O$$

It is a white powder and is not reacted with common acids except sulphuric acid which gives $Sn(SO_4)_2$. The latter on dilution gives SnO_2. Tin dioxide is also soluble in alkalis.

$$SnO_2 + 2KOH \rightarrow K_2SnO_3 + H_2O$$

Lead forms five oxides, namely, monoxide (PbO), dioxide (PbO_2), mixed oxides (Pb_3O_4, red lead), suboxide (Pb_2O) and sesquioxide (Pb_2O_3).

Lead monoxide exists in two forms, yellow powder called *massicot* and reddish yellow crystalline mass called *litharge*. Massicot is obtained when lead is heated in air at 575 K. At higher temperature of 1150 K, massicot fuses to give litharge. Heating of lead nitrate or carbonate gives lead monoxide. This oxide is amphoteric and dissolves in acids as well as alkalis.

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O; \quad PbO + 2NaOH \rightarrow \underset{\text{sodium plumbite}}{Na_2PbO_2} + H_2O$$

Lead dioxide may be obtained by oxidizing lead salt with bleaching powder containing some slaked lime.

$$(CH_3COO)_2Pb + Ca(OH)_2 \rightarrow Pb(OH)_2 + (CH_3COO)_2Ca$$
$$Pb(OH)_2 + CaOCl_2 \rightarrow PbO_2 + CaCl_2 + H_2O$$

Alkaline hypochlorite can also be used for the oxidation.

$$PbCl_2 + NaOCl + 2NaOH \rightarrow PbO_2 + 3NaCl + H_2O$$

Fusion of monoxide with $KClO_3$ or KNO_3 also produces PbO_2.

It is a chocolate brown powder and is a powerful oxidizing agent. It dissolves in concentrated HCl as well as in concentrated NaOH.

$$PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O; \qquad PbO_2 + 2NaOH \rightarrow \underset{\text{sodium plumbate}}{Na_2PbO_3} + H_2O$$

A few reactions showing oxidizing nature of PbO_2 are as under.

$$PbO_2 + SO_2 \rightarrow PbSO_4; \qquad PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$$

$$2Mn^{2+} + 5\ PbO_2 + 6H^+ \rightarrow \underset{\text{pink colour}}{2HMnO_4} + 5\ Pb^{2+} + 2H_2O$$

Red lead (Pb_3O_4) is, in fact, a mixed oxides ($2PbO \cdot PbO_2$). This has a orange-red colour and is obtained by heating PbO in air at 575 K–850 K.

$$6PbO + O_2 \underset{\text{above 850K}}{\overset{\text{575K–850 K}}{\rightleftharpoons}} 2Pb_3O_4$$

It oxidizes HCl to Cl_2 and gives oxygen with hot concentrated H_2SO_4.

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2; \qquad 2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$$

With nitric acid, PbO gives $Pb(NO_3)_2$ while PbO_2 remains as such.

$$Pb_3O_4 + 4HNO_3 \rightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$

Red lead is used as a protective paint for iron and steel and as an oxidizing agent in a laboratory.

Lead suboxide (Pb_2O) is obtained when lead oxalate is heated in absence of air.

$$2PbC_2O_4 \rightarrow Pb_2O + 3CO_2 + CO$$

Lead sesquioxide (Pb_2O_3) is obtaind when lead monoxide is heated in air up to 775 K.

$$4PbO + O_2 \rightarrow 2Pb_2O_3$$

Chlorides Tin forms two chlorides—stannous and stannic chlorides. Of these, the former is more ionic than the latter.

Stannous chloride is formed when tin is dissolved in concentrated HCl followed by evaporation when $SnCl_2 \cdot 2H_2O$ is deposited. Anhydrous chloride cannot be prepared by dehydrating the hydrated salt as it undergoes hydrolysis to give basic chloride, Sn(OH)Cl. However, this can be prepared by heating tin in a current of dry hydrochloric acid gas. Also, distillation of excess of tin with Hg_2Cl_2 gives $SnCl_2$ as the residue.

Stannous chloride is soluble in water. However on standing, the precipitates of Sn(OH)Cl are obtained. In the presence of HCl, this hydrolysis is prevented.

Stannous chloride in concentrated HCl is a powerful reducing agent. A few examples are

(a) $2Hg^{2+} + 2Cl^- + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+}$

$Hg_2Cl_2 + Sn^{2+} \rightarrow 2Hg + Sn^{4+} + 2Cl^-$

(b) $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

(c) $2Cu^{2+} + 2Cl^- + Sn^{2+} \rightarrow 2\ CuCl + Sn^{4+}$

(d) $2Au^{3+} + 3Sn^{2+} \rightarrow 2Au + 3Sn^{4+}$

(e) $I_2 + Sn^{2+} \rightarrow 2I^- + Sn^{4+}$

(f) $C_6H_5NO_2 + 6H^+ + 3Sn^{2+} \rightarrow C_6H_5NH_2 + 2H_2O + 3Sn^{4+}$

(g) $2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$

(h) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

With ammonia, $SnCl_2$ forms a number of double salts ($SnCl_2 \cdot NH_3$, $SnCl_2 \cdot 2NH_3$ and $3SnCl_2 \cdot 2NH_3$).

Anhydrous stannous chloride is an angular covalent molecule because of the repulsion between a lone pair of electrons on Sn and the two bonding pair of electrons.

Stannic chloride is a colourless fuming liquid. It is a covalent compound as it is soluble in benzene. With limited water, it forms a series of hydrated salts ($SnCl_4 \cdot 3H_2O$, $SnCl_4 \cdot 5H_2O$, $SnCl_4 \cdot 6H_2O$ and $SnCl_4 \cdot 8H_2O$). With excess water, it is hydrolysed.

$$SnCl_4 + H_2O \rightleftharpoons Sn(OH)Cl_3 + HCl; \qquad Sn(OH)Cl_3 + 3H_2O \rightleftharpoons Sn(OH)_4 + 3HCl$$

The crystals of hydrochlorostannic acid, $H_2[SnCl_6] \cdot 6H_2O$ are obtained when $SnCl_4$ is evaporated with hydrochloric acid. Similarly, salts of $(NH_4)_2\ [SnCl_6]$ and $K_2[SnCl_6]$ are obtained when $SnCl_4$ is crystallized in the presence of NH_4Cl and KCl, respectively. Stannic chloride also forms double salt with ammonia, $SnCl_4 \cdot 4NH_3$.

Lead also forms two chlorides—plumbous and plumbic chlorides. Of these, the former is more ionic than the latter. Lead(II) chloride is soluble in hot water but reappears on cooling. The solubility of $PbCl_2$ is decreased in hydrochloric acid solution due to the common ion but in presence of concentrated HCl, the solubility is increased due to the formation H_2PbCl_4. With ammonium chloride, the crystals of $(NH_4)_2[PbCl_6]$ are obtained.

IRON

Ferrous Sulphate It is also known as *green vitriol*. It can be obtained by treating scrap iron with dilute sulphuric acid. It is crystallized as $FeSO_4 \cdot 7H_2O$. Commercially, it is obtained by exposing big heaps of moist iron pyrites to air when slow oxidation takes place.

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

On standing, there is a loss of water of crystallization and also it turns brown on exposure to air due to oxidation to basic ferric sulphate.

$$4FeSO_4 + 2H_2O + O_2 \rightarrow 4Fe(OH)(SO_4)$$

Heating of ferrous sulphate gives ferric oxide with the evolution of SO_2 and SO_3.

$$2FeSO_4 \xrightarrow[\text{heat}]{} Fe_2O_3 + SO_2 + SO_3$$

Ferrous ion is a good reducing agent. It can reduce MnO_4^- to Mn^{2+} in acidic medium, $Cr_2O_7^{2-}$ to Cr^{3+} in acidic medium, nitric acid to nitric oxide, Hg^{2+} to Hg and Sn^{4+} to Sn^{2+}.

The solution of ferrous sulphate becomes black when NO_2 is passed through it. It is due to the formation of $FeSO_4 \cdot NO$.

Ferrous sulphate is not a primary standard in volumetric analysis as it is susceptible to aerial oxidation and dehydration.

Mohr's Salt It is a double salt with composition $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. It is sufficiently stable to be used as a primary standard in volumetric analysis. It can be obtained by mixing freshly prepared ferrous sulphate in solution with equal molar amounts of ammonium sulphate and then allow the solution to crystallize.

Oxide Ferrous oxide is obtained when ferrous oxalate is heated to about 430 K in the absence of air.

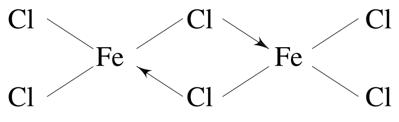
$$(COO)_2Fe \rightarrow FeO + CO + CO_2$$

In air, it burns to give more stable ferric oxide. The latter can be obtained by heating carbonate, nitrate or oxalate in the presence of air.

Heating of ferrous sulphate gives bright red Fe_2O_3 which is used as a pigment under the name *Venetian red*. It is amphoteric in nature and is soluble in both acids and alkalis.

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O; \qquad Fe_2O_3 + Na_2CO_3 \rightarrow \underset{\text{sodium ferrite}}{Na_2Fe_2O_4} + CO_2$$

Ferric Chloride The reaction of dry chlorine with heated iron gives ferric chloride which sublimes over as deep red crystalline plates. The anhydrous salt is deliquescent and soluble in water, alcohol and ether. The aqueous solution undergoes hydrolysis and is acidic towards litmus. In the gaseous state and in some organic solvents, ferric chloride exists as a dimer.



In aqueous acidic solution, it may be crystallised as $FeCl_3 \cdot 6H_2O$.

Potassium Ferrocyanide, $K_4Fe(CN)_6$ Hydrated iron oxide used in the purification of coal gas reacts with HCN present to the extent of about 0.3% in coal gas giving Prussian blue, $Fe_4[Fe(CN)_6]_3$. This is boiled with lime and the resultant $Ca_2Fe(CN)_6$ is extracted with water. The latter on treating with K_2CO_3 gives $K_4Fe(CN)_6$.

$$Ca_2Fe(CN)_6 + 2K_2CO_3 \rightarrow K_4Fe(CN)_6 + 2CaCO_3$$

On strong heating, $K_4Fe(CN)_6$ decomposes according to the reaction

$$K_4Fe(CN)_6 \rightarrow 4KCN + FeC_2 + N_2$$

On heating with conc. H_2SO_4, carbon monoxide is evolved.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$$

It is reducing agent and is oxidized to potassium ferricyanide ($K_3Fe(CN)_6$) by H_2O_2, Cl_2, $KMnO_4$ and O_3.

Potassium ferricyanide in alkaline medium is an oxidizing agent and is reduced to $K_4Fe(CN)_6$ by H_2S, PbO and Cr^{3+} compounds.

With ferrous salts, $K_3Fe(CN)_6$ gives a dark blue precipitate of Turnbull's blue which is believed to be identical with Prussian blue. This is due to mutual oxidation and reduction of ferrous ions and ferricyanide ions.

$$Fe^{2+} + [Fe(CN)_6]^{3-} \rightleftharpoons Fe^{3+} + [Fe(CN)_6]^{4-}$$

COPPER, ZINC AND SILVER

Copper Sulphate It is crystallized as $CuSO_4 \cdot 5H_2O$ and is also known as *blue vitriol.* It is best represented as $[Cu(H_2O)_4]SO_4 \cdot H_2O$. It may be prepared by reacting either CuO or $CuCO_3$ with dilute H_2SO_4. On an industrial scale, it is obtained by blowing air through a hot mixture of Cu and dil. H_2SO_4 : $Cu + 4H^+(aq) + O_2 \rightarrow 2Cu^{2+} + 2H_2O$ When exposed to air, blue colour fades to pale blue due to the conversion $CuSO_4.5H_2O \rightarrow CuSO_4.3H_2O$

The salt loses water of crystallization on heating.

$$CuSO_4 \cdot 5H_2O \underset{-\,4H_2O}{\overset{100°C}{\rightleftharpoons}} CuSO_4 \cdot H_2O \underset{-H_2O}{\overset{350°C}{\rightleftharpoons}} CuSO_4 \xrightarrow{\text{strong heat}} CuO + SO_3.$$

With ammonia, the cupric hydroxide is first precipitated which dissolves in more of ammonia giving tetramminecopper(II) sulphate complex, $[Cu(NH_3)_4]SO_4$.

With KI, Cu^{2+} ions in solution liberates iodine.

$$\begin{array}{l} 2I^- \rightarrow I_2 + 2e^- \\ 2Cu^{2+} + 2I^- + 2e^- \rightarrow 2CuI \\ \hline 2\ Cu^{2+} + 4I^- \rightarrow 2\ CuI + I_2 \end{array}$$

Copper(I) compounds if not insoluble disproportionates in aqueous solution.

$$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

ZINC

Oxide Zinc oxide is formed when zinc carbonate, nitrate or hydroxide is strongly heated. It is also obtained by burning zinc in air. It is a white powder commonly named as Philospher's wool. Its colour changes to yellow on heating because of the partial lose of oxygen. It is an amphoteric oxide, soluble in both HCl and NaOH.

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

Zinc oxide is used as a white paint base and is called *zinc white*.

Sulphate Zinc sulphate, $ZnSO_4 \cdot 7H_2O$, is known as *white vitriol*. It can be prepared by the action of dilute H_2SO_4 on zinc or its oxide and carbonate. It is used to prepare lithopone, a white pigment.

SILVER

Silver Nitrate Silver nitrate is known as *lunar caustic*. It is prepared by dissolving the silver metal in dilute nitric acid and crystallizing the solution. When large rhombic plates of $AgNO_3$ are obtained.

On heating, silver nitrate decomposes to give silver, nitrogen dioxide and oxygen.

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

It gives a black stain when it comes in contact with skin or cloth due to its reduction to metallic silver.

With dilute sodium thiosulphate solution, silver nitrate gives a white precipitate which changes colour to yellow, brown and finally black.

$$S_2O_3^{2-} + 2Ag^+ \rightarrow \underset{\text{white}}{Ag_2S_2O_3}; \quad Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{black}}{Ag_2S} + H_2SO_4$$

With a concentrated solution of sodium thiosulphate, silver nitrate gives no precipitate. Instead, a complex is formed.

$$Ag_2S_2O_3 + 3S_2O_3^{2-} \rightarrow 2\,[Ag(S_2O_3)_2]^{3-}$$

In an ammoniacal solution, Ag^+ ions exist as $[Ag(NH_3)_2]^+$ ions. It is because of this complex formation, silver chloride and bromide are soluble in ammonium hydroxide.

Bromide Silver bromide is obtained by adding soluble bromide to a silver salt solution. In a current of chlorine, silver bromide gives silver chloride. It is used in photographic emulsions. It dissolves in sodium thiosulphate during the fixing process.

$$AgBr + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

For the fast photographic emulsions, some AgI is used along with AgBr. These emulsions are used to take photographs when the intensity of light is low or for photographing moving objects when the exposure must be very short.

Potassium Permanganate It is the most important compound of + 7 manganese. It is manufactured by fusing MnO_2 with potassium hydroxide followed by oxidation of formed potassium manganate either electrolytically or by passing Cl_2 (or O_3) into solution.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Electrolytic oxidation $\quad MnO_4^{2-} \rightarrow MnO_4^- + e^-$

Oxidation by Cl_2 or O_3 $\quad 2MnO_4^{2-} + Cl_2 \rightarrow 2MnO_4^- + 2Cl^-$

$$2MnO_4^{2-} + O_3 + H_2O \rightarrow 2MnO_4^- + 2OH^- + O_2$$

On concentrating the solution, potassium permanganate crystallizes out.

The compound is a powerful oxidizing agent in acidic, neutral and alkaline media.

Oxidation in acidic medium Permanganate ion is reduced to Mn^{2+} ion.

$$MnO_4^- + 8H^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

In this medium, ferrous is oxidized to ferric, oxalate to carbon dioxide, nitrite to nitrate, iodide to iodine, halogen acids to halogens, etc.

Oxidation in neutral medium In this medium, MnO_4^- is reduced to MnO_2.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

Oxidation in alkaline medium In this medium, MnO_4^- is first changed to MnO_4^{2-} which is further reduced to MnO_2 in the presence of a reducing agent.

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}; \qquad MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$$

The net reaction is

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

which is the same as in a neutral medium.

Examples of oxidation by $KMnO_4$ in alkaline medium includes I^- to IO_3^- and nitrotoluene to nitrobenzoate ion.

Example of oxidation by $KMnO_4$ in neutral medium includes $MnSO_4$ to MnO_2. The reaction is

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

Potassium dichromate This is prepared by fusing chromite ore ($FeCr_2O_4$) with sodium hydroxide or sodium carbonate in the presence of air when soluble sodium chromate is obtained.

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow \underset{\text{(soluble)}}{8Na_2CrO_4} + \underset{\text{(insoluble)}}{2Fe_2O_3} + 8H_2O$$

The solution is filtered and the filtrate is made acidic with dilute sulphuric acid to obtain sodium dichromate.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

The solution is treated with potassium chloride to get less soluble potassium dichromate which crystallizes as orange crystals.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium dichromate is a powerful oxidizing agent:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

It can oxidise Fe^{2+} to Fe^{3+}, I^- to I_2, SO_3^{2-} to SO_4^{2-} and S^{2-} to S.

Potassium dichromate reacts with chloride ions in the presence of concentrated sulphuric acid to give red vapours of chromyl chloride.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + H_2Cr_2O_7$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4$$

$$H_2Cr_2O_7 + 4HCl \rightarrow 2CrO_2Cl_2 + 3H_2O$$

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

When the vapours of CrO_2Cl_2 are passed through water or alkaline solution, a yellow solution of H_2CrO_4 is obtained.

$$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl; \qquad CrO_2Cl_2 + 2OH^- \rightarrow H_2CrO_4 + 2Cl^-$$

The addition of lead acetate in this solution gives yellow precipitate of $PbCrO_4$.

$$Pb^{2+} + H_2CrO_4 \rightarrow PbCrO_4 + 2H^+$$

The above entire procedure is used to test Cl^- ions in a laboratory.

On heating, potassium dichromate decomposes to green chromic oxide and oxygen.

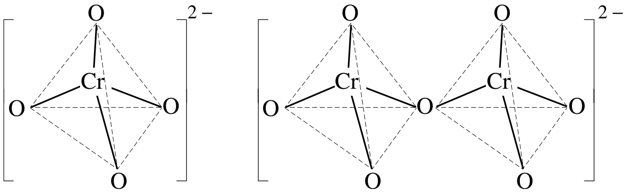
$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

In a solution, dichromate and chromate ions exist in equilibrium with each other

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

In acidic medium, solution contains $Cr_2O_7^{2-}$ ions whereas in alkaline medium, solution contains CrO_4^{2-} ions.

The structure of CrO_4^{2-} and $Cr_2O_7^{2-}$ are as follows.



Potassium dichromate is used in dyeing, chrome tanning, calico printing and photography.

Straight Objective Type

Sodium and Potassium

1. The oxide that gives hydrogen peroxide on treatment with a dilute acid is
   (a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2 (1985)
2. The molecular formula of Glauber's salt is
   (a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$ (c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$ (1985)
3. Solvay process is used for the manufacture of
   (a) NaOH (b) $NaCO_3 \cdot 10H_2O$ (c) K_2CO_3 (d) Na_2O_2
4. Which of the following statements is **not** correct?
   (a) The main raw materials required in Solvay process are NaCl and NH_4Cl
   (b) $NaHCO_3$ is less soluble in water as compared to NH_4Cl

(c) The by-product in Solvay process is $CaCl_2$
(d) $Na_2CO_3 \cdot 10H_2O$ is commonly known as washing soda or soda ash

5. Which of the following statements is **not** correct?
(a) $NaHCO_3$ is more soluble than Na_2CO_3
(b) NaOH is known as caustic soda
(c) $NaHCO_3$ is used as antacid
(d) Na_2CO_3 is used in the manufacture of soap and glass

6. Which of the following equations is not involved in the Solvay process?
(a) $CaCO_3 \xrightarrow[\text{heat}]{} CaO + CO_2$
(b) $NaCl + NH_3 + H_2O + CO_2 \rightarrow NH_4Cl + NaHCO_3$
(c) $CaO + 2NH_4Cl \rightarrow 2NH_3 + H_2O + CaCl_2$
(d) $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

7. Which of the following statements is **not** correct?
(a) KCl is a substitute for NaCl for patients of high blood pressure.
(b) KOH is a stronger alkali than NaOH.
(c) KOH is used in the manufacture of soft soap.
(d) NaOH is a non-deliquescent white crystalline solid.

8. Which of the following statements regarding the oxides of alkali and alkaline metals is **not** correct?
(a) The reactivity of K_2O towards water is more than that of Na_2O towards water.
(b) The oxides of alkaline earth metals are more basic than those of alkali metals.
(c) MgO is used as a refractory material for lining electric furnaces.
(d) The milk of lime and lime water are two different solutions.

9. Which of the following statement is **not** correct?
(a) KOH is less strong alkali than NaOH.
(b) Milk of magnesia is an aqueous solution of $Mg(OH)_2$.
(c) Mg^{2+} ions are not precipitated with the addition of NH_4OH in the presence of NH_4Cl.
(d) CaO_2 is less stable than MgO_2.

10. The oxidation number of oxygen in potassium superoxide is
(a) –2 (b) +1/2 (c) –1/2 (d) –1

11. Which of the following reactions occur at cathode when an aqueous solution of sodium chloride is electrolysed?
(a) Cl^- ions are oxidized (b) Water is oxidized (c) Na^+ ions are reduced (d) Water is reduced

12. The pair of compounds which cannot exist together in aqueous solution is
(a) Na_2CO_3 and $NaHCO_3$ (b) $NaHCO_3$ and NaOH (c) Na_2CO_3 and NaOH (d) $NaHCO_3$ and NaCl

13. K_2CO_3 cannot be obtained by a method similar to Solvay's method because
(a) $KHCO_3$ is more soluble in water than $NaHCO_3$
(b) $KHCO_3$ is less soluble in water than $NaHCO_3$
(c) $KHCO_3$ is not stable in solution
(d) KCl is not available in the pure form

14. Chemically, potash alum is
(a) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$ (b) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$
(c) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 18H_2O$ (d) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

15. Sodium carbonate reacts with SO_2 in aqueous medium to give
(a) $NaHCO_3$ (b) $NaHSO_3$ (c) Na_2SO_3 (d) Na_2SO_4

16. The number of water molecules of crystallization in sodium carbonate is
(a) 2 (b) 5 (c) 7 (d) 10

17. In aqueous solution, which of the following species has a largest value of a molar conductivity?
(a) Na^+ (b) K^+ (c) Li^+ (d) F^-

18. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^- (c) KO_2 only (d) BaO_2 only (1997)

19. The order of basicity of hydroxides of alkali metals is
(a) NaOH > KOH > RbOH (b) NaOH > RbOH > KOH
(c) RbOH > KOH > NaOH (d) RbOH > NaOH > KOH

20. Which of the following hydroxides of alkali metals is least soluble in water?
(a) LiOH (b) NaOH (c) KOH (d) RbOH

21. The crystal structure of oxides of Li, Na, K and Rb is
(a) primitive unit cell structure (b) body-centred unit cell structure
(c) rock-salt structure (d) anti-fluorite structure

22. The superoxides of alkali metals are
(a) diamagnetic (b) paramagnetic with one unpaired electron
(c) paramagnetic with two unpaired electrons (d) colourless

23. The bond order of superoxide ion is
(a) 1.0 (b) 1.5 (c) 2.0 (d) 2.5

24. Potassium superoxide (KO_2) is used in space capsules, submarines, and breathing masks, because it is
(a) diamagnetic in nature (b) high melting compound
(c) helpful in removing CO_2 and producing O_2 (d) unstable compound.

25. Which of the following statements regarding peroxides and superoxides of the metal ions is correct?
(a) stability increases with increase is the size of metal ion.
(b) stability decreases with increase in the size of metal ion.
(c) stability is not affected by the size of metal ion.
(d) initially increases followed by a decrease as the size of metal ion increases.

26. Which of the following compounds decomposes to oxide on heating?
(a) Li_2CO_3 (b) Na_2CO_3 (c) K_2CO_3 (d) $RbCO_3$

27. Strong heating of $MgCl_2 \cdot 6H_2O$ gives
(a) $MgCl_2$ (b) Mg(OH)Cl (c) MgO (d) $Mg(OCl)_2$

28. Which of the following alkali metal gives monoxide as the major product with treated with excess of oxygen?
(a) Li (b) Na (c) K (d) Rb

29. Which of the following alkali metal gives peroxide as the major product when treated with excess of oxygen?
(a) Li (b) Na (c) K (d) Rb

30. Which of the following alkali metal does not give superoxide as the major product when treated with excess of oxygen?
(a) K (b) Rb (c) Cs (d) Na

Magnesium and Calcium

31. The compound insoluble in acetic acid is
(a) CaO (b) $CaCO_3$ (c) Calcium oxalate (d) $Ca(OH)_2$ (1986)

32. The composition of Sorel's cement is
(a) $MgCl_2 \cdot 5H_2O$ (b) $MgCl_2 \cdot 5MgO \cdot nH_2O$ (c) $MgCO_3 \cdot 5H_2O$ (d) $MgCO_3 \cdot 5MgO \cdot nH_2O$

33. Magnesium chloride crystallizes as
(a) $MgCl_2 \cdot 2H_2O$ (b) $MgCl_2 \cdot 4H_2O$ (c) $MgCl_2 \cdot 6H_2O$ (d) $MgCl_2 \cdot 8H_2O$

34. The composition of epsom salt is
(a) $MgSO_4 \cdot H_2O$ (b) $MgSO_4 \cdot 3H_2O$ (c) $MgSO_4 \cdot 5H_2O$ (d) $MgSO_4 \cdot 7H_2O$

35. Quick lime is
(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) CaO (d) $CaSO_4$

36. Limestone is
(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) CaO (d) $CaSO_4$

37. Slacked lime is
(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) CaO (d) $CaSO_4$

38. Milk of lime is
(a) solid $Ca(OH)_2$ (b) suspension of $Ca(OH)_2$ in water
(c) suspension of $CaCO_3$ in water (d) suspension of CaO in water

39. Plaster of paris is
(a) $CaSO_4$ (b) $CaSO_4 \cdot \frac{1}{2} H_2O$ (c) $CaSO_4 \cdot H_2O$ (d) $CaSO_4 \cdot 2H_2O$

40. Which of the following statements is **not** correct?
(a) $MgCO_3$ is thermally less stable than $BaCO_3$.
(b) The carbonates of magnesium and calcium decompose below their melting point.
(c) The bicarbonates of magnesium and calcium are stable crystalline substances.
(d) Anhydrous magnesium chloride cannot be obtained by heating the hydrated magnesium chloride.

41. Which of the following oxides is most acidic in nature?
(a) BeO (b) MgO (c) CaO (d) BaO

42. Solubility of alkaline earth metal sulphates decreases down the Group 2 because
(a) they become more ionic
(b) lattice energy of sulphates does not vary significantly
(c) hydration energy decreases rapidly from Be^{2+} to Ba^{2+}
(d) lattice energy plays more predominant role than hydration energy

43. The solubility of hydroxides of alkaline earth metals increases down the group because
(a) the decrease in lattice energy is more predominant than the decrease in hydration energy
(b) the decrease in lattice energy is less predominant than the decrease in hydration energy
(c) the salts become less ionic
(d) lattice energy increases and hydration energy decreases as we move from Be^{2+} to Ba^{2+}.

44. Which of the following hydrated salts will give anhydrous salt on heating?
(a) $MgCl_2 \cdot 6H_2O$ (b) $CaCl_2 \cdot 6H_2O$ (c) $AlCl_3 \cdot 6H_2O$ (d) $SnCl_2 \cdot 2H_2O$

45. Which of the following oxides is present in the highest amount in Portland cement?
(a) MgO (b) CaO (c) SiO_2 (d) Al_2O_3

46. Which of the following oxides has the lowest percentage in a usual sample of Portland cement?
(a) CaO (b) MgO (c) SiO_2 (d) Al_2O_3

47. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order
K_2CO_3(I) $MgCO_3$(II) $CaCO_3$(III) $BeCO_3$(IV)
(a) I < II < III < IV (b) IV < II < III < I (c) IV < II < I < III (d) II < IV < III < I
(1996)

48. Gypsum is
(a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$ (c) $CaSO_4 \cdot \frac{1}{2} H_2O$ (d) $CaSO_4 \cdot 2H_2O$ (1978)

49. The temporary hardness of water due to calcium bicarbonate can be removed by adding.
(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) $CaCl_2$ (d) HCl (1979)

50. The order of solubility of hydroxides of alkaline earth metals in water is
(a) $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2$ (b) $Mg(OH)_2 < Sr(OH)_2 < Ca(OH)_2$
(c) $Ca(OH)_2 < Mg(OH)_2 < Sr(OH)_2$ (d) $Ca(OH)_2 < Sr(OH)_2 < Mg(OH)_2$

51. The order of solubility of carbonates of alkaline earth metals in water is
(a) $MgCO_3 < CaCO_3 < SrCO_3$ (b) $MgCO_3 < SrCO_3 < CaCO_3$
(c) $SrCO_3 < CaCO_3 < MgCO_3$ (d) $SrCO_3 < MgCO_3 < CaCO_3$

52. The order of solubility of sulphates of alkaline earth metals in water is
(a) $MgSO_4 < CaSO_4 < SrSO_4$ (b) $MgSO_4 < SrSO_4 < CaSO_4$
(c) $SrSO_4 < MgSO_4 < CaSO_4$ (d) $SrSO_4 < CaSO_4 < MgSO_4$

53. The order of thermal stability of carbonates of alkaline earth metals is
(a) $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3$ (b) $BeCO_3 < CaCO_3 < MgCO_3 < SrCO_3$
(c) $CaCO_3 < BeCO_3 < MgCO_3 < SrCO_3$ (d) $CaCO_3 < MgCO_3 < SrCO_3 < CaCO_3$

54. Which of the following statements reganding alkaline earth element in liquid ammonia is **not** correct?
(a) Dilute solutions of elements in ammonia are bright blue in colour.
(b) The blue colour of the element in ammonia is due to the spectrum from the solvated electrons.
(c) Evaporation of ammonia from the elements of Group II in ammonia yields metals.
(d) The concentrated solutions of the elements of Group II in ammonia are bronze in colour due to the formation of metal clusters.

55. Which of the following hydroxides is amphoteric in nature?
(a) $Be(OH)_2$ (b) $Mg(OH)_2$ (c) $Ca(OH)_2$ (d) $Ba(OH)_2$

56. The basic strength of hydroxides of alkaline earth elements follows the order
(a) $Mg(OH)_2 > Ca(OH)_2 > Sr(OH)_2$ (b) $Mg(OH)_2 > Sr(OH)_2 > Ca(OH)_2$
(c) $Ca(OH)_2 > Sr(OH)_2 > Mg(OH)_2$ (d) $Ca(OH)_2 > Mg(OH)_2 > Sr(OH)_2$

57. Which of the following salts is used as mild laxative?
(a) $MgSO_4 \cdot 7H_2O$ (b) anhydrous $MgSO_4$ (c) $CaSO_4 \cdot 2H_2O$ (d) anhydrous $CaSO_4$

58. The thermal stability of sulphates of alkaline earth elements follows the order
(a) $MgSO_4 > CaSO_4 > SrSO_4$ (b) $MgSO_4 > SrSO_4 > CaSO_4$
(c) $SrSO_4 > MgSO_4 > CaSO_4$ (d) $SrSO_4 > CaSO_4 > MgSO_4$

59. The formula of basic beryllium nitrate is
(a) $[Be_4O(NO_3)_4]$ (b) $[Be_4O_2(NO_3)_4]$ (c) $[Be_4O(NO_3)_6]$ (d) $[Be_4O_3(NO_3)_3]$

60. The least stable hydride of alkaline earth elements is
(a) BeH_2 (b) MgH_2 (c) CaH_2 (d) SrH_2

61. Which of the following hydrides is covalent and exists as polymeric form?
(a) BeH_2 (b) MgH_2 (c) CaH_2 (d) SrH_2

62. In the polymeric BeH_2 structure, each beryllium is bound to
(a) 2 hydrogen atoms (b) 3 hydrogen atoms
(c) 4 hydrogen atoms (d) alternatively to 2 and 4 hydrogen atoms

Aluminium

63. Which of the following statements about anhydrous aluminium chloride is correct?
(a) It exists as $AlCl_3$ molecules. (b) It is not easily hydrolysed.
(c) It sublimes at 100 °C under vacuum. (d) It is a strong Lewis base. (1981)

64. Hydrogen gas will not reduce
(a) heated cupric oxide (b) heated ferric oxide
(c) heated stannic oxide (d) heated aluminium oxide (1985)

65. Which of the following statements regarding aluminium chloride is **not** correct?
(a) Fused aluminium chloride does not conduct electricity.
(b) Aluminium chloride exists as dimer in organic solvents such as benzene and ether.
(c) Aluminium chloride exists as monomer in organic solvents such as benzene and ether.
(d) Aluminium chloride forms double salt $AlCl_3 \cdot 6NH_3$ with ammonia.

66. Which of the following characteristics of aluminium chloride dimer is correct?
(a) All bond lengths are identical.
(b) All bond angles are identical.
(c) All bond lengths and angles are different.
(d) The terminal Al—Cl bond length and the terminal bond angle Cl—Al—Cl are different from those involving bridged atoms.

67. Which of the following statements is **not** correct?
(a) Anhydrous aluminium chloride cannot be prepared by heating hydrated salt.
(b) Aluminium chloride solution is acidic.
(c) In the temperature range (420K-480 K) aluminium chloride exists as monomer in the vapour phase.
(d) At very high temperature, aluminium chloride exists as monomer.

68. The general formula of aluminium alums is
(a) $[M^I(H_2O)_4][Al(H_2O)_4](SO_4)_2$ (b) $[M^I(H_2O)_6][Al(H_2O)_6](SO_4)_2$
(c) $[M^I(H_2O)_5][Al(H_2O)_5](SO_4)_2$ (d) $M^I Al^{III}(SO_4)_2$ in nonpolar solvents

69. Anhydrous aluminium chloride in nonpolar solvents exists as
(a) monomer (b) dimer (c) ionic form (d) polymer

70. Which of the following hydroxide is amphoteric in nature?
(a) $B(OH)_3$ (b) $Al(OH)_3$ (c) $Ga(OH)_3$ (d) $Tl(OH)$

Tin and Lead

71. Which of the following oxides is amphoteric?
(a) Na_2O (b) CaO (c) K_2O (d) SnO_2 (1993)

72. Which of the following represents white lead?
(a) $Pb(OH)_2 \cdot 2PbCO_3$
(b) $Pb(OH)_2 \cdot Pb(CH_3COO)_2$
(c) $Pb(OH)_2$
(d) PbO

73. The molecular formula of red lead is
(a) PbO (b) PbO_2 (c) Pb_2O_3 (d) Pb_3O_4

74. Lead suboxide is
(a) PbO (b) PbO_2 (c) Pb_2O (d) Pb_2O_3

75. Lead sesquioxide is
(a) PbO (b) PbO_2 (c) Pb_2O (d) Pb_2O_3

76. Which of the following characteristics is **not** correct?
(a) SnO_2 is an amphoteric oxide
(b) The dissolution of SnO_2 in NaOH produces sodium stannate
(c) SnO_2^{2-} is known only in aqueous solution
(d) SnO_2^{2-} is a powerful reducing agent

77. Lead dioxide is a/an
(a) neutral oxide (b) acidic oxide (c) basic oxide (d) amphoteric oxide

78. Which of the following is known as butter of iron?
(a) $SnCl_2 \cdot 2H_2O$ (b) $SnCl_2 \cdot 3H_2O$ (c) $SnCl_2 \cdot 4H_2O$ (d) $SnCl_2 \cdot 5H_2O$

79. Which of the following halides does not exist?
(a) PbF_4 (b) $PbCl_4$ (c) $PbBr_4$ (d) PbI_4

80. Which of the following statements is **not** correct?
(a) Anhydrous stannous chloride cannot be prepared by heating $SnCl_2 \cdot 2H_2O$
(b) Stannous chloride is a linear molecule
(c) Stannous chloride in concentrated HCl is a powerful reducing agent
(d) With ammonia, $SnCl_2$ forms a number of double salts.

81. Which of the following statement is **not** correct?
(a) Stannic chloride is a colourless fuming liquid
(b) Stannic chloride is soluble in benzene
(c) Stannic chloride is not hydrolysed
(d) Stannic chloride forms more than one hydrated salt.

82. Which of the following statements is **not** correct?
(a) Sn(II) salts or lead(II) compounds are essentially ionic whereas tetravalent are generally covalent.
(b) Lead(II) compounds are more stable than lead(IV) compounds.
(c) Sn(II) are good oxidizing agent.
(d) Sn(IV) salts are more stable than Sn(II) salts.

83. Which of the following statements is **not** correct?
(a) Pb(II) halides are more stable than Pb(IV) halides
(b) The only stable tetrahalide is PbF_4
(c) The ionic character of lead(II) halides increases with increase in atomic number of the halogen
(d) Lead(IV) iodide does not exist

84. Litharge is
(a) PbO (b) PbO_2 (c) PbO_2 (d) Pb_3O_4

85. Which of the following statements is **not** correct?
(a) Lead(II) chloride is soluble in hot water and reappears on cooling.
(b) In dilute HCl, the solubility of $PbCl_2$ is diminished in comparison to that in water.
(c) In concentrated HCl, the solubility of $PbCl_2$ is very much diminished in comparison to that in water.
(d) Lead(II) chloride forms the complex $(NH_4)_2[PbCl_6]$.

86. Which of the following oxides is used in lead accumulators?
(a) PbO (b) PbO_2 (c) Pb_2O (d) Pb_3O_4

87. Brown SnO is a/an
(a) acidic oxide (b) alkaline oxide (c) neutral oxide (d) amphoteric acid

88. Which of the following halides is least stable and has doubtful existence?
(a) CI_4 (b) GeI_4 (c) SnI_4 (d) PbI_4 (1996)

89. Which gas is evolved when PbO_2 is treated with concentrated HNO_3?
(a) NO_2 (b) O_2 (c) N_2 (d) N_2O (2005)

90. Inert pair effect causes
(a) increase in stability of the (+IV) oxidation state on descending the group.
(b) decrease in stability of the (+IV) oxidation state on descending the group.
(c) decrease in stability of the (+II) oxidation state on descending the group.
(d) the decrease in tendency to form dimer.

91. Which of the following statement is correct?
(a) Pb^{II} is a reducing agent while Sn^{II} is not a reducing agent.
(b) Both Pb^{II} and Sn^{II} are reducing agents
(c) Both Pb^{II} and Sn^{II} are not reducing agents
(d) Sn^{II} is a reducing agent while Pb^{II} is not a reducing agent.

Iron

92. The brown complex compound is formulated as $[Fe(H_2O)_5NO^+]SO_4$. The oxidation state of iron is
(a) 1 (b) 2 (c) 3 (d) 0 (1987)

93. Which of the following statements regarding ferric chloride is **not** correct?
(a) In the vapour phase, ferric chloride corresponds to the dimer structure.
(b) The aqueous solution of ferric salt is alkaline.
(c) Ferric chloride is used as an antiseptic.
(d) Ferric alum is $Fe(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$.

94. Which of the following represents green vitriol?
(a) $CuSO_4 \cdot 5H_2O$ (b) $FeSO_4 \cdot 5H_2O$ (c) $FeSO_4 \cdot 7H_2O$ (d) $ZnSO_4 \cdot 7H_2O$

95. The colour of anhydrous $FeSO_4$ is
(a) green (b) blue (c) violet (d) white

96. The formula of the brown coloured compound formed in the brown ring test is
(a) $[Fe(H_2O)(NO_2)_5]SO_4$ (b) $[Fe(H_2O)_3(NO)_3]SO_4$
(c) $[Fe(H_2O)_5(NO)]SO_4$ (d) $[Fe(H_2O)_4(NO)_2]SO_4$

97. The formula of Mohr's salt is
(a) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (b) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 12H_2O$
(c) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 18H_2O$ (d) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 24H_2O$

98. The colour of anhydrous ferric chloride is
(a) white (b) blue (c) green (d) deep red

99. Which of the following statements is **not** correct?
(a) $FeSO_4 \cdot 7H_2O$ acts as a primary standard in volumetric analysis.
(b) On standing, the crystals of ferrous sulphate becomes brown.
(c) On strong heating, ferrous sulphate decomposes as $2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$
(d) Ferrous sulphate is a reducing agent.

100. Ferrous oxide is a/an
(a) neutral oxide (b) acidic oxide (c) basic oxide (d) amphoteric oxide

101. Ferric sulphate on heating gives
(a) SO_2 and SO_3 (b) SO_3 only (c) SO_2 only (d) S (1978)

102. Which one of the following oxides is neutral?
(a) CO (b) SnO_2 (c) ZnO (d) SiO_2 (1996)

103. Anhydrous ferric chloride is prepared by
(a) heating hydrated ferric chloride at a high temperature in a stream of air.
(b) heating metallic iron in a stream of dry chlorine gas
(c) reaction of ferric oxide with hydrochloric acid
(d) reaction of metallic iron with hydrochloric acid (2002)

104. FeO is nonstoichiometric and its commonly formula is
(a) $Fe_{0.6}O$ (b) $FeO_{0.6}$ (c) $Fe_{0.95}O$ (d) $FeO_{1.2}$

105. Hydrated ferrous chloride is
(a) $FeCl_2{\cdot}2H_2O$ (b) $FeCl_2{\cdot}4H_2O$ (c) $FeCl_2{\cdot}6H_2O$ (d) $FeCl_2{\cdot}8H_2O$

Copper and Silver

106. Which of the following statements regarding copper salts is **not** true?
(a) Copper(I) disproportionates to Cu and Cu(II) in aqueous solution.
(b) Copper(I) can be stabilized by the formation of insoluble complex compounds such as $CuCl_2^-$ and $Cu(CN)_2^-$.
(c) Copper(II) oxide is red powder.
(d) The water of crystallization of copper sulphate is five.

107. Which of the following compounds is known as blue vitriol?
(a) $FeSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$ (c) $ZnSO_4 \cdot 7H_2O$ (d) $FeSO_4 \cdot 5H_2O$

108. Which of the following salts is not formed when $CuSO_4 \cdot 5H_2O$ is exposed to air or heated?
(a) $CuSO_4 \cdot 3H_2O$ (b) $CuSO_4 \cdot 2H_2O$ (c) $CuSO_4 \cdot H_2O$ (d) $CuSO_4$

109. The compound commonly known as Philospher's wool is
(a) CuO (b) ZnO (c) SnO (d) FeO

110. Which of the following is known as white vitriol?
(a) $CuSO_4 \cdot 5H_2O$ (b) $FeSO_4 \cdot 7H_2O$ (c) ZnO (d) $ZnSO_4 \cdot 7H_2O$

111. Zinc oxide is a/an
(a) neutral oxide (b) acidic oxide (c) basic oxide (d) amphoteric oxide

112. Lithopone is a
(a) white pigment (b) yellow pigment (c) red pigment (d) blue pigment

113. Which of the following halides of silver is commonly used in photography?
(a) AgF (b) AgCl (c) AgBr (d) AgI

114. Which of the following halides of silver is used in preparing fast films?
(a) AgF (b) AgCl (c) AgBr (d) AgI

115. The colour of anhydrous copper sulphate is
(a) white (b) blue (c) green (d) yellow

116. The black image on an exposed and developed photographic film is composed of
(a) Ag (b) AgBr (c) Ag_2O (d) $Ag(S_2O_3)_2^{3-}$

117. Which of the following is known as Lunar caustic?
(a) NaOH (b) KOH (c) $AgNO_3$ (d) $Fe(NO_3)_2$

118. In dilute sodium thiosulphate solution, silver nitrate finally gives
(a) white precipitate of $Ag_2S_2O_3$
(b) white precipitate of $Ag_2S_2O_3$ which dissolves in more of sodium thiosulphate
(c) black precipitate of Ag_2S
(d) black precipitate of Ag

119. In concentrated sodium thiosulphate solution silver nitrate gives
(a) white precipitate of $Ag_2S_2O_3$
(b) no precipitate but a soluble complex $Na_3[Ag(S_2O_3)_2]$.
(c) black precipitate of Ag_2S
(d) black precipitate of Ag

120. AgCl dissolves in aqueous ammonia and not in water because
(a) aqueous ammonia is a better solvent than water
(b) ammonia is a stronger base than water
(c) silver ions forms soluble complex with ammonia
(d) chloride has more affinity for NH_3

121. Sodium thiosulphate is used in photography to
(a) reduce the AgBr grains to metallic Ag
(b) convert the metallic Ag to Ag salt

(c) remove undecomposed AgBr as a soluble silver thiosulphate complex
(d) remove reduced silver

122. Which of the following dissolves in hot concentrated solution of NaOH?
(a) Fe (b) Zn (c) Cu (d) Ag (1980)

123. Which of the following is the weakest base?
(a) NaOH (b) $Ca(OH)_2$ (c) KOH (d) $Zn(OH)_2$ (1980)

124. Identify the correct order of acidic strengths of CO_2, CuO, CaO and H_2O.
(a) $CaO < CuO < H_2O < CO_2$ (b) $H_2O < CuO < CaO < CO_2$
(c) $CaO < H_2O < CuO < CO_2$ (d) $H_2O < CO_2 < CaO < CuO$ (2002)

Potassium Permanganate and Potassium Dichromate

125. The oxidation state of Mn in $KMnO_4$ is
(a) +2 (b) +6 (c) +7 (d) +8

126. In acidic medium, $KMnO_4$ acts as a strong oxidizing agent. Its equivalent mass is molar mass divided by
(a) 2 (b) 3 (c) 4 (d) 5

127. The oxidation state of Mn in K_2MnO_4 is
(a) +2 (b) +6 (c) +7 (d) +8

128. In a reaction MnO_4^- is changed to MnO_2. The change in oxidation state of Mn is
(a) −3 (b) +3 (c) −1 (d) +1

129. The oxidation state of Cr in $K_2Cr_2O_7$ is
(a) +2 (b) +4 (c) +6 (d) +8

130. Chromyl chloride is represented by the formula
(a) CrOCl (b) $CrOCl_2$ (c) CrO_2Cl_2 (d) Cr_2OCl_2

131. Ammonium dichromate is used in some fireworks. The green coloured powder blown in air is
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) $CrO(O_3)$ (1997)

132. In the dichromate dianion,
(a) four Cr—O bonds are equivalent (b) six Cr—O bonds are equivalent
(c) all Cr—O bonds are equivalent (d) all Cr—O bonds are nonequivalent (1999)

133. On heating ammonium dichromate, the gas evolved is
(a) oxygen (b) ammonia (c) nitrous oxide (d) nitrogen (1999)

134. In alkaline medium, MnO_4^- oxidises I^- to
(a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^- (2004)

135. In alkaline medium, MnO_4^- in oxidation reaction is converted into
(a) MnO_4^{2-} (b) Mn^{2+} (c) MnO_2 (d) MnO_3^+

136. The equivalent mass of $KmnO_4$ in its oxidation reaction in alkaline medium is equal to
(a) molar mass (b) molar mass/3 (c) molar mass/4 (d) molar mass/5

137. In acidic medium $K_2Cr_2O_7$ acts as a strong oxidizing agent. Its equivalent mass is molar mass divided by
(a) 2 (b) 3 (c) 4 (d) 6

138. On adding NaOH in $K_2Cr_2O_7$ solution, the $Cr_2O_7^{2-}$ species is changed to
(a) Cr^{3+} (b) Cr_2O_3 (c) CrO_4^{2-} (d) Cr_2O_5

Multiple Correct Choice Type

1. Which of the following statement(s) is are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with concentrated H_2SO_4?
(a) A deep red vapour is evolved
(b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(c) Chlorine gas is evolved
(d) Chromyl chloride is formed (1998)

2. Sodium nitrate decomposes above ~ 800 °C to give
(a) N_2 (b) O_2 (c) NO_2 (d) Na_2O (1998)

3. The pair(s) of compounds which can exist together in aqueous solution is/are
(a) Na_2CO_3 and $NaHCO_3$ (b) Na_2CO_3 and NaOH (c) $NaHCO_3$ and NaOH (d) $K_2Cr_2O_7$ and NaOH

4. Which of the following statements is/are correct?
   (a) Sodium dichromate is more soluble in water than potassium dichromate.
   (b) Chromate and dichromate ions are interconvertible by changing the pH of the solution.
   (c) The equivalent mass of oxidising agent $KMnO_4$ in acidic medium is its molar mass divided by five.
   (d) The equivalent mass of oxidising agent $KMnO_4$ in acidic medium is its molar mass divided by five.

5. Anhydrous aluminium chloride
   (a) exists as a dimer.
   (b) does not react with water.
   (c) is used as a catalyst in Fries rearrangement.
   (d) is used as a catalyst in Friedel Crafts reaction.

6. Lead
   (a) is a true metal.
   (b) forms $PbCl_4$ a strong oxidising agent.
   (c) does not react with concentrated HCl.
   (d) reacts with NaOH to form $Pb(OH)_4$.

7. Which of the following statements is/are **not** correct?
   (a) All alkali metals from oxides on burning in air.
   (b) The solubilities of chlorides and hydroxides of alkaline-earth metals in water increase on decending the group.
   (c) $Be(OH)_2$ is basic in nature.
   (d) The tendency of complex formation of alkaline earth metals increases down the group.

8. Which of the following statements is/are correct?
   (a) The main raw material required in Solvay process are NaCl and NH_4Cl.
   (b) $NaHCO_3$ is less soluble in water as compared to NH_4Cl.
   (c) The byproduct in Solvay process is $CaCl_2$.
   (d) $Na_2CO_3 \cdot 10H_2O$ is commonly known as washing soda.

9. Which of the following statements is/are correct with reference to the ferrous and ferric ions?
   (a) Fe^{3+} gives brown colour with potassium ferricyanide.
   (b) Fe^{2+} gives blue precipitate with potassium ferricyanide.
   (c) Fe^{3+} gives red colour with potassium thiocyanate.
   (d) Fe^{2+} gives brown colour with ammonium thiocyanate. (1998)

10. Which of the following statements are **not** correct?
   (a) Solubility of sodium hydroxide increases with increase in temperature.
   (b) Sodium monoxide can be prepared by burning sodium in air.
   (c) The reactivity of K_2O with water is less than that of Na_2O with water.
   (d) The compound Na_2O_2 is sodium dioxide.

11. Which of the following statements are correct?
   (a) Potassium superoxide is diamagnetic in nature.
   (b) The thermal stability of hydroxides of Group 1 decreases on moving down the group.
   (c) Potassium carbonate cannot be prepared by Solvay process as potassium bicarbonate is highly soluble in water.
   (d) The solubility of bicarbonates of Group 1 is less soluble than the corresponding carbonates.

12. Which of the following statements are correct?
   (a) Amongst Group 1 elements, Li^+ ion has the highest enthalpy of hydration.
   (b) All chlorides of Group 1 elements are ionic except LiCl.
   (c) The metallic oxides of Group 1 elements become more basic on going down the group.
   (d) The ionic size of Li^+ in water is minimum in comparison to other alkali ion.

13. Which of the following statements are correct?
   (a) $MgCl_2 \cdot 6H_2O$ on heating gives anhydrous $MgCl_2$.
   (b) The oxides of alkaline earth metals are more basic than the oxides of alkali metals.
   (c) The carbonates of Mg and Ca are thermally unstable and decompose below their melting points.
   (d) The bicarbonates of Mg and Ca are not stable in the crystalline salt.

14. Which of the following statements are correct?
   (a) Unlike magnesium chloride, calcium chloride can be obtained by heating $CaCl_2 \cdot 6H_2O$.
   (b) Halides of elements of Group 2 with the exception of $BeCl_2$ are ionic.
   (c) The decrease in the solubility from $BeSO_4$ to $BaSO_4$ is primarily due to decrease in the hydration energy as one moves from Be^{2+} to Ba^{2+}.

(d) The increase in the solubility of chlorides and hydroxides of alkaline earth metals is primarily due to the decrease in lattice energy from Be to Ba salts.

15. Which of the following statements are correct?
(a) Milk of lime is a clear solution of $Ca(OH)_2$ in water.
(b) Potassium chloride is less soluble than magnesium chloride.
(c) On standing, stannous chloride solution becomes white due to the formation of Sn(OH)Cl.
(d) Stannic chloride forms double salt with ammonia with molecular formula $SnCl_4 \cdot NH_3$.

16. Which of the following statements are **not** correct?
(a) Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons.
(b) All the Al—Cl bonds in Al_2Cl_6 are equivalent.
(c) Aluminium exists in two polymorphic forms, namely, α-Al_2O_3 and γ-Al_2O_3.
(d) Anhydrous aluminium chloride can be prepared by heating hydrated salt.

17. Which of the following statements are **not** correct?
(a) Aluminium chloride exists as a monomer.
(b) Aluminium chloride is an ionic compound. It is thus insoluble in organic solvents such as alcohol, ether and benzene.
(c) Aluminium oxide is not an amphoteric oxide.
(d) Aluminium chloride acts as a Lewis acid.

18. Which of the following statements are correct?
(a) Alums are used as mordants in dyeing.
(b) Ferric chloride exists as a dimer in gaseous phase.
(c) Thermal stability of halide series CCl_4, $SiCl_4$, $SnCl_4$ and $PbCl_4$ decreases with increasing atomic mass of the central atom.
(d) Ferric chloride solution is alkaline in nature.

19. Which of the following statements are correct?
(a) When PbO_2 reacts with a dilute acid, it gives hydrogen peroxide.
(b) Pb(II) salts are more stable than Pb(IV) compounds.
(c) Divalent tin or lead compounds are essentially ionic in nature whereas tetravalent compounds are generally covalent.
(d) Massicot is yellow crystalline PbO.

20. Which of the following statements are correct?
(a) PbO is an amphoteric oxide.
(b) PbO_2 is lead peroxide.
(c) The solubility of $PbCl_2$ is increased in concentrated HCl.
(d) Lead chloride is soluble in hot water but reappears on cooling.

21. Which of the following statements are correct?
(a) $SnCl_2$ is a nonlinear molecule.
(b) Sn(II) salts are more stable than Sn(IV) compounds.
(c) Stannous oxide is an amphoteric oxide.
(d) Sodium stannite can be obtained in the crystalline form.

22. Which of the following statements are **not** correct?
(a) Anhydrous stannous chloride can be prepared by dehydrating the hydrated salt.
(b) Anhydrous stannous chloride is a linear molecule.
(c) Stannic chloride is insoluble in benzene.
(d) Stannic chloride crystallizes with no water of crystallization.

23. Which of the following statements are **not** correct?
(a) SnO_2 is a basic oxide.
(b) All the elements of Group 16 show inert-pair effect.
(c) Tin(II) chloride is a powerful oxidizing agent.
(d) Tin(II) chloride is used as a mordant in dying industry.

24. Which of the following statements are **not** correct?
(a) Heating of ferrous sulphate produces ferric oxide and sulphur dioxide.
(b) In volumetric analysis, ferrous sulphate is used as a primary standard.

(c) In volumetric analysis, Mohr's salt is used as a parimary standard.
(d) Heating of ferrous oxalate in the absence of air to about 430 K produces ferric oxide.

25. Which of the following statements are correct?
(a) Cu^+ disproportionates to Cu^{2+} and elemental copper in solution.
(b) Strong heating of anhydrous copper sulphate produces CuO and SO_2.
(c) The colour of ZnO changes to yellow on heating.
(d) ZnO is an amphoteric oxide.

26. Which of the following statements are **not** correct?
(a) In aqueous solution, free copper(I) disproportionates to give copper(0) and copper(II).
(b) Copper(II) reduces I_2 to I^-.
(c) Copper sulphate is $CuSO_4 \cdot 4H_2O$.
(d) Strong heating of $CuSO_4$ gives CuO and SO_3.

27. Which of the following statements are **not** correct?
(a) Silver fluoride is fairly soluble in water.
(b) Silver nitrate is a thermally stable substance.
(c) Silver nitrate gives white precipitate with sodium thiosulphate which changes its colour to yellow, brown and finally black due to the formation of silver.
(d) Silver nitrate gives white precipitate with concentrated solution of sodium thiosulphate.

28. Which of the following statements are correct?
(a) Silver chloride dissolves in ammonia forming $Ag(NH_3)_2^+$ complex.
(b) A current of chlorine displaces bromide from silver bromide.
(c) The chlorides of both silver and alkali metals are isomorphous.
(d) Silver bromide is used in photographic emulsion.

29. Which of the following statements are correct?
(a) Mn^{2+} can be oxidized to MnO_4^- by PbO_2.
(b) If metal ions of group III are precipitated by NH_4Cl and NH_4OH without prior oxidation by concentrated HNO_3, Fe^{3+} is not completely precipitated.
(c) Silver chloride is sparingly soluble in water because its lattice energy is greater than hydration energy.
(d) The salts $FeSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ are isostructural.

30. Which of the following statements are **not** correct?
(a) Sodium monoxide reacts with liquid ammonia to give $NaNH_2$ and NaOH.
(b) Sodium peroxide absorbs carbon monoxide producing $NaHCO_3$.
(c) Burning of potassium in oxygen produces KO_2.
(d) The oxidation state of oxygen in potassium superoxide is –1/2.

31. Which of the following statements are **not** correct?
(a) Potassium hydroxide is a weaker base than sodium hydroxide.
(b) Potassium hydroxide is insoluble in alcohol.
(c) Sodium carbonate is prepared industrially by Solvay process.
(d) Sodium carbonate crystallizes with ten molecules of water of crystallization.

32. Which of the following statements are **not** correct?
(a) Sodium bicarbonate is known as baking soda. (b) Sodium carbonate is known as washing soda.
(c) Lithium carbonate is soluble in water. (d) Glauber's salt is $Na_2SO_4 \cdot 7H_2O$.

33. Which of the following statements are **not** correct?
(a) The biproduct in Solvay process is $CaCl_2$.
(b) The composition of carnallite is $KCl \cdot MgCl_2 \cdot 7H_2O$
(c) The composition of schonite is $K_2SO_4 \cdot MgSO_4 \cdot 7H_2O$
(d) The composition of quicklime is CaO.

34. Which of the following statements are **not** correct.
(a) Calcium peroxide is more stable than magnesium peroxide.
(b) All elements except Be of Group 2 form monoxide and peroxides.
(c) All oxides of elements of Group 2 are basic with the exception of BeO which is amphoteric.
(d) The thermal stability of peroxides of elements of Group 2 decreases on descending the group.

35. Which of the following statements are
   (a) The solubility of the hydroxides of elements of Group 2 decreases on descending the group.
   (b) The basic character of hydroxides of elements of Group 2 decreases on descending the group.
   (c) Anhydrous calcium chloride melts at a temperature higher than that of anhydrous magnesium chloride because the charge: radius ratio is higher for Mg^{2+} as compared to Ca^{2+} ions.
   (d) Epsom salt is $CaSO_4 \cdot 2H_2O$

36. Which of the following statements are **not** correct?
   (a) Plaster of paris is $2CaSO_4 \cdot H_2O$
   (b) The solubility of sulphates of alkaline earth metals increases on descending the group.
   (c) The salt of magnesium which is used as a refractory material for lining electric furnaces is MgO.
   (d) Sorel's cement contains CaO and MgO.

37. Which of the following statements are correct?
   (a) Calcium peroxide is crystallized with the molecular formula $CaO_2 \cdot 8H_2O$.
   (b) An aqueous suspension of $Mg(OH)_2$ is known as milk of magnesia.
   (c) Magnesium chloride is crystallized with molecular formula $MgCl_2 \cdot 7H_2O$
   (d) Calcium sulphate is crystallized with the molecular formula $CaSO_4 \cdot 2H_2O$

38. Which of the following statements are **not** correct?
   (a) Aluminium chloride is crystallized with molecular formula $AlCl_3 \cdot 6H_2O$
   (b) The molecular formula of potash alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$
   (c) In concentrated HNO_3, aluminium gets a coating of Al_2O_3 and becomes passive.
   (d) The slaked lime is CaO.

39. Which of the following statements are **not** correct?
   (a) Tin(II) oxide on dissolution in NaOH produces sodium stannate.
   (b) Stannite ion is a powerful reducing agent.
   (c) Tin(IV) oxide on dissolution in NaOH produces sodium stannite.
   (d) In acidic medium, $SnCl_2$ reduces nitrobenzene to aniline.

40. Which of the following statements are **not** correct?
   (a) Litharage is crystalline mass having molecular composition PbO.
   (b) Pb_3O_4 is known as red lead.
   (c) The molecular formula of lead suboxide is PbO.
   (d) The molecular formula of lead sesquioxide is Pb_2O.

41. Which of the following statements are **not** correct?
   (a) Lunar Caustic is $AgNO_3$
   (b) With an excess of $SnCl_2$, $HgCl_2$ gives black precipitate due to the formation of mercurous chloride.
   (c) Chemical composition of white lead is $Pb(OH)_2$
   (d) Chrome yellow is $PbCrO_4$.

42. Which of the following statements are **not** correct?
   (a) Green vitriol is ferrous sulphate.
   (b) Ferrous sulphate crystallized with seven water of crystallization.
   (c) The basic ferric sulphate is $Fe(OH)_2SO_4$
   (d) The venetian red is FeO.

43. Which of the following statements are **not** correct?
   (a) Philospher's wool is ZnO.
   (b) White vitriol is $ZnSO_4$.
   (c) Zinc sulphate crystallizes with six water of crystallization.
   (d) A lead compound which is used as an antiknocking agent is $Pb(CH_3)_4$.

44. Which of the following statements are correct?
   (a) In medicine, $MgSO_4 \cdot 7H_2O$ is used as purgative.
   (b) Fusion of solid KNO_3 with solid K produces K_2O and N_2.
   (c) KNO_3 is commonly known as salt petre.
   (d) $NaNO_3$ is commonly known as chile salt peter.

45. Which of the following statements are **not** correct?
   (a) The water of crystallization associated with ferric chloride is six.

(b) An aqueous solution of ferric chloride is acidic in nature.
(c) Heating of $CuSO_4 \cdot 5H_2O$ at 100 °C produces $CuSO_4$.
(d) The compound $YBa_2Cu_3O_7$, which shows superconductivity, has copper in oxidation state +3. Assume that the rate earth element yttrium is in it usual +3 oxidation state.

46. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because:
(a) the hydration energy of sodium sulphate is more than its lattice energy.
(b) the lattice energy of barium sulphate is more than its hydration energy.
(c) the lattice energy has no role to play in solubility
(d) the hydration energy of sodium sulphate is less than its lattice energy. (1989)

47. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with
(a) H^+ ions (b) Ca^{2+} ions (c) SO_4^{2-} ions (d) Mg^{2+} ions (1990)

48. Which of the following oxides is/are amphoteric?
(a) Na_2O (b) CaO (c) Al_2O_3 (d) SnO_2 (1993)

49. The compound(s) formed upon combustion of sodium metal in excess air is (are)
(a) Na_2O_2 (b) Na_2O (c) NaO_2 (d) NaOH (2009)

50. Which of the following oxides are used as a refractory?
(a) BeO (b) MgO (c) CaO (d) SrO

51. Which of the following statements regarding ferric chloride is correct?
(a) Anhydrous ferric chloride has deep red colour
(b) Ferric chloride solution is acidic in nature
(c) Ferric chloride occurs as monomer in gaseous state
(d) Ferric chloride in acidic medium crystallizes as $FeCl_3 \cdot 6H_2O$.

Linked Comprehension Type

1. Born-Haber cycle for the formation MCl(s), where M is alkali-metal ion, requires that

$$\Delta_f H°(\text{MCl}) = \Delta_{\text{sub}}H°(\text{M}) + \Delta_{\text{ioniz}}H°(\text{M(g)}) + \frac{1}{2}\Delta_{\text{diss}}H°(\text{Cl}_2) + \Delta_{\text{ea}}H°(\text{Cl}) + \text{Lattice energy.}$$

Based on this expression, answer the following three questions for MX(s).

(i) The elements having minimum and maximum values of $\Delta_{\text{subl}}H°$, respectively, are
(a) Rb, Li (b) Cs, Li (c) Na, Rb (d) Cs, Na

(ii) The elements having minimum and maximum values of $\Delta_{\text{ioniz}}H°$ respectively, are
(a) Rb, Na (b) Rb, K (c) Cs, Li (d) Cs, Na

(iii) The minimum and maximum negative values of $\Delta_f H°(\text{MCl(s)})$, respectively, are
(a) Li, Cs (b) Li, Rb (c) K, Na (d) K, Cs

2. The standard enthalpies of formation of halides (X^-) of Group I metal ions (M^+) follow the regular trends depending on the nature of M^+ and X^-. Based on this information, answer the following three questions for MX(aq).

(i) The order of numerical values of standard enthalpy of formation (i.e. $-\Delta_f H°$) of M^+X^- where M^+ is any one of the ions (Li^+, Na^+, or K^+ ion) and X^- is any one of the halide ions (F^-, Cl^- or Br^-) is
(a) MF > MCl > MBr (b) MF > MCl < MBr
(c) MBr > MF > MCl (d) MF > MCl > MBr

(ii) The order of numerical values of enthalpy of formation (i.e. $-\Delta_f H°$) for M^+X^- (where M^+ is any one of the ions Li^+, Na^+ or K^+ and X is F^-) is
(a) LiF > NaF > KF (b) LiF > KF > NaF
(c) KF > LiF > NaF (d) KF > NaF > LiF

(iii) The order of numerical values of enthalpy of formation (i.e. $-\Delta_f H°$) for MX (where M^+ is any one of the ions Li^+, Na^+ or K^+ and X^- is any one of the ions Cl^- or Br^- or I^-) is
(a) LiX > NaX > KX (b) LiX > KX > NaX
(c) KX > LiX > NaX (d) KX > NaX > LiX

Assertion and Reason Type

The following questions contain two statements. Based on the following keys, answer correctly each question.

(a) Statement – 1 is correct, Statement – 2 is correct and is also a correct explanation for Statement – 1.
(b) Statement – 1 is correct, Statement – 2 is correct and is not a correct explanation for Statement – 1.
(c) Statement – 1 is correct and Statement – 2 is not correct.
(d) Statement – 1 is not correct and Statement – 2 is correct.

	Statement-1	**Statement-2**
1.	The alkali metals can form ionic hydrides which contain the hydride ion, H^-.	The alkali metals have low electronegativity; their hydrides conduct electricity when fused and liberate hydrogen at the anode. (1994)
2.	$Al(OH)_3$ is amphoteric in nature.	Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$. (1998)
3.	LiCl is predominantly a covalent compound.	Electronegativity difference between Li and Cl is too small. (1998)
4.	Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.	The higher oxidation states for the Group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.
5.	Temporary hardness of water can be removed while permanent hardness cannot be removed.	Temperary hardness of water is due to the presence of bicarbonates of magnesium and calcium while permanent hardness is due to their sulphate salts.
6.	The stability of the peroxide and superoxides of alkali elements increases as the metal ions become larger.	Similar sizes of positive and negative ions leads to higher coordination number which provides higher lattice energy and hence stability to the salt.
7.	Peroxides of alkali metals are stronger oxidizing agent than superoxides.	Peroxide provides H_2O_2 while superoxide provides H_2O_2 and O_2 when treated with water.
8.	Solvay process cannot be adopted to manufacture potassium carbonate.	The intermediate $KHCO_3$ is less soluble in water as compared to $NaHCO_3$.
9.	The solubility of sulphates of Group 2 decreases on descending the group.	Trends in solubility are dependent on the relative variations in lattice energy and hydration energy of the salt.
10.	Tin(IV) salts are more stable than tin(II) salts while reverse is true to lead salts.	Inert pair effect controls the stability of heavier elements in Group 14.
11.	The intense blue colour of Prussian blue and Turnbull's blue is due to electron transfer between Fe(+II) and Fe(+III) present in these compounds.	Prussian blue and Turnbull's blue differ in the oxidation states of iron inside and outside of the coordination sphere of the compounds.
12.	The solutions of alkali metals in liquid ammonia conduct electricity better than any salt in any liquid.	Conduction in solution of alkali metal in ammonia is due mainly to the presence of solvated electrons.
13.	The blue colour of alkali metals in liquid ammonia slowly fades on standing for a longer time	The fading is due to evaporation of ammonia from the solution.
14.	The solubility of fluorides and hydroxides of metals decreases on descending the Group II.	The numerical value of lattice energy decreases more rapidly than the numerical value of hydration energy in case of fluorides and hydroxides of metals on descending the Group II.

15.	The solubility of sulphates of metals decreases on descending the Group II.	The numerical value of lattice energy increases more rapidly than the numerical value of hydration energy in case of sulphates of metals on descending Group II.
16.	Acidic solution of $KMnO_4$ is stored in dark bottles.	$KMnO_4$ in acidic medium decomposes slowly and this decomposition is catalysed by sun light.
17.	On adding acid to aqueous solution of K_2CrO_4, its colour changes from yellow to orange.	CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium over wide range of pH from 2 to 6.
18.	$BeCl_2$ is not easily hydrolysed.	The hydrolysis of $BeCl_2$ may occur because it is an electron-deficient compound.

Matrix Match Type

1. Column I lists the names of some chemicals which are listed in Column II. Match correctly each entry of Column I with those given Column II.

Column I	**Column II**
(a) Baking powder	(p) Na_2CO_3
(b) Gun powder	(q) $NaHCO_3$
(c) Washing soda	(r) $NaNO_3$
(d) Chile salt peter	(s) KNO_3 + S + Charcoal
	(t) KNO_3

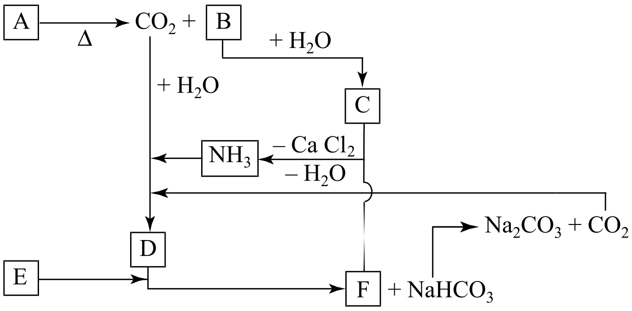
2. Column I lists the names of some chemicals which are listed in Column II. Match correctly each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Epsom salt	(p) $CaSO_4\cdot\frac{1}{2}H_2O$
(b) Plaster of pairs	(q) mixture of $Ca(OCl)_2\cdot Ca(OH)_2\cdot CaCl_2\cdot 2H_2O$
(c) Gypsum	(r) $CaSO_4\cdot H_2O$
(d) Bleaching powder	(s) $MgSO_4\cdot 7H_2O$
	(t) $CaSO_4\cdot 2H_2O$

3. Column I lists the names of some chemicals which are listed in Column II. Match correctly each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Green vitrol	(p) $CuSO_4\cdot 5H_2O$
(b) While vitrol	(q) $PbCrO_4$
(c) Blue vitrol	(r) $FeSO_4\cdot 7H_2O$
(d) Philospher's wool	(s) $ZnSO_4\cdot 6H_2O$
	(t) ZnO

4. The following is the scheme to manufacture of sodium carbonate. This scheme is known as Solvay process.



Column I lists the labeling A, B, …, and Column II mentiones their chemical formula. Match each entry of Column I with those given in Column II.

Column I	Column II
(a) A	(p) $Ca(OH)_2$
(b) B	(q) NH_4Cl
(c) C	(r) NaCl
(d) D	(s) CaO
(e) E	(t) $CaCO_3$
(f) F	(u) NH_4HCO_3

ANSWERS

Straight Objective Type

1. (b) **2.** (d) **3.** (b) **4.** (a) **5.** (a) **6.** (d) **7.** (d)
8. (b) **9.** (a) **10.** (c) **11.** (d) **12.** (b) **13.** (a) **14.** (d)
15. (c) **16.** (d) **17.** (b) **18.** (c) **19.** (c) **20.** (a) **21.** (d)
22. (b) **23.** (b) **24.** (c) **25.** (a) **26.** (a) **27.** (c) **28.** (a)
29. (b) **30.** (d) **31.** (c) **32.** (b) **33.** (c) **34.** (d) **35.** (c)
36. (a) **37.** (b) **38.** (b) **39.** (b) **40.** (c) **41.** (a) **42.** (c)
43. (a) **44.** (b) **45.** (b) **46.** (c) **47.** (b) **48.** (d) **49.** (b)
50. (a) **51.** (c) **52.** (d) **53.** (a) **54.** (c) **55.** (a) **56.** (c)
57. (a) **58.** (d) **59.** (c) **60.** (a) **61.** (a) **62.** (c) **63.** (c)
64. (d) **65.** (c) **66.** (d) **67.** (c) **68.** (b) **69.** (b) **70.** (b)
71. (d) **72.** (a) **73.** (d) **74.** (c) **75.** (d) **76.** (b) **77.** (d)
78. (d) **79.** (d) **80.** (b) **81.** (c) **82.** (c) **83.** (c) **84.** (a)
85. (c) **86.** (b) **87.** (a) **88.** (d) **89.** (b) **90.** (b) **91.** (d)
92. (a) **93.** (b) **94.** (c) **95.** (d) **96.** (c) **97.** (a) **98.** (d)
99. (a) **100.** (c) **101.** (b) **102.** (a) **103.** (b) **104.** (c) **105.** (b)
106. (c) **107.** (b) **108.** (b) **109.** (b) **110.** (d) **111.** (d) **112.** (a)
113. (c) **114.** (d) **115.** (a) **116.** (a) **117.** (c) **118.** (c) **119.** (b)
120. (c) **121.** (c) **122.** (b) **123.** (d) **124.** (a) **125.** (c) **126.** (d)
127. (b) **128.** (a) **129.** (c) **130.** (c) **131.** (b) **132.** (b) **133.** (d)
134. (a) **135.** (c) **136.** (b) **137.** (d) **138.** (c)

Multiple Correct Choice Type

1. (a), (b), (d) **2.** (a), (b), (d) **3.** (a), (b) **4.** (a), (b), (c)
5. (a), (d) **6.** (a), (b) **7.** (c), (d) **8.** (b), (c), (d)
9. (b), (c) **10.** (a), (b), (c), (d) **11.** (c), (d) **12.** (a) (b), (c)
13. (c), (d) **14.** (a), (b), (c), (d) **15.** (b), (c), (d) **16.** (a), (b), (d)
17. (a), (b), (c), (d) **18.** (a), (b) **19.** (b), (c) **20.** (a), (c), (d)
21. (a), (c) **22.** (a), (b), (c), (d) **23.** (a), (b), (c) **24.** (a), (b), (d)
25. (a), (c), (d) **26.** (b), (c) **27.** (b), (c), (d) **28.** (a), (b), (c)
29. (a), (b), (c), (d) **30.** (b), (c) **31.** (a), (b) **32.** (c), (d)
33. (b), (c) **34.** (a), (d) **35.** (a), (b) **36.** (b), (d)
37. (a), (b), (d) **38.** (b), (d) **39.** (a), (c) **40.** (c), (d)
41. (b), (c) **42.** (c), (d) **43.** (b), (c) **44.** (a), (b), (c), (d)
45. (c), (d) **46.** (a), (b) **47.** (b), (d) **48.** (c), (d)
49. (a), (b) **50.** (a), (b) **51.** (a), (b), (d)

Assertion and Reason Type

1. (a) **2.** (c) **3.** (c) **4.** (c) **5.** (a) **6.** (a) **7.** (d)
8. (c) **9.** (b) **10.** (a) **11.** (a) **12.** (a) **13.** (c) **14.** (d)
15. (a) **16.** (a) **17.** (a) **18.** (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (c) **(iii)** (a)
2. **(i)** (d) **(ii)** (a) **(iii)** (d)

Matrix Match Type

1. (a)–(q); (b)–(s); (c)–(p); (d)–(r) **2.** (a)–(s); (b)–(p); (c)–(t); (d)–(q)
3. (a)–(r); (b)–(s); (c)–(p); (d)–(t) **4.** (a)–(t); (b)–(s); (c)–(p); (d)–(u); (e)–(r); (f)–(q)

Hints and Solutions

Straight Objective Type

1. Na_2O_2 is sodium peroxide. This gives H_2O_2 with dilute acid.
2. Glauber's salt is $Na_2SO_4 \cdot 10H_2O$
3. Solvay process is used to manufacture $Na_2CO_3 \cdot 10H_2O$.
4. Raw materials in Solvay process are $CaCO_3$ and NaCl.
5. $NaHCO_3$ is less soluble than Na_2CO_3.
6. The correct reaction is $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
7. NaOH is a deliquescent white solid.
8. Oxides of alkali metals are more basic than alkaline earth metals.
9. Strength of base increases on descending the group.
10. Potassium superoxide is KO_2. The oxidation number of oxygen is –1/2
11. Water is reduced in preference to sodium ion.
12. The reaction $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$ occurs.
13. $KHCO_3$ is more soluble in water than $NaHCO_3$.
14. Potash alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.
15. The reaction is $Na_2CO_3 + SO_2 \rightarrow NaSO_3 + CO_2$. **16.** The formula is $Na_2CO_3 \cdot 10H_2O$.
17. Due to hydration of ions, K^+ ion has the smallest size in comparison to Li^+, Na^+ and F^- ions. Hence, K^+ has larger molar conductivity.
18. O_2^- in KO_2 has one unpaired electron.
19. Basicity of hydroxides of alkali metals increases on the descending the group.
20. Solubility of hydroxides increases on descending the group.
21. The oxides of Li, Na, K and Rb has anti-fluorite structure.
22. Superoxide is O_2^-. Its electronic configuration is KK $(\sigma 2s)^2(\sigma {}^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$. It has one unpaired electron.
23. O_2^- has 8 electrons in bonding orbitals and 5 electrons in antibonding orbitals. Its bond order is (8 – 5)/2 = 1.5.
24. KO_2 reacts with CO_2 liberating O_2. $4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2$.
25. The larger cations can be stabilized by larger anions. This results in larger lattice energy.
26. Thermal stability increases on ascending the group.
28. Lithium mainly forms the monoxide (and some peroxide) sodium mainly forms peroxide (and some oxide). Rest of alkali metals form superoxides.
29. See, Q.28. **30.** See, Q.28.
31. Calcium oxalate is insoluble in dilute acetic acid. **32.** Sorel's cement is $MgCl_2 \cdot 5MgO \cdot nH_2O$
33. Magnesium chloride crystallizes as $MgCl_2 \cdot 6H_2O$ **34.** Epsom salt is $MgSO_4 \cdot 7H_2O$.
35. Quick lime is CaO. **36.** Lime stone is $CaCO_3$.
37. Slacked lime is $Ca(OH)_2$ **38.** Milk of lime is a suspension of $Ca(OH)_2$ in water.

39. Plaster of paris is $CaSO_4 \cdot \frac{1}{2} H_2O$.

40. The bicarbonates of magnesium and calcium are stable only in solution.

41. Acidic nature decreases and basic nature increases on descending the group.

42. Solubility of alkaline earth metal sulphates decreases on descending the group because of rapid decrease in hydration energy of cations.

43. Solubility of alkaline earth metal hydroxides increases down the group because the decrease in lattice energy is more rapid than decrease in hydration energy.

45. CaO is present in Portland cement.

46. The lowest percentage is that of SiO_2.

47. Thermal stability increases on descending the group.

48. Gypsom is $CaSO_4 \cdot 2H_2O$.

49. By adding $Ca(OH)_2$, temporary hardness is removed due to the reaction $Ca(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons 2CaCO_3 + 2H_2O$

50. See, Q.43.

51. Same as in Q.42

52. See, Q.42.

53. See, Q.47.

54. Evaporation of ammonia leads to the formation of hexammoniates of the metals which slowly decompose to amides: $M(NH_3)_6 \rightarrow M(NH_2)_2 + 4NH_3 + H_2$.

55. The basic strength of hydroxides increases on descending the group. $Be(OH)_2$ is amphoteric.

56. See. Q.55.

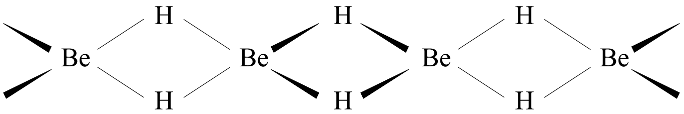
57. $MgSO_4 \cdot 7H_2O$ is used as mild laxative.

58. Thermal stability of sulphates increases on descending the group.

59. The basic beryllium nitrate is $[Be_4O(NO_3)_6]$

60. BeH_2 is least stable.

61. The structure of BeH_2 is



62. See. Q.61.

63. At low temperatures $AlCl_3$ exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes. On heating, Al_2Cl_3 is formed.

64. Aluminium has a very strong affinity for oxygen. Thus, Al_2O_3 is not reduced by H_2.

65. In organic solvents, aluminium chloride exists as dimer.

66. Terminal Al—Cl distance is 206 pm while bridge Al—Cl distance is 221 pm.

69. See, Q.67.

70. $Al(OH)_3$ is an amphoteric hydroxide.

71. SnO_2 is an amphoteric oxide.

72. White lead is $Pb(OH)_2 \cdot 2PbCO_3$.

73. Red lead is Pb_3O_4.

74. Lead suboxide is Pb_2O.

75. Lead sesquioxide is Pb_2O_3.

76. The dissolution of SnO_2 in NaOH produces sodium stannite.

77. PbO_2 is an amphoteric oxide.

78. Butter of iron is $SnCl_2 \cdot 5H_2O$

79. PbI_4 does not exist.

80. Stannous chloride is a bent, molecule.

81. Sn^{2+} ions are hydrolysed mainly to $[Sn_3(OH)_4]^{2+}$ with small amounts of $[Sn(OH)]^+$ and $[Sn_2(OH)_2]^{2+}$.

82. Sn(II) is not an oxidizing agent. It is more stable than Sn(IV).

83. Ionic character of lead(II) halides decreases with increase in atomic number of the halogen.

84. Litharge is PbO.

85. The solubility of $PbCl_2$ decreases in the presence of concentrated HCl due to common ion.

86. PbO_2 is used in lead accumulators.

87. Brown SnO is an acidic oxide.

88. Stability of MI_4 decreases on descending Group 14.

89. The reaction is $2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + O_2$

90. Inert pair effect represents the inactiveness of pair of electrons and thus the stability of M(+II) is increased in comparison to M(+IV).

91. Pb(+II) is more stable than Sn(+II).

92. The oxidation state of Fe in $[Fe(H_2O)_5NO^+]SO_4$ is +1.

93. Ferric chloride in aqueous solution is acidic due to hydrolysis of Fe^{3+} ions.

94. Green vitriol is $FeSO_4 \cdot 7H_2O$.

95. Anhydrous $FeSO_4$ is white.

96. The brown coloured compound is $[Fe(H_2O)_5(NO)]SO_4$.

97. Mohr's salt is $FeSO_4 \cdot (NH_4)2SO_4 \cdot 6H_2O$.

98. Anhydrous ferric chloride is red in colour.

99. $FeSO_4 \cdot 7H_2O$ is not a primary standard in volumetric analysis.

100. FeO dissolves in acids and is completely basic.

101. $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$

102. CO is a neutral oxide.

103. Anhydrous ferric chloride is prepared by heating metallic iron in a stream of dry chlorine gas.

104. FeO is a nonstoichiometric compound with average composition of $Fe_{0.95}O$.

105. Ferrous chloride with four water of crystallization.

106. CuO is black crystalline oxide.

107. Blue vitriol is $CuSO_4 \cdot 5H_2O$.

108. $CuSO_4 \cdot 2H_2O$ is not formed.

109. Philospher's wool is ZnO.

110. White Vitrial is $ZnSO_4 \cdot 7H_2O$.

111. ZnO is an amphoteric oxide.

112. Lithopone is white pigment.

113. AgBr is used in photographic emulsions.

114. AgI is used in making fast films.

115. Anhydrous copper sulphate is white.

116. The black image is due deposition of silver.

117. $AgNO_3$ is known as lunar caustic.

118. In dilute solution, black precipitate of Ag_2S is obtained.

119. In concentrated solution, a soluble complex of $Na_3[Ag(S_2O_3)_2]$ is obtained.

120. Solubility is due to the formation $[Ag(NH_3)_2]^+$ complex ion.

121. Sodium thiosulphate is used to remove undecomposed AgBr.

122. Zn dissolves in hot concentrated solution of NaOH.

123. $Zn(OH)_2$ is the weak base amongst the given bases.

124. CaO is the weakest one and CO_2 is the strongest one.

125. The oxidation state of Mn in $KMnO_4$ is +7.

126. Five electrons are involved per MnO_4^- ion. Hence, equivalent mass = molar mass/5.

127. The oxidation state of Mn in K_2MnO_4 is +6.

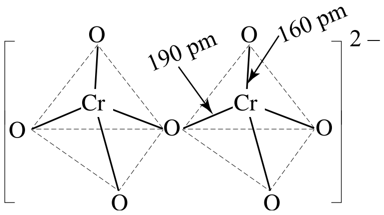
128. The change in oxidation number is from +7 to +4. The change is $+ 4 - 7 = - 3$.

129. The oxidation state of Cr in $K_2Cr_2O_7$ is +6.

130. Chromyl chloride is CrO_2Cl_2.

131. The green colour is due to Cr_2O_3.

132. Six Cr—O bonds are equivalent. The structure of $Cr_2O_7^{2-}$ is



133. $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$.

134. I^- is oxidized to IO_3^-.

135. In alkaline medium, MnO_4^- is reduced to MnO_2.

136. In alkaline medium, MnO_4^- is reduced to MnO_2. There is a change of –3 of oxidation number of Mn. Hence, equivalent mass=molar mass/3.

137. $Cr_2O_7^{2-}$ is changed to $2Cr^{3+}$. There is a total change of +6 of oxidation number of Cr. Hence, equivalent mass = molar mass/6.

138. There exists equilibrium $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$

Multiple Correct Choice Type

10. (a) Sodium hydroxide dissolves in water with the evolution of heat. Hence, its solubility decreases with increase in temperature.

(b) Burning of sodium produces both monoxide and peroxide. Monoxide can be produced by fusion Na and $NaNO_3$ or by heating sodium azide.

(c) The reactivity increases in going from Na_2O to K_2O.

(d) It is sodium peroxide as it liberates hydrogen peroxide with water.

11. (a) The superoxide, O_2^-, contains one unpaired electrons, so it is paramagnetic.

(b) The thermal stability increases down the group.

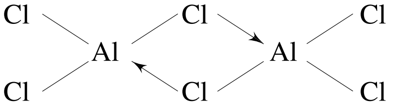
12. (a) Li^+ has the smallest size as compared to other alkali ions. Consequently, it has maximum charge density and thus is more extensively hydrated.

13. (b) These are less basic.

15. (a) A paste of lime in water is known as milk of lime whereas clear solution is known as lime water.

16. (a) $AlCl_3$ is a Lewis acid because it accepts rather than donating electrons.

(b) The structure of Al_2Cl_6 is



The terminal bonds are different from the bridge Al—Cl bonds.

17. (a) It exists as a dimer.

(b) It is a covalent compound and is thus soluble in alcohol, ether and benzene.

(d) It as Lewis base.

19. (a) PbO_2 is a dioxide and not peroxide.

(b) This is due to inert-pair effect.

(d) It is a yellow powder.

20. (b) It is lead dioxide.

(c) It is due to the formation of H_2PbCl_4.

21. (d) Sodium stannite is known only in aqueous solution. It is readily oxidized by atmospheric oxygen to sodium stannate.

22. (a) On heating hydrated salt, basic chloride, Sn(OH)Cl, is formed.

(b) It is an angular covalent molecule because of repulsion between a lone pair of electrons on Sn and two bonding pairs of electrons.

(c) It is a covalent molecule soluble in benzene.

(d) Stannic chloride forms a series of hydrated salts ($SnCl_4{\cdot}3H_2O$, $SnCl_4{\cdot}5H_2O$, $SnCl_4{\cdot}6H_2O$ and $SnCl_4{\cdot}8H_2O$).

23. (a) It is an ampoteric oxide.

(c) It is a reducing agent due to the reaction $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

24. (a) It produces ferric oxide, SO_2 and SO_3.

(b) It is susceptible to aerial oxidation and dehydration.

(d) Heating upto 430 K produces FeO, CO and CO_2. Only in the presence of air, ferric oxide is formed.

25. (a) The reaction $2Cu^+ \rightarrow Cu^{2+} + Cu$ is possible as $E^\circ_{Cu^+\,|\,Cu} > E^\circ_{Cu^{2+}\,|\,Cu}$

(b) The products are CuO and SO_3.

26. (b) Copper(II) oxidizes I^- to I_2. The reaction is $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

27. (a) The solubility of halides of silver varies as AgF > AgCl > AgBr > AgI.

(b) Silver nitrate decomposes as $2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$ on heating.

(c) There does occur change in colour but the final product is Ag_2S and not Ag.

(d) With concentrated solution of sodium thiosulphate, no precipitate is obtained. Instead, a complex ion $[Ag(S_2O_3)_2]^{3-}$ is obtained.

CHAPTER 15

COMPOUNDS OF NONMETALS

HYDROGEN PEROXIDE

In laboratory, hydrogen peroxide may be obtained by the addition of sodium peroxide or hydrated barium peroxide to icecold dilute sulphuric acid.

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$
$$BaO_2 \cdot 8H_2O + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2 + 8H_2O$$

On cooling, sodium sulphate precipitates out as $Na_2SO_4 \cdot 10H_2O$. The remaining solution is distilled under vacuum to give 30% H_2O_2. Anhydrous barium oxide is not used, as the coating of insoluble barium sulphate on the surface of barium oxide stops the reaction.

Commercially, hydrogen peroxide is manufactured by the electrolysis of potassium acid sulphate or 60% sulphuric acid at 0 °C. Peroxosulphate ion is formed at the platinum anode, the hydrolysis of which produces hydrogen peroxide.

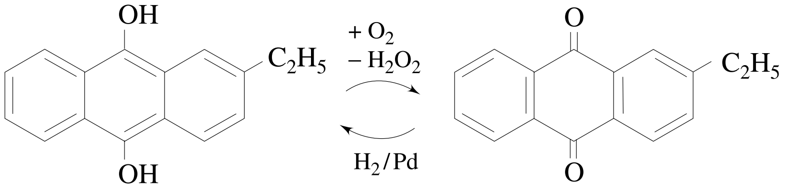
Anodic reaction $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$

Cathodic reaction $2H^+ + 2e^- \rightarrow H_2$

The product at the anode is isolated and subjected to distillation under vacuum to give hydrogen peroxide.

The recent method is based on the auto-oxidation of 2-alkylanthraquinol. In this process 2-ethylanthraquinone is dissolved in organic solvent (alcohol/hydrocarbon) and is reduced by hydrogen using Raney nickel or palladium as catalyst, to give 2-ethylanthraquinol. After the removal of catalyst, the latter is oxidized in current of air producing 2-ethylanthraquinone and hydrogen peroxide.



Hydrogen peroxide is a weak acid. It ionizes as

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^- \qquad HO_2^- + H_2O \rightleftharpoons H_3O^+ + O_2^{2-}$$

It is unstable due to the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$

This reaction is catalysed by impurities and sunlight. It is because of this reason, it is kept in coloured bottles.

Hydrogen peroxide is an oxidizing as well as a reducing agent.

$$\underset{\text{(oxidizing agent)}}{H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O} \qquad \underset{\text{(reducing agent)}}{H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-}$$

Based on the reduction potentials

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E° = 1.77$ V $\quad O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E° = 0.68$ V

$H_2O_2 + 2e^- \rightarrow 2OH^-$ $E° = 0.87$ V $\quad O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$ $E° = -0.15$ V it may be concluded that

H_2O_2 is a more powerful oxidizing agent in acidic medium as compared to alkaline medium. On the other hand H_2O_2 is a more powerful reducing agent in alkaline medium as compared to acidic medium.

In general, H_2O_2 will act as an oxidizing agent in acidic or alkaline medium, but only towards very strong oxidizing agents such as MnO_4^- it will behave as a reducing agent.

Kinetically, oxidation with hydrogen peroxide is slow in acidic medium but proceeds rapidly in alkaline medium. Decomposition of H_2O_2 occurs most rapidly in basic solution, hence excess of H_2O_2 may be destroyed in alkaline solution on heating.

Reactions exhibiting oxidizing nature of H_2O_2 are as follows.

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

$$NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O$$

$$2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$$

$$2I^- + 2H^+ + H_2O_2 \rightarrow 2H_2O + I_2$$

$$2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \rightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$$

$$2Cr(OH)_3 + 4OH^- + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 8H_2O$$

$$H_3AsO_3 + H_2O_2 \rightarrow H_3AsO_4 + H_2O$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$$

$$2HCHO + H_2O_2 \xrightarrow[\text{pyrogallol}]{}\!\!\!\!\!\!\!\! \xrightarrow[\text{alkaline}]{} 2HCOOH + H_2$$

With chromates and titanic sulphates in acidic solution, hydrogen peroxide gives the bright blue perchromate CrO_5 and the bright yellow titanium trioxide TiO_3, respectively. The peroxo compound of chromium in aqueous solution is unstable, it rapidly decomposes into green chromic sulphate with evolution of oxygen.

$$K_2Cr_2O_7 \xrightarrow{H_2SO_4} H_2Cr_2O_7$$

$$H_2Cr_2O_7 + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$$

$$4CrO_5 + 6H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$$

Reactions exhibiting reducing characteristics of H_2O_2 are as follows.

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

In alkaline medium, the reactions are

$$2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2KOH$$

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

$$KIO_4 + H_2O_2 \rightarrow KIO_3 + H_2O + O_2$$

Hydrogen peroxide is a bleaching agent for delicate materials, e.g. hair, wool, silk, ivory and feathers. It destroys bacteria and is used as an antiseptic (3% solution) and germicide.

Structure of Hydrogen Peroxide Hydrogen peroxide has a twisted structure in which two hydroxyl groups do not lie in the same plane (Fig. 15.1). There is a change in structural parameters in going from gaseous to crystalline phase. This is due to the hydrogen bonding.

Strength of Hydrogen Peroxide Solution The strength of hydrogen peroxide is usually represented in terms of oxygen at STP that one volume of hydrogen peroxide gives on heating. For example, '30 volume H_2O_2' means that one litre of 30 volume H_2O_2 will produce 30 L of O_2 at STP. This way of expressing strength can be conveniently conveted into percentage strength or strength in g L^{-1} as shown in the following.

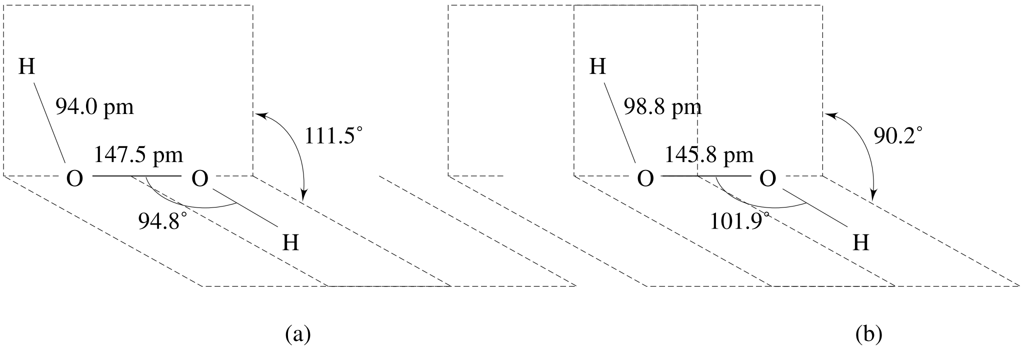


Fig. 15.1 Structure of H_2O_2 in (a) gaseous, and (b) crystalline phase

The decomposition reaction is $2H_2O_2 \rightarrow 2H_2O + O_2$
that is, 2 mol of H_2O_2 would produce 1 mol of oxygen. Suppose we have 20 volume H_2O_2. It means, 1 L of H_2O_2 would produce 20 L of O_2 at STP. Now, the amount of O_2 in 20 L at STP would be

$$n(O_2) = \frac{20\,\text{L}}{22.414\,\text{L mol}^{-1}}$$

Amount of H_2O_2 producing this amount of oxygen would be $n(H_2O_2) = 2n(O_2) = \frac{2 \times 20}{22.414}$ mol = 1.785 mol

Hence, Molarity of H_2O_2 = 1.785 mol L^{-1}

Strength of H_2O_2 = molarity × molar mass = (1.785 mol L^{-1}) (34 g mol^{-1}) = 60.69 g L^{-1}

Assuming density of 20 volume H_2O_2 to be 1 g mL^{-1}, we will have

Mass per cent of H_2O_2 = 6.069

BORON

Boranes The hydrides of boron are known as boranes. They fall into two series; (a) nido-boranes (B_nH_{n+4}) and (b) less stable series, arachno-boranes (B_nH_{n+6}).

Boranes were first prepared by Alfred Stock by heating Mg and B followed by the treatment of orthophosphoric acid.

$$3Mg + 2B \xrightarrow[\Delta]{} Mg_3B_2 \xrightarrow{H_3PO_4} \text{mixture of boranes mainly } B_4H_{10} \xrightarrow[\Delta]{} B_2H_6 \text{ diborane}$$

Diborane can also be prepared as follows.

$$B_2O_3 + 3H_2 + 2Al \xrightarrow[150\ °C]{250\ \text{atm}} B_2H_6 + Al_2O_3$$

$$\underset{\text{gas}}{2BF_3} + 6NaH \xrightarrow{180\ °C} \underset{\text{gas}}{B_2H_6} + 6NaF$$

In a laboratory, the following methods may be used.

1. Reducing the etherate complexes of the boron halide with $Li[AlH_4]$.

$$4[Et_2O{\cdot}BF_3] + 3Li[AlH_4] \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4] + 4Et_2O$$

2. Reacting $Na[BH_4]$ and iodine in the solvent diglyme (which is polyether $CH_3OCH_2CH_2OCH_2CH_2OCH_3$).

$$2Na[BH_4] + I_2 \xrightarrow[\text{solution}]{\text{in diglyme}} B_2H_6 + H_2 + 2NaI$$

3. Reducing BF_3 with $Na[BH_4]$ in diglyme

$$4[Et_2O{\cdot}BF_3] + 3Na[BH_4] \xrightarrow{\text{in diglyme}} 2B_2H_6 + 3Na[BF_4] + 4Et_2O$$

Diborane is a colourless gas. It is highly reactive gas. It catches fire spontaneously in air and explodes with oxygen. It is instantly hydrolysed by water. The involved reactions are

$$B_2H_6 + 3O_2 \rightarrow 2B_2O_3 + 3H_2O; \qquad B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 3H_2$$

Higher boranes are obtained by heating diborane in a sealed tube. The compounds formed are B_4H_{10}, B_5H_{11}, B_6H_{12} and $B_{10}H_{14}$.

One of the important reactions shown by B_2H_6 is the process of *hydroboration*. This involves the following steps.

1. Reaction of B_2H_6 with an alkene or alkyne

$$B_2H_6 + 6RCH{=\!=}CH_2 \rightarrow 2B(CH_2CH_2R)_3; \qquad B_2H_6 + 6RC{\equiv}CR \rightarrow 2B(RC{=\!=}CHR)_3$$

The reaction is carried out in the atmosphere of nitrogen as the product is very reactive.

The net reaction is a *cis*-addition reaction across a double or triple bond. The reactions follow anti-Markovnikov rule, that B attaches to the least substituted C atom.

2. Conversion of alkylborane into other stable products.
   (a) Treatment with carboxylic acids yields a hydrocarbon

$$B(CH_2CH_2R)_3 + 3CH_3COOH \rightarrow 3RCH_2CH_3 + B(CH_3COO)_3$$

   (b) Treatment with alkaline H_2O_2 yields an alcohol

$$B(CH_2CH_2R)_3 + 3H_2O_2 \rightarrow 3RCH_2CH_2OH + H_3BO_3$$

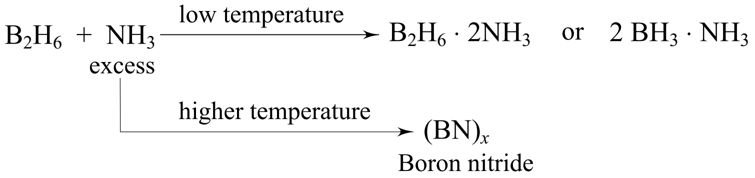
   (c) Oxidation with chromic acid yields a ketone or a carboxylic acid.

$$B(CH(R)R')_3 \xrightarrow{H_2CrO_4} RCOR'; \qquad B(CH_2CH_3)_3 \xrightarrow{H_2CrO_4} CH_3COOH$$

All the boranes are electron-deficient compounds. They form simple adducts with amines

$$B_2H_6 + 2(CH_3)_3N\!: \rightarrow 2[(CH_3)_3N \rightarrow BH_3]$$

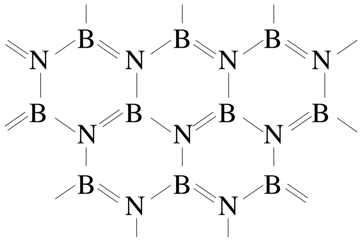
Their reactions with ammonia depend on the experimental conditions.

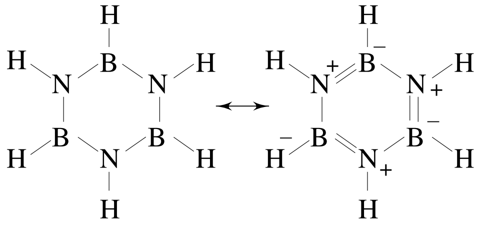


$$\underset{\text{excess}}{B_2H_6 + NH_3} \xrightarrow{\text{low temperature}} B_2H_6 \cdot 2NH_3 \quad \text{or} \quad 2\,BH_3 \cdot NH_3; \qquad \xrightarrow{\text{higher temperature}} \underset{\text{Boron nitride}}{(BN)_x}$$

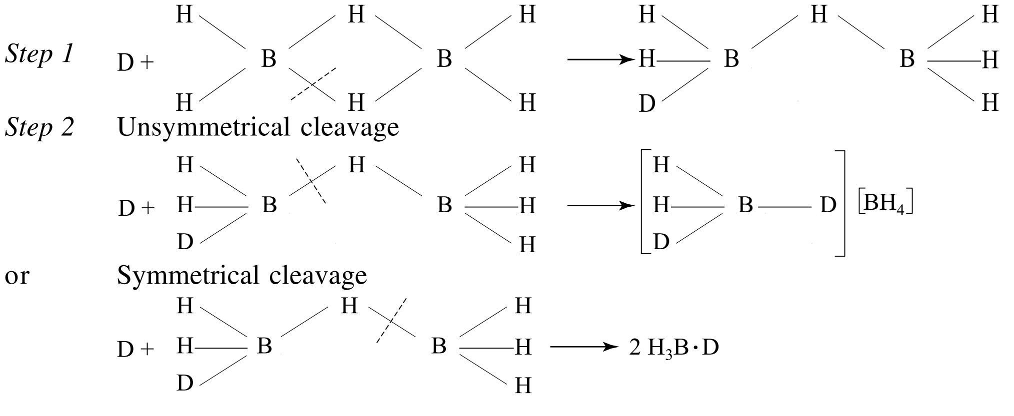
If the ratio of B_2H_6 and NH_3 is 1:2, the product obtained at higher temperature is borazine ($B_3N_3H_6$).

The structure of boron nitride is very similar to graphite (as the sum of valence electrons of B and N is equal to that of two C atoms). Borazine is known as inorganic benzene.


Boron nitride


Borazine

The reaction between B_2H_6 and electron-donor compound D (such as ammonia or alkylamines) at low temperatures proceeds in two steps.



Selection of one or the other of the two boron atoms as the point of attack by the second donor atom in step 2 decides the formation of the final product. Most of the compounds favour unsymmetrical cleavage. However, if the compound D is large or bulky, steric congestion favours the attack to the second boron atom.

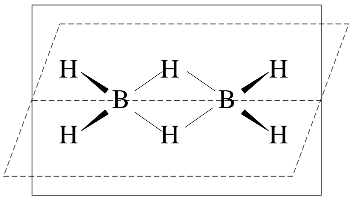
NH_3 and CH_3NH_2 shows greater tendency for unsymmetrical cleavage. With $(CH_3)_2NH$, this tendency is small while with $(CH_3)_3N$, there is no such tendency.

Diborane is a powerful electrophilic reducing agent for certain functional groups. For example,

$$RCN \xrightarrow{B_2H_6} RCH_2NH_2; \qquad RNO_2 \xrightarrow{B_2H_6} RNH_2; \qquad RCHO \xrightarrow{B_2H_6} RCH_2OH$$

The structure of diborane is

Terminal B—H is 2c—2e bond with bond length 119 pm.
Bridged B—H is 3c—2e bond with bond length 133 pm.
Bridged H atoms are perpendicular to the planar skeleton of rest of atoms.



Higher boranes have open cage structures.

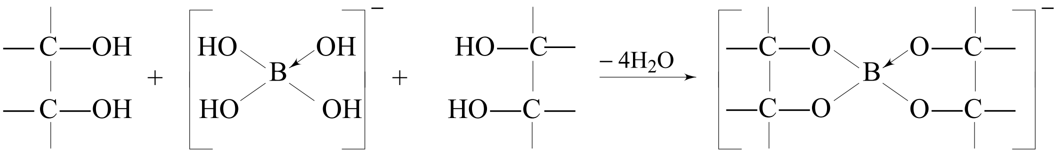
Boric Acid Boric acid, also known as orthoboric acid, is H_3BO_3, i.e. $B(OH)_3$. It behaves as a weak monobasic acid. It does not donate proton but accepts OH^-. It is therefore a Lewis acid. Its $pK_a = 9.25$.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

Boric acid cannot be titrated with NaOH as a sharp end point is not obtained. In the presence of certain polyhydroxy compounds such as glycerol, mannitol or sugars, boric acid acts as a strong monobasic acid. It can be titrated with NaOH using phenolphthalein indicator.

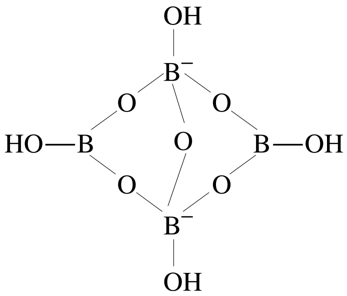
The added compound must be a *cis*-diol which forms very stable complex with the $[B(OH)_4]^-$.

$$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$$



In boric acid, B is sp^2 hybridized forming planar triangle structure. In the solid the boric acid units are hydrogen bonded together into two-dimensional sheets with almost hexagonal symmetry.

Borax Borax is usually written as $Na_2B_4O_7 \cdot 10H_2O$. Its structure is



It contains two tetrahedral units and two triangular units.

Its actual formula is $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

Borax is used as a primary standard for titrating acids. $Na_2B_4O_7 \cdot 10H_2O + 2HCl \rightarrow 2NaCl + 4H_3BO_3 + 5H_2O$

Since the products contain boric acid, methyl orange (pH range 3.1-4.4) is used as the indicator. One mole of borax reacts with two moles of acid. The actual reactions are

$$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 + 2[B(OH)_4]^-$$
$$2[B(OH)_4]^- + 2H_3O^+ \rightarrow 2B(OH)_3 + 4H_2O$$

Borax is also used for making buffer solution as its aqueous solution contains equal amounts of weak acid and its salts.

Borax Bead Test In the borax bead test, B_2O_3 or borax is heated in a Bunsen burner flame with metal oxides on a loop of platinum wire. The mixture fuses to give a glass-like metaborate bead.

$$CoO + B_2O_3 \rightarrow \underset{\substack{\text{Cobalt metaborate}\\ \text{(blue colour)}}}{Co(BO_2)_2}$$

Metaborate beads of many transition metals have characteristic colours and thus borax bead test is used to identify the metal.

CARBON

Monoxide The burning of carbon in a limited supply of air or in a deficiency of oxygen produces carbon monoxide. A few reactions producing carbon monoxide are as follows.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$\begin{array}{l}COOH\\ \;|\\ COOH\end{array} \xrightarrow{\text{concentrated } H_2SO_4} CO + CO_2 + H_2O$$

$$HCOOH \xrightarrow{\text{concentrated } H_2SO_4} CO + H_2O$$

$$CO_2 + Zn \xrightarrow[\text{heat}]{} CO + ZnO$$

$$K_4Fe(CN)_6 + \underset{\text{concentrated}}{6H_2SO_4} + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Carbon monoxide is an extremely poisonous gas. A concentration of one in 800 volumes of air will lead to death in 30 minutes. It combines with haemoglobin of the blood to give more stable carboxyhaemoglobin and thus renders it useless as an oxygen carrier. In air, it burns with a blue flame to give carbon dioxide. The gas readily dissolves in ammoniacal or acidic solution of cuprous chloride giving the additional product $CuCl\cdot CO\cdot 2H_2O$. Some of the reactions shown by carbon monoxide are given below.

$$CO + NaOH \xrightarrow[\text{heat}]{\text{pressure}} \underset{\text{sodium formate}}{HCOONa}$$

$$Fe_2O_3 + 3CO \xrightarrow{875\,-\,1175\text{ K}} 2Fe + 3CO_2$$

$$CO + Cl_2 \xrightarrow{h\nu} COCl_2$$

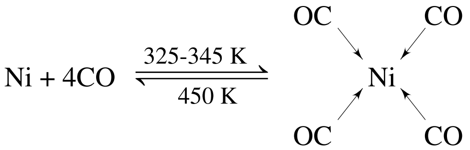
$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

$$CO + 2H_2 \xrightarrow[425\,-\,675\text{ K}]{\text{ZnO + Cu powder}} CH_3OH$$

The structure of carbon monoxide may be represented as $:\overset{-}{C}\vdots\vdots\overset{+}{O}:$ or $:C \overset{\leftarrow}{\equiv} O:$

Carbon atom is considered to be sp hybridized. One sp orbital being used to form a single bond with oxygen atom while the other sp orbital which points away from the C—O bond contains a lone pair of electrons. The sideways overlap of singly filled 2p orbitals on carbon and oxygen atoms produces a π bond. The second π bond is formed by the overlap of doubly filled 2p orbital on oxygen with the vacant 2p orbital on carbon. But once the bond is formed, it is not possible to distinguish the two π bonds.

Because of the directed lone pair of electrons on carbon, the molecule forms carbonyls with a number of metal in which the coordinate bond is formed through carbon atom and not through oxygen atom. With nickel, it forms tetracarbonyl which decomposes at higher temperature.



The poisonous nature of carbon monoxide is due to its ability to form a bond with iron atom in the haemoglobin of blood.

In the form of producer gas (CO + N_2), water gas (CO + H_2) or semiwater gas (mixture of producer and water gases), it is used as fuel.

Dioxide Carbon dioxide can be prepared by any of the following reactions.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$2NaHCO_3 \xrightarrow[\text{heat}]{} Na_2CO_3 + H_2O + CO_2$$

$$MgCO_3 \xrightarrow[\text{heat}]{} MgO + CO_2$$

Solid carbon dioxide is known as *dry ice* and is used as a refrigerant.

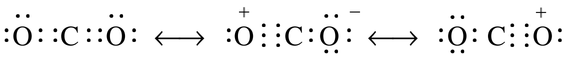
Carbon dioxide is an acidic oxide. $CO_2 + H_2O \rightleftharpoons H_2CO_3$

With reactive metals, it is reduced to CO.

$$2Na + 2CO_2 \rightarrow Na_2CO_3 + CO; \qquad 2Mg + CO_2 \rightarrow 2MgO + C$$

Carbon doxide is absorbed by green plants in the presence of sunlight and is ultimately transformed into starch and cellulose in the chloroplast. This process is known as *photosynthesis*.

Carbon dioxide is a linear molecule with carbon-oxygen bond equal to 115 pm, which is intermediate between those calculated for carbon-oxygen double and triple bonds. It is thus considered to be the resonance hybrid of the following structures.



$$:\ddot{O}::C::\ddot{O}: \longleftrightarrow :\overset{+}{O}\vdots\vdots C:\underset{..}{\overset{..\;-}{O}}: \longleftrightarrow :\underset{..}{\ddot{O}}:C\vdots\vdots\overset{+}{O}:$$

Carbon in CO_2 is sp hybridized. The two sp orbitals form two bonds with two oxygen atoms. The two p orbitals not included in hybridization give rise two π bonds.

Carbides These are prepared by direct combination of metals with carbon at elevated temperatures or indirectly, the heating of metallic oxide with carbon. The carbides may be classified into three groups, namely, ionic, covalent and interstitial.

Ionic carbides are formed by metals of Group 1, 2 and 3. These compounds, in general occur as transparent crystals and in the solid state they are nonconductors of electric current. They give hydrocarbons when treated with water or acids. On the basis of anions, these have been classified as methanides (C^{4-}), acetylides (C_2^{2-}) and allylides. (C_3^{4-}).

The examples are

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4 \qquad Al_2C_6 + 6H_2O \rightarrow 2Al(OH)_3 + 3C_2H_2$$

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4 \qquad Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3C{\equiv}CH$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Covalent carbides formed by the elements of Groups 16 and 17 are discrete molecules (CH_4, CO_2, CS_2, etc.). Some covalent carbides are giant molecules, e.g. carborundum (SiC) and boron carbide (B_4C_3). These are characterized by high decomposition temperature, chemical inertness and extreme hardness. Carborundum has a diamond like structure.

Interstitial (or metallic) carbides are formed by the transition elements such as TiC, HfC, W_2C, MoC, Mo_2C, Cr_3C_2 and Cr_4C. In these the small carbon atoms occupy interstitial positions in the crystal lattices of the metals. These compounds are characterized by hardness, chemical inertness and high electric conductivity.

SILICON

Silicones Silicones are polymeric organosilicon compounds containing individual or cross-linked Si—O chains or rings in which some of the oxygens of SiO_4 tetrahedron are replaced by —OH,—CH_3,—C_2H_5 and—C_6H_5 groups. For example, dialkyldichlorosilane (R_2SiCl_2), which is produced by the reaction

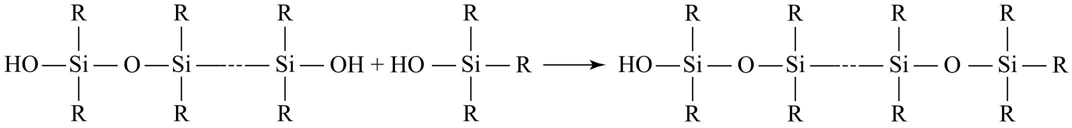
$$2RCl + Si(Cu) \rightarrow R_2SiCl_2$$

reacts with water producing dialkyldihydrosilane. This, in turn, may be dehydrated to give a linear polymer.

$$R_2SiCl_2 + 2H_2O \rightarrow R_2Si(OH)_2 + 2HCl$$

$$nR_2Si(OH)_2 \xrightarrow[-H_2O]{} \underset{\text{silicone}}{(R_2SiO)_n}, \text{ i.e. } [O - R_2Si - O]_n$$

Polymerization of $R_2Si(OH)_2$ is due to the active hydroxyl groups which exist at the two ends of the straight chain. However, if some trialkylchlorosilane, R_3SiCl, is mixed with R_2SiCl_2 and hydrolysed, the R_3SiCl helps blocking the end of straight chain produced by R_2SiCl_2.



$$\mathrm{HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}\cdots\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-R \longrightarrow HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}\cdots\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-R}$$

The hydrolysis of $RSiCl_3$ produces a complex cross-linked polymer.

Silicones have good thermal and oxidative stability. These are excellent water repellants, good electrical insulators, and chemically inert substances. Silicon rubber is not attacked by ozone. Liquid silicones are used as excellent lubricants. These are mixed with paints and enamels to increase the resistance to the effects of high temperatures, sunlight and chemicals.

Silicates Silicon forms a very large number of compounds containing SiO_4^{4-} anion as the basic unit. The structure of this basic unit is a tetrahedron in which oxygen atoms are arranged tetrahedrally around a silicon atom. Depending on the number of corners (0, 1, 2, 3 or 4) of SiO_4^{4-} tetrahedron shared with other tetrahedra, a variety of silicates are obtained.

Orthosilicates These contain individual discrete SiO_4^{4-} tetrahedra. Examples are phenacite (Be_2SiO_4), willemite (Zn_2SiO_4), and zircon ($ZnSiO_4$) minerals.

Pyrosilicates These contain discrete $Si_2O_7^{6-}$ ions formed by the sharing of one oxygen atom between the two SiO_4^{4-} tetrahedra. The structure is known as an island structure. Examples include thortveitite ($Sc_2Si_2O_7$) and hemimorphite ($Zn_4(OH)_2\,Si_2O_7$).

Chain and Cyclic Silicates These silicates are formed when two oxygen atoms of SiO_4^{4-} tetrahedron are shared with two other tetrahedra. The resulting structure may be the chain type or the cyclic type. The general formula of these silicates is $(SiO_3)_n^{2n-}$. Examples of cyclic silicates are benitoite ($BaTiSi_3O_9$), catapleite ($Na_2Zr\,Si_3O_9{\cdot}2H_2O$), dioptase ($Cu_6Si_6O_{18}{\cdot}6H_2O$) and beryl ($Be_3Al_2Si_6O_{18}$).

Infinite chain are formed when two oxygen atoms of SiO_4^{4-} tetrahedron are shared with the adjacent tetrahedra. If further sharing of oxygen atoms occurs by half of the silicon atoms, a double chain or band structure is formed. Examples of the former include enstatite $MgSiO_3$ and diopside $CaMg(SiO_3)_2$. Asbestos also contains silicate chains. The band structure contains the basic $Si_4O_{11}^{6-}$ repeating unit. An example is $Ca_2Mg_5(OH)_2(Si_4O_{11})_2$.

Layer and Sheet Silicates These are formed by sharing of three oxygen atoms by each tetrahedron giving an infinite two-dimensional sheet of the empirical formula $(Si_2O_5)_n^{2n-}$. Examples include kaolin $[Al_2(OH)_4Si_2O_5]$, talc $[Mg_3(OH)_2Si_4O_{10}]$ and the micas.

Three-Dimensional Silicates In these silicates, all the four oxygen atoms of a SiO_4^{4-} tetrahedron are shared with other tetrahedra resulting in a three-dimensional lattice. The formula of such a silicate is SiO_2(quartz).

Carbide Silicon carbide, also known as *carborundum*, is a very hard substance. It is made by heating sand and coke in an electric furnace at very high temperature of 2000–2500 °C.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

$$Si + C \rightarrow SiC$$

Chemically, silicon carbide is extremely inert and is not attacked by even hydrofluoric acid. When fused with alkalis, it is decomposed to give silicate and carbonate.

$$SiC + 4NaOH + 2O_2 \rightarrow Na_2SiO_3 + 2H_2O + Na_2CO_3.$$

It is used as an abrasive for cutting and grinding glass.

NITROGEN

Oxides Five oxides of nitrogen are known. These are: nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2) and nitrogen pentoxide (N_2O_5).

Nitrous Oxide In the laboratory, nitrous oxide can be prepared by heating ammonium nitrate or a mixture of sodium nitrate and ammonium sulphate (or ammonium chloride).

$$NH_4NO_3 \rightarrow N_2O + 2H_2O; \qquad 2NaNO_3 + (NH_4)_2SO_4 \rightarrow 2N_2O + 4H_2O + Na_2SO_4$$

It can also be prepared by the action of sodium nitrite on hydroxylamine hydrochloride in aqueous solution.

$$NH_2OH \cdot HCl + NaNO_2 \rightarrow N_2O + NaCl + 2H_2O$$

It is fairly soluble in cold water but lesser soluble in hot water. It is also known as laughing gas as it produces hysterical laughter when inhaled in small quantities. Large dose is fatal. Mixed with oxygen, it is used as an anaesthetic.

Nitrous oxide decomposes on heating to give $2N_2O \rightarrow 2N_2 + O_2 \quad \Delta H = -163.2 \text{ kJ mol}^{-1}$

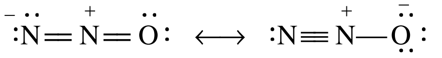
Because of the availability of oxygen, nitrous oxide supports the combustion of a glowing splinter, burning phosphorus and sulphur.

$$C + 2N_2O \rightarrow 2N_2 + CO_2; \qquad P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$$

$$S + 2N_2O \rightarrow SO_2 + 2N_2$$

It is reduced to N_2 when passed over hot copper.

Nitrous oxide is a linear molecule. It is considered to be resonance hybrid of the following structures.



$$:\overset{-}{\ddot{N}}=\overset{+}{N}=\ddot{O}: \longleftrightarrow :N\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}:$$

Nitrous oxide is a neutral oxide.

Nitric Oxide The action of 50% HNO_3 on Cu produces nitric oxide.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

In laboratory, pure nitric oxide may be obtained by reducing KNO_3 with ferrous sulphate acidified with concentrated H_2SO_4.

$$2NO_3^- + 6Fe^{2+} + 8H^+ \rightarrow 2NO + 6Fe^{3+} + 4H_2O$$

Nitric oxide can be produced commercially by the catalytic oxidation of ammonia.

$$4NH_3 + 5O_2 \xrightarrow[1070\text{ K}]{\text{Pt gauze}} 4NO + 6H_2O$$

This gas is also formed in the atmosphere during lightning flashes.

Nitric oxide is a colourless gas. It spontaneously combines with oxygen giving brown fumes of nitrogen peroxide. When passed through cold ferrous sulphate solution, it gives dark brown liquid due to $Fe[(NO)(H_2O)_5] \cdot SO_4$ which decomposes on heating giving back nitric oxide. This fact is made use of in the purification of this oxide.

Nitric oxide is reduced to nitrogen when passed over heated copper or sparked with hydrogen.

$$2Cu + 2NO \rightarrow 2CuO + N_2; \qquad 2H_2 + 2NO \rightarrow 2H_2O + N_2$$

It is reduced to N_2O by sulphurous acid and to NH_3 by hydrogen in presence of heated platinum.

$$2NO + H_2SO_3 \rightarrow N_2O + H_2SO_4; \qquad 2NO + 5H_2 \xrightarrow{\text{Pt black}} 2NH_3 + 2H_2O$$

Reduction by tin and hydrochloric acid produces hydroxylamine. $2NO + 6[H] \rightarrow 2NH_2OH$

In aqueous solution a powerful oxidizing agent oxidizes nitric oxide to nitrate ions.

$$3MnO_4^- + 4H^+ + 5NO \rightarrow 3Mn^{2+} + 5NO_3^- + 2H_2O$$

$$3I_2 + 4H_2O + 2NO \rightarrow 6I^- + 2NO_3^- + 8H^+$$

Concentrated nitric acid oxidizes NO to NO_2. $2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$

This equation explains why concentrated nitric acid reacts with metals producing NO_2 while with dilute nitric acid containing excess of water, NO is produced. With moderately strong nitric acid, both the gases are evolved.

Nitric oxide is a neutral oxide. The coordination complexes of NO with transition metal ions are known as nitrosyls. Examples are $[Fe(H_2O)(NO)]^{2+}$ and sodium nitroprusside $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. Nitric oxide in these complexes is attached through nitrogen atom.

Nitric oxide has 11 valence electrons. The presence of an odd electron makes the molecule paramagnetic. Under ordinary conditions, it is not dimerized. However in the liquid and solid state it is dimerized (O—N—N—O) to give a diamagnetic molecule.

The bond length N—O is 115 pm which is intermediate between a double and a triple bond. Its electronic configuration based on molecular orbital theory is

$$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\pi^* 2p)^1$$

Thus the bond order of NO is 2.5. The species NO^+ (nitrosonium ion) has bond order of 3 and the bond length in it is 106 pm which is less than that in NO.

Nitric oxide is considered to be the resonance hybrid of the following structures.

$$:\dot{N} = n\ddot{O}: \qquad \leftrightarrow \qquad :\overset{-}{\dot{N}} \equiv \overset{+}{\dot{O}}:$$

Dinitrogen Trioxide It is also known as nitrogen sesquioxide. It is stable only in the liquid state, in the gaseous state it dissociates readily into nitric oxides.

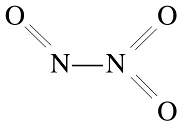
$$N_2O_3 \rightleftharpoons NO + NO_2$$

N_2O_3 can be obtained by condensing equimolar quantities of NO and NO_2. Thus, it is a mixed oxide. In the liquid or solid state, it has a blue colour.

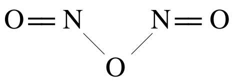
It is an acidic oxide and is the anhydride of nitrous acid HNO_2. With alkali it forms nitrites. N_2O_3 reacts with the concentrated acids, forming nitrosyl salts.

$$N_2O_3 + 2HClO_4 \rightarrow 2NO[ClO_4] + H_2O; \qquad N_2O_3 + 2H_2SO_4 \rightarrow 2NO[HSO_4] + H_2O$$

N_2O_3 exists in two different forms which are interconvertible by using the appropriate wave length.



asymmetrical form



symmetrical form

The N—N bond length in asymmetrical form is 186.4 pm which is exceptionally large, indicating a weak bond as compared to the N—N bond in hydrazine which has a bond length of 145 pm.

Nitrogen Dioxide In laboratory, NO_2 can be prepared by heating dry lead nitrate.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

On cooling, NO_2 condenses as a brown liquid which turns paler on cooling and eventually becomes a colourless solid due to the formation of dimerized NO_2 i.e. N_2O_4.

NO_2 is an odd electron molecule and is paramagnetic and very reactive. N_2O_4 does not contain unpaired electrons and is diamagnetic. It is a mixed anhydride as nitric and nitrous acids are produced on reacting with water.

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

The HNO_2 formed decomposes to give NO. $\qquad 2HNO_2 \rightarrow NO_2 + NO + H_2O$

The moist NO_2 and N_2O_4 gases are strongly acidic.

Nitrogen dioxide can also be produced on the basis of the following reactions.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$NaNO_2 + 2HNO_3 \rightarrow NaNO_3 + H_2O + 2NO_2$$

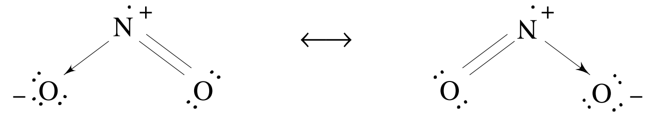
The NO_2–N_2O_4 system is a strong oxidizing agent. A few reactions illustrating this fact are

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO \qquad 2I^- + H_2O + NO_2 \rightarrow I_2 + 2OH^- + NO$$

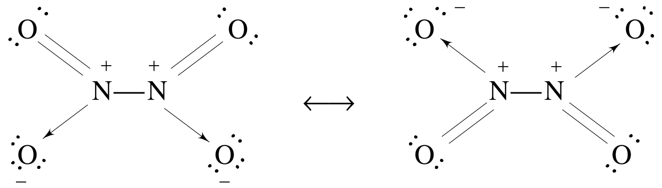
$$H_2S + NO_2 \rightarrow S + NO + H_2O \qquad CO + NO_2 \rightarrow CO_2 + NO$$

Nitrogen dioxide is oxidized by $KMnO_4$. $\qquad 2MnO_4^- + 10NO_2 + 2H_2O \rightarrow 2Mn^{2+} + 4H^+ + 10NO_3^-$

The NO_2 molecule is angular with an O—N—O angle of 132°. The bond length O—N of 120 pm is intermediate between a single and a double bond. The resonating structures of NO_2 are



The N_2O_4 molecule is planar with N—N bond length of 164 pm. It is a weaker bond as it is much larger than N—N bond length (147 pm) in hydrazine.



Liquid N_2O_4 is useful as a nonaqueous solvent. It ionizes as $N_2O_4 \rightleftharpoons \underset{\text{acid}}{NO^+} + \underset{\text{base}}{NO_3^-}$

In N_2O_4 substances containing NO^+ are acids and those containing NO_3^- are bases. A typical acid-base reaction is

$$\underset{\text{acid}}{NOCl} + \underset{\text{base}}{NH_4NO_3} \rightarrow \underset{\text{salt}}{NH_4Cl} + \underset{\text{solvent}}{N_2O_4}$$

Nitrogen Pentoxide This oxide is prepared by carefully dehydrating HNO_3 with P_2O_5 at low temperatures.

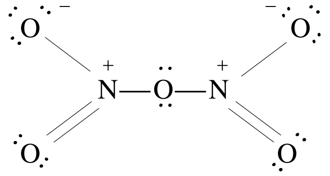
$$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$$

It is a colourless, deliquescent solid, which is highly reactive, is a strong oxidizing agent and is light sensitive. It is the anhydride of HNO_3. It decomposes slowly at room temperature.

$$2N_2O_5 \rightleftharpoons 4NO_2 + O_2$$

At very low temperature, NO_2 is formed when O_3 is passed through N_2O_5.

Solid N_2O_5 is ionic $NO_2^+\ NO_3^-$ (nitronium nitrate). In solution and in the gaseous phase it is covalent, with the structure



Oxoacids

Nitrous Acid It is unstable except in dilute solution. It is easily made by acidifying a solution of nitrite. Barium nitrite and sulphuric acid are commonly used as these give insoluble $BaSO_4$ which can be easily removed. On heating, nitrous acid decomposes as

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

Nitrite of Group 1 are fairly stable and can be obtained by heating nitrate, either on their own or with Pb.

$$2NaNO_3 \xrightarrow{\text{heat}} 2NaNO_2 + O_2$$

$$NaNO_3 + Pb \xrightarrow{\text{heat}} NaNO_2 + PbO$$

Nitrous acid and nitrites are weak oxidizing agents and will oxidize Fe^{2+} to Fe^{3+}, and I^- to I_2, they themselves are reduced to N_2O or NO.

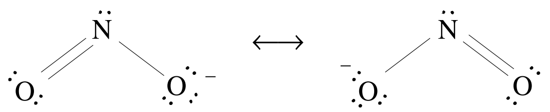
$$Fe^{2+} + 2H^+ + NO_2^- \rightarrow Fe^{3+} + H_2O + NO$$

$$2I^- + 4H^+ + 2NO_2^- \rightarrow I_2 + 2H_2O + 2NO$$

With strong oxidizing agents ($KMnO_4$ and Cl_2), HNO_2 and nitrite are oxidized to NO_3^-.

$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

The nitrite ion is angular and a resonance hybrid.



Nitric Acid Pure nitric acid is a colourless liquid but on exposure to light it turns slightly brown because of slight decomposition into NO_2 and O_2.

$$4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O$$

It is a strong acid and is completely dissociated in dilute aqueous solutions into H_3O^+ and NO_3^-.

The first synthetic method to manufacture HNO_3 is due to Brikeland-Eyde. In this method, N_2 and O_2 are sparked together in an electric arc furnace. The nitric oxide in air forms nitric dioxide which on dissolving in water gives nitric acid.

$$N_2 + O_2 \xrightarrow{\text{spark}} NO \xrightarrow{+\,O_2} NO_2 \xrightarrow{H_2O} HNO_3$$

These days, NO is prepared by catalytic oxidation of ammonia.

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{catalyst, 5atm, 850°C}]{\text{Platinium/Rhodium}} 4NO(g) + 6H_2O(g)$$

Nitric acid with water forms azeotropic mixture containing 68% of nitric acid. Concentrated nitric acid contains 98% acid and is produced by dehydrating with concentrated sulphuric acid or by mixing with a 72% magnesium nitrate solution followed by distillation.

When nitric acid is mixed with concentrated sulphuric acid, the nitronium ion NO_2^+ is formed. This is an active species which is used for the nitration of organic compounds. Covalent nitrates are less stable than ionic nitrates. Nitroglycerine, nitrocellulose, trinitrotoluene and fluorine nitrate are all explosive.

Nitric acid displays a wide range of oxidising action. It is reduced successively as follows.

$$\overset{+5}{HNO_3} \rightarrow \overset{+4}{NO_2} \rightarrow \overset{+2}{NO} \rightarrow \overset{+1}{N_2O} \rightarrow \overset{-3}{NH_3}$$

The degree of reduction of nitric acid depends both on its concentration and the reductant. In general, the more dilute the acid, the greater the reduction. Concentrated acid is reduced to NO_2, dilute acid is reduced to NO and very dilute acid (with electropositive element) is reduced to NH_3 which forms NH_4NO_3 with excess acid.

A few reactions are as follows.

$$3Cu + \underset{\text{(dilute)}}{8HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O; \quad Zn + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

$$Cu + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O; \quad 4Sn + 10HNO_3 \xrightarrow[\text{(dilute)}]{\text{cold}} 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$4Zn + \underset{\text{(very dilute)}}{10HNO_3} \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O; \quad 5Sn + \underset{\text{(conc.)}}{20HNO_3} \rightarrow H_2Sn_5O_{11}\cdot 4H_2O + 20NO_2 + 5H_2O$$

Nonmetals are oxidised to their highest oxoacids.

$$S + 2HNO_3 \rightarrow H_2SO_4 + 2NO; \quad As + \underset{\text{(conc.)}}{5HNO_3} \xrightarrow{\text{hot}} H_3AsO_4 + 5NO_2 + H_2O$$

$$P_4 + 10HNO_3 + H_2O \rightarrow 4H_3PO_4 + 5NO + 5NO_2; \quad 3I_2 + \underset{\text{(conc.)}}{10HNO_3} \xrightarrow{\text{hot}} 6HIO_3 + 10NO + 2H_2O$$

$$As + \underset{\text{(dilute)}}{3HNO_3} \rightarrow H_3AsO_3 + 3NO_2;$$

Nitric acid oxidises a number of reducing agents Fe^{2+} to Fe^{3+}, Sn^{2+} to Sn^{4+}, H_2S to S and I^- to I_2.

The reactions are

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$7SnCl_2 + 14HCl + 2HNO_3 \rightarrow 7SnCl_4 + NH_2OH + NH_3 + 5H_2O$$
$$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$$
$$6KI + 8HNO_3 \rightarrow 6KNO_3 + 2NO + 4H_2O + 3I_2$$

A mixture of one volume of nitric acid and three volumes of hydrochloric acid is known as *aqua regia*. It can dissolve metals like gold and platinum.

$$Au + \underbrace{3HCl + HNO_3}_{\text{aqua regia}} \rightarrow AuCl_3 + NO + 2H_2O$$

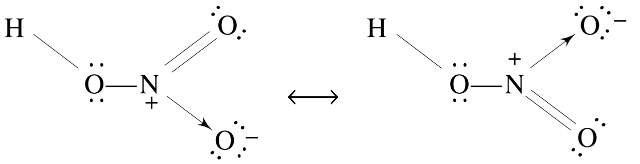
$AuCl_3$ dissolved in HCl as $HAuCl_4$ whereas NO is oxidized to NO_2 by HNO_3. The net reaction is

$$Au + 3HNO_3 + 4HCl \rightarrow HAuCl_4 + 3NO_2 + 3H_2O$$

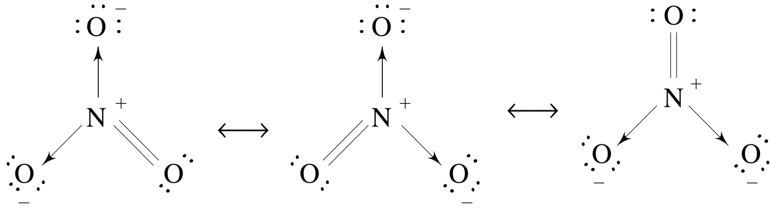
By employing Devarda's alloy (45% Al, 5% Zn and 50% Cu) in alkaline solution, nitric acid and nitrates can be converted quantitatively into ammonia.

$$4Zn + NO_3^- + 7OH^- + 6H_2O \rightarrow 4[Zn(OH)_4]^{2-} + NH_3$$

Nitric acid in vapour phase is planar. It involves two resonating structures.



The shape of nitrate ion is planar triangle.



Ammonia It is a colourless gas with a pungent odour. It can be prepared by decomposing ammonium salts with caustic alkalis or lime. In the laboratory, ammonia can be prepared by heating ammonium chloride with slaked lime.

$$2NH_4Cl + CaO \rightarrow CaCl_2 + H_2O + 2NH_3$$

Ammonia cannot be dried over concentrated sulphuric acid, calcium chloride or phosphorus pentoxide as the gas reacts with these substances. However, quicklime can be used.

Commercially, ammonia is produced by Haber's process based on the following reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.38 \text{ kJ mol}^{-1}$$

Low temperature and high pressure favours the formation of ammonia. Optimum conditions used are 500°C and 200 atm pressure. The rate of reaction is slow even at this temperature, so a catalyst of pure iron, mixed with a promoter like alumina and potassium oxide is used.

Another method is based on the hydrolysis of calcium cyanamide with superheated steam at 450 K.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

Aqueous ammonia contains uncombined ammonia (46.2%), hydrated ammonia ($H_3N \cdots HOH$, 52.4%) and relatively few (1.4%) NH_4^+ and OH^- ions. 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.

Ammonia burns in oxygen with a greenish-yellow flame. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

A mixture of NH_3 and oxygen explodes by the passage of electric spark through it. In the presence of platinum gauze at 500°C, the reaction occurring is $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Over heated metallic oxides, CuO and PbO, it is oxidized to nitrogen. $3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2$

When heated with alkali metals and barium, amides are formed. $2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$

With calcium, calcium hydride and nitrogen are formed. With chlorine, the reaction occurring is

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

whereas, with excess of chlorine, the reaction occurring is $NH_3 + 3Cl_2 \rightarrow \underset{\text{explosive}}{NCl_3} + 3HCl$

Aqueous ammonia precipitates many metallic hydroxides from solutions of their salts. In same cases, the precipitated hydroxides dissolve in excess ammonia giving complex ammines.

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 \downarrow + (NH_4)_2SO_4; \qquad 2AgNO_3 + 2NH_4OH \rightarrow Ag_2O \downarrow + H_2O + 2NH_4NO_3$$

$$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4](OH)_2; \qquad Ag_2O + 4NH_4OH \rightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

Sodium hypochlorite with ammonia solution in presence of a little glue or gelatine forms hydrazine. The reaction proceeds with the formation of NH_2Cl which reacts with NH_3 forming hydrazine.

$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$; $NH_2Cl + NH_3 \rightarrow H_2NNH_2 + HCl$

$HCl + NaOH \rightarrow NaCl + H_2O$

Glue or gelatine serves as a protective colloid which inhibits the secondary reaction.

$N_2H_4 + 2NH_2Cl \rightarrow 2NH_4Cl + N_2$

The characteristic tests of ammonia are as follows.

It gives yellow-brown colour or precipitate with Nessler's reagent.

$$\underset{\text{(Nessler's reagent)}}{2K_2HgI_4} + 3KOH + NH_3 \rightarrow \underset{\text{(iodide of Millon's base)}}{H_2NHgOHgI} + 7KI + 2H_2O$$

It gives yellow precipitate of ammonium chloroplatinate with chloroplatinic acid.

$$2NH_4Cl + H_2PtCl_6 \rightleftharpoons (NH_4)_2PtCl_6 + 2HCl$$

It gives a white precipitate of ammonium acid tartarate with a saturated solution of sodium hydrogen tartarate.

$$NH_4Cl + NaHC_4H_4O_6 \rightarrow NH_4HC_4H_4O_6 + NaCl$$

Liquid ammonia is an excellent ionizing solvent. It ionizes as $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

Thus, ammonium and amide salts act as acids and bases, respectively, in liquid ammonia.

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{solvent}}{2NH_3}$$

Liquid ammonia dissolves the alkali metals and, to a lesser extent Ca, Sr and Ba to produce deep blue solutions which are excellent reducing agents. The deep blue solutions are excellent electrical conductors as they contain solvated electrons.

PHOSPHORUS

Phosphine (PH_3)

The reaction of phosphides with water produces phosphine.

$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$; $Na_3P + 3H_2O \rightarrow PH_3 + 3NaOH$

Aluminium phosphide is decomposed with dilute sulphuric acid . $2AlP + 3H_2SO_4 \rightarrow 2PH_3 + Al_2(SO_4)_3$

Heating of phosphorous acid produces phosphine. $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

In a laboratory, phosphine can be produced by treating phosphorus with concentrated sodium hydroxide solution in an inert atmosphere of carbon dioxide.

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

Phosphine burns in air or oxygen to give P_4O_{10}. It is a colourless gas with odour of rotten fish. It is highly poisonous in nature. It is feebly basic as it reacts with halogen acids

$$PH_3 + HI \rightarrow \underset{\text{Phosphonium iodide}}{PH_4I}$$

When passed through metallic salt solutions, it precipitates phosphides and finally reduces them to the metals.

$3CuSO_4 + 2PH_3 \rightarrow \underset{\text{copper phosphide}}{Cu_3P_2} + 3H_2SO_4$; $PH_3 + 6Ag^+ + 3H_2O \rightarrow 6Ag + H_3PO_3 + 6H^+$

Phosphine reacts with Cl_2 to give PCl_3.

Oxides Phosphorus forms three oxides, trioxide (P_4O_6), tetroxide (P_4O_8) and pentoxide (P_4O_{10}).

Phosphorus trioxide Burning of phosphorus in a limited supply of air gives phosphorus trioxide. It is a colourless crystalline solid with odour of garlic. It exists as dimer both in naphthalene and in the vapour phase.

It dissolves in cold water giving phosphorous acid (H_3PO_3) whereas in hot water it gives phosphoric acid (H_3PO_4) and phosphine (PH_3).

$P_4O_6 + \underset{\text{cold}}{6H_2O} \rightarrow 4H_3PO_3$ $P_4O_6 + \underset{\text{hot}}{6H_2O} \rightarrow 3H_3PO_4 + PH_3$

In its structure, four P atoms lie at the corners of a tetrahedron and six oxygen atoms along the edges (Fig. 15.2). The P—O bond distance is 165.6 pm which is shorter than the expected single bond distance (184 pm). This suggests that there exists a considerable double bond character in the P—O bonds because of the formation of a pπ–dπ bond with oxygen donor.

Phosphorus tetroxide Liquid phosphorus trioxide when heated in a sealed tube at 440°C, changes into tetroxide.

$$4P_4O_6 \rightarrow 3P_4O_8 + 4P$$

Phosphorus tetroxide is a mixed anhydride as it gives both phosphorous and phosphoric acids with water.

$$P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$$

The structure of P_4O_8 is shown in Fig. 15.3.

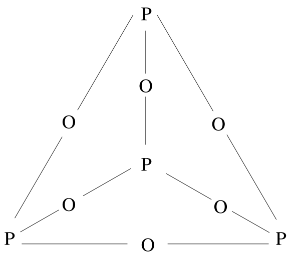


Fig. 15.2 Structure of P_4O_6

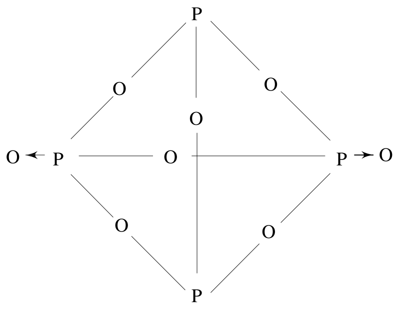


Fig. 15.3 Structure of P_4O_8

Phosphorus pentoxide Burning of phosphorus in an excess of dried air or oxygen gives phosphorus pentoxide. It is a white solid which sublimes on heating. It is odourless when pure. It dissolves in cold water giving metaphosphoric acid.

$$P_4O_{10} + \underset{\text{hot}}{2H_2O} \rightarrow 4HPO_3$$

With hot water, orthophosphoric acid is formed. $P_4O_{10} + \underset{\text{hot}}{6H_2O} \rightarrow 4H_3PO_4$

It is a strong dehydrating agent. For example, H_2SO_4 and HNO_3 are converted into corresponding anhydride.

$$2H_2SO_4 + P_4O_{10} \rightarrow 2SO_3 + 4HPO_3; \qquad 4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$$

Acetamide gives acetonitrile. $2CH_3CONH_2 + P_4O_{10} \rightarrow 2CH_3CN + 4HPO_3$

On heating with carbon, it is reduced to phosphorus. $P_4O_{10} + 10C \rightarrow P_4 + 10CO$

In the structure of P_4O_{10}, each P atom forms three bonds to oxygen atoms and also an additional coordinate bond with an oxygen atom (Fig. 15.4). Terminal coordinate P—O bond is 143 pm which is much shorter than the expected bond length of 162 pm. This shows the presence of considerable pπ-dπ back bonding because of the lateral overlap of full p orbitals on oxygen with empty d orbitals on phosphorus.

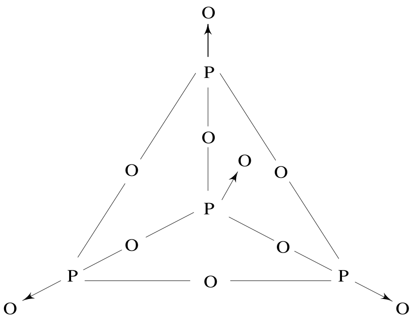


Fig. 15.4 Structure fo P_4O_{10}

Oxoacids Six important oxoacids are described in the following.

Hypophosphorous Acid (H_3PO_2) Heating of phosphorus with barium hydroxide solution forms barium hypophosphite in the solution. Excess of barium hydroxide is removed by passing carbon dioxide in the solution. It is filtered and the filtrate is evaporated to give crystals of barium hypophosphite. The latter is treated with the calculated quantity of H_2SO_4 when the acid is set free.

$$2P_4 + 3Ba(OH)_2 + 6H_2O \rightarrow 2PH_3\uparrow + 3Ba(H_2PO_2)_2$$
$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_3PO_2$$

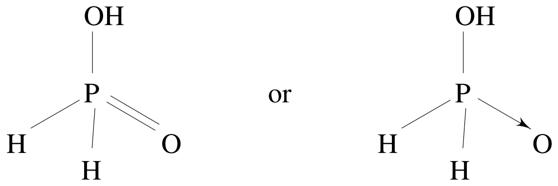
The acid and its salt decomposes on heating.

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3; \qquad 3NaH_2PO_2 \rightarrow NaH_2PO_3 + Na_2HPO_3 + PH_3$$

At higher temperature, phosphorous acid further disproportionates as $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

The acid and its salts are powerful reducing agent. The salts of Ag, Au, Pt, Hg and Bi are reduced to the corresponding metals.

It is a strong monobasic acid. Its structure is

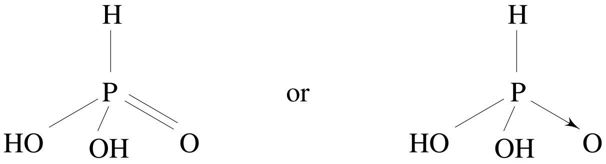


Orthophosphorus acid (H_3PO_3) This acid can be prepared by dissolving P_4O_6 in cold water. The hydrolysis of PCl_3 also produces this acid.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

The solution is evaporated until the temperature rises to 453 K and then cooled when the acid H_3PO_3 crystallized out as white solid.

H_3PO_3 is a dibasic acid, so only two hydrogen atoms are bonded to oxygen atoms. Thus its structure is



The acid ionizes as

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-; \qquad H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$$

The acid and its salts are strong reducing agents. It reduces mercury salts to mercurous salts and gold, silver and cupric salts to their respective metals.

$$H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$$
$$2HgCl_2 + 2e^- \rightarrow Hg_2Cl_2 + 2Cl^-$$

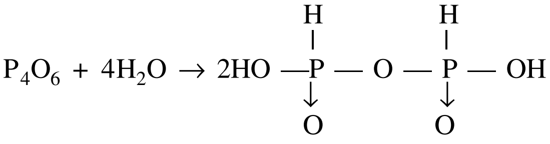
$$2HgCl_2 + H_3PO_3 + H_2O \rightarrow Hg_2Cl_2 + H_3PO_4 + 2H^+ + 2Cl^-$$

Its reducing action is due to the one hydrogen atom directly attached to phosphorus atom.

H_3PO_3 disproportionates on heating: $H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

The reaction with PCl_5 is $H_3PO_3 + 3PCl_5 \rightarrow PCl_3 + 3POCl_3 + 3HCl$

Pyrophosphorous acid ($H_4P_2O_5$) Controlled hydrolysis of P_4O_6 gives pyrophosphorous acid.



$$P_4O_6 + 4H_2O \rightarrow 2HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{H}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{H}{|}}{P}}-OH$$

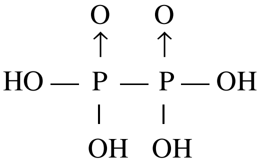
It is also a dibasic acid and possesses reducing characteristics.

Metaphosphorous Acid ($H_nP_nO_{2n}$) The treatment of phosphine with oxygen at a low pressure gives metaphosphorous acid.

$$nPH_3 + nO_2 \xrightarrow{25\ \text{mmHg}} (HPO_2)_n + nH_2$$

It is a polymerized species.

Hypophosphoric Acid ($H_4P_2O_6$) This acid is formed when white phosphorus partially immersed in water is allowed to be oxidized in a limited supply of air. Its structure is



$$HO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\uparrow}}{P}}-\underset{\underset{OH}{|}}{\overset{\overset{O}{\uparrow}}{P}}-OH$$

On heating, this acid decomposes to give phosphorous acid and metaphosphoric acid.

$$H_4P_2O_6 \rightarrow H_3PO_3 + HPO_3$$

It is tetrabasic acid with no reducing characteristics. In warm water, it undergoes hydrolysis.

$$H_4P_2O_6 \xrightarrow{H_2O} \underset{\text{phosphorous acid}}{H_3PO_3} + \underset{\text{phosphoric acid}}{H_3PO_4}$$

Orthophosphoric acid (H_3PO_4) The dissolution of P_2O_5 in water and then boiling the solution produces this acid.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

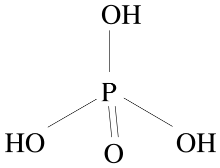
The hydrolysis of PCl_5 also produces this acid. The oxidation of red phosphorus with 50% nitric acid in the presence of a flake of iodine as a catalyst also produces H_3PO_4.

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Orthophosphoric acid is manufactured by heating rock phosphate with sulphuric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$$

H_3PO_4 is a tribasic acid. It structure is

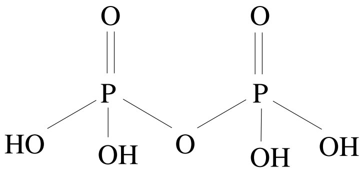


On heating it is dehydrated as follows. $\underset{\text{orthophosphoric acid}}{2H_3PO_4} \xrightarrow{520\text{ K}} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow{870\text{ K}} \underset{\text{metaphosphoric acid}}{2HPO_3}$

Pyrophosphoric Acid ($H_4P_2O_7$) Heating of orthophosphoric acid to 523–533 K produces this acid. It may also be obtained by heating an equimolar mixture of the ortho- and metaphosphoric acids at 100°C.

$$HPO_3 + H_3PO_4 \rightarrow H_4P_2O_7$$

$H_4P_2O_7$ is a tetrabasic acid. Its structure



On boiling with water pyro-acid is converted to ortho-acid $H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$

On strong heating, it produces metaphosphoric acid. $H_4P_2O_7 \xrightarrow{-H_2O} 2HPO_3$

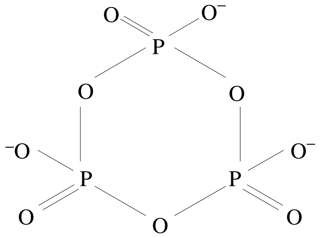
Only two series of salts are formed by this acid, e.g. $Na_2H_2P_2O_7$ and $Na_4P_2O_7$.

Metaphosphoric Acid (HPO_3) Heating orthophosphoric acid or pyrophosphoric acid to red heat produces metaphosphoric acid.

$$H_3PO_4 \rightarrow HPO_3 + H_2O \qquad H_4P_2O_7 \rightarrow 2HPO_3 + H_2O$$

It is a transparent glassy solid. On boiling with water, it is reconverted to ortho-acid. It is a monobasic acid. The metaphosphoric acid is also known as glacial phosphoric acid.

The structures of the various metaphosphoric acids are uncertain. Metaphosphate ions are built up from PO_4 units and are cyclic as opposed to linear structures. The trimetaphosphate ion, $P_3O_9^{3-}$, is



Fertilizers To meet the requirement of nutrients for the healthy growth of plants, chemical manures or fertilizers are added. These compounds contain nitrogen, phosphorus and potassium. The fertilizers may be classified as nitrogenous, phosphatic and potash fertilizers. Example of nitrogenous fertilizers are calcium cyanamide, CaNCN; ammonium sulphate, $(NH_4)_2SO_4$; basic calcium nitrate, $Ca(NO_3)_2 \cdot CaO$; urea, H_2NCONH_2; and calcium ammonium nitrate (CAN).

Examples of phosphatic fertilizers are superphosphate of lime, $Ca(H_2PO_4)_2 + 2CaSO_4$; triple superphosphate, $Ca(H_2PO_4)_2$; nitrophos, $Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$; ammoniated phosphates $NH_4H_2PO_4$, and calcium superphosphate nitrate, $Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$.

Examples of potash fertilizers are potassium chloride, potassium sulphate and potassium nitrate.

SULPHUR

Oxides The common oxides of sulphur are dioxide (SO_2) and trioxide (SO_3). In addition to these, monoxide (SO), sesquioxide (S_2O_3), tetroxide (SO_4) and heptoxide (S_2O_7) are also known.

Sulphur Dioxide It may be prepared based on the following reactions.

$$Cu + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O \qquad 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$S + O_2 \rightarrow SO_2 \qquad 2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

With water, it forms sulphurous acid (H_2SO_3). The latter has not been isolated in the free state. However, crystals of $SO_2 \cdot 7H_2O$ has been obtained from concentrated sulphurous acid. The salts of sulphurous acid are known.

$$KOH(aq) + SO_2 \rightarrow KHSO_3(aq) \qquad 2KOH(aq) + SO_2 \rightarrow K_2SO_3(aq) + H_2O$$

Sulphur dioxide is frequently used as a strong reducing agent. A few reactions exhibiting this characteristic are as follows.

$$Br_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \qquad Hg_2(NO_3)_2 + SO_2 + 2H_2O \rightarrow 2Hg + H_2SO_4 + 2HNO_3$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad 2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$2FeCl_3 + SO_2 + 2H_2O \rightarrow 2FeCl_2 + 2HCl + H_2SO_4 \qquad K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

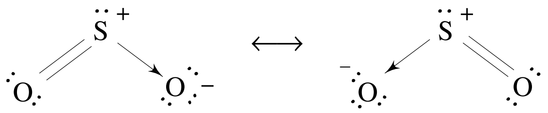
$$2HgCl_2 + SO_2 + 2H_2O \rightarrow Hg_2Cl_2 + 2HCl + H_2SO_4 \qquad 2KIO_3 + 5SO_2 + 4H_2O \rightarrow I_2 + 3H_2SO_4 + 2KHSO_4$$

Sulphur dioxide also acts as an oxidizing agent towards stronger reducing agents:

$$4FeCl_2 + SO_2 + 4HCl \rightarrow 4FeCl_3 + 2H_2O + S$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

Gaseous sulphur dioxide is a bent and symmetrical molecule. The bond angle is 119.5° which is close to the structure predicted from sp^2 hybridization. The S—O bond distance is 146 pm which is smaller than the expected value. This suggests pπ-dπ bonding between O and S. Two resonating forms are



Sulphur Trioxide It may be prepared by dehydrating concentrated sulphuric acid with phosphorus pentoxide or by heating sulphates.

$$2H_2SO_4 + P_4O_{10} \rightarrow 2SO_3 + 4HPO_3; \qquad Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

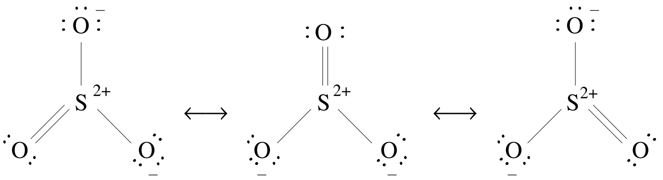
Large quantities of sulphur trioxide are produced for the manufacture of sulphuric acid. This is obtained by the oxidation of sulphur dioxide.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -188.3 \text{ kJ mol}^{-1}$$

Low temperature and high pressure favour the formation of sulphur trioxide. The optimum temperature is 450 °C. A catalyst is used to increase the rate of reaction. Platinized asbestos, used earlier, is replaced by vanadium pentoxide. Other catalysts used are finely divided platinum deposited on magnesium sulphate and a mixture of ferric oxide and cupric oxide. The above catalysts are used in the modern Contact process for the manufacture of sulphuric acid. The other older process is lead chamber process where oxides of nitrogen are used as catalyst.

Solid sulphur trioxide exists in three forms. These are known as α–, β–, and γ– sulphur trioxide. It is an acidic oxide which on dissolving in water gives sulphuric acid.

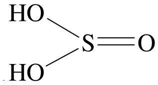
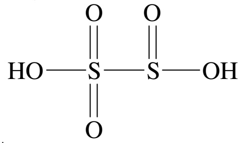
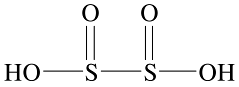
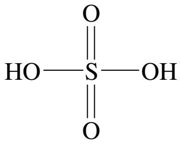
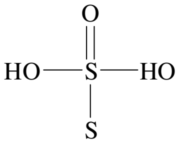
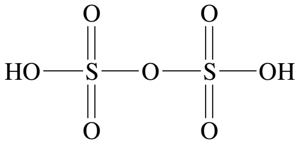
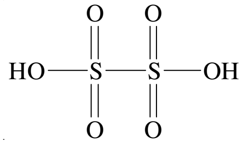
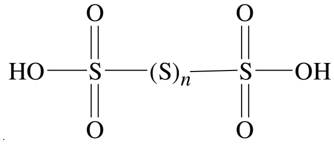
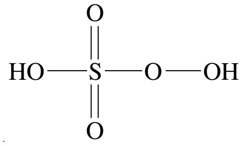
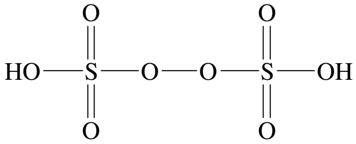
The molecules of SO_3 is triangular planar containing sp^2 hybridized sulphur atom. The S—O double bond arises from pπ-dπ bonding due to the lateral overlap of the p orbitals of oxygen with d orbitals of sulphur. It may be represented by the following resonating structures.



Oxoacids Sulphur forms a large number of oxoacids. Many of them do not exist as free acids but their salts are known. Acids ending in '-ous' have sulphur(IV) and form salts ending in '-ite'. Acids ending in '-ic' have sulphur(VI) and form salts ending in '-ate'.

The oxoacids of sulphur have been classified into four series. These are described in Table 15.1.

Table 15.1 Oxoacids of sulphur

Acid	*Formula*	*Oxidation state of* S
1. Sulphurous acid series		
Sulphurous acid, H_2SO_3	 $(HO)_2S{=}O$	(+IV)
Di- or pyrosulphurous acid, $H_2S_2O_5$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}\overset{\overset{O}{\Vert}}{S}{-}OH$	(+V), (+III)
Dithionous acid, $H_2S_2O_4$	 $HO{-}\overset{\overset{O}{\Vert}}{S}{-}\overset{\overset{O}{\Vert}}{S}{-}OH$	(+III)
2. Sulphuric acid series		
Sulphuric acid, H_2SO_4	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}OH$	(+VI)
Thiosulphuric acid, $H_2S_2O_3$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{S}{\vert}}{S}}{-}HO$	(+VI), (–II)
Di– or pyrosulphuric acid, $H_2S_2O_7$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}OH$	(+VI)
3. Thionic acid series		
Dithionic acid, $H_2S_2O_6$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}OH$	(+V)
Polythionic acid, $H_2S_nO_6$ $(n = 1 - 12)$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}(S)_n{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}OH$	(+V), (0)
4. Peroxoacid series		
Peroxomonosulphuric acid, or Caro's acid, H_2SO_5	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}O{-}OH$	(+VI)
Peroxodisulphuric acid, or Marshall's acid, $H_2S_2O_8$	 $HO{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}O{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}OH$	(+VI)

Two most common oxoacids of sulphur are sulphurous acid and sulphuric acid.

Sulphurous Acid Dissolution of SO_2 in water produces sulphurous acid which exists only in the solution. Its salt, the sulphite form stable crystalline solids. Acidic or alkaline solutions of sulphites or hydrogen sulphites are powerful reducing agents. In alkaline medium, the reducing properties are due to the sulphite ion, in acidic solution they arise from the presence of sulphur dioxide. From the standard potentials

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O \qquad E^\circ = 0.17\ \text{V}$$

$$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^- \qquad E^\circ = -0.93\ \text{V}$$

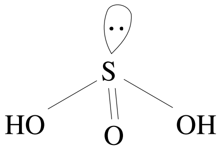
It may be concluded that the sulphites are stronger reductants in alkaline solution than sulphur dioxide in acidic solution. Examples of reducing action are

$$2Fe^{3+} + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2Fe^{2+} + 2H^+$$

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$$

Sulphites and SO_2 are oxidizing agents for more powerful reducing agents, such as H_2S.

The structure of sulphurous acid is tetrahedral including the lone pair of electrons on sulphur.



Sulphuric Acid Dissolution of SO_3 in water produces sulphuric acid. Fuming sulphuric acid or oleum is produced when SO_3 is absorbed in H_2SO_4.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{oleum}}{H_2S_2O_7}$$

Sulphuric acid with water forms an azeotropic solution containing approximately 9% of the acid.

Pure sulphuric acid is dense and has high boiling point. It is due to the hydrogen bonding.

Concentrated H_2SO_4 is used as dehydrating agent as it has a strong affinity for water. Hot concentrated sulphuric acid is a weak oxidizing agent, but this property is rapidly lost on dilution. The reduction product of the acid may be SO_2, S or H_2S depending upon the reductant. Nonmetals and lesser electropositive elements are weak reducing agents and reduce sulphuric acid to SO_2, e.g.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

More electropositive elements are more powerful reducing agents and reduce the acid to S or H_2S, e.g.

$$4Mg + 5H_2SO_4 \rightarrow 4MgSO_4 + 4H_2O + H_2S$$

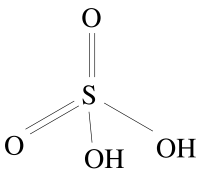
$$3Zn + 4H_2SO_4 \rightarrow 3ZnSO_4 + 4H_2O + S$$

Hydrogen bromide and iodide reduce sulphuric acid.

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$$

$$8HI + H_2SO_4 \rightarrow 4I_2 + 4H_2O + H_2S$$

The structure of sulphuric acid is



Sodium Thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) This salt is also known as hypo. Thiosulphate salts are produced by boiling aqueous sulphite salts with sulphur.

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

Hypo solution is used to titrate iodine in volumetric analysis.

$$2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$$

$Na_2S_2O_3$ is used in the bleaching industry to destroy any excess of Cl_2 on fabrics after they have been through a bleach bath. Similarly, $Na_2S_2O_3$ is sometimes used to remove the taste from heavily chlorinated drinking water. Since Cl_2 is a stronger oxidizing agent than I_2, HSO_4^- is formed rather than tetrathionate ion.

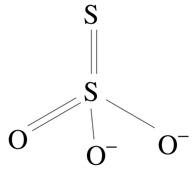
$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$$

Hypo is used in photography for fixing films and prints. Photographic emulsions are made of $AgNO_3$, AgCl and AgBr. Parts of the film exposed to light begin to decompose to Ag, thus forming a negative image. The process is enhanced by the developer solution, which is a solution of mild reducing agent, usually containing quinol. Its purpose is to reduce more silver halide from the place where silver atoms are already present. Thus, a developer solution intensifies the latent image on the film so that it becomes visible. After developing, the film or print is put in a solution of hypo which removes unchanged silver salts in the photographic emulsion.

$$Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 + 2NaBr$$

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3[Ag(S_2O_3)_2]$$

The structure of thiosulphate ion is



In laboratory, sodium thiosulphate can be tested by mixing a dilute solution of $Na_2S_2O_3$ with a solution of $AgNO_3$ when a white precipitate which quickly changes colour to yellow, brown and finally black is obtained.

$$\underset{\text{(white precipitate)}}{S_2O_3^{2-} + 2Ag^+ \rightarrow Ag_2S_2O_3} \qquad Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{(black)}}{Ag_2S} + H_2SO_4$$

With concentrated solution of $Na_2S_2O_3$, no such precipitate is formed as $Ag_2S_2O_3$ quickly combines with $Na_2S_2O_3$ to give a soluble complex of $Na_3[Ag(S_2O_3)_2]$.

Hydrogen Sulphide In the laboratory, hydrogen sulphide can be prepared by the action of dilute HCl (or H_2SO_4) on iron(II) sulphide.

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

The gas can be collected over water. It is contaminated with hydrogen produced by the action of HCl on iron which is present as impurity in the sample of ferrous sulphide.

In water, H_2S behaves as a diprotic acid. It is an important precipitating reagent in qualitative analysis.

H_2S is a good reducing agent. A few reactions exhibiting this characteristic are

$$H_2S + X_2 \rightarrow 2HX + S \; ; \qquad (X = Cl, Br, I)$$

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$$

$$2HNO_3 + H_2S \rightarrow 2NO_2 + 2H_2O + S$$

With excess of Cl_2 and HNO_3, sulphur is further oxidized to sulphuric acid.

In an alkaline medium, H_2S gives violet colouration with sodium nitroprusside.

$$Na_2S + Na_2[Fe(NO)(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$$

HALOGENS

Hydrohalic Acids Solutions of hydrogen halides are known as hydrohalic acids. In the gaseous state, hydrogen halides are covalent with the following enthalpy of dissociation.

$$\varepsilon(\text{H—F}) = 566 \text{ kJ mol}^{-1} \qquad \varepsilon(\text{H—Br}) = 366 \text{ kJ mol}^{-1}$$

$$\varepsilon(\text{H—Cl}) = 431 \text{ kJ mol}^{-1} \qquad \varepsilon(\text{H—I}) = 299 \text{ kJ mol}^{-1}$$

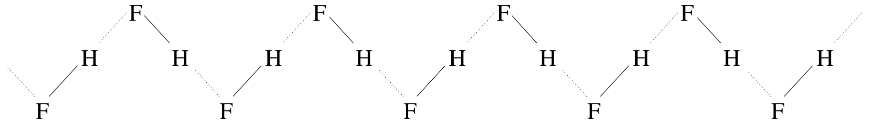
Thus, the strength of hydrogen-halogen bond follows the order. H—F > H—Cl > H—Br > H—I

In water, HCl, HBr, and HI ionize almost completely and are therefore strong acids. HF only ionizes slightly and is therefore a weak acid.

The aqueous solutions form azeotropic mixtures with maximum boiling points, because of a negative deviation from Raoult's law. In lesser ionic solvent, the acid strength of hydrohalic acids follows the order

$$HI > HBr > HCl > HF$$

Of the four hydrogen halides, HF has the highest boiling point due to the hydrogen bonds which persist even in the gaseous phase. In liquid and solid, HF forms zig-zag chains as shown in the following figure.



In the gaseous phase, a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF are formed. HCl, HBr and HI are not hydrogen bonded in the gas and liquid, though HCl and HBr are weakly hydrogen bonded in the solid.

Liquid HF has been used as a non-aqueous solvent. It undergoes self ionization.

$$2HF \rightleftharpoons [H_2F]^+ + F^-$$

Acid-base reactions occur in this solvent system. Mineral acids HNO_3, H_2SO_4 and HCl behave as bases in HF solvent. Perchloric acid behaves as an acid in HF. The fluoride acceptors compounds (SbF_5, NbF_5, AsF_5 and BF_3) also act as acids in HF.

Oxides of Chlorine

1. **Dichlorine monoxide, Cl_2O**

   This is prepared by heating freshly precipitated mercuric oxide with halogen gas diluted with dry air.

   $$2\,Cl_2 + 2\,HgO \xrightarrow{575\text{ K}} HgCl_2{\cdot}HgO + Cl_2O$$

   It is a yellow-brown gas which explodes in the presence of reducing agent or NH_3, on heating

   $$3\,Cl_2O + 10\,NH_3 \rightarrow 6\,NH_4Cl + 2\,N_2 + 3\,H_2O$$

   Cl_2O is acidic anhydride of hypochlorous acid.

   $$Cl_2O + H_2O \rightleftharpoons 2\,HOCl$$

   Cl_2O is angular shape with bond angle ClOCl equal to 111°. The bond length Cl—O is 170 pm. Oxygen in Cl_2O is sp^3 hybridized with two lone pairs of electrons. The increase in bond angle from 109°28′ to 111° is due to the removal of steric crowding of the larger chlorine atoms.

2. **Chlorine dioxide, ClO_2**

   This is prepared in situ and is used after diluting with air or CO_2.

   Laboratory preparation

   $$2\,NaClO_3 + 2(COOH)_2 \xrightarrow[90^\circ C]{H_2O} 2ClO_2 + 2CO_2 + (COONa)_2 + 2H_2O$$

   Commercial Preparation

   $$2\ NaClO_3 + SO_2 + H_2SO_4 \xrightarrow[NaCl]{\text{trace of}} 2ClO_2 + NaHSO_4$$

   $$2\ HClO_3 + 2\ HCl \rightarrow ClO_2 + Cl_2 + 2H_2O$$

ClO_2 is a powerful oxidizing, bleaching and chlorinating agent. It is used for the purification of water and for bleaching purposes.

The ClO_2 is an old electron molecule and is thus paramagnetic. The odd electron is delocalized over the entire molecule and thus ClO_2 does not show any tendency for dimerization.

The bond length Cl—O is 147 pm and it is shorter than for a single bond. This indicates the delocalization of odd electron on the entire molecule.

Dichloro Hexoxide, Cl_2O_6

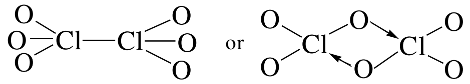
This oxide exists in equilibrium with ClO_3. $Cl_2O_6 \rightleftharpoons 2\ ClO_3$

Cl_2O_6 is made from ClO_2 and O_3. It is a strong oxidizing agent. It undergoes hydrolysis:

$$Cl_2O_6 + H_2O \rightarrow HClO_3 + HClO_4$$

$$Cl_2O_6 + 2\ NaOH \rightarrow NaClO_3 + NaClO_4 + H_2O$$

Its structure is not known. Probable structures are



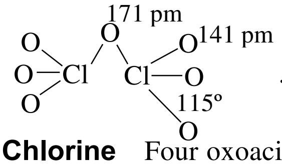
or $ClO_2^+\ ClO_4^-$

Dichlorine heptoxide Cl_2O_7

It is obtained by dehydration of perchloric acid with P_4O_{10}.

$$2\ HClO_4 \xrightarrow[-H_2O]{P_2O_5} Cl_2O_7$$

Its structure is



. Two ClO_4 tetrahedral are linked through an oxygen atom.

Oxoacids of Chlorine Four oxoacids of chlorine are known. These are

Hypochlorous acid, HOCl	Chlorous acid, $HClO_2$
Chloric acid, $HClO_3$	Perchloric acid, $HClO_4$

The structures of these acids are shown in Fig. 15.5.

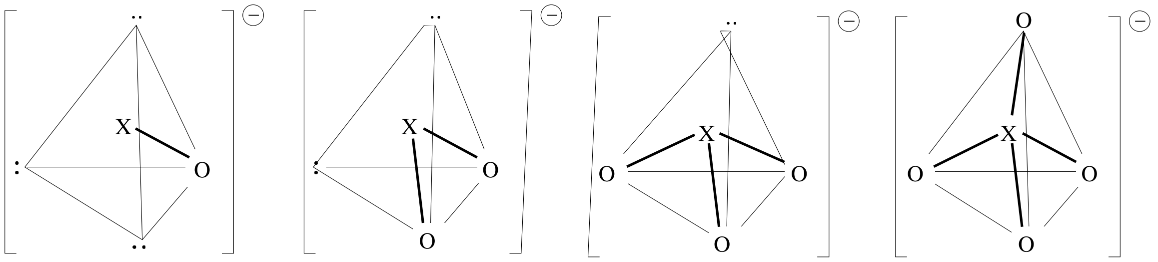


Fig. 15.5 Structures of oxoacids

All the structures shown in Fig. 15.5 are based on a tetrahedron. The sp^3 hybrid orbitals used for bonding form only weak σ bonds because s and p orbitals of chlorine differ appreciably in energy. However, the ions are stabilized by strong pπ-dπ bonding between full 2p orbitals on oxygen with empty d orbitals on the halogen atoms.

Hypochlorous Acid This acid is not very stable, and is known only in aqueous solution. However, its salt sodium hypochlorite (NaOCl) is well known. HOCl can be prepared by shaking chlorine with freshly precipitated HgO in water.

$$2HgO + H_2O + 2Cl_2 \rightarrow HgO \cdot HgCl_2 + 2HOCl$$

The chlorine dissolves in water to some extent, about two-thirds exists as hydrated chlorine and the rest as HCl and HOCl.

HOCl is a weak acid and is an oxidizing agent in acidic medium.

Sodium hypochlorite is extensively used for bleaching cotton fabric. It is also used as a disinfectant and sterilizing agent. Commercially, it is prepared by electrolysing cold brine with vigorous stirring. During electrolysis hydrogen is liberated at the cathode. This increases the concentration of OH^- in the solution. The stirring mixes Cl_2, which is produced at the anode, with OH^- ions

$$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$$

Hypohalite ions disproportionate in solution, particularly in basic solution. The rate of disproportionation reaction increases with temperature.

$$3OCl^- \xrightarrow[hot]{} 2Cl^- + ClO_3^-$$

Chlorous Acid This acid exists only in solution. It is a weak acid, but is stronger than HOCl.

$HClO_2$ is made by treating barium chlorite with H_2SO_4.

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HClO_2$$

Salts of $HClO_2$ are called chlorites, and are made either from ClO_2 and sodium hydroxide or ClO_2 and sodium peroxide.

$$2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$$

$$2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2$$

In alkaline medium, chlorites are stable but in acidic medium they disproportionate, particularly when heated

$$4HClO_2 \rightarrow 2ClO_2 + HCl + HClO_3 + H_2O$$

Chloric Acid $HClO_3$ is made by treating barium chlorate with H_2SO_4.

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow 2HClO_3 + BaSO_4\downarrow$$

$HClO_3$ is not very stable, but is known in solution as its salt. If heated to dryness, the acid decomposes as

$$4HClO_3 \rightarrow 4ClO_2 + 2H_2O + O_2$$

The salts chlorate may be made either passing Cl_2 in a hot solution of NaOH or electrolysing hot chloride solutions that are vigorously stirred.

$$6NaOH + 3Cl_2 \xrightarrow{80°C} NaClO_3 + 5NaCl + 3H_2O$$

Perchloric Acid $HClO_4$ may be prepared based on the following reactions.

$$NaClO_4 + H_2SO_4 \xrightarrow{\qquad} NaHSO_4 + \underset{\text{distilled under reduced pressure}}{HClO_4}$$

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$

Hot, concentrated perchloric acid can explode in the presence of slight amount of reducing agents, especially organic reducing agents. Hot $HClO_4$ solutions are strong oxidizing agent. Perchloric acid is the strongest amongst the all four oxoacids of chlorine.

The strengths of oxoacids follow the order $HClO_4 > HClO_3 > HClO_2 > HOCl$

This is due to the fact that in the series HOCl, $HClO_2$, $HClO_3$, $HClO_4$, an increasing number of oxygen atoms are bonded to the chlorine atom. The more oxygen atoms that are bonded, the more the electrons will be pulled away from the O—H bond (as oxygen is more electronegative than phosphorus), and thus more this bond will be weakend. Hence, $HClO_4$ requires the least energy to break the O—H bond and HClO requires the maximum energy. Hence, $HClO_4$ is the strongest acid while HClO is the weakest acid.

Bleaching Powder It is obtained by the interaction of chlorine and dry slaked lime.

$$Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)Cl + H_2O$$

Bleaching powder is a mixture of calcium hypochlorite, $Ca(OCl)_2$ and the basic chloride, $CaCl_2\cdot Ca(OH)_2\cdot H_2O$. A commercial sample of bleaching powder is evaluated from its available chlorine which is liberated when treated with acid.

$$Cl^- + OCl^- + 2H^+ \rightarrow H_2O + Cl_2$$

The liberated Cl_2 is estimated iodometrically.

$$Cl_2 + 2KI \rightarrow 2KCl + I_2; \qquad 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Bleaching powder is extensively used as a disinfectant, as a bleaching agent for paper pulp, cotton and linen goods.

Xenon Fluorides Based on the fact that PtF_6 can oxidise O_2 and the fact that the ionisation energy of O_2 to give O_2^+ is nearly the same as that of xenon ($Xe \rightarrow Xe^+ + e^-$), it was though that PtF_6 should also be able to oxidise Xe:

$$PtF_6 + O_2 \rightarrow O_2^+[PtF_6]^-; \qquad PtF_6 + Xe \rightarrow Xe^+[PtF_6]^-$$

In 1962, N. Bartlett prepared a yellow-red powder corresponding to $Xe^+\ PtF_6^-$. Followed by this reaction, fluoro compounds of xenon were prepared by the interaction of xenon and fluorine. The product obtained depends on the temperature, pressure and mixing ratio of the constituents. Thus,

$$Xe + F_2 \xrightarrow[675\ K]{\text{sunlight or}} XeF_2 \qquad Xe + 2F_2 \xrightarrow[6\times10^5\ Pa]{675\ K} XeF_4$$

(2:1 volume mixture) (1:5 volume mixture)

$$Xe + 3F_2 \xrightarrow[50-60\times10^5\ Pa]{575-675\ K} XeF_6$$

(1:20 volume mixture)

In XeF_2, there are five pairs of electrons around Xe and thus its geometry is trigonal bipyramidal. The fluorine atoms occupy linear positions while the three lone pairs occupy equatorial positions. Thus, XeF_2 is a linear molecule (Fig. 15.6).

In XeF_4, there are six pairs of electrons around Xe and thus its geometry is octahedral. The fluorine atoms occupy the positions in the plane giving a square planar molecule. Two lone pairs are perpendicular to this plane (Fig. 15.7).

In XeF_6, there are seven pairs of electrons around Xe and thus its geometry is distorted octahedron (Fig. 15.8).

The structure of oxygen containing compounds of Xe are as follows.

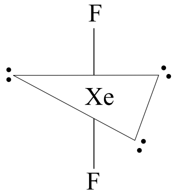


Fig. 15.6 Structure of XeF_2

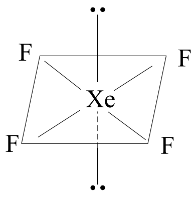


Fig. 15.7 Structure of XeF_4

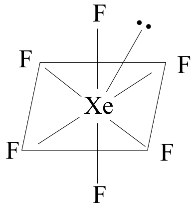


Fig. 15.8 Structure of XeF_6

The above structures can be explained on the basis VSEPR theory.

Xenon fluorides are oxidising and fluorinating agents. Some of the reactions are as follows.

$XeF_2 + H_2 \rightarrow 2HF + Xe$

$XeF_4 + 2H_2 \rightarrow 4HF + Xe$

$XeF_6 + 3H_2 \rightarrow 6HF + Xe$

$XeF_2 + 2HCl \rightarrow 2HF + Xe + Cl_2$

$XeF_4 + 4KI \rightarrow 4KF + Xe + 2I_2$

$SO_4^{2-} + XeF_2 + Ce_2(SO_4)_3 \rightarrow 2Ce(SO_4)_2 + Xe + F_2$

$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_6$

$XeF_4 + Pt \rightarrow Xe + PtF_4$

$XeF_4 + C_6H_6 \rightarrow Xe + C_6H_5F + HF$

Xenon fluorides also undergo hydrolysis reactions.

$2XeF_2 + 2H_2O \rightarrow 2Xe + 4\ HF + O_2$ (slow reaction)

$3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + (3/2)O_2$ (violent reaction)

$XeF_6 + 6H_2O \rightarrow XeO_3 + 6HF$ (violent reaction)

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

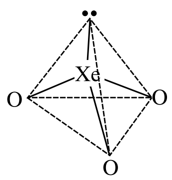
(small quantity)

The compound $XeOF_4$ is obtained when XeF_6 reacts with SiO_2. $2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$

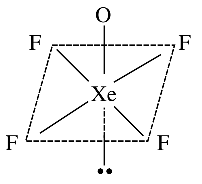
Xenon fluoride acts as a fluoride donor and forms complexes with covalent pentafluorides (PF_5, AsF_5, SbF_5, transition metal pentafluorides). Their structure are

$XeF_2\cdot MF_5$	$[XeF]^+\ [MF_6]^-$;	$XeF_2\cdot 2MF_5$	$[XeF]^+\ [M_2F_{11}]^-$
$2XeF_2\cdot MF_5$	$[Xe_2F_3]^+\ [MF_6]^-$		

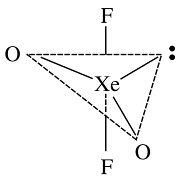
The structures of XeO_3, $XeOF_4$, XeO_2F_2, XeO_6 and XeO_4 are as follows.



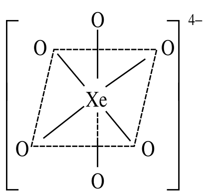
XeO_3; Pyramidal



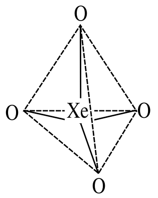
$XeOF_4$; Square pyramidal



XeO_2F_2



$[XeO_6]^{4-}$



XeO_4; Tetrahedral

INTERHALOGENS

The halogens react with each other forming the following types of interhalogen compounds.

Type AX : ClF, BrF, BrCl, ICl, IBr, IF (unstable)

Type AX_3 : ClF_3, BrF_3, $(ICl_3)_2$, IF_3 (unstable)

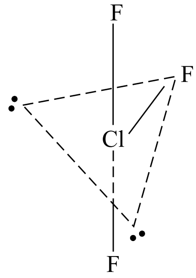
Type AX_5 : ClF_5, BrF_5, IF_5

Type AX_7 : IF_7

Because of the small difference in the electronegativity values, interhalogens involve covalent bonding. Compare to halogens, these bondings are weak resulting more reactivity to interhalogens. The order of reactivity is

$$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF > IF_3 > IF$$

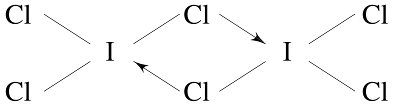
The structures of ClF_3 and BrF_3 are T-shaped with sp^3d hybridization. The trigonal bipyramid is not regular due to lone pair-lone pair repulsion.



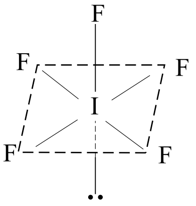
FClF bond angle is 87° 40°
Equatorial bond length 159.8 pm
Apical bond lengths 169.8 pm

$(ICl_3)_2$ in the liquid form exists as $(ICl_3)_2 \rightleftharpoons ICl_2^+ + ICl_4^-$ resulting enhanced conductivity.

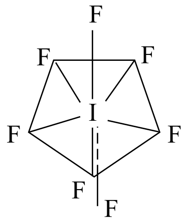
In the solid state it exists as



The structure of AX_5 is squared based pyramid with sp^3d^2 hybridization.



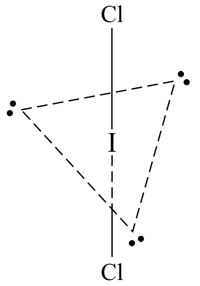
The structure of IF_7 is based on pentagonal bipyramide.



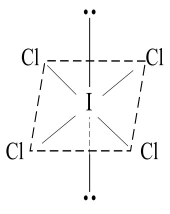
POLYHALIDES

Halids ions often react with molecules of halogens forming polyhalides. Examples are $K[I_3]$, $K[ICl_2]$, $K[ICl_4]$, $K[BrF_4]$, $Cs[IBrF]$, $K[IF_6]$ and $K[IBrCl]$.

The structures of $[ICl_2]^-$ and $[ICl_4]^-$ are:



Linear shape



Square planaar

PSEUDOHALOGENS

A few ions are known which show properties similar to those of halide ions. These are known as pseudohalide ions. A few examples are CN^-, SCN^-, $SeCN^-$, OCN^-, NCN^{2-}, ONC^- and N_3^-. The best known example is CN^-.

Straight Objective Type

Compounds of Boron

1. The molecular formula of nido-boranes is given by

(a) B_nH_{n+2} (b) B_nH_{n+4} (c) B_nH_{n-2} (d) B_nH_{n+6}

2. The molecular formula of arachno-boranes is given by

(a) B_nH_{n+2} (b) B_nH_{n+4} (c) B_nH_{n-2} (d) B_nH_{n+6}

3. Which of the following statements regarding diborane is **not** correct?

(a) Diborane is a colourless gas (b) It is least reactive gas

(c) It is hydrolysed by water (d) It combines with oxygen to give B_2O_3

4. The product obtained in the reaction between diborane and excess of ammonia at low temperature is

(a) $B_2H_6 \cdot NH_3$ (b) $B_2H_6 \cdot 2NH_3$ (c) $(BN)_x$ (d) Borazine

5. The product obtained in the reaction of diborane with excess of ammonia at higher temperatures is

(a) $B_2H_6 \cdot NH_3$ (b) $B_2H_6 \cdot 2NH_3$ (c) $(BN)_x$ (d) Borazine

6. If the ratio of B_2H_6 and NH_3 is 1:2, then the product obtained at higher temperature is

(a) $B_2H_6 \cdot NH_3$ (b) $B_2H_6 \cdot 2NH_3$ (c) $(BN)_x$ (d) Borazine

7. In diborane, boron involves

(a) no hybridization (b) sp hybridization (c) sp^2 hybridization (d) sp^3 hybridization

8. Which of the following facts regarding boric acid is **not** correct?

(a) Boric acid is a strong monobasic acid

(b) Boric acid does not donate proton but accepts OH^-

(c) Phenolphthalein can be used as the indicator in the titration between boric acid and sodium hydroxide in the presence of glycerol

(d) Boron atom in boric acid is sp^2 hybridized.

9. Which of the following statements regarding borax is **not** correct?

(a) The molecular formula of borax is $Na_2B_4O_7 \cdot 10H_2O$

(b) In borax, two of the boron atoms are sp^2 hybridized and the rest of two atoms are sp^3 hybridized

(c) Borax is used as a primary standard in the acid-base titrations

(d) Phenolphthalein can be used as the indicators in the titration between borax and sodium hydroxide.

10. Which of the following statements regarding diborane is correct?

(a) Diborane is a planar molecule

(b) All bond lengths B—H are of the same length

(c) Terminal B—H is 2c-2e bond while bridged B—H is 3c–2e bond

(d) Terminal B—H is 3c-2e bond while bridged B—H is 2c–2e bond.

11. Boric acid is a

(a) weak monobasic Lewis acid

(b) weak monobasic Arrhenius acid only

(c) weak monobasic Bronsted acid only

(d) weak monobasic Arrhenius as well as Bronsted acid.

12. In the presence of which of the following species, boric acid can be titrated against sodium hydroxide solution?

(a) *trans*-1, 2-diol (b) *cis*-1, 2-diol

(c) Borax (d) Sodium hydrogen phosphate (2006)

13. Which of the following statements regarding borax is not true?
(a) Borax may be used as a primary standard to standardize acids.
(b) The indicator used in the titration of borax solution with HCl solution is phenolphthalein.
(c) Equivalent mass of borax in its titration with HCl solution is molar mass divided by two.
(d) Borax involves two triangular BO_3 units and two tetrahedral BO_4.

14. Which of the following boron halides does not produce boric acid on hydrolysis?
(a) BF_3 (b) BCl_3 (c) BBr_3 (d) BI_3

15. Boron halides act as Lewis acid. The correct order of acid strength is
(a) $BF_3 > BCl_3 > BBr_3$ (b) $BF_3 > BBr_3 > BCl_3$
(c) $BBr_3 > BF_3 > BCl_3$ (d) $BBr_3 > BCl_3 > BF_3$

16. BF_3 forms a tetrahedral complex with the compounds which can donate lone pair of electrons. The bond length B—F in BF_3 is
(a) equal to that existing in the tetrahedral complex
(b) greater than that existing in the tetrahedral complex
(c) smaller than that existing in the tetrahedral complex
(d) greater than or smaller than or equal to that existing in tetrahedral complex depending upon the nature of the electron-donor compound.

17. Inoraganic benzene refers to the compound
(a) boron nitride (b) borazine (c) graphite (d) $H_3N \rightarrow BF_3$

18. Which of the following amines has little tendency to show the reaction $B_2H_6 + 2X \rightarrow [BH_2(X)_2]^+ [BH_4^-]$
(a) NH_3 (b) CH_3NH_2 (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

Compounds of Carbon

19. Among the following, the molecule that is linear is
(a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2 (1982)

20. Carbon monoxide with nickel powder gives
(a) NiCO (b) $Ni(CO)_2$ (c) $Ni(CO)_3$ (d) $Ni(CO)_4$

21. Which of the following statements regarding carbon monoxide is correct?
(a) It involves sp orbitals of carbon (b) It contains a lone pair only on carbon
(c) It contains a lone pair only on oxygen (d) In carbonyl, oxygen end is attached to the metal atoms

22. Which of the following compounds is an ionic carbide?
(a) Al_4C_3 (b) SiC (c) MoC (d) Cr_3C

23. Which of the following compounds is a covalent carbide?
(a) Al_4C_3 (b) SiC (c) MoC (d) Cr_3C

24. Which of the following compounds is an interstitial carbide?
(a) Al_4C_3 (b) SiC (c) B_4C_3 (d) MoC

25. Which of the following carbides is a methanide?
(a) Be_2C (b) CaC_2 (c) Al_2C_6 (d) Mg_2C_3

26. Which of the following carbides is an acetylides?
(a) Be_2C (b) Al_4C_3 (c) CaC_2 (d) Mg_2C_3

27. Which of the following carbides is an allylides?
(a) Be_2C (b) Al_4C_3 (c) CaC_2 (d) Mg_2C_3

28. Which of the following carbides represents carborundum?
(a) SiC (b) B_4C_3 (c) TiC (d) MoC

29. The number and type of bonds between two carbon atoms in CaC_2 are
(a) one sigma (σ) and one pi (π) bond
(b) one sigma (σ) and two pi (π) bonds
(c) one sigma (σ) and one and a half pi (π) bonds
(d) one sigma (σ) bond (1996)

Compounds of Silicon

30. Which of the following statements is correct?
(a) All compounds of silicon are collectively known as silicones
(b) Silicon hydrides are known as silicones
(c) Silicon halides are known as silicones
(d) Silicones are polymeric organosilicon compounds

31. Which of the following statements regarding silicones is **not** correct?
(a) Silicones have good thermal stability
(b) Liquid silicones are lubricants
(c) Silicones are chemical inert substances
(d) Silicone rubber is not attack by ordinary chemical reagents except ozone

32. The structure of orthosilicates involves
(a) the discrete SiO_4^{4-} tetrahedra
(b) the sharing of one oxygen atom between two SiO_4^{4-} tetrahedra
(c) the sharing of two oxygen atoms of one SiO_4^{4-} tetrahedra with two other tetrahedra
(d) the sharing of three oxygen atoms of one SiO_4^{4-} tetrahedron with three other tetrahedra

33. The structure of pyrosilicates involves
(a) the discrete SiO_4^{4-} tetrahedra
(b) the sharing of one oxygen atom between two SiO_4^{4-} tetrahedra
(c) the sharing of two oxygen atoms of one SiO_4^{4-} tetrahedron with two other tetrahedra
(d) the sharing of three oxygen atoms of one SiO_4^{4-} tetrahedron with three other tetrahedra

34. The silicates having chain and cyclic structures involve
(a) the discrete SiO_4^{4-} tetrahedra
(b) the sharing of one oxygen atom between two SiO_4^{4-} tetrahedra
(c) the sharing of two oxygen atoms of one SiO_4^{4-} tetrahedron with two other tetrahedra
(d) the sharing of three oxygen atoms of one SiO_4^{4-} tetrahedron with three other tetrahedra

35. The silicates having layer and sheet structures involves
(a) the discrete SiO_4^{4-} tetrahedra
(b) the sharing of one oxygen atom between two SiO_4^{4-} tetrahedra
(c) the sharing of two oxygen atoms of one SiO_4^{4-} tetrahedron with two other tetrahedra
(d) the sharing of three oxygen atoms of one SiO_4^{4-} tetrahedron with three other tetrahedra

36. The basic unit in orthosilicates is
(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $(SiO_3)_n^{2n-}$ (d) $(Si_2O_5)_n^{2n-}$

37. The basic unit in pyrosilicates is
(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $(SiO_3)_n^{2n-}$ (d) $(Si_2O_5)_n^{2n-}$

38. The basic unit in chain and cyclic silicates is
(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $(SiO_3)_n^{2n-}$ (d) $(Si_2O_5)_n^{2n-}$

39. The basic unit in layer and sheet silicates is
(a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $(SiO_3)_n^{2n-}$ (d) $(Si_2O_5)_n^{2n-}$

40. In three-dimensional silicates, the number of oxygen atoms per SiO_4^{4-} tetrahedron is
(a) one (b) two (c) three (d) four

41. $(CH_3)_2SiCl_2$ on hydrolysis produces
(a) $(CH_3)_2Si(OH)_2$ (b) $(CH_3)_2Si = O$
(c) $[O—(CH_3)_2Si—O]_n$ (d) $(CH_3)_2SiCl(OH)$ (2003)

42. Which of the following silicates is formed when three oxygen atoms of SiO_4^{4-} tetrahedral units are shared?
(a) Pyrosilicates (b) Cyclic silicates
(c) Linear chain silicates (d) Sheet silicates (2005)

43. The chemical used to stop the grow of polymerization of linear polymer formed from the hydrolysis of R_2SiCl_2 is
(a) R_3SiCl (b) R_4Si (c) $SiCl_3$ (d) $SiCl_2$

Compounds of Nitrogen

44. Nitrogen dioxide cannot be obtained by heating
(a) KNO_3 (b) $Pb(NO_3)_2$ (c) $Cu(NO_3)_2$ (d) $AgNO_3$ (1985)

45. Which of the following oxides of nitrogen is a coloured gas?
(a) N_2O (b) NO (c) N_2O_4 (d) NO_2 (1987)

46. Amongst the trihalides of nitrogen, the least basic is
(a) NF_3 (b) NCl_3 (c) NBr_3 (d) NI_3 (1988)

47. Which one of the following is the strongest base?
(a) AsH_3 (b) NH_3 (c) PH_3 (d) SbH_3 (1989)

48. Amongst the oxides of nitrogen, the neutral oxide is
(a) N_2O_5 (b) N_2O (c) N_2O_3 (d) NO_2

49. Nitrosonium ion is isoelectronic with
(a) NO (b) CO (c) NO_2 (d) CO_2^+

50. The oxide of nitrogen isoelectronic with CO_2 is
(a) NO (b) N_2O_3 (c) NO_2^+ (d) N_2

51. Highest oxidation state of nitrogen is achieved in
(a) nitrogen dioxide (b) dinitrogen trioxide
(c) dinitrogen tetroxide (d) dinitrogen pentoxide

52. In the brown ring test of nitrate ion, the compound formed is
(a) $[Fe(H_2O)_5(NO)]^{2+}$ (b) $[Fe(H_2O)_5NO]^{3+}$ (c) $[Fe(H_2O)_4(NO)_2]^{2+}$ (d) $[Fe(H_2O)_3(NO)_3]^{2+}$

53. Which of the following equations is **not** correctly formulated?
(a) Concentrated HNO_3 acquires a yellow coloration due to the reaction

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$$

(b) $Cu + \underset{\text{dilute}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
(c) $4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$
(d) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 4H_2O + 20NO_2$

54. Which of the following statements regarding nitrous oxide is **not** correct?
(a) The solubility of N_2O is more in cold solution as compared to a hot solution
(b) The solubility of N_2O is more in hot solution as compared to a cold solution
(c) The gas N_2O is known as laughing gas
(d) Nitrous oxide mixed with oxygen is used as anaesthetic

55. Which of the following statements regarding nitrous oxide is **not** correct?
(a) Nitrous oxide supports the combustion of phosphorus and sulphur
(b) Nitrous oxide is reduced to nitrogen when passed over hot copper
(c) Nitrous oxide is a bent molecule with the arrangement of atoms as NON
(d) Nitrous oxide is a linear molecule with the arrangement of atoms as NNO.

56. Which of the following statements regarding nitric oxide is **not** correct?
(a) Nitric oxide is a colourless gas
(b) Sulphurous acid converts nitric oxide to nitrogen dioxide
(c) Nitric oxide is paramagnetic in nature
(d) Nitric oxide is a neutral oxide

57. Which of the following statements regarding nitric oxide is **not** correct?
(a) Nitric oxide dimerizes under ordinary conditions
(b) The bond order of nitrosonium ion is 3
(c) There is a decrease in nitrogen-oxygen bond length in going from NO to NO^+
(d) In nitrosyls, nitric oxide is attached to the metal through nitrogen atom

58. Which of the following statements regarding nitrogen sesquioxide is **not** correct?
(a) Nitrogen sesquioxide is stable only in the liquid state. It dissociates in the vapour phase
(b) Dinitrogen sesquioxide is a neutral oxide
(c) Dinitrogen sesquioxide contains a weak N—N bond
(d) Dinitrogen sesquioxide exists in two different crystalline forms.

59. Which of the following oxides of nitrogen is a white solid?
(a) NO (b) NO_2 (c) N_2O_3 (d) N_2O_5

60. Which of the following statements regarding nitrogen dioxide is **not** correct?
(a) Nitrogen dioxide is a paramagnetic substance
(b) Solid nitrogen dioxide is brown in colour
(c) Nitrogen dioxide readily dimerizes to dinitrotetroxide
(d) Nitrogen dioxide is a mixed anhydride

61. Which of the following statements regarding nitrogen dioxide is **not** correct?
(a) The moist NO_2 is strongly acidic
(b) Dimerized nitrogen dioxide is paramagnetic
(c) Nitrogen dioxide is an angular molecule with O—N—O bond angle equal to 132°
(d) Nitrogen dioxide has two resonating structures

62. Which of the following statements regarding N_2O_4 is **not** correct?
(a) The molecule of N_2O_4 is planar (b) The molecule of N_2O_4 contains weak N—N bond
(c) In liquid N_2O_4, NOCl acts as a base (d) The dipole moment of N_2O_4 is zero

63. Which of the following statements regarding nitrogen pentoxide is **not** correct?
(a) Nitrogen pentoxide is a colourless, deliquescent solid
(b) Nitrogen pentoxide is the anhydride of nitric acid
(c) Solid N_2O_5 is a covalent molecule
(d) The molecule of N_2O_5 is planar

64. Which of the following statements is **not** correct?
(a) Nitrous acid is unstable except in dilute solution
(b) In the oxidation reaction with nitrous acid, the latter is reduced to either N_2O or NO
(c) Nitrous acid gives stable salt with members of Group 1
(d) Nitrite ions has a linear structure

65. Which of the following statements is **not** correct?
(a) Pure nitric acid is a light yellow liquid
(b) Nitric acid with water forms an azeotropic mixture containing 98% of acid
(c) Nitric acid when mixed with concentrated H_2SO_4 produces nitronium ion
(d) Covalent nitrates are less stable than ionic nitrates

66. Which of the following equations is **not** correctly formulated?
(a) $3Cu + \underset{\text{(dilute)}}{8HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
(b) $3Zn + \underset{\text{(v.dilute)}}{8HNO_3} \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$
(c) $4Sn + \underset{\text{(dilute)}}{10HNO_3} \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
(d) $As + \underset{\text{(dilute)}}{3HNO_3} \rightarrow H_3AsO_3 + 3NO_2$

67. Which of the following equations is **not** correctly formulated?
(a) $Cu + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(b) $Zn + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$
(c) $Sn + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Sn(NO_3)_2 + 2H_2O + 2NO_2$
(d) $As + \underset{\text{(conc.)}}{5HNO_3} \xrightarrow{\text{hot}} H_3AsO_4 + 5NO_2 + H_2O$

68. Ammonia can be dried by
(a) concentrated H_2SO_4 (b) P_4O_{10} (c) CaO (d) anhydrous $CuSO_4$
(2000)

69. The volume of ammonia gas obtained when 6 dm^3 of H_2 reacts with excess of nitrogen (all volumes measured at STP) would be
(a) 2 dm^3 (b) 3 dm^3 (c) 4 dm^3 (d) 6 dm^3

70. With excess of Cl_2, ammonia forms
(a) NH_4Cl (b) N_2 (c) NCl_3 (d) $NH_3 \cdot NCl_3$

71. Which of the following hydrides is most stable?
(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3

72. Concentrated nitric acid oxidizes iodine to
(a) HI (b) HIO_3 (c) HIO_4 (d) I_2O_7

73. Which of the following statements regarding ammonia is **not** correct?
(a) Low temperatures and high pressure favour the formation of ammonia
(b) The hydrolysis of calcium cyanamide with superheated steam produces ammonia
(c) Aqueous ammonia is ammonium hydroxide
(d) Ammonia is oxidized to nitrogen when passed over heated CuO

74. Which of the following statements regarding ammonia is **not** correct?
(a) The formation of ammonia is an exothermic reaction
(b) Haber's process of manufacturing ammonia involves the use of a catalyst of pure iron mixed with a promoter like alumina and potassium oxide
(c) The burning of ammonia produces NO_2 and water
(d) Ammonium salt in liquid ammonia acts as a strong acid

75. Which of the following equations is **not** correctly formulated?
(a) $2Na + 2NH_3 \xrightarrow[\text{heat}]{} 2NaNH_2 + H_2$
(b) $8NH_3 + 3Cl_2 \xrightarrow[\text{excess}]{} N_2 + 6NH_4Cl$
(c) $NH_3 + 3Cl_2 \xrightarrow[\text{excess}]{} NCl_3 + 3HCl$
(d) $4NH_3 + 2NaOCl \xrightarrow[\text{glue}]{} 2NH_4Cl + 2NaNH_2 + O_2$

76. Aqua regia is
(a) 3 parts concentrated HNO_3 + 1 part concentrated HCl
(b) 1 part concentrated HNO_3 + 3 parts concentrated HCl
(c) 2 parts concentrated HNO_3 + 2 parts concentrated HCl
(d) 1 part concentrated HNO_3 + 2 parts concentrated HCl

77. Among the following species, identify the isostructural pairs.
(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$ (b) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$ (d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$ (1996)

78. Ammonia, on reaction with hypochlorite anion, can form
(a) NO (b) NH_4Cl (c) N_2H_4 (d) HNO_2 (1999)

79. The hybridization of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+, respectively, are
(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

80. Dehydration of concentrated HNO_3 with phosphorus pentoxide at low temperature produces
(a) NO (b) N_2O (c) NO_2 (d) N_2O_5

81. A pale blue liquid obtained by equimolar mixture of two gases at – 30°C is
(a) nitric oxide (b) nitrogen trioxide (c) nitrogen tetroxide (d) nitrogen pentoxide

82. Which of the following oxides of nitrogen is a mixed anhydride?
(a) N_2O (b) NO (c) N_2O_4 (d) N_2O_5

83. Which of the following oxides of nitrogen is a neutral oxide?
(a) NO (b) N_2O_3 (c) NO_2 (d) N_2O_5

84. Which of the following oxides of nitrogen is mixed oxide?
(a) NO (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

85. Heating a solution of NH_4NO_3 acidified with HCl produces
(a) NO (b) N_2O (c) NO_2 (d) N_2O_3

86. Which of the following statements regarding N_2O_4 is **not** correct?
(a) It is a planar molecule
(b) It is used as nonaqueous solvent
(c) It involves N—N bond which is shorter than the N—N bond in hydrazine.
(d) NOCl in N_2O_4 acts as on acid.

87. Which of the following order regarding bond angle O—N—O in the following species is correct?
(a) $NO_2^+ > NO_2 > NO_2^-$ (b) $NO_2^+ < NO_2 > NO_2^-$
(c) $NO_2^+ > NO_2 < NO_2^-$ (d) $NO_2^+ < NO_2 < NO_2^-$

88. Of the following statements regarding hydrazine, which one is **not** correct?
(a) It is a monofunctional base
(b) Anhydrous N_2H_4 is a fuming colourless liquid.
(c) The enthalpy of formation of hydrazine is positive
(d) Aqueous solution of hydrazine is powerful reducing agent in basic solution.

89. Of the following statements regarding dinitrogen trioxide, which one is **not** correct?
(a) It is an anhydride of nitrous acid (b) In liquid form, it has intense blue colour
(c) The stable form has a stronger N—N bond (d) It readily dissociates to give NO and NO_2.

Compounds of Phosphorus

90. Phosphorous acid has
(a) one hydrogen atom attached to phosphorus (b) two hydrogen atoms attached to phosphorus
(c) three hydrogen atoms attached to phosphorus (d) no hydrogen atom attached to phosphorus

91. Distillation of concentrated HNO_3 with phosphorus pentaoxide produces
(a) NO (b) N_2O (c) NO_2 (d) N_2O_5

92. Which of the following statements regarding phosphorus trioxide is **not** true?
(a) It dimerizes in naphthalene and not in the vapour phase
(b) With cold nitric acid, it produces phosphorous acid
(c) With hot nitric acid, it produces phosphoric acid
(d) The P—O bond in phosphorus trioxide is shorter than the expected single bond distance

93. Which of the following statements regarding phosphorus tetroxide is **not** correct?
(a) Phosphorus tetroxide is a mixed anhydride
(b) It is obtained by heating trioxide in a sealed tube at 440 °C
(c) It produces phosphoric acid when treated with water
(d) Two of the phosphorus atoms in P_4O_8 are attached to oxygen through coordinate bonds

94. Which of the following statements regarding phosphorus pentoxide is **not** correct?
(a) It is an anhydride of metaphosphoric acid
(b) It is a strong dehydrating agent
(c) In phosphorus pentoxide, each phosphorus is attached to three oxygen atoms and also with another oxygen atom through coordinate bond
(d) The dehydrated product of HNO_3 obtained by treating with phosphorus pentoxide is nitrogen dioxide

95. Hypophosphorous acid is
(a) monobasic (b) dibasic (c) tribasic (d) neutral

96. Hypophosphorous acid contains
(a) one hydrogen attached to P (b) two hydrogen atoms attached to P
(c) three hydrogen atoms attached to P (d) no hydrogen attached to P

97. Orthophosphorous acid is
(a) monobasic (b) dibasic (c) tribasic (d) neutral

98. The number of hydrogen atoms attached to phosphorus in orthophosphorus acid is
(a) one (b) two (c) three (d) zero

99. Which of the following statements regarding orthophosphorous acid is **not** correct?
(a) It is produced by dissolving P_4O_6 in cold water
(b) It disproportionates on heating giving orthophosphoric acid and phosphine
(c) It is a strong oxidizing agent
(d) It is a dibasic acid

100. The number of hydrogen atoms attached to each phosphorus atoms in pyrophosphorous acid is
(a) one (b) two (c) three (d) none

101. Pyrophosphorous acid has the molecular formula
(a) H_3PO_3 (b) H_3PO_4 (c) $H_4P_2O_5$ (d) $H_4P_2O_7$

102. Pyrophosphorous acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

103. Hypophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

104. The number of hydrogen atoms attached to each phosphorus atom in hypophosphoric acid is
(a) zero (b) one (c) two (d) three

105. Orthophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

106. The number of hydrogen atoms attached to phosphorus atom in orthophosphoric acid is
(a) zero (b) one (c) two (d) three

107. Which of the following equations is **not** correctly formulated?
(a) $P_4O_{10} + 6H_2O \underset{\text{cold}}{\rightarrow} 4H_3PO_3 + 2O_2$
(b) $P_4 + 20HNO_3 \xrightarrow{I_2} 4H_3PO_4 + 20NO_2 + 4H_2O$
(c) $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
(d) $Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow[\text{heat}]{} 3CaSO_4 + 2H_3PO_4$

108. The formula of pyrophosphoric acid is
(a) H_3PO_3 (b) H_3PO_4 (c) $H_4P_2O_5$ (d) $H_4P_2O_7$

109. Pyrophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

110. Which of the following statements regarding pyrophosphoric acid is **not** correct?
(a) It is obtained by heating equimolar mixture of ortho- and meta-phosphoric acid at 100 °C
(b) On boiling with water, it produces orthophosphoric acid
(c) On strong heating, it produces metaphosphoric acid
(d) It forms four series of salts, e.g. $NaH_3P_2O_7$, $Na_2H_2P_2O_7$, $Na_3HP_4O_7$ and $Na_4P_2O_7$

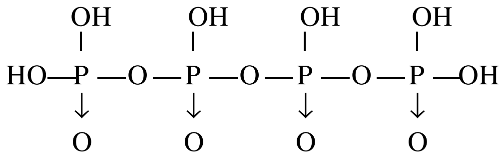
111. The number of hydrogen atoms attached to each phosphorus atom in pyrophosphoric acid is
(a) zero (b) one (c) two (d) three

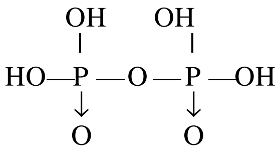
112. Which of the following statements regarding metaphosphoric acid is **not** correct?
(a) It is also known as glacial phosphoric acid
(b) It is a transparent liquid
(c) It is a monobasic acid
(d) It produces orthophosphoric acid on treating with water

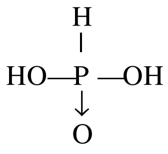
113. Which of the following represents metaphosphoric acid?
(a) HPO_3 (b) H_3PO_3 (c) H_3PO_4 (d) $H_4P_2O_7$

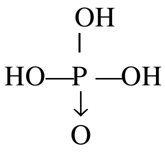
114. The anhydride of orthophosphorous acid is
(a) P_4O_6 (b) P_4O_8 (c) P_4O_{10} (d) P_2O_4

115. Which of the following oxoacids of phosphorus is reducing in character?

(a) 
$HO{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}O{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}O{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}O{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}OH$

(b) 
$HO{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}O{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}OH$

(c) 
$HO{-}\overset{H}{\underset{\substack{\downarrow\\O}}{P}}{-}OH$

(d) 
$HO{-}\overset{OH}{\underset{\substack{\downarrow\\O}}{P}}{-}OH$

116. One mole of calcium phosphide on reaction with excess water gives
(a) one mole of phosphoric acid (b) two moles of phosphoric acid
(c) two moles of phosphine (d) one mole of phosphorus pentoxide (1999)

117. The number of P—O—P bonds in cyclic metaphosphoric acid is
(a) zero (b) two (c) three (d) four (2000)

118. Polyphosphates are used as water softening agents because they
(a) form soluble complexes with anionic species (b) precipitate anionic species
(c) form soluble complexes with cationic species (d) precipitate cationic species (2002)

119. Which of the following statements is correct?
(a) H_3PO_3 is dibasic and reducing (b) H_3PO_3 is tribasic and reducing
(c) H_3PO_3 is tribasic and nonreducing (d) H_3PO_3 is dibasic and nonreducing (2003)

120. The reaction of P_4 with X leads selectively to P_4O_6. The X is
(a) Dry O_2 (b) A mixture of O_2 and N_2
(c) Moist O_2 (d) O_2 in the presence of aqueous NaOH (2009)

121. Which of the following statements regarding P_4O_{10} is **not** correct?
(a) Each P atom is bonded to four O atoms.
(b) P atoms are arranged tetrahedrally with respect to each other.
(c) Each P—O bond has identical bond length.
(d) Each P is bonded to one O atom with considerable pπ-dπ back bonding.

Compounds of Oxygen

122. Heavy water is
(a) $H_2^{18}O$ (b) Water obtained by repeated distillation
(c) D_2O (d) Water at 4 °C (1983)

123. The volume strength of 0.75 M H_2O_2 solution is
(a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0 (1991)

124. The maximum possible number of hydrogen bonds a water molecule can form is
(a) 2 (b) 4 (c) 3 (d) 1 (1992)

125. Which of the following equations depicts the oxidizing nature of H_2O_2?
(a) $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$
(b) $2Fe^{3+} + 2OH^- + H_2O_2 \rightarrow 2Fe^{2+} + 2H_2O + O_2$
(c) $2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O$
(d) $KIO_4 + H_2O_2 \rightarrow KIO_3 + H_2O + O_2$

126. The oxidation state of oxygen in hydrogen peroxide is
(a) 0 (b) +1 (c) −1 (d) −2

127. Which of the following statements regarding hydrogen peroxide is **not** true?
(a) Hydrogen peroxide is a pale blue viscous liquid
(b) Hydrogen peroxide can act as oxidizing as well as reducing agent
(c) The two hydroxyl groups in hydrogen peroxide lie in the same plane.
(d) In the crystalline phase, H_2O_2 is paramagnetic

128. Oxygen atoms in hydrogen peroxide has
(a) sp orbitals (b) sp^2 orbitals (c) sp^3 orbitals (d) pure p orbitals

129. The oxide that gives H_2O_2 on treating with a dilute acid is
(a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2

130. Which of the following statements regarding hydrogen peroxide is **not** true?
(a) H_2O_2 is a linear molecule
(b) The concentration of H_2O_2 in water is generally expressed as 20 or 30 volumes of H_2O_2
(c) H_2O_2 is an oxidizing agent
(d) H_2O_2 is a reducing agent

131. Which of the following methods is not the commercial method of preparing hydrogen peroxide?
(a) Electrolysis of potassium acid sulphate (b) Electrolysis of 60% H_2SO_4 at 0 °C
(c) Auto-oxidation of 2-alkylanthraquinol (d) Addition of dilute H_2SO_4 on Na_2O_2

132. The correct order of acid strength is
(a) $Cl_2O_7 > SO_2 > P_4O_{10}$ (b) $CO_2 > N_2O_5 > SO_3$
(c) $Na_2O > MgO > Al_2O_3$ (d) $K_2O > CaO > MgO$ (2000)

133. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is
(a) H_2O because of hydrogen bonding (b) H_2Te because of higher molar mass
(c) H_2S because of hydrogen bonding (d) H_2Se because of lower molar mass

134. Which of the following order regarding electronegativity is correct?
(a) $O^- > O > O^+$ (b) $O^- > O < O^+$ (c) $O^- < O > O^+$ (d) $O^- < O < O^+$

135. Of the following statements regarding H_2O_2, which is **not** correct?
(a) In acid solution, the oxidation by H_2O_2 is slow.
(b) In alkaline solution, the oxidation by H_2O_2 is slow.
(c) It disproportionates in basic solution.
(d) It may be produced by electrolytic oxidation of H_2SO_4 followed by hydrolysis

Compounds of Sulphur

136. Sodium thiosulphate is used in photography because of its
(a) reducing behaviour (b) oxidizing behaviour
(c) complex forming behaviour (d) reaction with light (1981)

137. There is no S—S bond in
(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$ (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$ (1991)

138. The most favourable conditions for the formation of SO_3 in the reaction

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \quad \Delta H = -95 \text{ kJ mol}^{-1} \text{ are}$$

(a) low temperature and low pressure (b) low temperature and high pressure
(c) high temperature and low pressure (d) high temperature and high pressure

139. Which of the following statements regarding sulphur dioxide is **not** correct?
(a) SO_2 is an angular molecule.
(b) SO_2 is an anhydride of sulphuric acid.
(c) SO_2 is an acidic oxide.
(d) The S—O bond length is smaller than the expected value.

140. Which of the following statements regarding sulphur trioxide is **not** correct?
(a) It exists in three polymorphic forms.
(b) It is an anhydride of sulphuric acid.
(c) Its geometry is square planar.
(d) Vanadium pentoxide is used as a catalyst in the conversion of SO_2 into SO_3.

141. Which of the following compounds produces SO_3 on heating?
(a) Na_2SO_4 (b) $CaSO_4$ (c) $CuSO_4$ (d) $Fe_2(SO_4)_3$

142. Marshall's acid is
(a) H_2SO_5 (b) $H_2S_2O_5$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

143. Caro's acid is
(a) H_2SO_5 (b) $H_2S_2O_5$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

144. Which of the following catalysts is used in the lead chamber process?
(a) V_2O_5 (b) Platinum gauge (c) Oxides of nitrogen (d) Finely divided nickel

145. Which of the following statements regarding sulphurous acid is **not** correct?
(a) Sulphurous acid can be isolated in the crystalline form
(b) In alkaline solution, reducing action of sulphurous acid is due to sulphite ion
(c) In acidic solution, reducing action of sulphurous acid is due to SO_2
(d) The structure of sulphurous acid is tetrahedral including the lone pair of electrons on sulphur

146. Which of the following statements regarding sulphuric acid is **not** correct?
(a) The absorption of SO_2 in sulphuric acid produces oleum
(b) Sulphuric acid with water forms an azeotropic mixture
(c) Concentrated sulphuric acid is a weak oxidizing agent
(d) Lesser electropositive elements reduce sulphuric acid to sulphur dioxide

147. Which of the following statements regarding sodium thiosulphate is **not** correct?
(a) Sodium thiosulphate is used in photography for fixing films and prints
(b) Sodium thiosulphate has five molecules of water of crystallization
(c) The reaction of Cl_2 and I_2 with sodium thiosulphate is $2Na_2S_2O_3 + X_2 \rightarrow Na_2S_4O_6 + 2NaX$
(d) The equivalent mass of sodium thiosulphate when it reacts with iodine is equal to its molar mass

148. Which of the following pairs of ions cannot be separated by H_2S in dilute HCl solution?
(a) Pb^{2+}, Bi^{3+} (b) Cu^{2+}, NI^{2+} (c) Hg^{2+}, Zn^{2+} (d) Cu^{2+}, Co^{2+}

149. Which of the following pairs of ions cannot be separated by H_2S in ammoniacal medium?
(a) Zn^{2+}, Ni^{2+} (b) Zn^{2+}, Mg^{2+} (c) Mg^{2+}, Ca^{2+} (d) Co^{2+}, Ca^{2+}

150. The dissolution of AgBr in $S_2O_3^{2-}$ produces
(a) $Ag(S_2O_3)^-$ (b) $Ag(S_2O_3)_2^{3-}$ (c) $Ag(S_2O_3)_3^{5-}$ (d) $Ag(S_2O_3)_4^{7-}$

151. Which of the following statements regarding sodium thiosulphate is **not** correct?
(a) The structure of $S_2O_3^{2-}$ is tetrahedral
(b) Sodium thiosulphate is used as antichlor in the textile industries
(c) Sodium thiosulphate acts as an oxidizing agent in its reaction with iodine
(d) The reaction of sodium thiosulphate and Cl_2 is $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$

152. The violet coloration when H_2S is passed through sodium nitroprusside is due to
(a) $[Fe(NOS)(CN)_5]^{4-}$ (b) $[Fe(NOS)_2(CN)_4]^{4-}$ (c) $[Fe(NOS)_3(CN)_3]^{4-}$ (d) $[Fe(NOS)_4(CN)_2]^{4-}$

153. Hydrolysis of one mole of peroxodisulphuric acid produces
(a) two moles of sulphuric acid
(b) two moles of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide
(1996)

154. Sodium thiosulphate is prepared by
(a) reducing Na_2SO_4 solution with H_2S (b) boiling Na_2SO_3 solution with S in alkaline medium
(c) neutralising $H_2S_2O_3$ solution with NaOH (d) boiling Na_2SO_3 solution with S in acidic medium
(1996)

155. The number of S—S bonds in sulphur trioxide trimer (S_3O_9) is
(a) three (b) two (c) one (d) zero (2001)

156. Which of the following oxoacids of sulphur has —O—O—linkage?
(a) $H_2S_2O_3$ (b) $H_2S_2O_5$ (c) $H_2S_2O_6$ (d) $H_2S_2O_8$ (2004)

157. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives
(a) $Na_2S_4O_6$ (b) $NaHSO_4$ (c) NaCl (d) NaOH (2008)

158. Which of the following acids does not involve S—S bond?
(a) Pyrosulphrous acid (b) Dithionous acid (c) Dithionic acid (d) Pyrosulphuric acid

Compounds of Halogens

159. Which of the following is the strongest acid?
(a) $ClO_3(OH)$ (b) $ClO_2(OH)$ (c) $SO(OH)_2$ (d) $SO_2(OH)_2$ (1989)

160. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is
(a) sp^3 (b) sp^2 (c) sp (d) none of these (1992)

161. Which of the following statements is correct for $CsBr_3$?
(a) It is a covalent compound (b) It contains Cs^{3+} and Br^- ions
(c) It contains Cs^+ and Br_3^- ions (d) It contains Cs^+, Br^- and lattice of Br_2 molecule.
(1996)

162. KF combines with HF to form KHF_2. The compound contains the species
(a) K^+, F^- and H^+ (b) K^+, F^- and HF (c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^- (1996)

163. Which one of the following species is not a pseudohalide?
(a) CNO^- (b) $RCCO^-$ (c) OCN^- (d) NNN^- (1997)

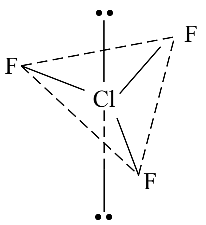
164. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl^-—E—Cl^- for different E are in order
(a) $B > P = As = Bi$ (b) $B > P > As > Bi$
(c) $B < P = As = Bi$ (d) $B < P < As < Bi$ (1999)

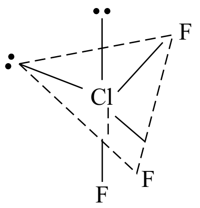
165. Which of the following type of interhalogen compounds is **not** known?
(a) AX (b) AX_2 (c) AX_3 (d) AX_5

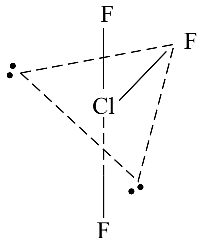
166. Which of the following interhalogen compound is most reactive?
(a) ClF_3 (b) ClF (c) BrF_3 (d) BrF

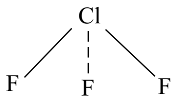
167. The structure of ICl_4^- is
(a) tetrahedral (b) square planar (c) trigonal bipyramid (d) pentagonal bipyramid

168. Which of the following structures for ClF_3 is correct?

(a)


(b)


(c)


(d)


169. The hydrogen halide having maximum dipole moment is
(a) HF (b) HCl (c) HBr (d) HI

170. Among the hydrohalic acids, the strongest one in water is
(a) HF (b) HCl (c) HBr (d) HI

171. Hypochlorous acid is
(a) HClO (b) $HClO_2$ (c) $HClO_3$ (d) $HClO_4$

172. The anhydride of perchloric acid is
(a) ClO_2 (b) ClO_2^- (c) Cl_2O_3 (d) Cl_2O_7

173. The strongest Bronsted base is
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

174. Which of the following hydrogen halides has maximum bond enthalpy?
(a) HF (b) HCl (c) HBr (d) HI

175. Which of the following hydrogen halides has maximum boiling point?
(a) HF (b) HCl (c) HBr (d) HI

176. The hydrogen bonding is maximum in
(a) HF (b) HCl (c) HBr (d) HI

177. The strengths of oxoacids follow the order
(a) $HClO_3 > HClO_2 > HOCl$ (b) $HClO_3 < HClO_2 < HOCl$
(c) $HClO_3 > HClO_2 < HOCl$ (d) $HClO_3 < HClO_2 > HOCl$

178. Of the following oxoacids of chlorine, the strongest acid is
(a) HOCl (b) $HClO_2$ (c) $HClO_3$ (d) $HClO_4$

179. Which of the following statements regarding hypochlorous acid is **not** correct?
(a) It is known only in aqueous solution
(b) The whole of chlorine dissolved in water exists as HCl and HOCl
(c) Salts of hypochlorous acid are known
(d) Hypochlorous ions disproportionate in aqueous solution

180. Which of the following statements regarding chlorous acid is **not** correct?
(a) The molecular formula of chlorous acid is $HClO_2$
(b) It exists only in solution
(c) In alkaline medium, chlorites are unstable whereas in acidic medium they are stable
(d) Chlorous acid is a weak acid

181. When chlorine reacts with cold and dilute solution of sodium hydroxide, the products obtained are
(a) $Cl^- + ClO^-$ (b) $Cl^- + ClO_2^-$ (c) $Cl^- + ClO_3^-$ (d) $Cl^- + ClO_4^-$

182. When iodine reacts with a hot and concentrated solution of sodium hydroxide, the products obtained are
(a) $I^- + IO^-$ (b) $I^- + IO_3^-$ (c) $I^- + IO_4^-$ (d) $I^- + I_2O_9^-$

183. Molecular shapes of SF_4, CF_4 and XeF_4 are
(a) the same with 2, 0 and 1 lone pairs of electrons respectively
(b) the same with 1, 1 and 1 lone pairs of electrons respectively

(c) different with 0, 1 and 2 lone pairs of electrons respectively
(d) different with 1, 0 and 2 lone pairs of electrons respectively (2000)

184. Which of the following interhalogens does not exist?
(a) ClF_7 (b) BrF_3 (c) BrF_5 (d) IF_5

185. Which of the following statements regarding interhalogens is not correct?
(a) Interhalogens involve covalent bonding
(b) Interhalogens are less reactive than halogens
(c) $(ICl_3)_2$ in liquid form shows enhanced conductivity.
(d) Interhalogens of the formula AX_4 are not observed.

Compounds of Inert Gas

186. In a sealed nickel vessel, Xe and F_2 were taken in 2:1 volume ratio and they were heated to 400 °C. The product obtained is
(a) XeF (b) XeF_2 (c) XeF_4 (d) XeF_6

187. In a sealed nickel vessel, Xe and F_2 were taken in 1 : 5 volume ratio and they were heated to 400 °C. The product obtained is
(a) XeF (b) XeF_2 (c) XeF_4 (d) XeF_6

188. In a sealed nickel vessel, Xe and F_2 were taken in 1 : 20 volume ratio and they were heated to 400 °C. The product obtained is
(a) XeF (b) XeF_2 (c) XeF_4 (d) XeF_6

189. In XeF_2, the number of pairs of electrons around Xe is
(a) 3 (b) 4 (c) 5 (d) 6

190. In XeF_4, the number of pairs of electrons around Xe is
(a) 3 (b) 4 (c) 5 (d) 6

191. In XeF_6, the number of pairs of electrons around Xe is
(a) 4 (b) 6 (c) 7 (d) 8

192. The state of hybridization of Xe in XeF_4 is
(a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2

193. The state of hybridization of Xe in XeF_2 is
(a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2

194. The number of lone pair of electrons around Xe in XeO_3 is
(a) 1 (b) 2 (c) 3 (d) 4

195. The number of lone pair of electrons around Xe in $XeOF_4$ is
(a) 4 (b) 3 (c) 1 (d) zero

196. Which of the following fluorides of xenon is not observed?
(a) XeF (b) XeF_2 (c) XeF_4 (d) XeF_6

Multiple Correct Choice Type

1. Nitrogen(I) oxide is produced by
(a) thermal decomposition of ammonium nitrate (b) disproportionation of N_2O_4
(c) thermal decomposition of ammonium nitrite (d) interaction of hydroxylamine and nitrous acid (1989)

2. The species that do not contain peroxide ions are
(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2 (1992)

3. Highly pure dilute solution of sodium in liquid ammonia
(a) shows blue colour (b) exhibits electrical conductivity
(c) produces sodium amide (d) produces hydrogen gas (1980)

4. Paramagnetism is shown by
(a) Cl_2O_7 (b) ClO_3 (c) O_2 (d) ClO_2

5. Which of the following statements about H_2O_2 is/are correct?
(a) H_2O_2 is a linear molecule.
(b) Concentrated H_2O_2 in water in generally expressed as 20 or 30 volumes of H_2O_2.

(c) H_2O_2 is an oxidising agent.
(d) H_2O_2 is a reducing agent.

6. H_2O_2 is obtained when dilute H_2SO_4 reacts with
(a) Na_2O_2 (b) BaO_2 (c) PbO_2 (d) MnO_2

7. Quicklime is used
(a) as basic lining in the furnaces. (b) as a purgative.
(c) In bleaching fabrics. (d) in drying alcohol and gases.

8. CO_2 is isostructural with
(a) $HgCl_2$ (b) $SnCl_2$ (c) C_2H_2 (d) NO_2

9. sp^3 hybridisation is involved in
(a) CO (b) CO_2 (c) SO_2 (d) SO_3

10. Dimerisation takes place in
(a) $AlCl_3$ (b) NO_2 (c) N_2O_3 (d) N_2O_5

11. Which of the following fluorides of xenon is/are known?
(a) XeF_2 (b) XeF_3 (c) XeF_4 (d) XeF_6

12. Which of the following statements regarding the elements of Group 13 is/are **not** correct?
(a) The stability of the (+I) oxidation state decreases down the group whereas that of (+III) increases.
(b) Boron does not form hydrated B^{3+} ion.
(c) Boric acid isonises as $H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$.
(d) Boron compounds act as Lewis acid.

13. Which of the following statements is/are not correct?
(a) Nitric oxide in the gaseous phase is paramagnetic.
(b) Nitric oxide is an anhydride of nitrous acid.
(c) Dimerisation of NO_2 is accompanied by increase in paramagnetism.
(d) N_2O_5 is a covalent in the solid phase.

14. Which of the following statements is/are **not** correct?
(a) Water is energetically less stable than hydrogen and oxygen taken separately.
(b) The molecular formula of pyrosulphurous acid is $H_2S_2O_3$.
(c) H_2O_2 is a strong oxidising as well as reducing agent.
(d) The dissolution of AgBr in $S_2O_3^{2-}$ produces $Ag(S_2O_3)^-$.

15. Highly pure dilute solution of sodium in liquid ammonia
(a) shows blue colour. (b) exhibits electrical conductivity.
(c) produces sodium amide (d) produces hydrogen gas. (1998)

16. Which of the following statements is/are correct?
(a) The electronic configuration of Cr is [Ar] $(3d)^5$ $(4s)^1$. (Atomic number of Cr = 24.)
(b) The magnetic quantum number may have a negative value.
(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47.)
(d) The oxidation state of nitrogen in NH_3 is – 3.

17. Which of the following statements are correct?
(a) In hydrogen peroxide both the hydroxyl groups lie in the same plane.
(b) The decomposition of H_2O_2 is catalyzed by impurities and sunlight.
(c) Hydrogen peroxide is oxidizing as well as reducing agent.
(d) Hydrogen peroxide is a more powerful oxidizing agent in acidic medium as compared to alkaline medium.

18. Which of the following statements are **not** correct?
(a) Hydrogen peroxide is a more powerful reducing agent in acidic medium as compared to alkaline medium.
(b) Decomposition of H_2O_2 is rapid in acidic medium but slow in alkaline medium.
(c) In an alkaline medium, hydrogen peroxide oxidizes $Cr(OH)_3$ to $Cr_2O_7^-$.
(d) With acid dichromate, hydrogen peroxide gives blue colour due to perchromate (CrO_5) which being unstable soon changes to green colour due to Cr^{3+} ions.

19. Which of the following statements are correct?
  (a) Hydrogen peroxide can be used to bleach delicate materials like silk, wool, etc.
  (b) Hydrogen peroxide in a linear molecule.
  (c) The oxidation number of oxygen in hydrogen peroxide is – 1.
  (d) The dipole moment of hydrogen peroxide is zero.

20. Which of the following statements are **not** correct?
  (a) In metal carbonyls, carbon monoxide is attached to the central atom through oxygen end.
  (b) The poisonous nature of carbon monoxide is due to its ability to form a bond with iron atom in the haemoglobin in blood.
  (c) Be_2C is a covalent carbide.
  (d) Magnesium carbide (Mg_2C_3) on treating with water gives ethyne.

21. Which of the following statements are correct?
  (a) Boron carbide is an ionic carbide.
  (b) In metallic carbides, carbon atoms occupy interstitial positions in the crystal lattices of metals.
  (c) Silicon rubber is not attached by ozone.
  (d) Dehydration of dialkyldihydrosilane produces linear silicon.

22. Which of the following statements are correct?
  (a) When carborundum is fused with alkalis, the products are sodium silicate and sodium carbonate.
  (b) Nitrous oxide is an acidic oxide.
  (c) Nitrous oxide is nonsupporter to combustion of burning phosphorus.
  (d) Commercially, nitric oxide is obtained by catalytical oxidation of ammonium in the presence of Pt gauze at 1070 K.

23. Which of the following statements are **not** correct?
  (a) The H—N—H bond angle in NH_3 is greater than H—As—H bond angle in AsH_3.
  (b) Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state.
  (c) Nitric oxide is reduced to nitrous oxide when heated over copper.
  (d) Nitric oxide is reduced to hydroxylamine by hydrogen in the presence of Pt black.

24. Which of the following statements are correct?
  (a) An acidified solution of potassium permangnate oxidizes nitric oxide to nitrate ion.
  (b) The reaction $2HNO_3 + NO \rightarrow 3NO_2 + H_2O$ completely moves in the forward direction.
  (c) The action of concentrated HNO_3 on metals produces NO_2 because the reaction $2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$ lies far towards right side.
  (d) The action of dilute HNO_3 on metals produces NO because the reaction $2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$ lies far towards left side.

25. Which of the following statements are **not** correct?
  (a) Nitric oxide is a diamagnetic molecule.
  (b) Bond order of nitrosonium ion is 2.5.
  (c) Nitric oxide contains a double bond between N and O atoms. Its bond length is the same as expected between these atoms.
  (d) Dinitrogen trioxide is stable in the gaseous state.

26. Which of the following statements are correct?
  (a) Nitrogen sesquioxide reacts with concentrated acids forming nitrosyl salts.
  (b) Nitrogen sesquioxide exists in two different forms—symmetrical and asymmetrical forms.
  (c) The N—N bond in dinitrogen oxide is weak in nature.
  (d) Heating dry lead nitrate produces NO_2 and O_2. On cooling, NO_2 crystallizes out.

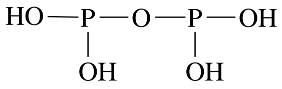
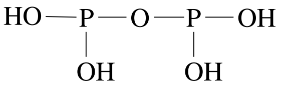
27. Which of the following statements are correct?
  (a) Nitrogen dioxide is a linear molecule.
  (b) Nitrogen tetroxide is a planar molecule with N—N bond length equal to the expected N—N single bond.
  (c) Nitrous acid is stable only in dilute solution.
  (d) Nitrous acid oxidizes I^- to I_2.

28. Which of the following statements are correct?
(a) Nitrite ion is a resonance hybrid of two resonating structures.
(b) Pure nitric acid is light yellow in colour.
(c) Nitric acid becomes brown due to dissolved NO_2 in it.
(d) 98 per cent nitric acid is obtained by dehydrating the azeotropic mixture of HNO_3 and H_2O by concentrated sulphuric acid.

29. Which of the following statements are **not** correct?
(a) Nitronium ion is NO^+.
(b) In the reaction between metal and nitric acid, the more dilute the acid, the lesser the reduction of NO_3^- ion.
(c) Nonmetals are oxidized to their highest oxoacids with concentrated nitric acid.
(d) Nitric acid is a nonplanar molecule with no resonating structures.

30. Which of the following statements are correct?
(a) Aqueous ammonia is a solution of ammonium hydroxide.
(b) Burning of ammonia produces nitrogen and water.
(c) When electric spark is passed through the mixture of NH_3 and O_2, nitric oxide is formed.
(d) Blue coloured crystals of molecular formula $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ is obtained when excess of aqueous ammonia is added to $CuSO_4$ solution.

31. Which of the following statements are correct?
(a) The P—O distance in P_4O_6 is such shorter than the expected value of single P—O bond which is 184 pm.
(b) Phosphorus pentoxide dehydrates HNO_3 to NO_2.
(c) Hypophosphorous acid contains one hydrogen atom directly attached to phosphorus.
(d) Orthophosphorous acid is a strong reducing agent.

32. Which of the following statements are **not** correct?
(a) Heating of phosphorous acid forms phosphoric acid and phosphorus.
(b) The structure of pyrophosphorous acid is 
$\mathrm{HO{-}\underset{\substack{|\\ OH}}{P}{-}O{-}\underset{\substack{|\\ OH}}{P}{-}OH}$
(c) The strucuture of hypophosphoric acid is 
$\mathrm{HO{-}\underset{\substack{|\\ OH}}{P}{-}O{-}\underset{\substack{|\\ OH}}{P}{-}OH}$
(d) Hypophosphoric acid produces phosphorous and metaphosphoric acids on heating.

33. Which of the following statements are **not** correct?
(a) Hypophosphoric acid is a reducing agent.
(b) Hypophosphoric acid on hydrolysis forms phosphoric acid.
(c) Hydrolysis of P_4O_{10} produces phosphorous acid.
(d) Boiling of pyrophosphoric acid with water produces phosphorous acid.

34. Which of the following statements are correct?
(a) Sulphurous acid is a white crystalline solid.
(b) Sulphurous acid is a strong reducing agent.
(c) The S—O bond in SO_2 is smaller than the expected value.
(d) Solid sulphur trioxide exists in three polymorphic forms.

35. Which of the following statements are correct?
(a) The molecule of SO_3 is triangular planar with no resonating structures.
(b) In alkaline medium, the reducing properties of sulphurous acid is due to the SO_3^{2-} ions while in acidic medium it is due to SO_2.
(c) Redox potential of SO_4^{2-} ions in acidic medium ($SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$) is smaller than in the alkaline medium ($SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$).
(d) Magnesium reduces H_2SO_4 acid to H_2S.

36. Which of the following statements are **not** correct?
(a) Sodium thiosulphate is an oxidizing agent.
(b) The reaction of sodium thiosulphate with Cl_2 is $2NaS_2O_3 + Cl_2 \rightarrow Na_2S_4O_6 + 2NaCl$
(c) HBr is a stronger acid than HI because of hydrogen bonding.
(d) Sodium thiosulphate is a primary standard in volumetric analysis.

37. Which of the following statements are correct?

(a) Chlorites are stable in acidic medium. (b) In alkaline medium, chlorites are stable.
(c) Chlorous acid exists as white crystalline solid. (d) Hypochlorous acid exists only in solution.

38. Which of the following statements are correct?

(a) Chloric acid on heating decomposes to give ClO_2, H_2O and O_2.
(b) Perchloric acid is the strongest oxidizing agent amongst oxoacids of chlorine.
(c) The structure of ClO_2 is analogous to that of NO_2.
(d) The ClO_2 molecule is paramagnetic.

39. Which of the following statements are correct?

(a) NO_2 dimerizes easily but NO does not dimerize easily.
(b) Solid PCl_5 exists as $PCl_4^+\ PCl_6^-$.
(c) The yellow colour of nitric acid can be removed by bubbling air through the warm acid.
(d) All atoms in NH_3 molecule lie in the same plane.

40. Which of the following statements are correct?

(a) Alkali metals form covalent carbides.
(b) Silicones are used as lubricants.
(c) Oxides of nitrogen are capable of depleting the ozone layer.
(d) Liquid ozone is not paramagnetic.

41. Which of the following statements are **not** correct?

(a) H_2O_2 when added to acidified $KMnO_4$ acts as an oxidizing agent.
(b) HF is a powerful oxidizing agent.
(c) The experimentally determined N—F bond length in NF_3 is greater than the sum of the single bond covalent radii of N and F.
(d) Pyrophosphoric acid forms four series of compounds.

42. Which of the following statements are correct?

(a) Nitrogen dioxide contains one unpaired electron(s) and is thus paramagnetic in nature.
(b) Dimerized nitrogen dioxide contains no unpaired electrons(s) and is thus diamagnetic in nature.
(c) Nitrogen dioxide is a mixed anhydride of HNO_2 and HNO_3 acids.
(d) Nitrogen dioxide is reduced to NO by acidified $KMnO_4$ solution.

43. Which of the following statements are **not** correct?

(a) NOCl acts as a base in liquid N_2O_4.
(b) NH_4NO_3 acts as an acid in liquid N_2O_4.
(c) Nitrogen pentoxide is anhydride of nitric acid.
(d) In solid, N_2O_5 is present as $NO_2^+\ NO_3^-$ nitronium nitrate.

44. Which of the following statements are correct?

(a) In the redox reaction between Fe^{2+} and HNO_2 in acidic medium, HNO_2 is changed into NO.
(b) In the redox reaction between MnO_4^- and HNO_2 in acidic medium, HNO_2 is changed into HNO_3.
(c) Nitric acid with water forms an azeotropic mixture containing 68 per cent of nitric acid.
(d) Copper reacts with dilute nitric acid producing NO_2 gas.

45. Which of the following statements are **not** correct?

(a) Copper reacts with concentrated nitric acid producing NO_2 gas.
(b) Zinc reacts with very dilute nitric acid producing NO gas.
(c) In the reaction between tin and dilute nitric acid, NO_3^- is reduced to NO.
(d) Aqua regia is a mixture of HCl and HNO_3 mixed in the volume ratio of 3 : 1.

46. Which of the following statements are correct?

(a) Devarda's alloy contains Al, Zn and Cu with mass per cents 45, 5 and 50, respectively.
(b) Devarda's alloy can convert NO_3^- in alkaline medium to NH_3.
(c) The shape of nitrate ion is planar triangle.
(d) Compound used to dry ammonia is CaO.

47. Which of the following statements are **not** correct?

(a) The favourable conditions for the formation of ammonia are high temperature and low pressure.
(b) In the Haber's process, catalyst used is pure iron mixed with a promoter like alumina.
(c) Hydrolysis of calcium cyanimide produces NH_3 gas.
(d) The reaction between NH_3 and Cl_2 produces NH_4Cl.

48. Which of the following statements are **not** correct?
(a) The reaction between NH_3 solution and sodium hypochlorite in the presence of glue or gelatine forms hydrazine.
(b) Ammonia with alkaline K_2HgI_4 solution produces brown colour or precipitate.
(c) Nessler's reagent is an alkaline solution of KI.
(d) NH_4Cl in liquid ammonia acts as an acid.

49. Which of the following statements are **not** correct?
(a) Alkali metals dissolve in liquid ammonia giving blue coloured solution due to the formation of solvated electrons.
(b) Burning of phosphorus in a limited supply to oxygen produces P_2O_3.
(c) Phosphorus trioxide exists as monomer both in naphthalene and in the vapour phase.
(d) Dissolution of phosphorus trioxide in cold water produces H_3PO_2.

50. Which of the following statements are correct?
(a) Dissolution of phosphorus trioxide in hot water produces H_3PO_4 and PH_3.
(a) In phosphorus trioxide, each phosphorus is attached to three oxygen atoms.
(c) The structure of P_4O_6 is tetrahedron with phosphorus atom lies on corners and oxygen atoms on the edges.
(d) Phosphorus tetraoxide is an anhydride of H_3PO_4 acid.

51. which of the following statements are **not** correct?
(a) Phosphorus pentoxide produces HPO_2 with cold water.
(b) Phosphorus pentoxide produces H_3PO_4 with hot water.
(c) In P_4O_{10}, each phosphorus atom is linked to four oxygen atoms.
(d) Hypophosphorous acid is H_3PO_3.

52. Which of the following statements are **not** correct?
(a) An aqueous solution of H_2O_2 is slightly acidic.
(b) H_2O_2 is obtained commercially by the catalytic reduction of 2-ethylanthraquione followed by auto-oxidation.
(c) Hydrogen peroxide is less powerful reducing agent in alkaline medium as compared to acidic medium.
(d) Hydrogen peroxide acts as an oxidizing agent due to the conversion of O_2^{2-} into O_2.

53. Which of the following statements are **not** correct?
(a) Hydrogen peroxide acts as a reducing agent due to the conversion of O_2^{2-} into O_2^{-}.
(b) The molarity of '20 volume H_2O_2' is 1.785 mol L^{-1}.
(c) The mass percent of H_2O_2 in '20 volume H_2O_2' is 0.2.
(d) The term 30 volume H_2O_2 means that 1 L of H_2O_2 would liberate 30 L of O_2 at STP.

54. Which of the following statements are **not** correct?
(a) The treatment of formic acid with concentrated sulphuric acid produces CO.
(b) The treatment of oxalic acid with concentrated sulphuric acid produces CO and CO_2 gases.
(c) The producer gas contains CO and H_2 gases.
(d) The water gas contains CO and N_2 gases.

55. Which of the following statements are correct?
(a) Semi-water gas is a mixture of producer and water gases.
(b) Dry ice is solid CO_2.
(c) Carbon dioxide is a linear molecule with C—O bond equal to 115 pm.
(d) Carbon in carbon dioxide is sp^2 hybridized.

56. Which of the following statements are correct?
(a) The carbides Be_2C and Al_4C_3 are known as methanides as they give methane gas on treating with water.
(b) The carbides CaC_2 and Al_2C_6 are known as methanides as they give methane gas on treating with water.
(c) Carborundum is SiC.
(d) Carborundum has a diamond like structure.

57. Which of the following statements are **not** correct?
(a) The heating of ammonium nitrate produces N_2 gas.
(b) The solubility of nitrous oxide in water increases with increase in temperature.
(c) The laughing gas is nitrous oxide.
(d) Mixed with O_2, nitrous oxide is used as anaesthetic.

58. Which of the following statements are **not** correct?
  (a) Nitrous oxide is a nonlinear molecule.
  (b) The oxide of nitrogen which gives dark brown liquid when passed through cold ferrous sulphate is nitric oxide. The colour is due to the formation of $[Fe(H_2O)_5\ (NO)]^{2+}$ species.
  (c) Sulphurous acid reduces nitric oxide to nitrous oxide.
  (d) Reduction of nitric oxide with Sn and HCl produces NH_3.

59. Which of the following statements are **not** correct?
  (a) Nitric oxide is neutral oxide.
  (b) The coordination complexes of NO with transition metal ions are known as nitrosyls.
  (c) The molecular formula of sodium nitroprusside is $Na_2[Fe(CN)_4(NO)_2]\cdot 2H_2O$
  (d) In nitrosyls, nitric oxide is attached to the central metal ion through oxygen end of the molecule.

60. Which of the following statements are **not** correct?
  (a) Nitric oxide is dimerized in the liquid state and not in gaseous state.
  (b) The bond order of nitric oxide is 2.
  (c) The bond length in NO^+ is larger than in NO.
  (d) Nitric oxide contains one unpaired electron(s) and is therefore paramagnetic in nature.

61. Which of the following statements are
  (a) Nitrogen sesquioxide is N_2O_3.
  (b) Nitrogen sesquioxide is basic oxide.
  (c) Nitrogen sesquioxide is an anhydride of nitrous acid.
  (d) Solid nitrogen dioxide is red. It is due to the formation dimer of nitrogen dioxide.

62. Which of the following statements are **not** correct?
  (a) At higher temperatures, phosphorous acid disproportionates to give H_3PO_3 and H_3PO_4.
  (b) Hypophosphorous acid is tribasic acid.
  (c) Orthophosphoric acid is dibasic acid with molecular formula H_3PO_3.
  (d) The number of hydrogen atoms directly attached to phosphorus atom in phosphorous acid is one.

63. Which of the following statements are **not** correct?
  (a) Pyrophosphorous acid is dibasic acid with molecular formula $H_2P_2O_5$.
  (b) Metaphosphorous acid is represented as $(HPO_2)_n$.
  (c) Hypophosphoric acid is tribasic acid with molecular formula $H_4P_2O_6$.
  (d) Orthophosphoric acid is tribasic acid with molecular formula H_3PO_3.

64. Which of the following statements are **not** correct?
  (a) On heating to 520 K, orthophosphoric acid is converted into pyrophosphoric acid.
  (b) On heating to 870 K, orthophosphoric acid is converted into metaphosphoric acid
  (c) Pyrophosphoric acid is tetrabasic acid with molecular formula $H_4P_2O_6$.
  (d) Metaphosphoric acid is a monobasic acid with molecular formula H_2PO_3

65. Which of the following statements are **not** correct?
  (a) The favourable conditions for the formation of SO_3 from SO_2 and O_2 are high temperature and low pressure.
  (b) In the contact process of manufacturing SO_3, the catalyst used is V_2O_5.
  (c) In the lead chamber process of manufacturing SO_3, the catalyst used is oxides of nitrogen.
  (d) SO_3 is a basic oxide.

66. Which of the following statements are **not** correct?
  (a) The structure of SO_3 molecule is triangular planar.
  (b) Sulphur atom in SO_3 is sp^2 hybridized.
  (c) Heating of pyrophosphoric acid with water produces phosphorous acid.
  (d) On strong heating, pyrophosphoric acid is changed into phosphoric acid.

67. Which of the following statements are **not** correct?
  (a) H_2SO_4 acts as a dehydrating agent on reaction with sugar.
  (b) The molecular shape of SO_2 is linear.
  (c) The bleaching action of SO_2 is due to oxidation reaction.
  (d) The absorption of SO_2 in concentrated H_2SO_4 produces oleum.

68. Which of the following statements are **not** correct?
(a) Dithionic acid has molecular formula $H_2S_2O_6$
(b) Thiosulphuric acid has molecular formula $H_2S_2O_3$.
(c) Caro's acid is H_2SO_6.
(d) Marshall's acid is H_2SO_8.

69. Which of the following statements are correct?
(a) The structure of sulphurous acid is tetrahedral including the lone pair of electrons.
(b) Sulphuric acid with water forms an azeotropic solution containing approximately 9% of the acid.
(c) Hot concentrated sulphuric acid is a strong oxidizing agent.
(d) Zinc reduces H_2SO_4 to SO_2.

70. Which of the following statements are correct?
(a) Copper reduces H_2SO_4 to SO_2.
(b) Violet colouration obtained on mixing S^{2-} and sodium nitroprusside is due to the formation of $[Fe(NOS)(CN)_5]^{4-}$ species.
(c) Sodium nitroprusside is $Na_2\ [Fe(NO)\ (CN)_5]$
(d) Amongst hydrogen halides, the maximum bond enthalpy is possessed by HI.

71. Which of the following statements are **not** correct?
(a) In a lesser ionic solvent, the maximum acid strength of hydrohalic acid is of HF.
(b) Acid HNO_3 behaves as a base in liquid HF.
(c) Perchloric acid behaves as a base in liquid HF.
(d) The fluoride acceptor compounds in liquid HF acts as an acid.

72. Which of the following statements are **not** correct?
(a) The structures of all oxoacids of chlorine are tetrahedron.
(b) Chlorous acid is a weaker acid than hypochlorous acid.
(c) Salts of chlorous acid are known as chlorites
(d) Chloric acid is $HClO_2$.

73. Which of the following statements are correct?
(a) Hypochlorous acid is HOCl.
(b) Chlorous acid is $HClO_2$.
(c) Perchloric acid is $HClO_3$.
(d) Salts of chloric acid are known as chlorites.

74. Which of the following statements are **not** correct?
(a) Amongst the oxoacids of chlorine, the strongest acid is $HClO_4$.
(b) Amongst the oxoacids of chlorine, the weakest acid is HClO.
(c) Bleaching powder is chemically written as $Ca(OCl)_2$.
(d) Bleaching powder is obtained when Cl_2 is passed through wet slaked lime.

75. Which of the following statements are **not** correct?
(a) Hydrohalic acid dissolving glass is HF.
(b) The hybridization of chlorine in hypochlorous acid is sp^2.
(c) Concentrated H_2SO_4 is not used to prepare HBr from KBr as it oxidises HBr.
(d) Dehydration of $HClO_4$ with P_4O_{10} gives ClO_3.

76. Which of the following statements are correct?
(a) A commercial sample of bleaching powder is evaluated from its available Cl_2 which is liberated when treated with acid.
(b) The fertilizer CAN is calcium ammonium nitrate.
(c) Superphosphate of lime is $Ca(H_2PO_4)_2 + 2CaSO_4$
(d) Triple super phosphate is $Ca(H_2PO_4)_2$.

77. Which of the following statements are **not** correct?
(a) The fertilizer nitrophos is $Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$
(b) Silicon chloride on hydrolysis produces SiO_2
(c) $(SiH_3)_3N$ is stronger base than $(CH_3)_3N$.
(d) Mg_3N_2 on reacting with water produces NO gas.

78. The compounds used as refrigerant are
(a) NH_3
(b) CCl_4
(c) CF_4
(d) CF_2Cl_2

79. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution starts. The colourless salt(s) H is (are).
(a) NH_4NO_3 (b) NH_4NO_2 (c) NH_4Cl (d) $(NH_4)_2SO_4$

80. The nitrogen oxide(s) that contain N—N bond(s) is/are (2009)
(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

81. In the reaction $2X + B_2H_6 \rightarrow [BH_2\ X_2]^+\ [BH_4^-]$, the amine(s) X is/are (2009)
(a) NH_3 (b) CH_3NH_2 (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

Linked Comprehension Type

1. Nitrogen form a series of oxides with oxygen. These are N_2O, NO, N_2O_3, NO_2 and N_2O_5. Based on these oxides, answer the following three questions.

(i) Which of the oxides of nitrogen is easily dimerized?
(a) N_2O (b) NO (c) NO_2 (d) N_2O_5

(ii) Which of the oxide of nitrogen exists as ionic solid?
(a) N_2O (b) NO (c) NO_2 (d) N_2O_5

(iii) Which of the oxide is considered to be mixed anhydride of nitrous and nitric acids?
(a) N_2O (b) NO (c) N_2O_3 (d) N_2O_5

2. Nitric oxide is absorbed by a cold solution of ferrous sulphate due to the formation of the dark brown nitrosyl complex ion, $[Fe(NO)(H_2O)_6]^{2+}$. Based on this, answer the following three questions.

(i) The number of unpaired electrons in the complex ion is
(a) 2 (b) 3 (c) 4 (d) 5

(ii) The magnetic moment of the complex in Bohr magneton is
(a) $\sqrt{3}$ (b) $\sqrt{6}$ (c) $\sqrt{15}$ (d) $\sqrt{35}$

(iii) The dark brown colour is due to
(a) increase in the energy gap between d orbitals of Fe^{2+} ion in the complex
(b) decrease in the energy gap between d orbitals of Fe^{2+} ion in the complex
(c) Fe and NO exist as Fe^+ and NO^+ and there occurs charge transfer
(d) the unpaired electron of NO

3. The noble gases have closed-shell electronic configuration and are monatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number + 2, + 4 and + 6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

(i) Argon is used in welding because its
(a) low reactivity with metal (b) ability to lower the melting point of metal
(c) flammability (d) high calorific value.

(ii) The structure of XeO_3 is
(a) linear (b) planar (c) pyramidal (d) T-shaped.

(iii) XeF_4 and XeF_6 are expected to be
(a) oxidising (b) reducing (c) unreactive (d) strongly basic (2007)

4. There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms larger number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus.

(i) Among the following, the correct statement is
(a) Phosphates have no biological significance in humans.
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
(d) Oxidation of nitrates is possible in soil.

(ii) Among the following, the correct statement is
- (a) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.
- (b) Between NH_3 and PH_3. PH_3, is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.
- (c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.
- (d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and less directional.

(iii) White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
- (a) dimerization reaction (b) disproportionation reaction
- (c) condensation reaction (d) precipitation reaction.

5. Phosphorus forms two series of acids. These are phosphorus acid series and phosphoric acid series. Based on these acids, answer the following three questions.

(i) Pyrophosphoric acid is
- (a) H_3PO_4 (b) $H_4P_2O_7$ (c) $H_5P_3O_{11}$ (d) $H_6P_4O_{13}$.

(ii) Which of the following acids does not contain P—O—P bond?
- (a) $H_4P_2O_7$ (b) $H_4P_2O_5$ (c) $H_4P_2O_6$ (d) $(HPO_3)_n$

(iii) Which of the following acids is a reducing agent?
- (a) $H_4P_2O_7$ (b) H_3PO_4 (c) $H_4P_2O_6$ (d) $H_4P_2O_5$

6. Phosphorus forms two series of acids. These are phosphorous acid series and phosphoric acid series. Based on these acids, answer the following.

(i) Which of the following acids is a tribasic acid?
- (a) Orthophosphorous acid (b) Orthophosphoric acid
- (c) Pyrophosphoric acid (d) Hypophosphoric acid

Which of the following acids is a dibasic acid?
- (a) Orthophosphorous acid (b) Orthophosphoric acid
- (c) Pyrophosphoric acid (d) Hypophosphoric acid

Which of the following acid is a tetrabasic as well as reducing acid?
- (a) Orthophosphorous acid (b) Orthophosphoric acid
- (c) Pyrophosphoric acid (d) Hypophosphoric acid

7. Phosphorus forms two series of acids. These are phosphorous acid series and phosphoric acid series. Based on these acids, answer the following three questions

(i) Which one of the following acids is a monobasic as well as reducing acid?
- (a) Hypophosphorous acid (b) Orthophosphorous acid
- (c) Pyrophosphorous acid (d) Hypophosphoric acid

(ii) Which one of the following acids is a dibasic as well as reducing acid?
- (a) Hypophosphorous acid (b) Orthophosphorous acid
- (c) Pyrophosphorous acid (d) Hypophosphoric acid

(iii) Which one of the following acids is a tetrabasic as well as nonreducing acid?
- (a) Hypophosphorous acid (b) Pyrophosphorous acid
- (c) Hypophosphoric acid (d) Tripolyphosphoric acid

8. Sulphur forms a number of acids. These can be broadly classified into four categories, namely, sulphurous acid series, sulphuric acid series, thionic acid series and peroxoacid series. Based on these acids, answer the following three questions.

(i) Which of the following acids does not include S—S bond?
- (a) $H_2S_2O_4$ (b) $H_2S_2O_5$ (c) $H_2S_2O_6$ (d) $H_2S_2O_7$

(ii) Which of the following acids include O—O bond?
- (a) $H_2S_2O_4$ (b) $H_2S_2O_5$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

(iii) Which of the following acids belongs to thionic acid series?
- (a) $H_2S_2O_4$ (b) $H_2S_2O_5$ (c) $H_2S_2O_6$ (d) $H_2S_2O_7$

Silicon forms a very large number of compounds containing SiO_4^{4-} anion as the basic unit. The structure of this basic unit is a tetrahedron in which oxygen atoms are arranged tetrahedrally around a silicon atom. Depending upon the number of corners of SiO_4^{4-} tetrahedron shared with other tetrahedra, a variety of silicates are obtained. Based on this information, answer the following questions.

9. Beryl involves the unit $Si_6O_{18}^{x}$. For this answer the following three questions.

(i) The charge carried by $Si_6O_{18}^{x}$ is

(a) −4 (b) −8 (c) −12 (d) −16

(ii) The number of oxygen shared per unit of SiO_4^{4-} is

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

(iii) The unit $Si_6O_{18}^{x-}$ represents

(a) linear silicate (b) cyclic silicate

(c) sheet silicate (d) three-dimensional silicate.

10. Talc involves the unit $Si_4O_{10}^{x}$. For this, answer the following three questions.

(i) The charge carried by $Si_4O_{10}^{x}$ is

(a) −4 (b) −6 (c) −8 (d) −10

(ii) The number of oxygen shared per unit of SiO_4^{4-} is

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

(iii) The unit $Si_4O_{10}^{x-}$ represents

(a) linear silicate (b) cyclic silicate

(c) sheet silicate (d) three-dimensional silicate

Assertion and Reason Type

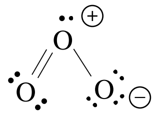
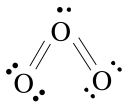
In the following questions, two statements are given. Answer each question based on the following keys.

(a) Statement – 1 is correct. Statement – 2 is correct and is correct explanation of Statement – 1.

(b) Statement – 1 is correct. Statement – 2 is correct and is not correct explanation of Statement – 1.

(c) Statement – 1 is correct. Statement – 2 is incorrect.

(d) Statement – 1 is incorrect. Statement – 2 is correct.

	Statement–1	**Statement–2**
1.	Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.	Phosphorus has lower electronegativity than nitrogen. (1994)
2.	The electronic structure of O_3 is 	 structure is not allowed because octet around O cannot be expanded. (1998)
3.	HNO_3 is a stronger acid than HNO_2	In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one. (1998)
4.	Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.	$SiCl_4$ is ionic and CCl_4 is covalent. (2001)
5.	Boric acid acts as a strong acid in the presence of a *cis*-diol (e.g. glycerol).	A *cis*-diol forms hydrogen bonding with oxygen of boric acid.
6.	The observed bond length of B—F in BF_3 is shorter than the sum of covalent radii of B and F atoms.	The B—F bond in BF_3 involves back bonding of lone pair of F to the empty p orbital of B.
7.	White phosphorus is a neutral species.	White phosphorous exists as monatomic solid.

8. Pyrophosphoric acid ($H_4P_2O_7$) is a reducing tetrabasic acid.	The reducing property of acids of phosphorus is due to hydrogen atom attached to phosphorus atom.
9. ClF_3 is a T-shaped molecule with two of Cl—F bonds have identical bond length but is different from the third third Cl—F bond.	Electrons around Cl in ClF_3 acquires bipyramidal orientations. Two of the F atom occupy apical positions and third occupies equaterial position.
10. Dihydrogen exists as two isomers, namely, *ortho*- and *para*-dihydrogen.	The two isomers of dihydrogen result from the two different spin orientations of its two electrons.
11. The bond angle in NH_3 is greater than in NF_3.	NH_3 involves more bonding pair-bonding pair electronic repulsion as the pairs are located near the nitrogen atom.
12. In water, orthoboric acid behaves as a weak monobasic acid.	In water, orthoboric acid acts as a proton donor.
13. Silicones are good electrical insulators.	Si—O bond is covalent and has a high bond energy.
14. CO_2 is a gas while SiO_2 is a crystalline solid.	Carbon can form multiple bond whereas Si is not able to form multiple bond.
15. The oxygen end of carbon monoxide carries negative charge.	Oxygen is more electronegative than carbon.
16. Carbides of transition metals such as Ti, Hf, W and Mo form are interstitial carbides	Interstitial carbides involve carbon atoms in the interstitial positions in the crystal lattices of the metals.
17. Low temperature and high pressure favour the formation of sulphur trioxide from the oxidation of SO_2.	The oxidation of SO_2 to SO_3 is exothermic and is accompanied with decrease in the number of gaseous species.
18. $N(SiH_3)_3$ has planar configuration while $N(CH_3)_3$ has pyramidal configuration.	N—Si bond besides σ bond also involves π bonding due to $p\pi$-$d\pi$ back bonding which makes $N(SiH)_3$ a planar molecule. No such bonding is present in $N(CH_3)_3$.
19. CF_3COOH acts as a strong acid while $(CF_3)_3N$ has no basic properties.	The high electronegativity of fluorine is responsible for these characteristics
20. (3c-4e) A—B—A bonds are weaker and longer than a normal (2c-2e) A—B bond.	In (3e-4e) bonds, only two electrons are present in the bonding molecular orbital and the remaining two electrons are present in nonbonding molecular orbitals.
21. PBr_5 in acetonitrile forms an electrolytically conducting solution.	The conductivity is due to presence of $[PBr_4]^+$ and $[PBr_6]^-$ ions.

Matrix Match Type

1. Match each of reactions given in Column I with the corresponding product(s) given in Column II.

Column I	**Column II**
(a) Cu + dil. HNO_3	(p) NO
(b) Cu + conc. HNO_3	(q) NO_2
(c) Zn + dil. HNO_3	(r) N_2O
(d) Zn + conc. HNO_3	(s) $Cu(NO_3)_2$
	(t) $Zn(NO_3)_2$

(2009)

2. Column I lists nature of some of oxides and Column II lists some of the examples of oxides. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Neutral oxide	(p) N_2O_3
(b) Acidic oxide	(q) N_2O_4
(c) Mixed oxide	(r) SnO
(d) Amphoteric oxide.	(s) NO
	(t) P_4O_6
	(u) N_2O

3. Column I lists four gases and these gases can be obtained by heating the appropriate inorganic compound mentioned in Column II. Match each gas mentioned in Column I with the compound(s) mentioned in Column II.

Column I	**Column II**
(a) N_2	(p) NH_4NO_2
(b) O_2	(q) NH_4NO_3
(c) NO_2	(r) HgO
(d) N_2O	(s) $(NH_4)_2Cr_2O_7$
	(t) $Cu(NO_3)_2$
	(u) $K_2Cr_2O_7$

4. Column I lists the reactants of four reactions and Column II gives one of the products in these reactions. Match each entry of column I with those given in Column II.

Column I	**Column II**
(a) P_4O_6 + cold H_2O	(p) H_3PO_3
(b) P_4O_6 + hot H_2O	(q) H_3PO_4
(c) P_4O_8 + H_2O	(r) PH_3
(d) P_4O_{10} + HNO_3	(s) HPO_3

ANSWERS

Straight Objective Type

1. (b) **2.** (d) **3.** (b) **4.** (b) **5.** (c) **6.** (d) **7.** (d)
8. (a) **9.** (d) **10.** (c) **11.** (a) **12.** (b) **13.** (b) **14.** (a)
15. (d) **16.** (c) **17.** (b) **18.** (d) **19.** (a) **20.** (d) **21.** (a)
22. (a) **23.** (b) **24.** (d) **25.** (a) **26.** (c) **27.** (d) **28.** (a)
29. (b) **30.** (d) **31.** (d) **32.** (a) **33.** (b) **34.** (c) **35.** (d)
36. (a) **37.** (b) **38.** (c) **39.** (d) **40.** (d) **41.** (c) **42.** (d)
43. (a) **44.** (a) **45.** (d) **46.** (a) **47.** (b) **48.** (b) **49.** (b)
50. (c) **51.** (d) **52.** (a) **53.** (b) **54.** (b) **55.** (c) **56.** (b)
57. (a) **58.** (b) **59.** (d) **60.** (b) **61.** (b) **62.** (c) **63.** (c)
64. (d) **65.** (a) **66.** (b) **67.** (c) **68.** (c) **69.** (c) **70.** (c)
71. (a) **72.** (b) **73.** (c) **74.** (c) **75.** (d) **76.** (b) **77.** (c)
78. (c) **79.** (b) **80.** (d) **81.** (b) **82.** (c) **83.** (a) **84.** (b)
85. (b) **86.** (c) **87.** (a) **88.** (a) **89.** (c) **90.** (a) **91.** (d)
92. (a) **93.** (c) **94.** (d) **95.** (a) **96.** (b) **97.** (b) **98.** (a)
99. (c) **100.** (a) **101.** (c) **102.** (b) **103.** (d) **104.** (a) **105.** (c)
106. (a) **107.** (a) **108.** (d) **109.** (d) **110.** (d) **111.** (a) **112.** (b)
113. (a) **114.** (a) **115.** (c) **116.** (c) **117.** (c) **118.** (c) **119.** (a)
120. (b) **121.** (c) **122.** (c) **123.** (b) **124.** (b) **125.** (c) **126.** (c)
127. (c) **128.** (c) **129.** (b) **130.** (a) **131.** (d) **132.** (a) **133.** (a)
134. (d) **135.** (b) **136.** (c) **137.** (d) **138.** (b) **139.** (b) **140.** (c)
141. (d) **142.** (d) **143.** (a) **144.** (c) **145.** (a) **146.** (a) **147.** (c)

148. (a) **149.** (a) **150.** (c) **151.** (c) **152.** (a) **153.** (c) **154.** (b)
155. (d) **156.** (d) **157.** (b) **158.** (d) **159.** (a) **160.** (a) **161.** (c)
162. (c) **163.** (b) **164.** (b) **165.** (b) **166.** (a) **167.** (b) **168.** (c)
169. (a) **170.** (d) **171.** (a) **172.** (d) **173.** (a) **174.** (a) **175.** (a)
176. (a) **177.** (a) **178.** (d) **179.** (b) **180.** (c) **181.** (a) **182.** (b)
183. (d) **184.** (a) **185.** (b) **186.** (b) **187.** (c) **188.** (d) **189.** (c)
190. (d) **191.** (c) **192.** (d) **193.** (c) **194.** (a) **195.** (c) **196.** (a)

Multiple Correct Choice Type

1. (a), (d) **2.** (a), (c) **3.** (a), (b) **4.** (b), (c), (d)
5. (b), (c), (d) **6.** (a), (b) **7.** (a), (d) **8.** (a), (c)
9. (c), (d) **10.** (a), (b) **11.** (a), (c), (d) **12.** (a), (c)
13. (b), (d) **14.** (a), (d) **15.** (a), (b) **16.** (a), (b), (c)
17. (b), (c), (d) **18.** (a), (b), (c) **19.** (a), (c) **20.** (a), (c), (d)
21. (b), (c), (d) **22.** (a), (d) **23.** (b), (c), (d) **24.** (a), (c), (d)
25. (a), (b), (c), (d) **26.** (a), (b), (c), (d) **27.** (c), (d) **28.** (a), (c), (d)
29. (a), (b), (d) **30.** (b), (c), (d) **31.** (a), (d) **32.** (a), (b), (c)
33. (a), (b), (c), (d) **34.** (b), (c), (d) **35.** (b), (d) **36.** (b), (c), (d)
37. (b), (d) **38.** (a), (b), (c), (d) **39.** (a), (b), (c) **40.** (b), (c)
41. (a), (b), (d) **42.** (a), (b), (c) **43.** (a), (b) **44.** (a), (b), (c)
45. (b), (c) **46.** (a), (b), (c), (d) **47.** (a), (d) **48.** (c), (d)
49. (c), (d) **50.** (a), (b), (c) **51.** (a), (d) **52.** (c), (d)
53. (a), (c) **54.** (c), (d) **55.** (a), (b), (c) **56.** (a), (c), (d)
57. (a), (b) **58.** (a), (d) **59.** (c), (d) **60.** (b), (c)
61. (b), (d) **62.** (a), (b) **63.** (c), (d) **64.** (c), (d)
65. (a), (d) **66.** (c), (d) **67.** (b), (c) **68.** (c), (d)
69. (a), (b) **70.** (a), (b), (c) **71.** (a), (c) **72.** (b), (d)
73. (a), (b), (c) **74.** (c), (d) **75.** (b), (d) **76.** (a), (b), (c), (d)
77. (c), (d) **78.** (a), (d) **79.** (a), (b) **80.** (a), (b), (c)
81. (a), (b), (c)

Linked Comprehension Type

1. **(i)** (c) **(ii)** (d) **(iii)** (c) **2.** **(i)** (b) **(ii)** (c) **(iii)** (c)
3. **(i)** (a) **(ii)** (c) **(iii)** (a) **4.** **(i)** (c) **(ii)** (c) **(iii)** (b)
5. **(i)** (b) **(ii)** (c) **(iii)** (d) **6.** **(i)** (b) **(ii)** (a) **(iii)** (d)
7. **(i)** (a) **(ii)** (b) **(iii)** (c) **8.** **(i)** (d) **(ii)** (d) **(iii)** (c)
9. **(i)** (c) **(ii)** (b) **(iii)** (b) **10.** **(i)** (a) **(ii)** (c) **(iii)** (c)

Assertion and Reason Type

1. (b) **2.** (a) **3.** (a) **4.** (c) **5.** (c) **6.** (a) **7.** (c)
8. (d) **9.** (a) **10.** (c) **11.** (a) **12.** (c) **13.** (b) **14.** (a)
15. (d) **16.** (a) **17.** (a) **18.** (a) **19.** (a) **20.** (b) **21.** (a)

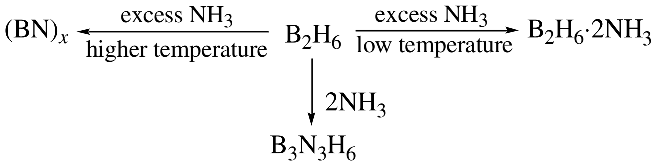
Matrix Match Type

1. (a)–(p), (s); (b)–(q), (s); (c)–(r), (t); (d)–(q), (t) **2.** (a)–(s), (u);(b)–(p), (q), (t); (c)–(p), (q);(d)–(r)
3. (a)–(p), (s); (b)–(r), (t), (u); (c)–(t); (d)–(q) **4.** (a)–(p);(b)–(q), (r); (c)–(p), (q); (d)–(s)

Hints and Solutions

Straight Objective Type

1. The formula of nido-boranes is B_nH_{n+4}.
2. The formula of arachno-boranes ins B_nH_{n+6}.
3. Diborane is highly reactive.
4. Diborane reacts with NH_3 as follows.



5. See. Q. 4.
6. See Q. 4.
7. B in B_2H_6 is sp^3 hybridized.
8. Boric acid is weak acid. it does not give H^+ but accepts OH^-. It is Lewis acid.
9. The reaction is $Na_2B_4O_7{\cdot}10H_2O + 2HCl \rightarrow 2NaCl + 4H_3BO_3 + 5H_2O$
Due to the formation of H_3BO_3, methyl orange is used as the indicator.
10. In B_2H_6, bridge B—H—B is 3c-2e bond.
12. The neutralization reaction is $B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4] + NaBO_2 + 2H_2O$ *cis*-diol forms a stable complex with the $[B(OH_4]^-$ and thus the neutralization reaction proceeds in the forward direction. Thus $B(OH)_3$ in the presence of *cis*-diol acts as a strong acid.
14. BF_3 hydrolyses incompletely and forms fluoborates.

$$\begin{array}{l} 4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF \\ 12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O \\ \hline 4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^- \end{array}$$

The other halides undergo complete hydrolysis $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$
15. Besides σ bond between boron and halogen atoms, there exist additional pπ-pπ bond between the two atoms resulting from back-donation of electrons from halide to boron (back bonding). The tendency to form back bonding is maximum in BF_3 and falls rapidly on passing to BCl_3 and BBr_3. The tendency to accept electron pair, therefore, increases from BF_3 to BBr_3.
16. Due to back bonding, B—F bond acquires some double bond character due to which its bond length is lesser than in the complex $F_3B \leftarrow NH_3$ where back bonding is not present.
17. Borazine has structure similar to that of benzene.
18. The hefty and crowded electron donor species involves symmetrical breaking of B_2H_6.
19. CO_2 is linear molecule while the other three are bent molecules.
20. The compound formed is $Ni(CO)_4$.
21. CO involves sp orbitals of carbon. It has lone pair of electrons on both C and O. The lone pair of C has more directional characteristics and is thus it binds to metals via carbon end.
22. Al_4C_3 is an ionic carbide. SiC is a covalent carbide, MoC and Cr_3C are metallic (or interstitial) carbides.
23. See Q. 22.
24. See Q. 22.
25. Be_2C and Al_4C_3 are methanides as they yield methane on reacting with water. CaC_2 is acetylides as it forms acetylene. Mg_2C_3 yields $CH_3—C \equiv CH$.
26. See Q. 25.
27. See. Q. 26.
28. Carborundum is SiC.
29. In CaC_2, the carbide ion is $(—C \equiv C—)^{2-}$.
30. Silicones are polymeric organosilicon compounds $-\!\!\left[O—Si(R_2)—O]_n\right]\!\!-$.
31. Silicon rubber is chemically inert straight-chain polymers. Methyl silicones can be used as light duty lubricating oil.
32. Orthosilicates contain discrete $(SiO_4)^{4-}$ tetrahedra unit.
33. Pyrosilicates involve sharing of one oxygen atom between two SiO_4^{4-} tetrahedral.
34. The sharing of two oxygen atoms of one SiO_4^{4-} tetrahedron with two other tetrahedra forms chain and cyclic silicates.

35. The sharing of three oxygen atoms lead to the layer and sheet structures.
36. The basic unit of orthosilicates is SiO_4^{4-}.
37. The basic unit of pyrosilicates is $Si_2O_7^{6-}$.
38. The basic unit of chain and cyclic silicates is $(SiO_3)_n^{2-}$.
39. The basic unit of layer and sheet silicates is $(Si_2O_5)_n^{2n-}$.
40. The sharing of all the four oxygens of SiO_4^{4-} leads to three-dimensional silicates.
41. Hydrolysis of $(CH_3)_2SiCl_2$ leads to the formation of silicones $-\!\left[\text{O—}(CH_3)_2\text{Si—O}]_n\right]\!-$.
42. See. Q. 35.
43. R_3SiCl serves as blocking compound as it will not have —OH as the end of the chain.
44. Heating of KNO_3 gives O_2.
45. NO_2 is a coloured gas.
46. NF_3 is least basic. The highly electronegativity of F atoms attract electrons and thus reduces the donor power of N atom.
47. NH_3 is the strongest base due to smaller size of N atom. The ability to act as electron donor decreases on descending the Group 15.
48. N_2O is a neutral oxide as it does not form hypronitrous acid $H_2N_2O_2$ with water. Also no hyponitrites are formed with alkali.
49. NO^+ and CO contain the same number of electrons.
50. NO_2^+ and CO_2 contain the same number of electrons.
51. The oxidation states are: $\overset{+4}{N}O_2$; $\overset{+3}{N_2}O_3$; $\overset{+4}{N_2}O_4$; $\overset{+5}{N_2}O_5$.
52. The brown ring is due to the formation of $[Fe(H_2O)_5\,(NO)]^{2+}$.
53. With dilute HNO_3, the reaction is $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
54. The solubility of N_2O is more in hot solution.
55. The N_2O molecule is linear with the arrangement NNO.
57. The electronic configuration of NO is KK $(\sigma\,2s)^2\ (\sigma\,{*}2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma\ 2p_z)^2\ (\pi{*}2p_x)^1$. In going from NO to NO^+, antibonding electron is removed. This increases bond order and hence decrease in bond length. Nitric oxide dimerizes only in the liquid and solid states.
58. N_2O_3 is a mixed oxide ($NO + NO_2$). It is an acidic oxide ($N_2O_3 + H_2O \rightarrow 2HNO_2$).
59. N_2O_5 in solid form is colourless.
60. NO_2 is colourless in solid form. It is present as N_2O_4.
61. Dimerized NO_2 is diamagnetic as there is no unpaired electrons.
62. Liquid N_2O_4 is a non-aqueous solvent. It self-ionizes as $N_2O_4 \rightleftharpoons \underset{\text{acid}}{NO^+} + \underset{\text{base}}{NO_3^-}$. Thus NOCl acts as an acid.
63. X-ray diffraction shows that solid N_2O_5 is ionic $NO_2^+\ NO_3^-$.
64. The nitrite ion NO_2^- has a planar trigonal structure, with N at the centre, two corners occupied by O atoms, and the third corner occupied by the lone pair. A three-centre bond covers the N and the two O atoms and the bond order of N—O is 1.5.
65. Pure nitric acid is a colourless liquid.
66. The reaction with Zn is $4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$.
67. The reaction with Sn is $5Sn + 20HNO_3 \rightarrow H_2Sn_5O_{11} \cdot 4H_2O + 20NO_2 + 5H_2O$.
68. NH_3 can be dried with CaO.
69. The reaction $N_2 + 3H_2 \rightarrow 2NH_3$. From this, it follows that 6 dm^3 of H_2 will produce 4 dm^3 ($= 2 \times 6\ dm^3/3$) of NH_3.
70. With excess of Cl_2, NH_3 forms NCl_3 ($NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$).
71. The stability of hydrides of Group 15 elements decreases on descending the group.
72. The reaction is $10HNO_3 + 3I_2 \rightarrow 6HIO_3 + 10NO + 2H_2O$
73. There exists an equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. The formation of ammonia is exothermic and is accompanied with decrease in gaseous species. Thus low T and high p favour the formation of NH_3.
74. The burning of ammonia produces N_2 and H_2O. ($4NH_3 + 3O_2 \rightarrow 2N_2 + 3H_2O$).

75. The complete reaction involves two steps.

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \quad \text{(fast)}$$
$$2NH_3 + NH_2Cl \rightarrow NH_2NH_2 + NH_4Cl \quad \text{(slow)}$$

76. Aqua regia is 1 part conc. HNO_3 and 3 parts conc. HCl.

77. NF_3 and H_3O^+ involve valence electrons each, and NO_3^- and BF_3 involve 24 valence electrons and these pairs are isostructural.

78. $2NH_3 + NaOCl \rightarrow H_2NNH_2 + NaCl + H_2O$

79. The number of paired electrons around N in NO_2^+, NO_3^- and NH_4^+ are 2, 3 and 4, respectively. Hence, these respectively involve sp, sp^2 and sp^3 hybridization.

80. P_2O_5 dehydrates HNO_3 at low temperature producing N_2O_5.

81. The gases NO and NO_2 on mixing gives N_2O_3

82. $N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$

83. NO is a neutral oxide.

84. See Q. 81.

85. $NH_4NO_3(aq) \xrightarrow[\Delta]{} N_2O + 2H_2O$

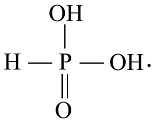
86. In N_2O_4, the N—N bond is long and weak as compared to normal N—N single bond.

87. NO_2^+, NO_2 and NO_2^- involve 16, 17 and 18 valence electrons. NO_2^+ involves sp hybridization, hence angle O—N—O is 180°. NO_2^- involves sp^2 hybridization, hence angle is 120°.

88. Hydrazine forms two series of salts.; $N_2H_4 + HX \rightarrow N_2H_5^+ + X^-$; $N_2H_4 + 2HX \rightarrow N_2H_6^{2+} + 2X^-$

89. The bond N—N is longer and weaker as compared to the normal N—N bond.

90. The structure of phosphorous acid is



$$\mathrm{H-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-OH}.$$

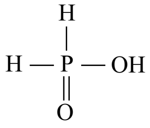
91. Distillation of HNO_3 with P_2O_5 produces N_2O_5.

92. P_2O_3 exists as P_4O_6 both in naphthalene and in the vapour phase.

93. $P_4O_8 \xrightarrow{+H_2O} H_3PO_4 + H_3PO_3$.

94. $HNO_3 \xrightarrow[P_2O_5]{} N_2O_5 + H_2O$.

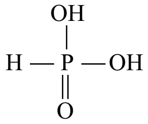
95. Hypophosphorous acid is



$$\mathrm{H-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-OH}$$

96. See Q. 95.

97. Orthophosphorous acid is

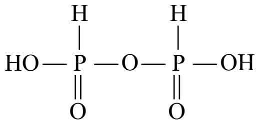


$$\mathrm{H-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-OH}$$

98. See Q. 97.

99. The orthophosphorous acid is a moderately strong reducing agent.

100. Pyrophosphorous acid is

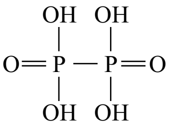


$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-OH}$$

101. See Q. 100

102. See Q. 100

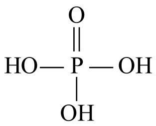
103. Hypophosphoric acid is



$$\mathrm{O{=}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{P}}-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{P}}{=}O}$$

104. See Q. 103

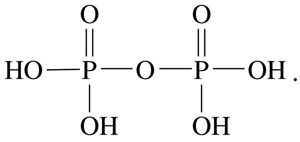
105. Orthophosphoric acid is



$$\mathrm{HO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$$

106. See Q. 105

107. The hydrolysis reaction is $P_4O_{10} + 6H_2O \xrightarrow[\text{cold}]{} 4H_3PO_4$

108. Pyrophosphoric acid is  $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$.

109. Pyrophosphoric acid is tetrabasic acid.

111. See, Q. 108.

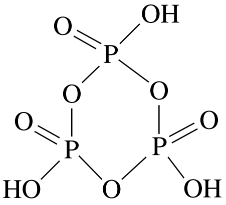
113. Metaphosphoric acid is HPO_3

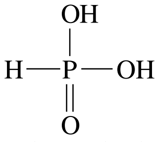
114. P_4O_6 is the anhydride of orthophosphorous acid.

115. Reducing oxoacid of phosphorus contains H atom directly attached to P

116. Reaction is $Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$

117. The cyclic metaphosphoric acid is



119. H_3PO_3,  $\mathrm{H{-}\underset{O}{\overset{OH}{P}}{-}OH}$, is dibasic as well as reducing, since it contains two hydrogen atoms attached to oxygen and one hydrogen attached to phosphorus.

120. P_4O_6 is formed in the limited supply of oxygen.

121. Terminal P—O has double bond characteristics while bridged P—O is normal single bond.

122. Heavy water is D_2O.

123. $\underset{2\ \text{mol}}{2H_2O_2} \rightarrow 2H_2O + \underset{1\ \text{mol}}{O_2}$

0.75 mol will produce (1/2) (0.75 mol) = 0.375 mol

1 mol O_2 occupies 22.414 L at STP. 0.375 mol O_2 will occupy (22.414 L) (0.375) of O_2, i.e. 8.4 L

Hence, volume strength is 8.4.

125. In the reaction, $2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O$, the oxidation number of O in H_2O_2 is changed from –1 to –2, i.e. H_2O_2 undergoes reduction, hence, it acts as oxidizing agent.

126. The oxidation number of O in H_2O_2 is – 1.

127. The two —OH bonds are not in the same plane.

128. Oxygen in H_2O_2 is sp^3 hybridized.

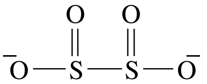
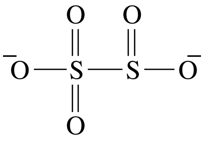
129. Na_2O_2 is peroxide, it gives H_2O_2 on treatment with dilute acid.

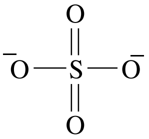
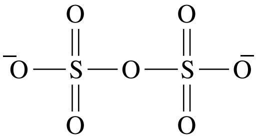
130. H_2O_2 is a nonlinear molecule.

132. The species Cl_2O_7, SO_2 and P_4O_{10} are the anhydride of $HClO_4$, H_2SO_3 and H_3PO_4, respectively. The acid strength of these acids follows the order $HClO_4 > H_2SO_3 > H_3PO_4$. The corresponding anhydrides also follow the same order.

134. The positive charge on atom increases its electronegativity while negative charge decreases its electronegativity.

135. Kinetically, oxidation with H_2O_2 is slow in acidic medium but proceeds rapidly in alkaline medium.

137. $S_2O_4^-$ is  $\mathrm{{}^{-}O{-}\overset{O}{S}{-}\overset{O}{S}{-}O^{-}}$; $S_2O_5^{2-}$ is  $\mathrm{{}^{-}O{-}\underset{O}{\overset{O}{S}}{-}\overset{O}{S}{-}O^{-}}$

$S_2O_3^{2-}$ is  $\mathrm{{}^{-}O{-}\underset{O}{\overset{O}{S}}{-}O^{-}}$; $S_2O_7^{2-}$ is  $\mathrm{{}^{-}O{-}\underset{O}{\overset{O}{S}}{-}O{-}\underset{O}{\overset{O}{S}}{-}O^{-}}$

138. The reaction is exothermic and is accompanied with decrease in the gaseous species. Hence, low temperature and high pressure favour the formation of SO_3.

139. SO_2 is the anhydride of H_2SO_3 and not H_2SO_4.

140. S is sp^2 hybridized. The structure is trigonal planar.

141. $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$

142. Marshall's acid is $H_2S_2O_8$. **143.** Caro's acid is H_2SO_5

144. In the lead chamber process, NO_2 is used as a homogeneous catalyst to oxidize SO_2 to SO_3 in the presence of water. In the contact process, V_2O_5 is used as a catalyst.

145. Sulphurous acid exists as hydrated SO_2. It exists in minute amounts in solution. In solid form, only its salts are available.

147. The reaction with Cl_2 is $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$

148. Both Pb^{2+} and Bi^{3+} are precipitated as sulphides in the second group of salt analysis.

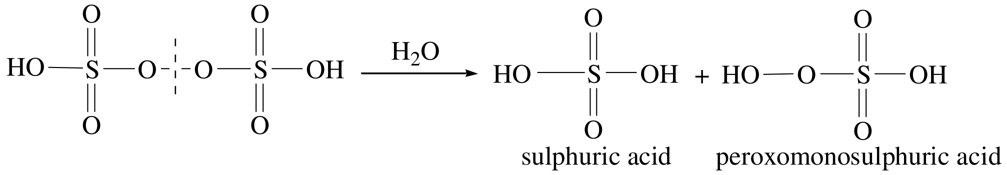
149. Both Zn^{2+} and Ni^{2+} are precipitated as sulphides in ammoniacal solution. These are precipitated in the fourth group of salt analysis.

150. The reaction is $Na_2S_2O_3 + 2AgBr \xrightarrow{-2NaBr} Ag_2S_2O_3 \xrightarrow{+5Na_2S_2O_3} 2Na_5[Ag(S_2O_3)_3]$

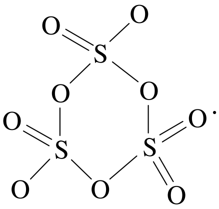
151. $S_2O_3^{2-}$ is reduced to $S_4O_6^{2-}$ in its reaction with I_2.

152. The violet colour is due $[Fe(NOS)(CN)_5]^{4-}$.

153. The reaction is

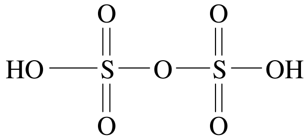


154. $Na_2SO_3 + S \xrightarrow[\text{medium}]{\text{alkaline}} Na_2S_2O_3$

155. The trimer is  .

156. $H_2S_2O_8$ is peroxo disulphuric acid. It contains —O—O—linkage.

157. See, Q. 147.

158. Pyrosulphuric acid is  $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$. All other given acids contain —S—S—linkage.

159. The oxidation state of Cl is the highest in $ClO_3(OH)$ and Cl is more electronegative than S.

160. ClO_2^- has V-shaped structure based upon a tetrahedral arrangement of two bonds and two lone pairs of electrons.

161. $CsBr_3$ may be represented as $Cs^+ \, Br_3^-$

162. $KHF_2 \rightarrow K^+ + HF_2^-$

164. BCl_3 has 24 valence electrons, B has three paired electrons around it and thus sp^2 hybridized. Angle Cl—B—Cl is expected to be 120°.

PCl_3 has 26 valence electrons, P has four paired electrons around it and thus sp^3 hybridized. Angle Cl—P—Cl is expected to be 109° 28′.

For As or Bi, the angle is more near to 90°.

165. Interhalogen AX_2 is not known.

166. ClF_3 is most reactive. The reactivity follows the order: $ClF_3 > ClF > BrF_3 > BrF$.

167. ICl_4^- has 36 valence electrons, I has six paired electrons around it and thus d^2sp^3 hybridized. The four Cl atoms form square planar structure.

169. HF has maximum dipole moment. **170.** HI is the strongest acid.

171. Hypochlorous acid is HClO.

172. Cl_2O_7 is the anhydride of perchloric acid. $Cl_2O_7 + H_2O \rightarrow 2HClO_4$

173. HClO is the weakest acid. Its conjugate base ClO^- is the strongest base.

174. Bond enthalpy of HF is maximum.

175. HF has the high boiling point due to more strong hydrogen bonding. **176.** See, Q. 175.

177. Larger the number of O atoms attached to Cl, larger the acid strength. **178.** See, Q. 177

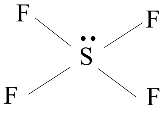
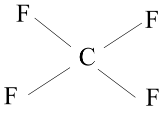
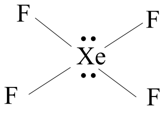
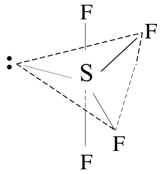
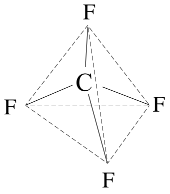
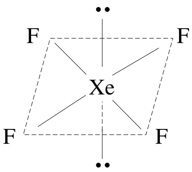
179. In a saturated solution of chlorine, about two thirds exists as hydrated molecules, and the rest as HCl and HOCl.

180. Chlorite ClO_2^- is stable in alkaline medium, but disproportionates in acidic medium: $2ClO_2^- \rightleftharpoons ClO_3^- + ClO^-$

181. $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

182. $3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$

183. For the given molecules, we have

	SF_4	CF_4	XeF_4
Number of valence electrons	34	32	36
Lewis structure			
Number of lone pairs on the central atom	1	0	2
Number of pairs of electrons (bonded + lone) around the central atom	5	4	6
Probable structure	trigonal bipyramidal 	tetrahedral 	octahedral 

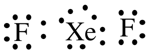
184. The interhalogen ClF_7 does not exist.

185. Interhalogens are more reactive than halogens.

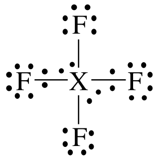
186. For the ratio Xe : F : : 2 : 1, the product is XeF_2.

187. For the ratio Xe : F : : 1 : 5, the product is XeF_4.

188. For the ratio Xe : F : : 1 : 20, the product is XeF_6.

189. Number of valence electrons in XeF_2 = 22. These are distributed as  .

There are five paired of electrons around Xe..

190. Number of valence electrons in XeF_4 = 36. These are distributed as  . There are six paired of electrons around Xe.

191. Working similarly as Q. 189 and 190, the number of unpaired electrons around Xe is seven.

192. In XeF_4, there six paired of electrons around Xe (Q. 190), the state of hybridization is sp^3d^2.

193. In XeF_2, there are five paired of electrons around Xe(Q. 189), the state of hybridization is sp^3d.

194. Valence electrons in XeO_3 = 8 + 3 + 6 = 26. Of these 24 electrons are distributed around three oxygens, hence, lone pair of electrons around Xe is (26 – 24)/2 = 1.

195. Valence electrons in $XeOF_4 = 8 + 6 + 4 \times 7 = 42$. Of these, 40 electrons are distributed around O and 4F atoms, hence, lone pair of electrons around Xe is (42 – 40)/2 = 1.

196. XeF is not observed.

Multiple Correct Choice Type

17. (a) The two hydroxyl groups lie in the different planes making an angle of 111.5° with each other.

18. (a) The reverse is true. (b) The reverse is true. (c) In an alkaline medium, Cr(VI) exists as CrO_4^{2-}.

20. (a) It is attached through carbon end. (c) It is an ionic carbide.
(d) The product is propyne.

21. (a) It is a covalent carbide.

22. (a) It is a neutral oxide.
(b) Decomposition of N_2O gives oxygen and nitric oxide. Thus, N_2O is a supporter of combustion of burning phosphorus.

23. (b) There occurs only partial dimerization of nitric oxide in the liquid state.
(c) It is reduced to nitrogen.
(d) It is reduced to ammonia.

24. (b) The reaction between nitric acid and nitric oxide is a reversible reaction

$$2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$$

25. (a) Nitric oxide contains one unpaired electron. It is paramagnetic in nature.
(b) Nitrosonium ion contains 10 valence electrons. Its molecular electronic configuration is $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$. Hence, its bond order is 3.
(c) The bond length N—O is 115 pm which is intermediate between the double and triple bonds.
(d) Dinitrogen trioxide is stable only in the liquid state. In the gaseous state it dissociates to nitric oxide and nitric dioxide.

26. (a) With HCl, salt formed is $NO[ClO_4]$ and with H_2SO_4, salt is $NO[HSO_4]$.

27. (a) Nitrogen dioxide is angular with O—N—O angle of 132°.
(b) Though the molecule is planar but N—N bond distance (164 pm) is much larger than the expected value (147 pm).

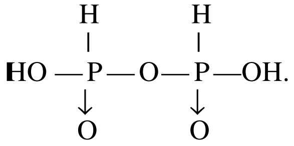
28. (a) It is a colourless liquid.

29. (a) It is NO_2^+. (b) The more dilute the acid, the greater the reduction.
(d) Nitric acid is a planar molecule with two resonating structures.

30. (a) Aqueous ammonia contains 46.2% of uncombined NH_3, 52.4% hydrated ammonia and 1.4% NH_4OH.

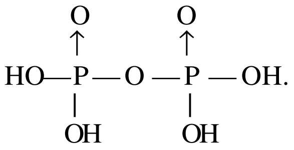
31. (b) It dehydrates HNO_3 to its anhydride which is N_2O_5.
(c) Two hydrogen atoms are directly attached to phosphorus atom.

32. (a) The products are phosphoric acid and phosphine.
(b) Pyrophosphorous acid is diabasic acid. Its structure is



$$\mathrm{HO{-}\overset{\displaystyle H}{\underset{\displaystyle \overset{\downarrow}{O}}{P}}{-}O{-}\overset{\displaystyle H}{\underset{\displaystyle \overset{\downarrow}{O}}{P}}{-}OH.}$$

(c) The structure is



$$\mathrm{HO{-}\overset{\displaystyle \overset{O}{\uparrow}}{\underset{\displaystyle OH}{P}}{-}O{-}\overset{\displaystyle \overset{O}{\uparrow}}{\underset{\displaystyle OH}{P}}{-}OH.}$$

33. (a) It is not a reducing agent as no hydrogen atom is attached to phosphorus.
(b) The products are phosphorous and phosphoric acids.
(c) The acid produced is phosphoric acid.
(d) The acid produced is phosphoric acid.

34. (a) Sulphurous acid has not been isolated in the free state.

35. (a) It is a triangular planar with three resonating structures.
(c) The reverse is true.

36. (a) It is a reducing agent.
(b) The reaction is $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$
(c) Stronger the hydrogen bonding, weaker the acid.

37. (a) In acidic medium, chlorite disproportionates as $4HClO_2 \rightarrow 2ClO_2 + HCl + HClO_3 + H_2O$
(c) Chlorous acid exists only in the solution.

41. (c) Lone pair—lone pair repulsion in N—F bond makes this bond longer than the sum of the single bond covalent radii of N and F.
(d) Only two series of salts ($Na_2H_2P_2O_7$ and $Na_4P_2O_7$) are formed.

CHAPTER 16

TRANSITION ELEMENTS

A transition element in its elementary form or in at least one of its oxidation states, possesses partially filled d orbitals in its penultimate shell. This definition excludes zinc, cadmium and mercury from the transition elements because they do not contain a partially filled d orbital either in the elementary state or in their oxidation states. However, their properties are an extension of the properties of transition elements, they are generally considered along with the transition elements.

Three series of elements are formed by filling the 3d, 4d and 5d shells by electrons. These are collectively known as d-block elements. The three series are as follows.

First series or 3d series : From scandium ($Z = 21$) to zinc ($Z = 30$)
Second series or 4d series : From yttrium ($Z = 39$ to cadmium ($Z = 48$)
Third series or 5d series : From lanthanum ($Z = 57$), hafnium ($Z = 72$) to mercury ($Z = 80$)

These elements are known as transition elements because their position in the periodic table is between the s-block and p-block elements.

The outer electronic configurations of the elements of the first transition series are given in Table 16.1.

Table 16.1 Electronic Configurations of 3 d Series

Atomic number	*Element name*	*Element Symbol*	*Electronic Configuration*
21	Scandium	Sc	$(3d)^1(4s)^1$
22	Titanium	Ti	$(3d)^2(4s)^2$
23	Vanadium	V	$(3d)^3(4s)^2$
24	Chromium	Cr	$(3d)^5(4s)^1$
25	Manganese	Mn	$(3d)^5(4s)^2$
26	Iron	Fe	$(3d)^6(4s)^2$
27	Cobalt	Co	$(3d)^7(4s)^2$
28	Nickel	Ni	$(3d)^8\ (4s)^2$
29	Copper	Cu	$(3d)^{10}(4s)^1$
30	Zinc	Zn	$(3d)^{10}(4s)^2$

From the above configurations, it is obvious that the electrons are added in a regular way: $3d^1$, $3d^2$, $3d^3$, ..., $3d^{10}$ with the exception of Cr and Cu. In these two elements, one of the s electrons move into the d shell, because of the additional stability of half-filled or completely-filled d shell.

The general characteristics of the transition elements are described in the following.

1. Variable Oxidation State Because of comparable energies of 3d and 4s electrons, the removal of successive electrons firstly from 4s orbital and then from 3d orbitals leads to the variable oxidation states of the transition elements.

Prior to the starting of transition elements, 4s orbital has lower energy than 3d orbitals. Consequently, 4s orbital is filled prior to 3d orbitals. But once a transition element is formed by putting electron(s) in 3d orbital(s), the removal of 4s electron(s) requires lesser energy than the 3d electron as the electronic repulsions amongst 3d and 4s electrons raises the energy of 4s electrons. Consequently, in going from the elemental form to ion, it is the 4s electrons which are removed prior to 3d electrons.

Table 16.2 describes the oxidation states exhibited by the transition elements of 3d-series. These form regular pyramid.

Table 16.2 Oxidation States

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			I					I	
II	II	II	II	II	II	II	II	II	II
III	III	III	III	III	III	III	III	III	
	IV	IV	IV	IV	IV	IV	IV		
		V	V	V	V	V			
			VI	VI	VI				
				VII					

Among the first five elements, the correlation between electronic structure and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are being used for bonding. Once the d^5 configuration is exceeded, i.e. in the last five elements, the tendency for all the d electrons to participate in bonding decreases. Because of successive increase in the effective nuclear charge and the availability of lesser number of half-filled orbitals, the number of oxidation states shown by these elements is also successively decreased.

The higher oxidation states occurs in fluorides, oxides, oxoanions and, to a limited extent, in the chlorides of the metals. Highly electronegative elements stabilize high oxidation states. The bonding in the higher state (V, VI and VII) is predominantly covalent, because the production of discrete, highly charged ions is energetically impossible in chemical systems. For the lower states (II and III) discrete ions can exists (e.g. in the oxides), but complex ion formation is an outstanding feature. In general, the lower oxidation states are reducing and the higher oxidation states are oxidizing.

2. Formation of Complexes Because of their small size, comparable high nuclear charge and availability of vacant d orbitals, the metals are capable of exerting strong electrostatic attraction to the molecule or ions containing a lone pair of electrons. This leads to the formation complex molecules. Examples include $[Co(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$ and $[Cu(NH_3)_4]\ SO_4$.

The groups that surround the metal ion are called *ligands*. The total number of the ligands bound around a metal ion is called the *coordination number* of the metal ion.

Ligands have been classified based on the number of donor atoms in a ligand. A few examples are as follows.

Monodentate : F^- ; OH^- ; NH_3 ; H_2O ; NO_2^- ; SCN^-
Bidentate : Ethylenediamine (en) ; 2,2 – bipyridine (bipy) hydrazine ; 1, 10 – phenanthroline ; dimethylglyoxime
Tridentate : Triaminopropane ; diethylenetriamine (dien)
Tetradentate : Triethylenetetramine (trien) ; triaminotriethylamine (tren)
Pentadentate : Tetraethylenepentamine (tetraen) ; ethylenediamine triacetate ion
Hexadentate : Ethylenediamine tetracetate ion

The International Union of Pure and Applied Chemistry (IUPAC) have suggested the following basic rules for naming a complex compound.

1. The positive ion is named first followed by the negative ion.
2. When writing the name of a complex, the ligands are quoted in alphabetical order, regardless of their charge (followed by the metal).
3. When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is named first, then the coordinated group are listed in the order : negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).
   (a) The names of negative ligands end in ‘-o’, e.g. fluoro (F^-), chloro (Cl^-), hydrido (H^-), thio (S^{2-}), nitro (NO_2^-) and so on.
   (b) Neutral groups have no special endings, e.g. ammine (NH_3), aqua (H_2O), carbonyl (CO) and nitrosyl, (NO).
   (c) Positive groups end in ‘-ium’, e.g. hydrazinium ($H_2NNH_3^+$)
4. Where there are several ligands of the same kind, we normally use the prefixes di, tri, tetra, penta and hexa to show the number of ligands of that type. For ligands already containing such number, the prefixes bis, tris and tetrakis are used to indicate the numbers of ligands. In such a case, ligand is written within the brackets immediately after the prefix.
5. The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the name without any intervening blank, e.g. cobalt(II) and cobalt(III).

6. Complex positive ions and neutral molecules have no special ending but complex negative ions end in '-ate'.
7. If the complex contains two or more metal atoms, the bridging ligands are indicated by the prefix μ.
8. Sometimes a ligand may be attached through different atoms. For example, M—NO_2 is called a nitro and M—ONO is called nitrito; M—SCN is called thiocyanato and M—NCS isothiocyanto.
9. Water or solvent of crystallization are indicated after the name of the complex. Arabic numerals are used to indicate the number of such molecules.

A few examples of naming the complex compounds are given in the following.

$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride	$Na_2[ZnCl_4]$	Sodium tetrachlorozincate (II)
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechlorocobalt (III) ion	$K_3[Fe(CN)_5(NO)]$	Potassium pentacyanonitrosoylferrate (II)
$[CoSO_4(NH_3)_4]NO_3$	Tetramminesulphatocobalt (III) nitrate	$Fe(C_2H_5)_2$	Bis(cyclopentadienyel)iron (II)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt (III)	$Cr(C_6H_6)_2$	Bis(benzene)chromium (0)

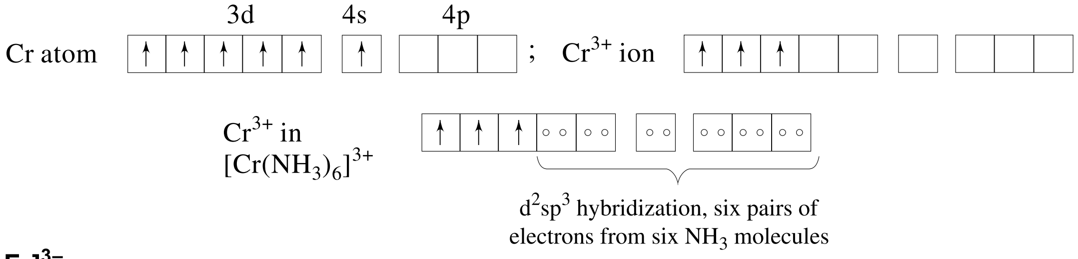
The simplest theory to explain bonding in complex compounds is the valence bond theory as developed by Linus Pauling. The salient features of the theory are as follows.

1. The central metal loses a requisite number of electrons to form the ion. The number of electrons lost is the valence of the resulting cation.
2. The cation makes available a number of orbitals equal to its coordination number, for the formation of covalent bonds with the ligands.
3. The cation orbitals hybridize to form a new set of equivalent hybrid orbitals with definite directional characteristics.
4. The nonbonding metal electrons occupy the inner d orbitals and do not participate in the hybridization.
5. Each ligand contains a lone pair of electrons. A covalent bond is formed by the overlap of a vacant hybrid metallic orbital and a filled orbital of the ligand.

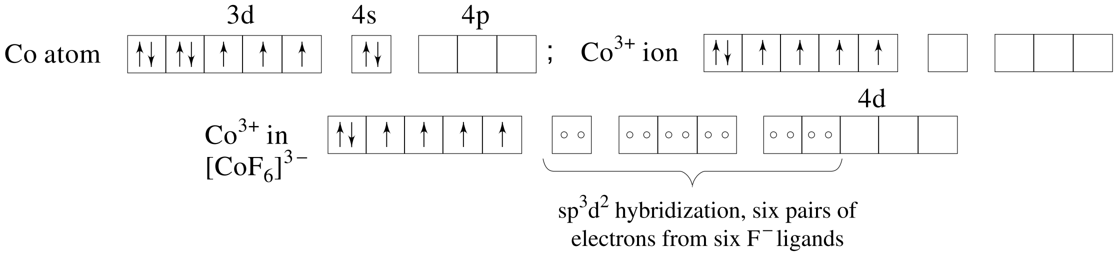
The above rules are illustrated with the following typical examples.

(i) $[Cr(NH_3)_6]^{3+}$

The outer electronic configuration of Cr is $(3d)^5(4s)^1$. Chromium in the above complex is in +3 oxidation state, hence, Cr(III) has the configuration of $(3d)^3$. There are six ligands, so six empty orbitals of chromium are required. These include two 3d orbitals, one 4s orbital and three 4p orbitals. These orbitals hybridize to give d^2sp^3 hybrid orbitals directed towards the corners of an octahedron. The final configuration of the complex will contain three unpaired electrons in three 3d orbitals of chromium. Hence, the complex will be paramagnetic. The above description is diagrametically represented as follows.



(ii) $[CoF_6]^{3-}$



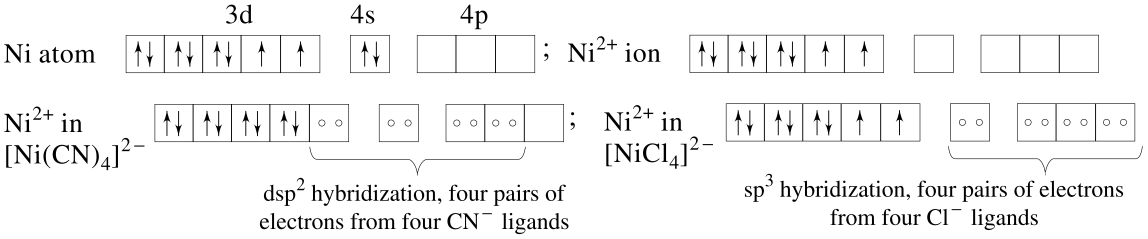
The complex $[CoF_6]^{3-}$ is octahedral and is strongly paramagnetic.

Inner and Outer Orbital Octahedral Complexes

In the inner orbital octahedral complexes, d^2sp^3 hybridization in the central metal occurs while in the outer orbital complexes, sp^3d^2 hybridization is involved.

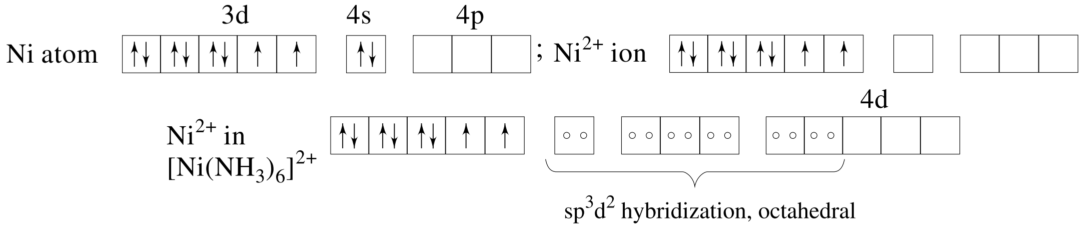
The inner orbital complexes involve lesser number of unpaired electrons and thus these are called as low spin complexes. On the other hand, the outer orbital complexes involve comparatively larger number of unpaired electrons and thus are called high spin complexes.

(iii) $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$



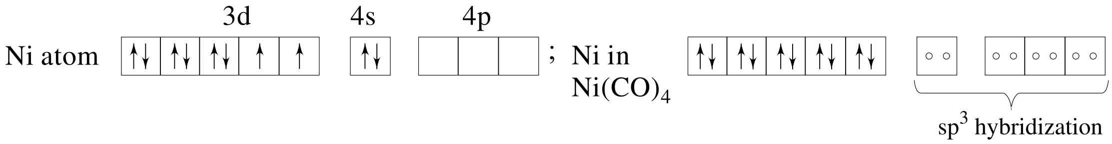
$[Ni(CN)_4]^{2-}$ is a square planar (dsp^2 hybridization) and diamagnetic (no unpaired electrons) while $[NiCl_4]^{2-}$ is tetrahedron (sp^3 hybridization) and paramagnetic (two unpaired electrons). The CN^- ligand is strong and it forces the two unpaired electrons to pair up.

(iv) $[Ni(NH_3)_6]^{2+}$



$[Ni(NH_3)_6]^{2+}$ has an octahedral structure and is paramagnetic (two unpaired electrons).

(v) $Ni(CO)_4$



$Ni(CO)_4$ has a tetrahedral structure and is diamagnetic (no unpaired electrons).

Isomerism in Coordination Compounds

Coordination compounds exhibit various types of isomerism. A brief description of these are as follows.

Ionization Isomerism The isomers involving the exchange of ligand in the coordination sphere and the anion present outside the coordination sphere are known as ionization isomers. For example, $[Co(NH_3)_5 Br]SO_4$ and $[Co(NH_3)_5 (SO_4)]Br$.

Linkage Isomerism The isomers involving the attachement of different donor atom of a ligand to the metal in the coordination sphere are known as linkage isomers. For example $[Co(NH_3)_5 (NO_2)]Cl_2$ and $[Co(NH_3)_5 (ONO)]Cl_2$

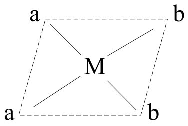
Coordination Isomerism The isomers involving the exchange of ligands between the complex cation and complex anion of a complex compound are known as coordinate isomers. For example, $[Cr(NH_3)_6]^{3+}[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}[Cr(CN)_6]^{3-}$.

Geometrical Isomerism The isomers involving the different geometrical arrangement of ligands around the central metal atom are known as geometrical isomers. The two identical ligands occupying the adjacent positions is known as *cis* isomer while those occupying the opposite positions are known as *trans* isomers.

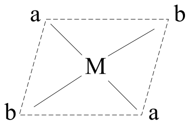
Representing monodentate by the lower case alphabets (such as a, b, c, ..) and bidentate by the upper case alphabets (such as AA and AB), the geometrical isomerism in complex compounds are as follows.

Geometical Isomerism in Square Planar Complexes

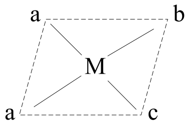
- The complexes $[Ma_4]$ and $[Ma_3b]$ do not exhibit geometrical isomerism.
- The complexes $[Ma_2b_2]$ and $[Ma_2bc]$ exhibit *cis* – *trans* isomers.



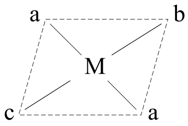
Cis



Trans

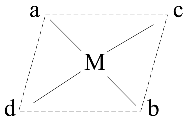


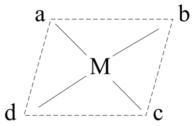
Cis

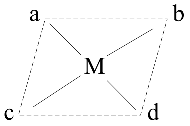


Trans

- The complex [Mabcd] exists in three isomeric forms

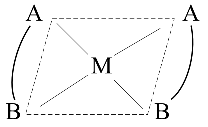




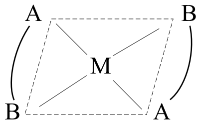


  This have different pairs of ligands at the *trans* positions.

- The complex $[M(AB)_2]$ also exists in *cis*- and *trans*-forms.



Cis



Trans

Geometrical Isomerism in Octahedral Complexes

In an octahedral complex, if the two similar ligands occupy positions at the two ends of the twelve edges of the octahedron, the complex is the *cis* isomer.

These positions are 1–2, 1–3, 2–3, 3–6, etc. as shown in Fig. 16.1

If the two similar ligands occupy positions at the end of a straight line passing through the centre of the octahedron (which is occupied by the central atom M), the complex is the *trans* isomer. These positions are 1–6, 2–4 and 3–5 shown in Fig. 16.1

Number of isomers of a complex The number of isomers for the complex [Mabcdef] may be computed as follows.

1. Keep one of the ligands (say, a) at the position 1 of the octahedron. Its *trans* position 6 can be occupied by any one of the remaining 5 ligands giving a total of 5 such configurations.
2. Leaving these two ligands, we have four remaining ligands which will occupy two *trans* positions 2–4 and 3–5. The number of ways of picking 2 ligands from the remaining four ligands is ${}^4C_2 = 4!/(2!\ 2!) = 6$
3. Since two such groups of ligands are to be chosen for the two remaining *trans* positions (2–4 and 3–5), the number of ways of picking two ligands together becomes 6/2 = 3.
   Thus, three configurations can be written for the fixed ligands at positions 1 and 6.
4. Since there are five ways of having fixed ligands, the total number of configurations or isomers for the complex [Mabcdef] becomes 5 × 3 = 15.

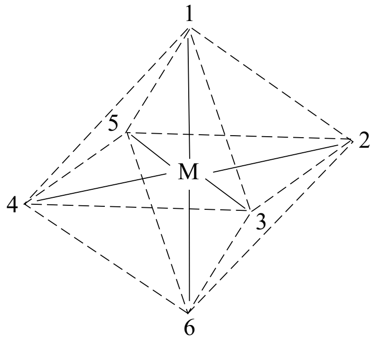


Fig. 16.1

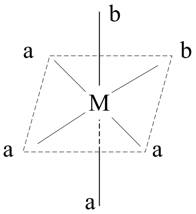
The above 15 isomers do not include enantiomer for an isomer which is asymmetric in nature. In fact, for six different ligands, each one will have its enantiomer.

The above procedure may be adopted for the complexes $[Ma_2bcde]$, $[Ma_2b_2cd]$, $[Ma_2b_2c_2]$, $[Ma_3b_3]$, [M(AA)bcde], [M(AB)bcde] and so on. From the fifteen configurations thus obtained, the repeated configurations are excluded for getting the number of isomers for a given complex compound.

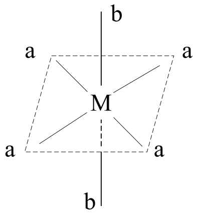
A brief account of geometrical isomers of a few complex compound is given below.

- The complexes $[Ma_6]$, $[Ma_5b]$ and $[M(AA)_3]$ do not show geometrical isomerism.
- The complexes $[Ma_4b_2]$, $[Ma_3b_3]$ and $[Ma_4bc]$ exhibit two isomers each.

$[Ma_4b_2]$



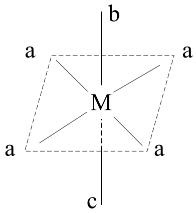
Cis-isomer



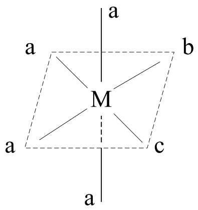
Trans-isomer

In *cis*–form, the two ‘b’ ligands occupy adjacent positions (e.g. 1 and 2).
In *trans*–form, the two ‘b’ ligands occupy opposite positions (e.g. 1 and 6)

$[Ma_4bc]$



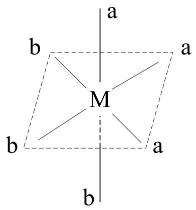
Cis-isomer



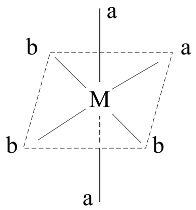
Trans-isomer

In *cis*–form, the two ‘a’ ligands have *cis* positions to each other.
In *trans*–form, the two a ligands have *trans* positions to each other.

$[Ma_3b_3]$



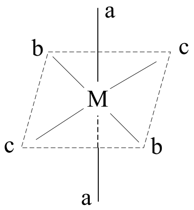
Cis-isomer



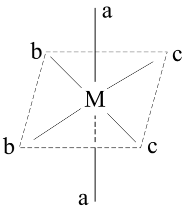
Trans-isomer

In *cis*–form, the three ligands ‘a’ occupy positions at the corners of a triangular face and the three ‘b’ ligands occupy positions at the corners of the opposite face. This isomer is also known as facial (abbreviation–face) isomer
The *trans*–form is known as meridonal (abbreviation–mer) isomer.

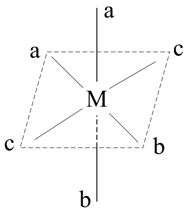
- The complex $[Ma_2b_2c_2]$ exists in five geometrical isomers, (there are five ways of distributing pairs of ligands in trans positions), one of which also has its enantiomer, thus there exists a total of six isomers.



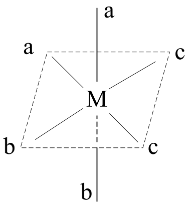
Trans positions:
aa; bb; cc



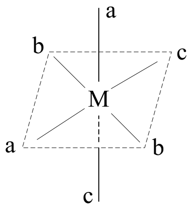
aa; bc; bc



ab; ab; cc

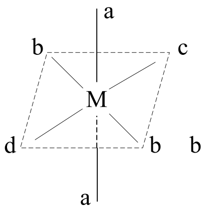


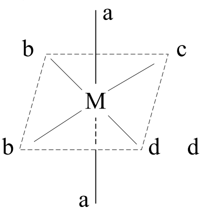
ab; ac; bc

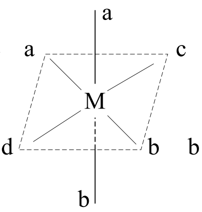


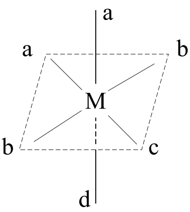
(enantiomer)
ac; bb; ac

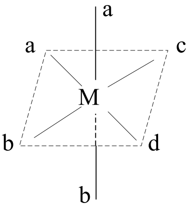
- A molecule having no plane of symmetry or centre of symmetry exists in two optically active configurations which are related to each other through the mirror image of each other and are not superimposable on each other.
- The complex $[Ma_2b_2cd]$ exhibits *six* geometrical isomers–there are six ways of distributing pairs of ligands in *trans* positions), two of which have enantiomers, thus making a total of eight isomers.



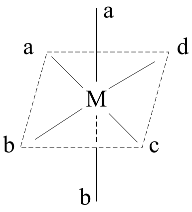






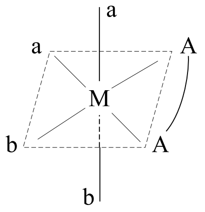


(and its enantiomer)

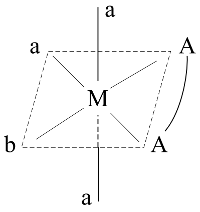


(and its enantiomer)

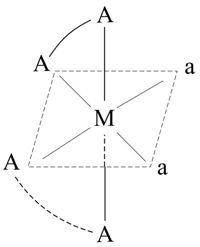
- The complex [Mabcdef] exhibits *fifteen* isomers (= ${}^6C_2$ = 6!/(4! 2!)) all of them have their enantiomers, making a total of 30 isomers.
- The complexes $[M(AA)a_2b_2]$, $[M(AA)_2a_2]$ and $[M(AA)_2ab]$, where AA is a symmetrical bidentate, exists in two forms, namely, *cis* and *trans* forms, of which *cis* form has its enantiomer.



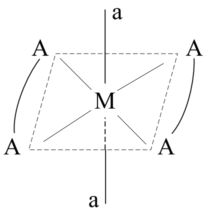
Cis-form
(and its enantiomer)



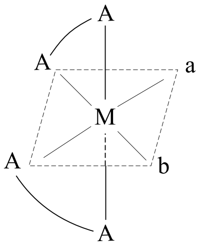
(*Trans*-form)



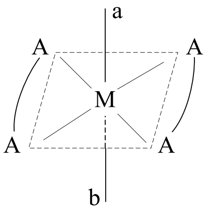
Cis-form
(and its enantiomer)



(*Trans*-form)

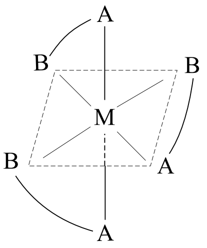


Cis-form
(and its enantiomer)

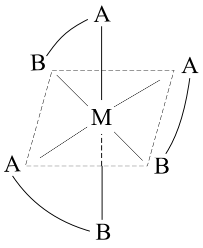


(*Trans*-form)

- The complex [M(AB)$_3$], where AB is unsymmetrical bidentate ligand in which A and B are two different donor atoms, exists in *cis*– and *trans*–forms. Each of the two also has its enantiomer.



Cis-form
(and its enantiomer)



Trans-form
(and its enantiomer)

Stability of Coordination Compounds

The stability of a complex compound depends on the nature of the metal and that of the ligand. In general, the higher the oxidation state of the metal, the more stable the complex. The cynao complexes are far more stable than those formed by halide ions. The stability of halide complexes increases in the order $Cl^- < Br^- < I^-$.

The stability of complexes also decreases with increase in the ionic size of the central metallic ion having the same charge number. For example, the stability of complexes formed from the same ligands increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+}, that is, the order of stability is

$$\underset{91\ \text{pm}}{Mn^{2+}} < \underset{83\ \text{pm}}{Fe^{2+}} < \underset{82\ \text{pm}}{Co^{2+}} < \underset{78\ \text{pm}}{Ni^{2+}} < \underset{69\ \text{pm}}{Cu^{2+}} > \underset{74\ \text{pm}}{Zn^{2+}}$$

This sequence is known as *Iriving-William order of stability* of complexes of M^{2+} ions.

The increasing order of influence of ligands (known as spectrochemical series) on the electronic configuration of central metal atom or ion is

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO^-_2 < CN^-$$

Thus, halogens are said to be weak ligands while NO_2^-, CN^- are said to be strong ligands.

3. Size of Atoms The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. The decrease is due to the increase in the effective nuclear charge. The exception at the end of the series is due to the more electronic repulsion amongst the electrons.

The elements of the first group in the d-block series show the expected increase in size Sc → Y → La. However, in the subsequent group there is an increase in the radius of 10 to 20 pm between the first and second member, but hardly any increase between the second and third elements. This is due to the lanthanide contraction which is interposed between first member (La) and second member (Hf) of 5d series. The gradual decrease in the size of the 14 lanthanide elements cancels almost exactly the normal size increase on descending a group of transition elements.

4. Density The atomic volumes of the transition elements are low as compared with elements in neighbouring Groups 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all electrons more strongly. Consequently, the densities of transition elements are high.

5. Melting and Boiling Points Because of increasing availability of d electrons, especially unpaired electrons, the transition elements have stronger metallic characteristics as compared to those belonging to Groups 1 and 2. Thus, their melting and boiling points are also higher than metals of Groups 1 and 2. In general, the melting and boiling points increase from the beginning towards the middle of each transition series, followed by decrease as electrons pairing increases toward the end of the transition series.

6. Ionization Energies The ionization energies of transition elements are intermediate between those of the s- and p-blocks. The values of ionization energy increase as one moves from left to right in each series. This is primarily due to increase in the effective nuclear charge. Generally, the compounds of transition elements in the lower oxidation states are ionic and in the higher oxidation states they are covalent.

7. Colour Many ionic and covalent compounds of transition elements are coloured. When light passes through a material, it absorbs some of the wavelengths due to electronic excitation. If absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complimentary colour to the colour of the light absorbed. The material looks coloured corresponding to the transmitted light.

In transition elements, the electronic excitation is due to d–d electronic excitation. In an isolated metal ions, d orbitals are degenerate. This degeneracy is lost when the ligands approach the metal ion. The energy of some of d orbitals is lowered while of the remaining orbitals the energy is raised. Electrons occupy the orbitals of lower energy and can be excited to higher ones with the absorption of wavelength which lies in the visible region.

Table 16.3 describes the relationship between the colour absorbed (in the visible region) and the complimentary colour observed. The colour of a transition metal ion may be related to the number of unpaired d electrons. This is shown in Table 16.4

Table 16.3 The Relationship between the Colour Absorbed and Complimentary Colour Observed

Colour Absorbed	*Complimentary Colour*
Violet	Yellow–green
Indigo	Yellow
Blue to blue green	Orange to red
Green to yellow green	Purple to violet
Orange	Blue
Red	Blue–green

Table 16.4 Colour of Some Transition Metal Ions

Number of Unpaired Electrons	*Metal Ions*	*Colour Observed*
0	Cu^+, Zn^{2+}, Sc^{2+}, Ti^{4+}	Colourless
1	Cu^{2+}, V^{4+}	Blue
2	Ni^{2+}, V^{3+}	Green
3	Co^{2+}	Pink
3	Cr^{3+}	Green
4	Fe^{2+}	Green
4	Cr^{2+}	Blue
5	Mn^{2+}	Pale pink
5	Fe^{3+}	Yellow

Crystal Field Splitting in the Complexes The ligands in a complex compound causes the splitting of d orbitals into two categories, namely, (d_{xy}, d_{xz}, d_{yz}) and ($d_{x^2-y^2}$, d_{z^2}), respectively. In the octahedron environment, the former has lower energy than in the latter categories. The reverse is observed in the tetrahedron environment. The difference in the energy levels is represented as Δ_0 and is set equal to 10 Dq. This energy difference is known as *crystal field splitting energy.* The category containing d_{xy}, d_{xz} and d_{yz} is known as t_{2g} level and is 0.4 Δ_0 (or 4Dq) from the original energy level of d orbitals. The category containing d_{z^2} and $d_{x^2-y^2}$ is known as e_g level and is 0.6 Δ_0 (or 6Dq) from the original energy level of d orbitals.

The crystal field splitting depends upon the influence power of the ligands. The ligands are said to be strong if the splitting is large and if the splitting is small, the ligands are said to be weak. It is possible to arrange ligands in the order of their increasing splitting power. This series, known *spectrochemical series*, as stated earlier is

$I^- <$ $Br^- < S^{2-} < SCN^- < Cl^- < NO_3^-$, $F^- <$ urea, $OH^- < Ox^{2-}$, $O^{2-} < H_2O < NCS^- <$ Py, $NH_3 <$ en $< NO_2^- < CH_3^- < CN^- < CO$

8. Metallic characteristics Due to decrease in atomic size and increase in ionization energy, the metallic characteristics decrease as one moves from left to right in a d–series elements. This is reflected in the decrease of basicity of metallic(II) oxides. For examples the basicity follows the order TiO > VO > CrO > FeO.

The oxides of a given transition element in lower oxidation states are basic. Those of the same metal in intermediate oxidation states are amphoteric while those of the metal in higher oxidation states are acidic. This also follows from the fact that covalent character of the metallic compounds increases on increasing the oxidation state of the metal. The following examples illustrate the above fact.

VO	; V_2O_3	; VO_2	; V_2O_5	
Basic	Basic	Amphoteric	Acidic	
CrO	; Cr_2O_3	; CrO_2	; CrO_3	
Basic	Amphoteric	Amphoteric	Acidic	
MnO	; Mn_3O_4	; Mn_2O_3	; MnO_2	; Mn_2O_7
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

9. Magnetic Properties A substance is paramagnetic if it contains unpaired electrons and is diamagnetic if there are no unpaired electrons. As the transition metal ions usually contain unpaird d–electrons, they are paramagnetic in nature. The magnetic moment (μ) of a paramagnetic species is related to the number of unpaired electrons through the expression $\mu = \sqrt{n\,(n+2)}\ \mu_B$ where μ_B is Bohr magneton ($= 9.273 \times 10^{-24}$ J T^{-1})

10. Catalytic Activity Many transition metals and their compounds have catalytic properties. Table 16.5 includes some of the important catalysts.

Table 16.5 Some Important Catalysts

Catalyst	*Reaction Catalysed*
$TiCl_4$	Polymerization of ethene and propene. This is known as Natta catalyst.
V_2O_5	Conversion of SO_2 to SO_3 in the contact process (formation of H_2SO_4)
MnO_2	Decomposition of $KClO_3$ to give O_2.
Fe	Manufacture of ammonia in the Haber process.
Pd	Hydrogenation, e.g. phenol to cyclohexanone.
Cr_2O_3 + ZnO	Conversion of CO and H_2 into CH_3OH
Ni	Hydrogenation of double bond
$PdCl_2$	Conversion of $C_2H_4 + H_2O + PdCl_2$ to $CH_3CHO + 2HCl + Pd$
Pt	Formely used in the contact process to convert SO_2 into SO_3.
Mn^{2+}	Autocatalyst in MnO_4^- and $(COOH)_2$ reaction.

INNER–TRANSITION ELEMENTS

The elements from ${}_{58}Ce$ to ${}_{71}Lu$ and from ${}_{90}Th$ to ${}_{103}Lw$ are called inner–transition elements, also known as f–block elements.

The elements from ${}_{58}Ce$ to ${}_{71}La$ are known as lanthanides (or lanthanones) while those from ${}_{90}Th$ to ${}_{103}Lw$ are known as actinides (or antinones). These names are from the elements ${}_{57}La$ (lanthanum) and ${}_{89}AC$ (actinium), respectively. The valence-shell electronic configurations of these elements may be represented as $(n–2)f^{0–14}\ (n–1)d^{0–2}ns^2$, where n = 6 and 7, respectively.

The fourteen lanthanides are as follows.

Cerium ($_{58}$Ce), Praseodymium ($_{59}$Pr), Neodymium ($_{60}$Nd), Promethium ($_{61}$Pm), Samarium ($_{62}$Sm), Europous ($_{63}$Eu), Gadolinium ($_{64}$Gd), Terbium ($_{65}$Tb), Dysprosium ($_{66}$Dy), Holomium ($_{67}$Ho), Erbium ($_{68}$Er), Thullium ($_{69}$Tm), Ytterbium ($_{70}$Yb) and Luteium ($_{71}$Lu).

The main oxidation state of the lanthanides is +3, although a few elements also show +2 and +4 oxidation states. The latter may be rationalized on the basis of attaining stable $4f^0$, $4f^7$ and $4f^{14}$ configurations.

The atomic and ionic radii of M^{3+} ion show steadily decrease with the increase in atomic number. This decrease, known as lanthanide contraction, can be explained on the basis of increase in effective nuclear charge due to the poor shielding of the nuclear charge by the incoming 4f electron. The consequences of this lanthanide contraction are as follows.

- The basic character of $M(OH)_3$ decreases with increase in the atomic number due to increase in the covalent character of the bond between M^{3+} and OH^- ion.
- The chemical properties are quite similar to each other.
- The atomic radii of the elements of 2nd transition series are almost equal to those for the elements of 3rd transition series. Due to the similarity in the covalent radii, the elements of 2nd and 3rd transition series show close similarity in their properties. Examples of the pairs of elements which show similar properties (and are also difficult to separate from each other) are Zr – Hf, Nb – Ta, Mo –W, Ru – Os, Rh – Ir, Pd – Pt and Ag – Au.

Other Characteristic Properties

- Most of M^{3+} ions are coloured. The ions having *n* electrons in 4f orbitals has the same colour as that of the element having 14 – *n* electrons.
- Magnetic properties of lanthanides are due to the unpaired electrons.
  The orbital motion of 4f electrons is not quenched as in the case of 3d electrons, consequently, the magnetic properties of 4f elements are decided by both the orbital as well as spin motion of electrons.
- The lanthanide ions have poor tendency to form complexes owing to the small value of charge–to–radius ratio.

ORGANOMETALLIC COMPOUNDS

Organometallic compounds contain at least one metal–carbon bond. The elements B, Si, Ge, As, Sb and Te are all considered as metals in organometallic compounds. The latter may be classified into three categories, namely, sigma bonded complexes, pi bonded complexes and complexes having both sigma and pi bonding. Examples of these are given below.

σ – *bonded* Grignard reagent, $Al_2(CH_3)_6$, $Al(C_6H_5)_6$, $Pb(CH_3)_4$, $Pb(C_2H_5)_4$, $Zn(C_2H_5)_2$ etc.
π – *bonded* Ferrocene, dibenzenechromium, and Zeise's salt.
σ *and* π *bonded* Tetracarbonylnickel(0), pentacarbonyliron(0), hexacarbonyl of Cr, Mo and W.

In π-bonded complexes, the number of carbon atoms boud to the metal is shown by prefixes η^2, η^5 and η^6 depending upon two, five and six carbon atoms, respectively.

Organometallic compounds find many applications in chemistry. For example, Grignard reagents are used in organic synthetic reactions, Wilkinson's catalyst is used in the homogeneous catalyst in the hydrogenation of alkenes and Zeigler Natta catalysts are used in the heterogeneous catalysts in the polymerization of olefins.

Straight Objective Type

General Characteristics

1. Which of the following facts is not shown by transition metals?
(a) Formation of coloured salts (b) Variable oxidation state
(c) Inert pair effect (d) Catalytic activity

2. A transition element containing only one electron in 4s orbital is
(a) $_{21}$Sc (b) $_{23}$Mn (c) $_{26}$Fe (d) $_{29}$Cu

3. The outer electronic configuration of copper is
(a) $(3d)^{10}(4s)^1$ (b) $(3d)^9(4s)^2$ (c) $(3d)^{10}(4s)^0$ (d) $(3d)^{10}(4s)^2$

4. The catalyst used in the Haber process for the manufacture of ammonia is
(a) Pt (b) Pd (c) Ni (d) Fe

5. The number of ions furnished per molecule of the complex $[Ni(NH_3)_4]Cl_2$ is
(a) 1 (b) 2 (c) 3 (d) 4

6. Chlorophyll is a/an
(a) magnesium complex (b) cobalt complex (c) iron complex (d) chromium complex

7. Haemoglobin is a/an
(a) iron(II) complex (b) cobalt(III) complex
(c) magnesium(II) complex (d) chromium(III) complex

8. Vitamin B_{12} is a complex of
(a) Cobalt(II) ion (b) Cobalt(III) ion (c) Chromium(II) ion (d) Chromium(III) ion

9. The number of ions produced by the complex $[Co(NH_3)_4Cl_2]Cl$ is
(a) 2 (b) 3 (c) 4 (d) 6

10. Which compound is formed when excess KCN is added to aqueous solution of copper sulphate?
(a) $Cu(CN)_2$ (b) $K_2[Cu(CN)_4]$ (c) $K[Cu(CN)_2]$ (d) $K_3[Cu(CN)_4]$ (1997)

11. Ionic radii of
(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < {}^{37}Cl^-$ (c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$ (1999)

12. Which of the following does not represent the correct sequence of indicated property?
(a) $Sc^{3+} > Fe^{3+} > Mn^{3+}$; stability of +3 oxidation state
(b) $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+}$; magnetic moment
(c) FeO > CoO > NiO; basic character
(d) Se < Ti < Cr < Mn; number of oxidation states

13. Lanthanide contraction is due to poor shielding of
(a) 4f electron from 5d electron (b) 4f electron from 6s electron
(c) 4f electron from 4f electron (d) 4f electron from 4d electron

14. Which of the following configurations would lead to the lowest value of third ionization energy?
(a) $(4f)^4(6s)^2$ (b) $(4f)^6(6s)^2$ (c) $(4f)^7(6s)^2$ (d) $(4f)^7(5d)^1(6s)^2$

15. The basic character of the transition metal monoxides follows the order
(a) CrO > VO > FeO > TiO (b) TiO > FeO > VO > CrO
(c) TiO > VO > CrO > FeO (d) VO > CrO > TiO > FeO (2003)
Given: Atomic numbers of Ti, V, Cr and Fe are 22, 23, 24 and 26, respectively.

16. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is
(a) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$ (b) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(c) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$ (d) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
Given: Atomic numbers of Y, Lu, Eu and La are 39, 71, 63 and 57, respectively. (2003)

17. How many ions are produced from $[Co(NH_3)_6]Cl_3$ in the solution?
(a) 3 (b) 4 (c) 5 (d) 6

18. Wilkinson's catalyst used as a homogeneous catalyst in hydrogenation of alkene contains
(a) iron (b) aluminium (c) rhodium (d) cobalt

19. The highest oxidation state of chromium is
(a) +4 (b) +5 (c) +6 (d) +7

20. Oxidation of Cr^{3+} in acid solution forms
(a) CrO_2^- (b) CrO_4^{2-} (c) $Cr_2O_7^{2-}$ (d) Cr^{2+}

21. Reduction of MnO_4^- in strongly basic solution produces
(a) Mn^{2+} (b) MnO_4^{2-} (c) MnO_2 (d) Mn_2O_7

22. The oxidation states of Mn in K_2MnO_4 and $KMnO_4$ respectively are
(a) +6, +7 (b) +6, +6 (c) +7, +7 (d) +7, +6

23. The oxidation states of Cr in $K_2Cr_2O_7$ and K_2CrO_4 respectively are
(a) +6, +7 (b) +7, +6 (c) +6, +6 (d) +7, +7

24. Which of the following complexes is stable?
(a) $[CdCl_4]^{2-}$ (b) $[CdBr_4]^{2-}$ (c) $[CdI_4]^{2-}$ (d) $[Cd(CN)_4]^{2-}$

25. Which of the following statements is **not** correct?
(a) The stability constant of $[Co(NH_3)_6]^{3+}$ is larger than that of $[Co(NH_3)_6]^{2+}$
(b) The cyano complexes are far more stable than those formed by halide ions

(c) The stability of halide complexes follows the order $I^- < Br^- < Cl^-$
(d) The stability constant of $[Cu(NH_3)_4]^{2+}$ is larger than that of $[Cd(NH_3)_4]^{2+}$

26. Which one of the following transition elements displays the highest oxidation state?
(a) Cr (b) Mn (c) Fe (d) V

27. The Irving–Williams order regarding the stability of the complexes of bivalent metal of the first transition series is
(a) Mn < Fe < Co < Ni < Cu < Zn (b) Mn > Fe > Co > Ni > Cu > Zn
(c) Mn < Fe < Co > Ni > Cu > Zn (d) Mn > Fe > Co < Ni < Cu < Zn

28. The number of unpaired electrons in V^{3+} ions is
(a) 1 (b) 2 (c) 3 (d) 5

29. The elements with the larger number of oxidation states is
(a) Co (b) V (c) Mn (d) Ti

30. Which one of the following exhibits oxidation state of +8 in its compounds?
(a) Iron (b) Osmium (c) Chromium (d) Manganese

31. The oxidation state of Ni in $Ni(CO)_4$ is
(a) zero (b) +1 (c) +2 (d) –1

32. The most characteristic oxidation state of lanthanide is
(a) +1 (b) +2 (c) +3 (d) +4

33. The element which follows the lanthanides in the 6th period is
(a) Hf (b) Zr (c) Nb (d) Mn

34. Which of the following has the maximum number of unpaired electrons?
(a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+} (1996)

35. The complex ion with 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) $[Cr(H_2O)_6]^{3+}$ (2001)

36. The fusion of MnO_2 with KOH in air produces
(a) purple coloured $KMnO_4$ (b) purple-green coloured K_2MnO_4
(c) reddish-brown coloured Mn_2O_7 (d) brown coloured Mn_2O_3

37. Excess of KCN is added to an aqueous solution of $CuSO_4{\cdot}5H_2O$. This causes
(a) the formation of $Cu(CN)_2$
(b) the formation of $Cu(OH)_2$
(c) the formation of complex ion $[Cu(CN)_4]^{2-}$
(d) the precipitation of CuCN which dissolves forming the complex ion $[Cu(CN)_4]^{3-}$ (2006)

38. Given:
$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag(NH_3)^+ + NH_3; \qquad K_1^o = 1.4 \times 10^{-4}$$
$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3; \qquad K_2^o = 4.3 \times 10^{-4}$$
The instability constant of the complex $Ag(NH_3)_2^+$ is equal to
(a) 7.14×10^3 (b) 2.33×10^3 (c) 6.02×10^{-8} (d) 1.66×10^7 (2006)

39. The bond length of CO is 112.8 pm. Its bond length in $Fe(CO)_5$ will be about
(a) 112.8 pm (b) 110 pm (c) 113 pm (d) 120 pm (2006)

40. Among the following metal carbonyls, the C—O bond order is lowest in
(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$ (c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$ (2007)

Complexes

41. When excess of NH_4OH is added to the aqueous solution of $CuSO_4$, the compound crystallized after the addition of alcohol is
(a) $[Cu(NH_3)_4](OH)_2$ (b) $[Cu[NH_3)_4]SO_4$ (c) $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ (d) $[Cu(NH_3)_4]SO_4{\cdot}2H_2O$

42. The IUPAC name of $[Fe(CN)_6]^{3-}$ ion is
(a) hexacyanoferrate(II) ion (b) hexacyanoferrate(III) ion
(c) hexacyanideiron(II) ion (d) iron(III) hexacyanide ion

43. The IUPAC name of $[Ni(CO)_4]$ is
(a) tetracarbonylnickel(II) (b) tetracarbonylnickel(0)
(c) tetracarbonylnickelate(II) (d) tetracarbonylnickelate(0)

44. The IUPAC name of $[Ni(CN)_4]^{2-}$ is
(a) tetracyanonickel(II) ion (b) tetracyanonickel(0) ion
(c) tetracyanonickelate(II) ion (d) tetracyanonicklate(0) ion

45. The IUPAC name of $K_3[Co(NO_2)_6]$ is
(a) potassium(I) hexanitrocobaltate(II) (b) potassium(I) hexanitrocobaltate(III)
(c) potassium hexanitrocobalt(0) (d) potassium hexanitrocobaltate(III)

46. The IUPAC name of $[Pt(NH_3)_4(NO_2)Cl]SO_4$ is
(a) tetramminechloronitroplatinum(II) sulphate (b) tetramminechloronitroplatinum(IV) sulphate
(c) chlorotetramminenitroplatinum(IV) sulphate (d) chloronitrotetrammineplatinum(IV) sulphate

47. en is an example of a
(a) monodentate ligand (b) bidentate ligand (c) tridentate ligand (d) hexadentate ligand

48. Which of the following is tridentate ligand?
(a) NO^-_2 (b) Oxalate ion (c) Glycinate ion (d) dien

49. Which of the following is tetradentate ligand?
(a) en (b) dien
(c) trien (d) ethylenediaminetriacetate

50. Which of the following is pentadentate ligand?
(a) en (b) dien
(c) trien (d) Ethylenediaminetriacetate ion

51. Which of the following is hexadentate ligand?
(a) dien (b) trien
(c) Ethylene bis(salicylaldimine) ion (d) Ethylenediaminetetracetate ion

52. The IUPAC name of $[CoCl_2(en)_2]Cl$ is
(a) bis(ethylenediammine)dichlorocobalt(III) chloride
(b) dichlorobis(ethylenediammine)cobalt(III) chloride
(c) dichlorobis(ethylenediammine)cobalt(I) chloride
(d) trichlorobis(ethylenediammine)cobalt(0)

53. Which of the following is not an example of σ-bonded organometallic compound?
(a) $Al_2(CH_3)_6$ (b) $Pb(CH_3)_4$ (c) $Zn(C_2H_5)_2$ (d) Ferrocene

54. Which of the following is not an example of π-bonded organometallic complex?
(a) Ferrocene (b) Dibenzenechromium (c) Zeise's salt (d) $Pb(CH_3)_4$

55. Which of the following statements is correct?
(a) Metal carbonyls are the examples of σ-bonded organometallic complexes
(b) Metal carbonyls are the examples of π-bonded organometallic complexes
(c) Metal carbonyls are the examples of organometallic complexes which involve both σ- and π-bonds between metal and carbon of carbonyl group
(d) Metal carbonyls involve both σ- and π-bonds between metal and oxygen of carbonyl group

56. Zeise's salt is
(a) $Fe(\eta^5 - C_5H_5)_2$ (b) $Cr(\eta^6 - C_6H_6)_2$ (c) $K[Pt\ (\eta^2 - C_2H_4)Cl_3]$ (d) $K[Pt\ (\eta^2 - C_2H_4)_2Cl_2]$

57. Dimethylglyoxime is coordinated to Ni^{2+} through
(a) two oxygen atoms (b) two nitrogen atoms
(c) two oxygen and one nitrogen atoms (d) two oxygen and two nitrogen atoms

58. Ferrocene is
(a) $Fe(\eta^2 - C_6H_5)_2$ (b) $Fe(\eta^5 - C_5H_5)_2$ (c) $Fe(\eta^6 - C_6H_6)_2$ (d) $Fe\ (\eta^3 - C_3H_3)_2$

59. In carbonyls, the carbon monoxide is linked to metal atom through
(a) carbon atom forming a weak σ bond and a weak π bond
(b) carbon atom forming a strong σ bond and a strong π bond
(c) oxygen atom forming a weak σ bond and a weak π bond
(d) oxygen atom forming a strong σ bond and a strong π bond

60. The complex $CuSO_4{\cdot}5H_2O$ is represented as
(a) $[Cu(H_2O)_5]SO_4$ (b) $[Cu(H_2O)_4]{\cdot}SO_4(H_2O)$
(c) $[Cu(H_2O)_4]\ SO_4]{\cdot}H_2O$ (d) $[Cu(H_2O)_2SO_4]{\cdot}3H_2O$

61. The IUPAC name of $[Ni(NH_3)_4]$ $[NiCl_4]$ is
(a) Tetrachloronickel(II)–tetraamminenickel(II) (b) Tetraamminenickel(II)–tetrachloronickel(II)
(c) Tetraamminenickel(II)–tetrachloronickelate(II) (d) Tetrachloronickel(II)–tetraamminenickelate(0)
(2008)

Geomety of Complexes

62. Which of the following statements about the complex $[CoF_6]^{3-}$ which is paramagnetic in nature is correct?
(a) Cobalt involves d^2sp^3 hybridization (b) Cobalt involves sp^3d^2 hybridization
(c) F is in zero oxidation state (d) Co is in +2 oxidation state

63. Which of the following statements is not correct?
(a) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the state of hybridization of nickel
(b) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the magnetic properties
(c) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the geometry
(d) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in primary valencies of nickel

64. Which of the following statements is **not** correct?
(a) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$differ in the state of hybridization
(b) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ differ in the magnetic properties
(c) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ differ in the primary valencies of nickel
(d) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ have nickel in the different oxidation states

65. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are
(a) both square planar (b) tetrahedral and square planar, respectively
(c) both tetrahedral (d) square planar and tetrahedral, respectively.
(1999)

66. A complex involving dsp^2 hybridization has
(a) a square planar geometry (b) a tetrahedral geometry
(c) an octahedral geometry (d) trigonal planar geometry

67. A complex involving d^2sp^3 hybridization is
(a) a square planar geometry (b) a tetrahedral geometry
(c) an octahedral geometry (d) trigonal planar geometry

68. Which of the following complex ions possesses d^2sp^3 hybridization?
(a) $[Ni(NH_3)_6]^{2+}$ (b) $[CoF_6]^{3-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[FeF_6]^{3-}$

69. Which of the following complexes ions possesses dsp^2 hybridization?
(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(CO)_4]$ (c) $[NiCl_4]^{2-}$ (d) $[Ni(PF_3)_4]$

70. Which of the following complexes has magnetic moment of 2.83 Bohr magneton?
(a) $[Co(H_2O)_6]Cl_3$ (b) $[Ni(H_2O)_6]Cl_2$ (c) $[Cu(NH_3)_6]Cl_2$ (d) $[Mn(H_2O)_6]Cl_2$

71. Which of the following complex ions possesses sp^3d^2 hybridization?
(a) $[Cr(NH_3)_6]^{3+}$ (b) $[FeF_6]^{3-}$ (c) $[Co(NO_2)_6]^{3-}$ (d) $[TiF_6]^{3-}$

72. Which of the following is not a tetrahedral complex?
(a) $Ni(CO)_4$ (b) $K_2[Ni(CN)_4]$ (c) $K_3[Cu(CN)_4]$ (d) $[NiCl_4]^{2-}$

73. The species having tetrahedral shape is
(a) $Ni(CO)_4$ (b) $[Ni(CN)_4]^{2-}$ (c) $[PdCl_4]^{2-}$ (d) $[Pd(CN)_4]^{2-}$ (2004)

74. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridizations of nickel in these complexes, respectively, are
(a) sp^3, sp^3 (b) sp^3, dsp^2 (c) dsp^2, sp^3 (d) dsp^2,dsp^2 (2008)

Magnetism of Complexes

75. Among 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) $FeSO_4 \cdot 6H_2O$ (c) $CuSO_4 \cdot 5H_2O$ (d) $NiSO_4 \cdot 6H_2O$ (1988)

76. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$
(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(b) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic
(d) $Ni(CO)_4$ is diamagnetic and, $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic (1991)

77. Amongst the following ions which one has the highest paramagnetism?
(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$ (c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$ (1990)

78. A substance which is not paramagnetic is
(a) $Cr(ClO_4)_3$ (b) $KMnO_4$ (c) $TiCl_3$ (d) $VOBr_2$

79. The expression of magnetic moment of a paramagnetic species in terms of Bohr magneton (μ_B) and number of unpaired electrons (n) is
(a) $\mu = n\,\mu_B$ (b) $\mu = \sqrt{n\,(n+1)}\ \mu_B$
(c) $\mu = \sqrt{n\,(n+2)}\ \mu_B$ (d) $\mu = \sqrt{n\,(n+1)\,(n+2)}\ \mu_B$

80. The ratio of mass of a paramagnetic substance in a magnetic field to its actual mass
(a) is greater than one (b) is less than one (c) is equal to one (d) cannot be predicted

81. The ratio of mass of a diamagnetic substance in a magnetic field to its actual mass
(a) is greater than one (b) is less than one (c) is equal to one (d) cannot be predicted

82. The calculated value of magnetic moment of $_{22}Ti^{3+}$ is
(a) 1.73 μ_B (b) 2.83 μ_B (c) 3.87 μ_B (d) 4.9 μ_B

83. The calculated value of magnetic moment of $_{23}V^{3+}$ is
(a) 1.73 μ_B (b) 2.83 μ_B (c) 3.87 μ_B (d) 4.90 μ_B

84. The calculated spin magnetic moment of Cr^{2+} ion is
(a) 0 (b) 1.73 μ_B (c) 4.90 μ_B (d) 6.9 μ_B

85. The calculated value of magnetic moment of $_{24}Cr^{3+}$ is
(a) 1.73 μ_B (b) 2.83 μ_B (c) 3.87 μ_B (d) 4.90 μ_B

86. The calculate value of magnetic moment of $_{26}Fe^{3+}$ is
(a) 1.73 μ_B (b) 3.87 μ_B (c) 4.90 μ_B (d) 5.92 μ_B

87. The calculated value of magnetic moment of chromium atom would be
(a) 3.87 μ_B (b) 4.90 μ_B (c) 5.92 μ_B (d) 6.92 μ_B

88. The magnetic moment of a transition metal of 3d series is 6.92 μ_B. Its electronic configuration would be
(a) $(3d)^4(4s)^2$ (b) $(3d)^5(4s)^1$ (c) $(3d)^{10}$ (d) $(3d)^5(4s)^0$

89. Which of the following electronic configuration would be associated with the highest magnetic moment?
(a) d^2 (b) d^4 (c) d^5 (d) d^7

90. Which of the following electronic configuration would be associated with the lowest magnetic moment?
(a) d^2 (b) d^3 (c) d^4 (d) d^9

91. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong?
(a) The complex involves d^2sp^3 hybridization and is octahedral in shape
(b) the complex is paramagnetic
(c) the complex is diamagnetic
(d) The complex gives white precipitate with silver nitrate

92. Which of the following complex is diamagnetic?
(a) $[CoF_6]^{3-}$ (b) $[NiCl_4]^{2-}$ (c) $[Ni(NH_3)_6]^{2-}$ (d) $[Ni(CN)_4]^{2-}$

93. In nitroprusside ion the iron and NO exists as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by
(a) estimating the concentration of iron (b) measuring the concentration of CN
(c) measuring the solid state magnetic moment (d) thermally decomposing the compound (1998)

94. Which of the following ions is expected to be paramagnetic?
(a) $_{29}Cu^+$ (b) $_{30}Zn^{2+}$ (c) $_{26}Fe^{2+}$ (d) $_{21}Sc^{3+}$

95. Which of the following ions is expected to be diamagnetic?
(a) $_{25}Mn^{2+}$ (b) $_{29}Cu^{2+}$ (c) $_{27}Co^{3+}$ (d) $_{24}Cr^{3+}$

96. Which of the following chemical species will exhibit magnetic moment of 1.73 Bohr magneton?
(a) $[Cu(NH_3)_4]^{2+}$ (b) $[Ni(CN)_4]^{2-}$ (c) $TiCl_4$ (d) $[CoCl_6]^{4-}$

97. Which of the following complexes is paramagnetic?
(a) $K_2[Ni(CN)_4]$ (b) $K_4[Fe(CN)_6]$ (c) $[Co(NH_3)_6]Cl_3$ (d) $[Cr(H_2O)_6]SO_4$

98. Which of the following statements is **not** true?
(a) $Ni(CO)_4$ is paramagnetic (b) $[Fe(CN)_6]^{3-}$ contains one unpaired electron
(c) $[FeF_6]^{3-}$ involves sp^3d^2 hybridization (d) $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic

99. Among the following, the compound that is both paramagnetic and coloured is
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2(TiCl_6)$ (c) $VOSO_4$ (d) $K_3[Cu(CN)_4]$ (1997)

100. The spin magnetic moment of cobalt in the compound $K_2[Co(SCN)_4]$ is
(a) $\sqrt{3}$ bohr magneton (b) $\sqrt{8}$ bohr magneton (c) $\sqrt{15}$ bohr magneton (d) $\sqrt{24}$ bohr magneton

101. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is
(a) 0 (b) 2.84 (c) 4.90 (d) 5.92 (2009)

102. Which of the following will exhibit the lowest degree of paramagnetism?
(a) $CuSO_4{\cdot}5H_2O$ (b) $MnSO_4{\cdot}4H_2O$ (c) $FeSO_4{\cdot}6H_2O$ (d) $NiSO_4{\cdot}6H_2O$

103. Which one of the following ions will exhibit the highest degree of paramagnetism?
(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$ (c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$

Colour of Complexes

104. If a transition–metal compound absorbs violet radiation in the visible region, its colour would be
(a) yellow-green (b) yellow (c) orange (d) blue

105. If a transition–metal compound absorbs indigo radiation from the visible region, its colour would be
(a) yellow green (b) yellow (c) orange (d) indigo

106. If a transition–metal compound absorbs blue to blue–green radiations from the visible region, its colour would be
(a) yellow (b) orange to red (c) purple to violet (d) blue–green

107. If the d–d transition of a compound requires orange radiation, then the colour of the compound would be
(a) orange (b) blue (c) red (d) green

108. The colour of Cu^+ compounds is
(a) white (b) blue (c) orange (d) yellow

109. The colour of $_{21}Sc^{3+}$ compounds would be
(a) white (b) blue (c) orange (d) yellow

110. Transition metal compounds are usually coloured. This is due to the electronic transition
(a) from p orbital to s orbital (b) from d orbital to s orbital
(c) from d orbital to p orbital (d) within the d orbitals

111. A solution of $Cr(NO_3)_2$ slowly turns green when concentrated HCl is added to it. It is due to the formation of
(a) $CrCl_3$ (b) Cr_2O_3 (c) CrO_4^{2-} (d) chloro complexes

112. Which of the following ions is expected to be colourless?
(a) $_{29}Cu^{2+}$ (b) $_{22}Ti^{4+}$ (c) $_{23}V^{3+}$ (d) $_{26}Fe^{2+}$

113. Which of the following hydrated transition metal ions is colourless?
(a) Ti(III) (b) Ti(IV) (c) Fe(II) (d) Fe(III)

114. Which of the following statement is not correct?
(a) $Ti(NO_3)_4$ is a colourless compound (b) $[Cu(NCCH_3)_4]^+ BF_4^-$ is a colourless compound
(c) $[Cr(NH_3)_6]^{3+}3Cl^-$ is a coloured compound (d) $K_3[VF_6]$ is a colourless compound

115. Which of the following compounds is expected to be coloured?
(a) Ag_2SO_4 (b) CuF_2 (c) MgF_2 (d) CuCl (1997)

116. Which of the following pairs is expected to exhibit same colour in solution?
(a) $VOCl_2$, $MnCl_2$ (b) $CuCl_2$, $VOCl_2$ (c) $VOCl_2$, $FeCl_2$ (d) $MnCl_2$, $FeCl_2$ (2005)

117. The colour of $_{71}Lu^{3+}$ is expected to be
(a) colourless (b) yellow (c) red (d) blue

118. The colour of $_{57}La^{3+}$ would be
(a) colourless (b) yellow (c) red (d) blue

119. The colour of $_{62}Sm^{3+}$ is yellow. The expected colour of $_{66}Dy^{3+}$ is
(a) colourless (b) yellow (c) red (d) blue

120. According to crystal field theory, octahedral splitting and tetrahedral splittings of d orbitals caused by the same ligands are related through the expression
(a) $\Delta_o = \Delta_t$ (b) $4\Delta_o = 9\Delta_t$ (c) $9\Delta_o = 4\Delta_t$ (d) $\Delta_o = 2\Delta_t$

121. The colour of a complex compound is due to
(a) promotion of 3d electrons of the central atom/ion to 4s orbital
(b) promotion of 3d electrons of the central atom/ion to 4p orbitals
(c) promotion of 3d electrons of the central atom/ion within d orbitals
(d) promotion of 4s electrons of the central atom/ion to 4p orbitals

122. Relative to the average energy in the spherical crystal field, the t_{2g} orbitals in octahedral field is
(a) raised by $(2/5)\Delta_o$ (b) lowered by $(2/5)\Delta_o$ (c) raised by $(3/5)\Delta_o$ (d) lowered by $(3/5)\Delta_o$

123. Relative to the average energy in the spherical crystal field, the t_{2g} orbitals in tetrahedral field is
(a) raised by $(2/5)\Delta_t$ (b) lowered by $(2/5)\Delta_t$ (c) raised by $(3/5)\Delta_t$ (d) lowered by $(2/5)\Delta_t$

124. Relative to the average energy in the spherical crystal field, the e_g orbitals in octahedral field is
(a) raised by $(2/5)\Delta_o$ (b) lowered by $(2/5)\Delta_o$ (c) raised by $(3/5)\Delta_o$ (d) lowered by $(3/5)\Delta_o$

125. Relative to the average energy in the spherical crystal field, the e_g orbitals in tetrahedral field is
(a) raised by $(2/5)\Delta_t$ (b) lowered by $(2/5)\Delta_t$ (c) raised by $(3/5)\Delta_t$ (d) lowered by $(3/5)\Delta_t$

126. Which of the following ligands are correctly represented in an spectrochemical series?
(a) $SCN^- < F^- < CN^-$ (b) $SCN^- < CN^- < F^-$ (c) $F^- < SCN^- < CN^-$ (d) $F^- < CN^- < SCN^-$

127. The spectrochemical series of ligands is
(a) $I^- < F^- < H_2O < NH_3 < CN^-$ (b) $F^- < Cl^- < Br^- < I^- < H_2O < CN^-$
(c) $I^- < Br^- < Cl^- < H_2O < NH_3 < CN^-$ (d) $I^- < H_2O < F^- < Br^- < Br^- < CN^- < NH_3$

128. Which of the following statements is **not** correct?
(a) Weak ligands like F^-, Cl^- form high-spin complexes.
(b) Strong ligands like CN^- form low-spin complexes.
(c) $[FeF_6]^{3-}$ is a high-spin complex.
(d) $Ni(CO)_4$ is a high-spin complex.

129. Which one of the following is a high spin or outer-orbital complex?
(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(CN)_6]^{3-}$ (c) $[CoF_6]^{3-}$ (d) $[Fe(CN)_6]^{2-}$

130. Among the following, the coloured compound is
(a) CuCl (b) $K_3[Cu(CN)_4]$ (c) CuF_2 (d) $[Cu(CH_3CN_4]BF_4$
(2008)

131. Of the following statements, which one is correct?
(a) $[CoF_6]^{3-}$ is a high spin complex and $[Co(NH_3)_6]^{3+}$ is a low spin complex
(b) $[CoF_6]^{3-}$ is a low spin complex and $[Co(NH_3)_6]^{3+}$ is a high spin complex
(c) Both $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ are low spin complexes
(d) Both $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ are high spin complexes

Isomerism in Complexes

132. The following square-planar complex shows *cis-trans* isomerism:
(a) $PtCl_4^{2-}$ (b) $PtCl_3NH_3^-$ (c) $PtCl_2(CN)_2^{2-}$ (d) $PtCl_2$ en

133. The following represents a pair of enantiomers:
(a) *trans*-$CrCl_2$ en_2^+ (b) *cis*-$CrCl_2$ en_2^+ (c) *trans*-$CrCl_2(NH_3)_4^+$ (d) *cis*-$CrCl_2(NH_3)_4^+$

134. The total number of possible isomers (*cis-trans* and optical) of $CrCl_2en_2^+$ is
(a) 1 (b) 2 (c) 3 (d) 4

135. The total number of possible isomers of $[CrCl_3(NH_3)_3]$ is
(a) 1 (b) 2 (c) 3 (d) 4

136. The total number of possible isomers of $[ZnCl_2F_2^-]$ is
(a) 1 (b) 2 (c) 3 (d) 4

137. The total number of possible isomers of $[CrCl_2CNNH_2en]$ is
(a) 3 (b) 4 (c) 5 (d) 6

138. The complexes $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$ are the examples of
(a) ionization isomers (b) linkage isomers (c) coordination isomers (d) optical isomers

139. The complexes $[CoNO_2(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$ are the examples of
(a) geometrical isomers (b) optical isomers
(c) coordination isomers (d) linkage isomers

140. The complexes $[Cr(NH_3)_6]$ $[Co(CN)_6]$ and $[Co(NH_3)_6]$ $[Cr(CN)_6]$ are the examples of
(a) geometrical isomers (b) optical isomers
(c) coordination isomers (d) linkage isomers

141. The compound $[PtCl_2(NH_3)_2]$ can form
(a) geometrical isomers (b) coordination isomers
(c) linkage isomers (d) optical isomers

142. The compound $[CoCl_2(NH_3)_2\ (en)]$ can form
(a) linkage isomers (b) coordination isomers
(c) optical isomers (d) linkage as well as optical isomers

143. The number of geometrical isomers including optical isomers for the complex of the type $[Ma_2b_2c_2]$ is
(a) 4 (b) 5 (c) 6 (d) 8

144. The number of geometrical isomers including optical isomers for the complex of the type [Mabcdef] is
(a) 20 (b) 26 (c) 28 (d) 30

145. Which type of isomerism is shown by $Co(NH_3)_4Br_2Cl$?
(a) Geometrical only (b) Ionization only
(c) Geometrical and ionization (d) Ionization and optical (2005)

146. Which of the following complexes has more than one geometrical isomers?
(a) $[Ma_4]$ (b) $[Ma_3b]$ (c) $[Ma_2b_2]$ (d) $[Ma_6]$

147. Which of the following complexes has more than two geometrical isomers?
(a) $[Ma_2b_2]$ (b) [Mabcd] (c) $[Ma_2bc]$ (d) $[Ma_3]$

148. Which of the following complexes has maximum number of geometrical isomers?
(a) [Mabcd] (b) $[Ma_2b_2c_2]$ (c) $[M(AA)_2a_2b_2]$ (d) [Mabcdef]

149. The number of optical isomers of a square planer complex [Mabcd] is
(a) zero (b) one (c) two (d) four

150. Which of the following complexes has no optical isomer?
(a) $[Ma_3b_3]$ (b) $[Ma_2b_2c_2]$ (c) $[M(AA)_2a_2]$ (d) $[M(AA)_2ab]$

151. Which of the following statements regarding the complex $[M(AA)_2a_2]$ is correct?
(a) *cis* – form is optically active while *trans* – form is inactive.
(b) *cis* – form is optically inactive while *trans* – form is active.
(c) Both *cis* – and *trans* – forms are optically active.
(d) Both *cis* – and *trans* – forms are optically inactive.

Inner-Transition Elements

152. Which of the following ions is coloured?
(a) $_{57}La^{3+}$ (b) $_{63}Eu^{3+}$ (c) $_{64}Gd^{3+}$ (d) $_{71}Lu^{3+}$

153. Which of the following species is coloured?
(a) $[Ti(H_2O)_6]^{2+}$ (b) $[Sn(H_2O)_6]^{2+}$ (c) $[Zn(H_2O)_6]^{2+}$ (d) $[Ag(NH_3)_2]^+$

154. Which of the following pairs is expected to exhibit the same colour?
(a) $_{58}Ce^{3+} - {}_{67}Ho^{3+}$ (b) $_{60}Nd^{3+} - {}_{68}Er^{3+}$ (c) $_{61}Pm^{3+} - {}_{69}Tm^{3+}$ (d) $_{63}Sm^{3+} - {}_{70}Yb^{3+}$

155. Which of the following pairs is expected to form colourless compound?
(a) $_{57}La^{3+} - {}_{59}Pr^{3+}$ (b) $_{57}La^{3+} - {}_{71}Lu^{3+}$ (c) $_{60}Nd^{3+} - {}_{61}Pm^{3+}$ (d) $_{63}Eu^{3+} - {}_{65}Tb^{3+}$

156. The most of inner-transition elements, show the valency of
(a) +2 (b) +3 (c) +4 (d) +5

157. Which of the following characteristics of lanthanides is correct?
(a) Reducing property decreases from La to Lu.
(b) Reducing property increases from La to Lu.
(c) Reducing property remains constant from La to Lu.
(d) Reducing property initially decreases followed by increase.

Multiple Correct Choice Type

1. The aqueous solutions of the following salts will be coloured in the case of
(a) $Zn(NO_3)_2$ (b) $LiNO_3$ (c) $Co(NO_3)_2$ (d) $CrCl_3$ (1990)

2. Potassium manganate (K_2MnO_4) is formed when
(a) Cl_2 is passed into an aqueous $KMnO_4$ solution
(b) MnO_2 is fused with KOH in air
(c) formaldehyde reacts with $KMnO_4$ in presence of strong alkali
(d) $KMnO_4$ reacts with concentrated H_2SO_4 (1988)

3. Identify the complexes which are expected to be coloured
(a) $Ti(NO_3)_4$ (b) $[Cu(NCCH_3)_4]^+ \ BF_4^-$
(c) $[Cr(NH_3)_6]^{3+} \ (Cl^-)_3$ (d) $K_3[VF_6]$ (1994)

4. Which of the following statements regarding lanthanides is/are correct?
(a) The compounds formed by lanthanides are covalent
(b) The colour of the compound of lanthanide element having *x*f electrons is often similar to that of the element having (14 – *x*)f electrons
(c) Except $_{57}La^{3+}$, $_{58}Ce^{4+}$ and $_{71}Lu^{3+}$ salts, all other compounds of lanthanides are paramagnetic
(d) The paors $_{40}Zr$ and $_{72}Hf$, $_{41}Nb$ and $_{73}Ta$, and $_{42}Mo$ and $_{74}W$ have nearly identical sizes

5. Which of the following statements is/are correct?
(a) The oxides of transition metals in their low oxidation state are generally basic
(b) The oxides of transition metals in their intermediate and high oxidation states are generally amphoteric and acidic, respectively
(c) Mixed iron oxides is found in the mineral magnetite
(d) Silver oxide is soluble in ammonium hydroxide forming the complex $Ag(NH_3)OH$

6. Which of the following statements is/are correct?
(a) Primary valency of the central metal of a complex is always satisfied by anions
(b) Secondary valency of the central metal of a complex may be satisfied by either negative ions or neutral molecules
(c) Species attached by primary valencies in a complex compound can be precipitated out
(d) Species attached through secondary valencies in a complex are Lewis acids

7. Which of the following statements is/are correct?
(a) The ionic radius of a cation generally increases with an increase in its coordination number.
(b) The octahedral radius of Mn^{2+} is larger than that of Fe^{2+}.
(c) The octahedral radius of Fe^{2+} is larger than that of Co^{2+}.
(d) The octahedral radii of divalent cations at the end of transition series generally show the upward trend.

8. Which of the following statements are **not** correct?
(a) The outer electronic configuration of the ground state chromium atom is $(3d)^4(4s)^2$.
(b) Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3d orbital of neutral atom.

(c) Both potassium ferrocyanide and potassium ferricyanide are diamagnetic.
(d) Copper has electronic configuration $(3d)^9(4s)^2$.

9. Which of the following statements are correct?
(a) Fe^{3+} ion has half–filled 3d orbitals.
(b) The paramagnetic character decreases from Sc to Mn and then increases to Zn.
(c) Copper(I) is diamagnetic wheras Cu(II) is paramagnetic.
(d) Iron(II) is more paramagnetic than iron(III).

10. Which of the following statements are correct?
(a) The complex ion $[Co(NH_3)_6]^{2+}$ is readily oxidized to $[Co(NH_3)_6]^{3+}$
(b) Fe^{3+} shows maximum paramagnetic character amongst the trivalent metal ions of the first transition series.
(c) Zinc unlike transition elements shows only one oxidation state of +II.
(d) The covalent radius of Cd is less than that of Ag.

11. Which of the following statements are correct?
(a) The melting points of transition elements are higher than the metals of Group 1 and 2 in the same period.
(b) The melting point/boiling point of the transition–element series increases first up to the middle followed by decrease.

(c) V_2O_5 is used as a catalyst in the contact process to convert SO_2 into SO_3.
(d) In the Haber process for the manufacture of NH_3, Mn is used as a catalyst

12. Which of the following statements are correct?
(a) $[Cu(NCCH_3)_4]^+ BF_4^-$ is a coloured compound.
(b) $Ti(NO_3)_4$ is a colourless compound.
(c) $K_3[VF_6]$ is a coloured compound.
(d) CuSCN is a yellow coloured compound

13. Which of the following statements are correct?
(a) The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is CrO_2Cl_2.
(b) The atomic radii of the transition elements of 5d series are very nearly the same as the corresponding element of 4d series. This is due to lanthanide contraction.
(c) The outer electronic configuration of chromium (atomic number 24) is $(3d)^4(4s)^2$.
(d) The outer electronic configuration of copper (atomic number 29) is $(3d)^{10}(4s)^1$.

14. Which of the following statements are **not** correct?
(a) The atomic radius of Zn is smaller than that of Cu.
(b) Copper(I) salts are colourless as there are no electrons in 3d orbitals.
(c) The value of Bohr magneton is 9.273×10^{-24} J T^{-1}.
(d) The magnetic moment of transition element containing two unpaired electrons would be nearly $\sqrt{8}$ Bohr magneton.

15. Which of the following statements are correct?
(a) The colour of the solution of a complex absorbing violet radiation would be yellow.
(b) A solution of a complex compound absorbs orange radiation. Its colour would be blue.
(c) The expression of magnetic moment in terms of number of unpaired electrons is $n(n+2)$ bohr magneton.
(d) The Natta catalyst is $TiCl_4$.

16. Which of the following statements are correct?
(a) The reaction between $KMnO_4$ and oxalic acid is catalysed by Mn^{2+} which is known as autocatalyst.
(b) The colour of compounds of transition elements is due to d–d electronic excitation.
(c) The atomic volumes of the transition elements are larger as compared to the elements in the nearby Groups 1 and 2.
(d) The maximum paramagnetic character in the 3d series elements is possessed by manangese atom.

17. Which of the following statements are correct?
(a) Amongst the bivalent metal ions of 3d series transition elements, the maximum paramagnetism is shown by the ion Mn^{2+}.
(b) The IUPAC name of $K[Ag(CN)_2]$ is potassium dicyanoargentate(I)
(c) The IUPAC name of $K_4[Fe(CN)_6]$ is potassium hexacyanoferrous
(d) The IUPAC name of $Na_2[Fe(CN)_5(NO)]$ is sodium nitrosylpentacyanoferrate(II)

18. Which of the following statements are correct?
(a) The complex ion $[Fe(CN)_6]^{4-}$ is diamagnetic. The state of hybridization of iron is d^2sp^3.
(b) The complex ion $[Fe(H_2O)_6]^{2+}$ is paramagnetic. The state of hybridization of iron is sp^3d^2.
(c) The magnetic moment of the $[Fe(H_2O)_6]^{2+}$ would be $\sqrt{20}$ bohr magneton.
(d) The complex ion $[Ni(CO)_4]$ is paramagnetic. The state of hybridization of Ni is sp^3.

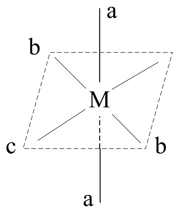
19. Which of the following statements are correct?
(a) The complex ion $[CuCl_4]^{2-}$ is paramagnetic. The state of hybridization of Cu is dsp^2.
(b) Of the ions Co^{2+} and Co^{3+}, the ion having lower magnetic moment is Co^{3+}.
(c) Of the two elements Fe and Zn, the element having higher melting point is Zn.
(d) Of the two elements Sc and Mn, the element having more oxidation state is Mn.

20. Which of the following statements are **not** correct?
(a) Of the two ions Cu^{2+} or Zn^{2+}, the diamagnetic ion is Cu^{2+}.
(b) Of the two ions Fe^{2+} or Fe^{3+}, the ion having higher magnetic moment is Fe^{2+}.
(c) The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is paramagnetism.
(d) The magnetic moment of Fe^{2+} is identical to that of Co^{3+}.

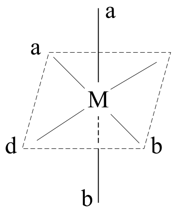
21. Which of the following statements are correct?]
(a) The IUPAC name of $[Co(NH_3)_6]Cl_3$ is hexaaminecobalt(II) chloride.
(b) The IUPAC name of $[Co(NH_3)_5ONO]Cl_2$ is petaamminenitrocobalt(III) chloride.
(c) The IUPAC name of $K_3[Cr(CN)_6]$ is potassium hexacyanochromate(III).

22. Which of the following pairs have identical atomic radii due to lanthanide contraction?
(a) Zn – Hf (b) Pd – Pt (c) Cu – Zn (d) Zn – Cd

23. Which of the following complex configurations are expected to exist also as their enantiomer?



(a)



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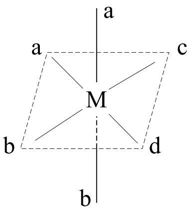

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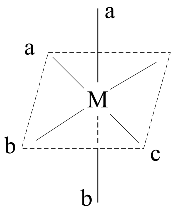


(d)

24. Which of the following alloys contain(s) Cu and Zn?
(a) Bronze (b) Brass (c) Gun metal (d) Type metal (1993)

25. Which of the following statements(s) is (are) correct with reference to the ferrous and ferric ions?
(a) Fe^{3+} gives brown colour with potassium ferricyanide.
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide.
(c) Fe^{3+} gives red colour with potassium thiocyanate.
(d) Fe^{3+} gives brown colour with ammonium thiocyanate. (1998)

26. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese
(a) gives hardness to steel (b) helps the formation of oxides of iron
(c) can remove oxygen and sulphur (d) can show highest oxidation state of +7 (1998)

27. The compound(s) that exhibits(s) geometrical isomerism is (are)
(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$ (c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2Cl_2]$ (2009)

28. Which of the following statements are correct?
(a) Dimethylglyoxime is a bidentate ligand.
(b) Dimethylglyoxime is a tetradentate ligand.
(c) Dimethylglyoxime forms a square planar complex with Ni^{2+} ions.
(d) Dimethylglyoxime form an octahedral complex with Ni^{2+} ions.

29. Which of the following facts regarding Prussian blue and Turnbull's blue are correct?
(a) $Fe^{3+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow$ Prussian blue
$Fe^{2+}(aq) + [Fe(CN)_6]^{3-}(aq) \rightarrow$ Turnbull's blue
(b) $Fe^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow$ Prussian blue
$Fe^{3+}(aq) + [Fe(CN)_6]^{3-}(aq) \rightarrow$ Turnbull's blue
(c) Both have the same molecular formula
(d) Blue colour of Turnbull's blue is less intense than that of Prussian blue.

Linked Comprehension Type

1. Ni^{2+} ions form the complex ions $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$. Based on these complexes, answer the following three questions.

(i) Which of the following statements is correct?
(a) $[NiCl_4]^{2-}$ is diamagnetic while $[Ni(CN)_4]^{2-}$ is paramagnetic
(b) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic
(c) Both the ions are diamagnetic
(d) Both the ions are paramagnetic

(ii) Which of the following statements is correct?
(a) $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridization while $[NiCl_4]^{2-}$ involves sp^3 hybridization
(b) $[Ni(CN)_4]^{2-}$ involves sp^3 hybridization while $[NiCl_4]^{2-}$ involves dsp^2 hybridization

(c) both the ions involves sp^3 hybridization
(d) both the ions involve dsp^2 hybridization

(iii) Which of the following statements is correct?
(a) $[Ni(CN)_4]^{2-}$ is green in colour while $[NiCl_4]^{2-}$ is yellow
(b) $[Ni(CN)_4]^{2-}$ is yellow in colour while $[NiCl_4]^{2-}$ is green
(c) both the ions are yellow in colour
(d) both the ions are green in colour

2. Ni^{2+} ions form the complexes $[NiCl_4]^{2-}$ and $Ni(CO)_4$. Based on these complexes, answer the following three questions.

(i) Which of the following statements is correct?
(a) $[NiCl_4]^{2-}$ is tetrahedral while $Ni(CO)_4$ is square planar
(b) $[NiCl_4]^{2-}$ is square planar while $Ni(CO)_4$ is tetrahedral
(c) both the ions are tetrahedral
(d) both the ions are square planar

(ii) Which of the following statements is correct?
(a) $[NiCl_4]^{2-}$ is diamagnetic while $Ni(CO)_4$ is paramagnetic
(b) $[NiCl_4]^{2-}$ is paramagnetic while $Ni(CO)_4$ is diamagnetic
(c) both the ions are diamagnetic
(d) both the ions are paramagnetic

(iii) Which of the following statements is correct?
(a) Both the ions have Ni in the same state of oxidation
(b) Both the ions differ in the oxidation state of Ni
(c) $[NiCl_4]^{2-}$ is volatile while $Ni(CO)_4$ is involatile
(d) $[NiCl_4]^{2-}$ decomposes on heating while $Ni(CO)_4$ is stable

3. For the ions $[Cr(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$, answer the following three questions.

(i) Which of the following statements is correct?
(a) Both the ions involve sp^3d^2 hybridization
(b) Both the ions involve d^2sp^3 hybridization
(c) $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridization while $[CoF_6]^{3-}$ involves sp^3d^2 hybridization
(d) $[Cr(NH_3)_6]^{3+}$ involves sp^3d^2 hybridization while $[CoF_6]^{3-}$ involves d^2sp^3 hybridization

(ii) Which of the following statements is correct?
(a) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[CoF_6]^{3-}$ is diamagnetic
(b) $[Cr(NH_3)_6]^{3+}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic
(c) Both the ions are diamagnetic
(d) Both the ions are paramagnetic

(iii) Which of the following statements is correct?
(a) $[Cr(NH_3)_6]^{3+}$ is named as hexaamminechromium(III) while $[CoF_6]^{3-}$ is named as hexafluorocobalt(III)
(b) $[Cr(NH_3)_6]^{3+}$ is named as hexaamminechromium(III) while $[CoF_6]^{3-}$ is named as hexafluorocobaltate(III)
(c) $[Cr(NH_3)_6]^{3+}$ is named as hexaamminechromate(III) while $[CoF_6]^{3-}$ is named as hexafluorocobaltate(III)
(d) $[Cr(NH_3)_6]^{3+}$ is named as hexaamminechromate(III) while $[CoF_6]^{3-}$ is named hexafluorocobalt(III)

4. Metal complexes are of immense importance in biological processes. Identify the metal ions in the complexes chlorophyll, haemoglobin and vitamin B_{12}.

(i) The metal ion present in chlorophyll is
(a) Mg^{2+} (b) Co^{3+} (c) Fe^{2+} (d) Fe^{3+}

(ii) The metal ion present in haemoglobin is
(a) Mg^{2+} (b) Co^{3+} (c) Fe^{2+} (d) Fe^{3+}

(iii) The metal ion present in vitamin B_{12} is
(a) Mg^{2+} (b) Co^{3+} (c) Fe^{2+} (d) Fe^{3+}

5. Ni^{2+} ions form the following complexes

$$Ni^{2+} \xrightarrow{KCN} \text{Complex I} \quad \text{and} \quad Ni^{2+} \xrightarrow[\text{excess}]{KCl} \text{Complex II}$$

Both the complexes have coordination number 4.

1. The IUPAC names of the complexes respectively are
- (a) potassium tetracyanonickel(II) and potassium tetrachloronickelate(II)
- (b) potassium tetracyanonickelate(II) and potassium tetrachloronickel(II)
- (c) potassium tetracyanonickel(II) and potassium tetrachloronickel
- (d) potassium tetracyanonickelate(II) and potassium tetrachloronickelate(II)

2. Which of the following statement is correct?
- (a) The cyano complex is diamagnetic and the chloro complex is paramagnetic
- (b) The cyano complex is paramagnetic and the chloro complex is diamagnetic
- (c) Both the complexes are diamagnetic
- (d) Both the complexes are paramagnetic

3. Nickel ion involves
- (a) dsp^2 hybridization in both complexes
- (b) sp^3 hybridization in both complexes
- (c) dsp^2 hybridization in cyano complex and sp^3 hybridization in chloro complex
- (d) sp^3 hybridization in cyano complex and dsp^2 hybridaziation in chloro complex (2006)

6. The compounds of transition metals are ionic in the lower oxidation state and are covalent in the higher oxidation state. In fact, the covalent character of the bond increases on increasing the oxidation state of the d–series element. This characteristic results into basic oxide in the lower oxidation state and acidic oxide in the higher oxidation state. In the intermediate oxidation states, oxides are amphoteric. Also, the basicity of MO decreases as one moves from left to right of d–series element. This also follows from the fact that the metallic characteristic decreases from left to right due to decrease in atomic size and increase in ionization energy of the element as the atomic number of transition metal is increased. Based on these facts, answer the following three questions.

(i) The basicity of MO of 3d–series elements follows the order

(a) $TiO > VO > CrO > FeO$ (b) $TiO > VO > FeO > CrO$
(c) $TiO > FeO > VO > CrO$ (d) $FeO > CrO > VO > TiO$

(ii) The acidity of oxides of Mn follows the order

(a) $MnO > Mn_2O_3 > MnO_2 > Mn_2O_7$ (b) $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$
(c) $MnO > MnO_2 > Mn_2O_3 > Mn_2O_7$ (d) $MnO < Mn_2O_7 < Mn_2O_3 < MnO_2$

(iii) The acidic character of chlorides of vanadium follows the order

(a) $VCl_2 > VCl_3 > VOCl_2$ (b) $VCl_2 > VOCl_2 > VCl_3$
(c) $VCl_3 > VOCl_2 > VCl_2$ (d) $VOCl_2 > VCL_3 > VCl_2$

Assertion and Reason Type

The questions below consists of two statements. Use the following key to choose the appropriate answer.
- (a) Both statements are correct and statement –2 is correct explanation of statement –1.
- (b) Both statements are correct and statement –2 is not correct explanation of statement –1.
- (c) Statement –1 is correct and statement –2 is incorrect.
- (d) Statement –1 is incorrect and statement –2 is correct.

	Statement–1	**Statement–2**
1.	If a strong acid is added to a solution of potassium chromate it changes its colour from yellow to orange.	The colour change is due to the oxidation of potassium dichromate. (1988)
2.	The pairs of elements such as Zr–Hf, Nb–Ta and Mo–W have nearly identical sizes.	The smaller size is due to lanthanide contraction.
3.	Zn^{2+} is diamagnetic	The electrons are lost from 4s orbital to form Zn^{2+} (1998)
4.	$[Fe(H_2O)_5NO]SO_4$ is paramagnetic	The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons (2008)
5.	The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically active	Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. (2008)

6.	The square planar complexes has no optical isomers.	The square planar complexes has plane of symmetry.
7.	An octahedron arrangements of ligands involves 12 *cis* positions and 3 *trans* positions.	There are 12 edges of an octahedron and three different ways of joining opposite species.
8.	According to Iriving – William order of stability of complexes of M^{2+} ions, the stability decreases from Mn^{2+} to Cu^{2+} then increases up to Zn^{2+}.	The stability of complexes of M^{2+} decreases with increase in the ionic size of the central metal ion.
9.	The complex $K_4[Fe(CN)_6]$ is less stable than $K_3[Fe(CN)_6]$.	The oxidation states of Fe in $K_4[Fe(CN)_6]$ is +2 while that in $K_3[Fe(CN)_6]$ is +3.
10.	The complex $[Cu(en)_2]Cl_2$ is more stable than $[Cu(NH_3)_4]Cl_2$.	The chelated complex is more stable than a non–cheated complex.
11.	The order of acidity of oxides of vanadium is $VO < VO_2 < V_2O_5$.	The compounds of a given transition metal becomes more and more acidic as the oxidation state of the transition metal increases.
12.	The basic character of the hydroxides of lanthanide decreases with increase in atomic number.	The decrease of ionic size with increase in atomic number of lanthanides increases the covalent character of M—OH bond
13.	The lanthanides show poor tendency to form complexes as compared to the transition elements.	Poor tendency to form complexed by lathanides may be attributed to smaller charge density of its M^{3+} ion.
14.	The atomic radii of elements of 5d series are almost identical to the corresponding elements of 4d series.	The screening effect of 4f electrons is similar to those of 3d electrons.
15.	The species $[Co(NH_3)_6]^{2+}$ is readily oxidized to $[Co(NH_3)_6]^{3+}$.	$[Co(NH_3)_6]^{3+}$ involves sp^3d^2 hybridization.

Matrix Match Type

1. Match the complexes in *Column I* with their properties listed in *Column II.*

Column I	**Column II**
(a) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(p) geometrical isomers
(b) $[Pt(NH_3)_2Cl_2]$	(q) paramagnetic
(c) $[Co(H_2O)_5Cl]Cl$	(r) diamagnetic
(d) $[Ni(H_2O)_6]Cl_2$	(s) metal ion with +2 oxidation state (2007)

2. Column I gives the classification of ligands and their examples are given in Column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Bidentate	(p) Triaminotriethylamine
(b) Tridentate	(q) Ethylenediaminetetracetate ion
(c) Tetradentate	(r) 1, 10 – Phenanthroline
(d) Pentadentate	(s) Ethylenediaminetriacetate ion
(e) Hexadentate	(t) Triethylenetetramine
	(u) Diethylenetriamine
	(v) Ethylenediamine
	(w) Dimethylglyoxide

3. Column I lists the possible number of geometrical isomers of the complex mentioned in Column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) One	(p) $[Ma_3b]$(planar)
(b) Two	(q) $[Ma_2b_2]$(planar)

(c) Three	(r) [Mabcd] planar
(d) Five	(s) $[Ma_3b_3]$ octahedron
	(t) $[Ma_2b_2c_2]$ octahedron
	(u) $[M(AA)_2a_2]$ octahedron

4. Column I includes some of the hybridization schemes of some complexes which are listed in Column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) sp^3	(p) $[FeF_6]^{3-}$
(b) dsp^2	(q) $[NiCl_4]^{2-}$
(c) sp^2d	(r) $[PtCl_6]^{2-}$
(d) d^2sp^3	(s) $[Cu(NH_3)]^{2+}$
(e) sp^3d^2	(t) $Ni(CO)_4$
	(u) $[Ni(CN)_4]^{2-}$

5. Column I includes number of unpaired electrons in the metal ions existing as complexes which are listed in column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Zero	(p) $[Cr(CN)_6]^{4-}$
(b) One	(q) $[Co(NH_3)_6]^{3+}$
(c) Two	(r) $[Cr(NH_3)_6]^{3+}$
(d) Three	(s) $[Fe(CN)_6]^{4-}$
	(t) $[TiF_6]^{3-}$
	(u) $[Ni(NH_3)_6]^{2-}$

6. Column I mentions some of the types of isomerism shown by complexes which are listed in Column II. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Geometrical isomerism	(p) $[Pt(NH_3)_2(py)_2Cl_2]SO_4$
(b) Linkage isomerism	(q) $[Co(en)_2(NH_3)Cl]SO_4$
(c) Coordination isomerism	(r) $[Co(NH_3)_4(H_2O)Cl]SO_4$
(d) Optical isomerism	(s) $[Co(NH_3)_5(NO_2)]Cl_2$
	(t) $[Co(NH_3)_6]$ $[Cr(CN)_6]$
	(u) $[Co(NH_3)_3Cl_3]$

ANSWERS

Straight Objective Type

1. (c)	**2.** (d)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (a)	**7.** (a)
8. (b)	**9.** (a)	**10.** (d)	**11.** (d)	**12.** (b)	**13.** (c)	**14.** (d)
15. (c)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (c)	**20.** (c)	**21.** (b)
22. (a)	**23.** (c)	**24.** (d)	**25.** (c)	**26.** (b)	**27.** (a)	**28.** (b)
29. (a)	**30.** (b)	**31.** (a)	**32.** (c)	**33.** (a)	**34.** (d)	**35.** (a)
36. (b)	**37.** (d)	**38.** (c)	**39.** (c)	**40.** (b)	**41.** (d)	**42.** (b)
43. (b)	**44.** (c)	**45.** (d)	**46.** (b)	**47.** (b)	**48.** (d)	**49.** (c)
50. (d)	**51.** (d)	**52.** (b)	**53.** (d)	**54.** (d)	**55.** (c)	**56.** (c)
57. (b)	**58.** (b)	**59.** (a)	**60.** (b)	**61.** (c)	**62.** (b)	**63.** (d)
64. (a)	**65.** (c)	**66.** (a)	**67.** (c)	**68.** (c)	**69.** (a)	**70.** (b)
71. (b)	**72.** (b)	**73.** (a)	**74.** (b)	**75.** (c)	**76.** (c)	**77.** (b)
78. (b)	**79.** (c)	**80.** (a)	**81.** (b)	**82.** (a)	**83.** (b)	**84.** (c)
85. (c)	**86.** (d)	**87.** (b)	**88.** (b)	**89.** (c)	**90.** (d)	**91.** (c)
92. (d)	**93.** (c)	**94.** (c)	**95.** (b)	**96.** (a)	**97.** (d)	**98.** (a)
99. (c)	**100.** (c)	**101.** (a)	**102.** (a)	**103.** (b)	**104.** (a)	**105.** (b)

106. (b) **107.** (b) **108.** (a) **109.** (a) **110.** (d) **111.** (d) **112.** (b)
113. (c) **114.** (d) **115.** (b) **116.** (b) **117.** (a) **118.** (a) **119.** (b)
120. (b) **121.** (c) **122.** (b) **123.** (a) **124.** (c) **125.** (d) **126.** (a)
127. (c) **128.** (d) **129.** (c) **130.** (c) **131.** (a) **132.** (c) **133.** (b)
134. (c) **135.** (b) **136.** (b) **137.** (d) **138.** (a) **139.** (d) **140.** (c)
141. (a) **142.** (c) **143.** (c) **144.** (d) **145.** (c) **146.** (c) **147.** (b)
148. (d) **149.** (a) **150.** (a) **151.** (a) **152.** (b) **153.** (a) **154.** (b)
155. (b) **156.** (b) **157.** (a)

Multiple Correct Choice Type

1. (c), (d) **2.** (b), (c) **3.** (c), (d) 4. (b), (c), (d)
5. (a), (b), (c) **6.** (a), (b), (c) **7.** (a), (b), (d) **8.** (a), (b), (c), (d)
9. (a), (c) **10.** (a), (b), (c) **11.** (a), (b), (c) **12.** (b), (c)
13. (a), (b), (d) **14.** (a), (b) **15.** (a), (b), (d) **16.** (a), (b)
17. (a), (b) **18.** (a), (b) **19.** (a), (d) **20.** (a), (b)
21. (b), (c) **22.** (a), (b) **23.** (c), (d) **24.** (a), (b), (c)
25. (b), (c) **26.** (a), (c) **27.** (c), (d) **28.** (a), (c)
29. (a), (c), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (a) **(iii)** (d)
2. **(i)** (c) **(ii)** (b) **(iii)** (b)
3. **(i)** (c) **(ii)** (d) **(iii)** (b)
4. **(i)** (a) **(ii)** (c) **(iii)** (b)
5. **(i)** (d) **(ii)** (a) **(iii)** (c)
6. **(i)** (a) **(ii)** (b) **(iii)** (d)

Assertion and Reason Type

1. (c) **2.** (a) **3.** (b) **4.** (a) **5.** (b) **6.** (a) **7.** (a)
8. (d) **9.** (b) **10.** (a) **11.** (a) **12.** (a) **13.** (a) **14.** (d)
15. (d)

Matrix Match Type

1. (a) – (p), (q), (s); (b) (p), (r), (s) (c) (q), (s); (d) – (q), (s)
2. (a) – (r), (v), (w); (b) – (u); (c) – (p), (t); (d) – (s); (e) – (q)
3. (a) – (p); (b) – (q), (s), (u); (c) – (r); (d) – (t)
4. (a) – (q), (t); (b) – (u); (c) – (s); (d) – (r); (e) – (p)
5. (a) – (q), (s); (b) – (t); (c) – (p), (u); (d) – (r)
6. (a) – (p), (r), (q), (u); (b) – (s); (c) – (t); (d) – (p), (q)

Hints and Solutions

Straight Objective Type

1. Inert pair effect is not shown by transition metals.
2. The electronic configuration of Cu is $(3d)^{10}(4s)^1$ **3.** Same as Q.2
4. Ni is used as a catalyst in Haber process.
5. $[Ni(NH_3)_4]Cl_2$ gives three ions $[Ni(NH_3)_4]^{2+}$ and $2Cl^-$ **6.** Chlorophyll is a complex of magnesium.
7. Haemoglobin is an iron(II) complex. **8.** Vitamin B_{12} is a complex of cobalt(III) ion.
9. The number of ions produced by the complex $[Co(NH_3)_4Cl_2]Cl$ is two, namely, $[Co(NH_3)_4Cl_2]^+$ and Cl^-.
10. The compound is $K_3[Cu(CN)_4]$.

11. The ionic radii of P^{3+} is larger than P^{5+} (larger the charge number of cation, the smaller the size). Mn^{7+} has smaller size than Ti^{4+}. K^+ has smaller size than Cl^-. $^{35}Cl^-$ and $^{37}Cl^-$ have more or less identical size.

12. The number of unpaired electrons of the ions in the given choices are Mn^{2+} (n = 5); Ni^{2+} (n = 2), Co^{2+} (n = 3) and Fe^{2+} (n = 4). The correct sequence of magnetic moment would be $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$.

13. Lanthanide contraction is due to poor shielding of 4f electron from 4f electron(s).

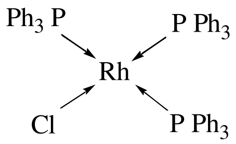
14. Third ionization potential means the removal of outer third electron. Since the configuration $(4f)^7$ $(5d)^1$ $(6s)^2$ would lead to the stable half-filled configuration after the removal of third electron, it is expected to have the lowest third ionization energy.

15. The size of given metals decreases whereas ionization energy increases from Ti to V to Cr to Fe. Hence, the metallic character of the metals decreases so is their basicity of oxides from Ti to V to Cr to Fe.

16. $_{63}Eu$ and $_{71}Lu$ are the members of lanthanide series. Due to the lanthanide contraction, the sizes of Eu, Lu and La follow the order Lu < Eu < La. The element $_{39}Y$ belongs to the fifth period while Lu belongs to the sixth period, we expect their sizes to follow the order Y < Lu. Hence, the correct order is Y < Lu < Eu < La.

17. The species $[Co(NH_3)_6]Cl_3$ produces four ions in solution, namely, $[Co(NH_3)_6]^{3+}$ and three Cl^-.

18. The Wilkinson's catalyst is *tris*(triphenylphosphine)chlororhodium (I).



19. The highest oxidation state is +VI as in K_2CrO_4 or $K_2Cr_2O_7$.

20. Cr^{3+} in acidic solution is oxidized to $Cr_2O_7^{2-}$.

21. In strongly basic solution, MnO_4^- is reduced to MnO_4^{2-}.

22. The oxidation states in K_2MnO_4 and $KMnO_4$ are +VI and +VII, respectively.

23. The oxidation states in $K_2Cr_2O_7$ and K_2CrO_4 are +VI and +VI, respectively.

24. $[Cd(CN)_4]^{2-}$ is a stable complex. **25.** The stability of halide complexes follows the order $I^- > Br^- > Cl$.

26. Mn displays the highest oxidation state of +VII as in $KMnO_4$.

27. For a given ligand the stability of the complexes of the metallic ions having the same charge decreases with the increase in the size of the central metal ion. The sequence of the given ions is $Mn^{2+} < Fe^{2+} < Co^{2+} < NI^{2+} < Cu^{2+} < Zn^{2+}$. This sequence is known as Irving – William order of stability of the complexes of M^{2+} ions.

28. The electronic configuration of $_{23}V^3$ ion is $3d^2$.

29. The maximum number of oxidation states of Co, V, Mn and Ti are 4, 4, 6 and 3, respectively.

30. Osmium in OsO_4 has oxidation state of +8. **31.** The oxidation state of Ni in $Ni(CO)_4$ is zero.

32. The most characteristic oxidation state of Li is +3.

34. The electronic configuration of the given ions are as follows.

$_{12}Mg^{2+}$	$(1s)^2(2s)^2(2p)^6$	No unpaired electrons
$_{22}Ti^{3+}$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^1$	One unpaired electrons
$_{23}V^{3+}$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2$	Two unpaired electrons
$_{26}Fe^{2+}$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^6$	Four unpaired electrons

35.

Central atom	*Oxidation state*	*Number of electrons*	*Configuration*
Mn	+7	25 – 7 = 18	$(1s)^2(2s)^2(2p)^6(3s)^3(3p)^6$
Co	+3	27 – 3 = 24	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^6$
Fe	+3	26 – 3 = 23	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^5$
Cr	+3	24 – 3 = 21	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^3$

36. The fusion reaction is $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

37. The addition of KCN to cupric salt solution causes the precipitation of cuprous cyanide.

$$2Cu^{2+} + 4CN^- \rightarrow 2CuCN + \underset{\text{cyanogen}}{C_2N_2}$$

The precipitate of cuprous cyanide dissolves in excess of potassium cyanide solution forming the complex ion $CuCN + 3CN^- \rightarrow [Cu(CN)_4]^{3-}$

38. The standard instability constant refers to the reaction $[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$

$$K^\circ_{ins} = \frac{[Ag][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]}\,\frac{[Ag^+][NH_3]}{[Ag(NH_3)]^+} = K_1^\circ\, K_2^\circ = (1.4 \times 10^{-4})\,(4.3 \times 10^{-4}) = 6.02 \times 10^{-8}$$

39. Bond length of CO in $Fe(CO)_5$ will be slightly larger than 112.8 pm due to decrease in bond order of CO because of dπ – pπ back bonding from metal to the ligand.

40. Larger the number of electrons on metal ion, larger will be back bonding to the ligand and smaller will be the bond order. $[Fe(CO)_5]$ has eight electrons while the other complexes have six electrons.

41. The crystallized compound is $[Cu(NH_3)_4]SO_4 \cdot 2H_2O$

42. The IUPAC name of $[Fe(CN)_6]^{3-}$ ion is hexacyanoferrate(III) ion.

43. The IUPAC name of $[Ni(CO)_4]$ is tetracarbonylnickel(0).

44. The IUPAC name of $[Ni(CN)_4]^{2-}$ is tetracyanonickelate(II) ion.

45. The IUPAC name of $K_3[Co(NO_2)_6]$ is potassium(I) hexanitratecobalate(III).

46. The IUPAC name of $[Pt(NH_3)_4(NO_2)Cl]SO_4$ is tetramminechloronitroplatinum(IV) sulphate.

47. en is an example of a bidentate ligand. **48.** dien is an example of a tridentate ligand.

49. trine is an example of a tetradentate ligand. **50.** Ethylenediaminetriacetate ion is a pendadentate ligand.

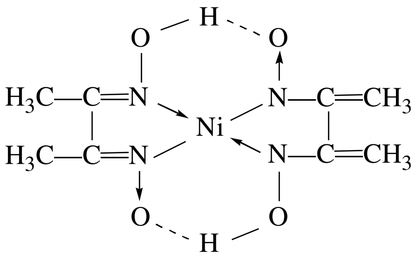
51. Ethylenediaminetetracetate ion is a hexadentate ligand.

52. The IUPAC name of $[CoCl_2(en)_2]Cl$ is dichlorobis(ethylenediamine)cobalt(III) chloride.

55. The σ and π bondings is through C of CO.

56. Zeise's salt is a metal–alkene complex $(K[Pt(C_2H_4)Cl_3] \cdot H_2O)$.

57. Dimethylglyoxime is coordinated to Ni^{2+} through two nitrogen atoms.

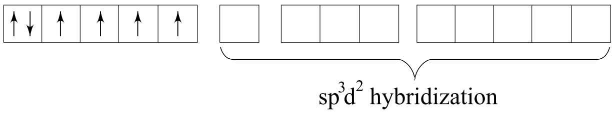


58. Ferrocene is $Fe(\eta^5 - C_5H_5)_2$ complex.

59. The carbonyls linkage to the metal involves a weak σ bond and a weak π bond.

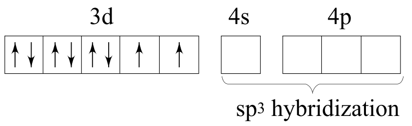
61. The positive ion is named first followed by the negative ion. The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the name. The complex negative ion ends in '– ate'. Thus, the name is tetraamminenickel(II) – tetrachloronickelate(II).

62. Cobalt in the complex exists as

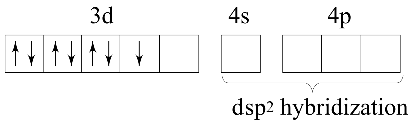


63. We have

Ni in $[Ni(Cl)_4]^{2-}$

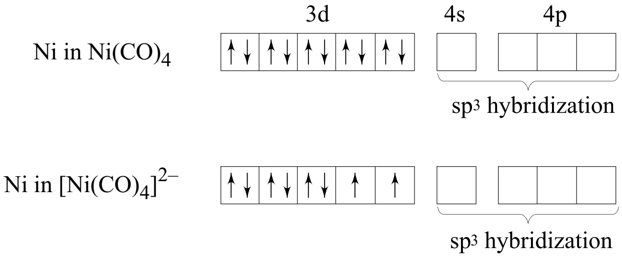


Ni in $[Ni(CN)_4]^{2-}$



The primary valencies of Ni in both the complexes are the same of +2.

64. We have



65. The gemoetry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are tetrahedral as both involves sp^3 hybridization.

68. $[Ni(NH_3)_6]^{2+}$, $[CoF_6]^{3-}$ and $[FeF_6]^{3-}$ involve sp^3d^2 hybridization while $[Co(NH_3)_6]^{3+}$ involves d^2sp^3 hybridization.

69. $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridization wheras $[Ni(CO)_4]$, $[NiCl_4]^{2-}$ and $[Ni(PF_3)_4]$ involve sp^3 hybridization.

70. 2.83 Bohr magneton implies two unpaired electrons according to the expression $\sqrt{n(n+2)}\mu_B$. The species Co, Ni, Cu and Mn in the given complexes have $(3d)^6$, $(3d)^8$, $(3d)^9$ and $(3d)^5$ electronic configurations, respectively. These involve sp^3d^2, sp^3d^2, sp^3d^2 and sp^3d^2, respectively. Thus, the complex $[Ni(H_2O)_6]^{2+}$ has two unpaired electrons.

71. The electronic configurations of Cr, Fe, Co and Ti in the complexes are $(3d)^3$, $(3d)^5$, $(3d)^6$ and $(3d)^1$ elecronic configurations, respectively. These involve d^2sp^3, sp^3d^2, d^2sp^3 and d^2sp^3 hybridization , respectively.

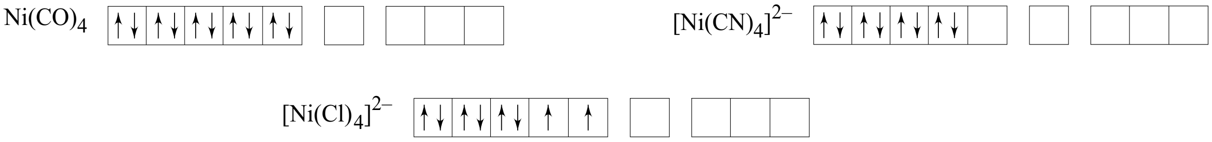
72. The complex ion [$Ni(CN)_4]^{2-}$ involves dsp^2 hybridization (see Q.63) and other given complexes involve sp^3 hybridization (see Q.64).

73. $Ni(CO)_4$ involves sp^3 hybridization (see Q.64) while in the rest of three secies dsp^2 hybridization exists.

74. $Ni(CO)_4$ involves sp^3 hybridization (see Q.64) and $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridization (see Q.63).

75. The electronic configurations of Mn^{2+}, Fe^{2+}, Cu^{2+} and Ni^{2+} are $(3d)^5$, $(3d)^6$, $(3d)^9$ and $(3d)^8$, respectively. The minimum number of unpaired electrons is present in Cu^{2+}.

76. The configurations of Ni in the given complexes are:



Thus, $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.

77. The electronic configurations of Cr^{3+}, Fe^{2+}, Cu^{2+} and Zn^{2+} are $(3d)^3$, $(3d)^6$, $(3d)^8$ and $(3d)^{10}$. Among these, Fe^{2+} has the largest unpaired electrons.

78. The electronic configurations of Cr^{3+}, Mn^{7+}, Ti^{3+} and V^{4+} are $(3d)^3$, $(3d)^0$, $(3d)^1$ and $(3d)^1$, respectively. Mn^{7+} contains no unpaired electrons, hence, $KMnO_4$ is not paramagnetic.

79. The expression is $\mu = \sqrt{n(n+2)}\,\mu_B$.

80. The ratio is greater than one.

81. The ratio is less than one.

82. $_{22}Ti^{3+}$ contains one unpaired electron ($3d^1$). Hence, $\mu = \sqrt{3}\,\mu_B = 1.73\,\mu_B$.

83. $_{23}V^{3+}$ contains two unpaired electrons ($3d^2$). Hence, $\mu = \sqrt{8}\,\mu_B = 2.83\,\mu_B$.

84. Cr^{2+} contains four unpaired electrons $(3d)^4$. Hence, $\mu = \sqrt{24}\,\mu_B = 4.9\,\mu_B$.

85. The electronic configuration of $_{24}Cr^{3+}$ is $(3d)^3$. Its magnetic moment will be $\sqrt{15}\,\mu_B = 3.87\,\mu_B$.

86. The electronic configuration of $_{26}Fe^{3+}$ is $(3d)^5$. Its magnetic moment will be $\sqrt{35}\,\mu_B = 5.92\,\mu_B$.

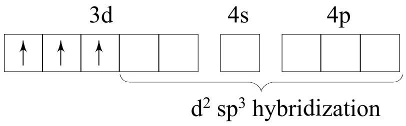
87. Cr contains six unpaired electrons. Its magnetic moment will be $\sqrt{48}\,\mu_B = 6.92\,\mu_B$.

88. The magnetic moment of 6.92 μ_B corresponds to six unpaired electrons. Hence, the configuration will be $(3d)^5(4s)^1$.

89. $(d)^5$ configuration contains maximum number of unpaired electrons.

90. $(d)^9$ configuration contains minimum number of unpaired electrons.

91. Chromium in the complex exists as



The complex involves d^2sp^3 hybridization. It has octahedral shape and is paramagnetic due to three unpaired electrons. The complex gives white precipitates with Cl^- ions.

92. There are 4, 2, 2 and 0 unpaired electrons in $[CoF_6]^{3-}$, $[NiCl_4]^{2-}$, $[Ni(NH_3)_6]^{2-}$ and $[Ni(CN)_4]^{2-}$ ions. Hence, $[Ni(CN)_4]^{2-}$ is diamagnetic.

93. The presence of Fe^{II} and NO^+ may be confirmed by measuring the solid state magnetic moment.

94. The electronic configurations are: $_{29}Cu^+$ $(3d)^{10}$; $_{30}Zn^{2+}$ $(3d)^{10}$; $_{26}Fe^{2+}$ $(3d)^6$; $_{21}Sc^{3+}$ $(3d)^0$. Fe^{2+} has four unpaired electrons, so it is paramagnetic.

95. The electronic configurations are: $_{25}Mn^{2+}$ $(3d)^5$; $_{29}Cu^+$ $(3d)^{10}$; $_{27}Co^{3+}$ $(3d)^6$; $_{24}Cr^{3+}$ $(3d)^3$. $_{29}Cu^+$ has no unpaired electrons, so it is diamagnetic

96. 1.73 Bohr magneton implies one unpaired electron according to the expression $\sqrt{n(n+2)}\mu_B$. The species Cu, Ni, Ti and Co in the given complexes have $(3d)^9$, $(3d)^8$, $(3d)^0$ and $(3d)^6$ electronic configurations, respectively. These involve sp^2d, dsp^2, sp^3 and d^2sp^3 hybridizations, respectively. Thus, the complex $[Cu(NH_3)_4]^{2+}$ has one unpaired electron.

97. The electronic configurations of Ni, Fe, Co and Cr in the given complexes are $(3d)^8$, $(3d)^6$, $(3d)^6$ and $(3d)^4$, respectively. These involve dsp^2, d^2sp^3, d^2sp^3 and d^2sp^3 hybridization, respectively. The complex $[Cr(H_2O)_6]SO_4$ will be paramagnetic as Cr contains two unpaired electrons.

98. $Ni(CO)_4$ involves sp^3 hybridization with $(3d)^{10}$ electronic configuration of Ni. It is diamagnetic.

99. For a compound to be paramagnetic and coloured it must have unpaired electron(s) in 3d orbital(s) of the central atom.

Compound	*Central atom*	*Electronic configuration*
$K_2Cr_2O_7$	$_{24}Cr(VI)$	$(3s)^2(3p)^6$
$(NH_4)_2(TlCl_6)$	$_{22}Tl(IV)$	$(3s)^2(3p)^6$
$VOSO_4$	$_{23}V(IV)$	$(3s)^2(3p)^6(3d)^1$
$K_3[Cu(CN)_4]$	$_{29}Cu(I)$	$(3s)^2(3p)^6(3d)^{10}$

100. Cobalt in $[Co(SCN)_4]^{2-}$ is present as Co^{2+}. It involves sp^3 hybridization with three unpaired electrons in 3d orbitals. Its magnetic moment will be $\sqrt{3(3+2)}\ \mu_B = \sqrt{15}\ \mu_B$

101. The electronic configuration of Cr is $Ar(3d)^5(4s)^1$. In order to accommodate six ligands and the fact that CO is a strong ligand, the electrons in Cr are paired to provide two unfilled 3d orbitals which are involves in d^2sp^3 hybridization. Thus, there are no unpaired electrons in $Cr(CO)_6$. Hence, its spin magnetic moment will be zero.

102. The electronic configurations of Cu^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+} are $(3d)^9$, $(3d)^5$, $(3d)^6$ and $(3d)^8$, respectively. The configuration $(3d)^9$ has the minimum unpaired electrons.

103. The given complexes involve outer hybridization of sp^3d^2. The electronic configurations of Cr^{3+}, Fe^{2+}, Cu^{2+} and Zn^{2+} in the given complexes are $(3d)^3$, $(3d)^6$, $(3d)^9$ and $(3d)^{10}$, respectively. The configuration $(3d)^6$ has largest number of unpaired electrons.

104. The complimentary colour of violet radiation is yellow-green.

105. The complimentary colour of indigo radiation is yellow.

106. The complimentary colour of blue-green radiation is orange to red.

107. The complimentary colour of orange is blue.

108. The electronic configuration of Cu^+ is $(3d)^{10}$. There is no unpaired electron. Hence, the compounds of Cu^+ are colourless (white).

109. The electronic configuration of $_{21}Sc^{3+}$ is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$. There is no unpaired electrons is d orbitals. Hence, the compounds of Sc^{3+} are white.

110. The colour in the transition metal. Compounds is due d – d transitions.

111. Green colour is due to chloro complexes.

112. The electronic configurations of $_{29}Cu^{2+}$, $_{22}Ti^{4+}$, $_{23}V^{3+}$ and $_{26}Fe^{2+}$ are $(3d)^9$, $(3d)^0$, $(3d)^1$ and $(3d)^6$, respectively. Hence, Ti^{4+} will be colourless.

113. The electronic configurations of Ti^{3+}, Ti^{4+}, Fe^{2+} and Fe^{3+} are $(3d)^1$, $(3d)^0$, $(3d)^6$ and $(3d)^5$, respectively. The hydrated transition metal ion Ti^{4+} contains no unpaired electron, hence, colourless.

114. The electronic configurations of Ti^{4+}, Cu^+, Cr^{3+} and V^{3+} are $(3d)^0$, $(3d)^{10}$, $(3d)^3$ and $(3d)^2$, respectively. Hence, $K_3[VF_6]$ is a coloured compound as it contains two unpaired electrons.

115. CuF_2 is expected to be coloured as Cu^{2+} contains one unpaired electron.

116. The colour of a transition metal ion may be related to its number of unpaired d electrons. We have $V^{4+}$and Cu^{2+} ($n = 1$), blue; Fe^{2+} ($n = 4$), green and Mn^{2+} ($n = 5$), pink.
Hence, $CuCl_2$ and $VOCl_2$ are expected to have the same colour.

117. The electronic configuration of ${}_{71}Lu^{3+}$ is $[Xe](4f)^{14}$. Hence, it is expected to be colourless.

118. The electronic configuration of ${}_{57}La^{3+}$ is that of Xe. Hence, there is no f electrons. The species La^{3+} is expected to be colourless.

119. The electronic configuration of ${}_{62}Sm^{3+}$ is $(4f)^5$ and that of ${}_{66}Dy^{3+}$ is $(4f)^9$. The colour of f^n and f^{14-n} are often identical.

120. We have $4\Delta_O = 9\,\Delta t$

121. The colour of the complex compound is due to d – d electronic transition.

122. t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) have lower energy by $(2/5)\Delta_O$

123. t_{2g} orbitals have higher energy by $(2/5)\Delta_t$.

124. e_g orbitals (d_{z^2}, $d_{x^2-y^2}$) have higher energies by $(3/5)\Delta_O$.

125. e_g orbitals have lower energies by $(3/5)\Delta_t$.

126. The order is $SCN^- < F^- < CN^-$.

127. The spectrochemical series of ligands is

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^-$$

128. F^- and Cl^- are weak ligands. These have small tendency of pairing metal electrons. Thus, these form high-spin complexes. The spacing of splitted orbitals of metal ions is small.
CN^- a strong ligand. It has high tendency of pairing metal electrons. Thus, it forms low-spin complexes. CO is a strong ligand and thus it forms low-spin complexes.

129. See Q.128

130. Only in CuF_2, copper exists as Cu^{2+} with one unpaired electron. Its colour is blue. In other choices, copper exists as Cu^+ with no unpaired electrons and thus are colourless.

131. F is a weak ligand and thus forms a high spin complex. NH_3 is a strong ligand and thus forms a low spin complex

132. $Pt(Cl_2)(CN)_2^{2-}$ will show *cis-trans* isomerism.

133. *cis*-$CrCl_2en_2^+$ exists as a pair of enantiomers.

134. The remaining three complexes have plane of symmetry. Hence, they are optically inactive.

135. There are only two isomers, *cis*-and *trans*-forms.

136. There are only two isomers, *cis*-and *trans*-forms.

137. There are three geometric isomers; one isomer of *cis*-dichloro and two isomers of *trans*-dichloro. All the three are optically active. Hence, there are six isomers.

138. There is exchange of ligand in the coordination sphere and the anion present outside the coordination sphere. Thus, the given complexes are ionization isomers.

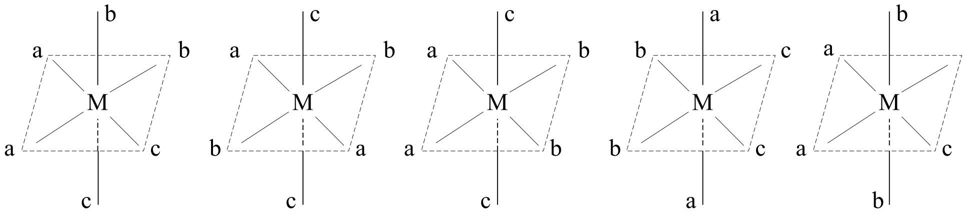
139. There is different donor atom of the ligand. Thus, the given isomers are linkage isomers.

140. There is a exchange of ligands between the complex cation and complex anion. Thus, the given isomers are coordination isomers;

141. $[PtCl_2(NH_3)_2]$ is square planar. The arrangement of two Cl or two NH_3 may be *cis* or trans. Thus, the given isomer forms geometrical isomers.

142. The compound $[CoCl_2(NH_3)_2(en)]$ has octahedral arrangement of ligands. It can form optical isomers.

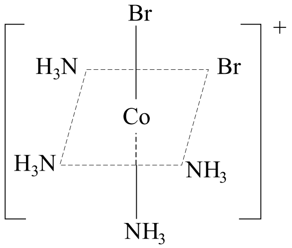
143. The complex $[Ma_2b_2c_2]$ can exist in five geometrical isomers. These are (i) all ligands occupy *cis* positions, (ii) all ligands occupy *trans* positions and (iii) three isomers in which one of the ligands occupy *trans* position. These are depicted below.



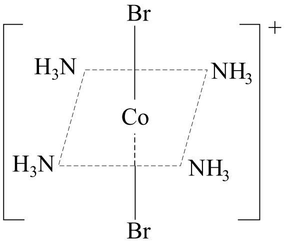
Cis-isomer exists in two optical (mirror image) isomers. Only this compound is asymmetrical.

144. The number of ways of arranging 6 ligands is $^6C_2$ which is equal to 15. (= 6 × 5/2 = 15). Each isomer is asymmetrical and thus also exists as optical isomer. Thus, there as 30 isomers.

145. Geometrical isomers are



and



Ionization isomers are $[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4Cl]Br$

152. The electronic configuration are: $_{57}La^{3+}$ $(4f)^0$; $_{63}Eu^{3+}$ $(4f)^6$; $_{64}Gd^{3+}$ $(4f)^7$; $_{71}Lu^{3+}$ $(4f)^{14}$
The ion $_{63}Eu^{3+}$ is expected to coloured due to possible f – f electronic transition.

153. The electronic configurations are: $_{22}Ti^{2+}$ $(3d)^2$; Sn^{2+} $(5s)^2$; Zn^{2+} $(3d)^{10}$; Ag^+ $(4d)^{10}$
The complex $[Ti(H_2O)_6]^{2+}$ is expected to be coloured due to d – d electronic transition.

154. The electronic configurations are:

$_{58}Ce^{3+}$ $(4f)^1$ — $_{67}Ho^{3+}$ $(4f)^{10}$
$_{60}Nd^{3+}$ $(4f)^3$ — $_{68}Er^{3+}$ $(4f)^{11}$
$_{61}Pm^{3+}$ $(4f)^4$ — $_{69}Tm^{3+}$ $(4f)^{12}$
$_{62}Sm^{3+}$ $(4f)^5$ — $_{70}Yb^{3+}$ $(4f)^{13}$

The ion having *n* electrons in 4f orbitals has the same colour as the ion having (14–*n*) electrons in 4f orbitals.

155. The configurations of $_{57}La^{3+}$ is $(4f)^0$ while that of $_{71}Lu^{3+}$ is $(4f)^{14}$. They are expected to be colourless.

156. Most of inner-transition elements show the valence of +3.

157. $E°$ value increases (becomes less negative) from La to Lu. Thus, the tendency of the reaction $M \rightarrow M^{3+} + 3e^-$ decreases.

Multiple Correct Choice Type

1. The electronic configurations of Zn^{2+}, Li^+, Co^{2+} and Cr^{3+} are $(3d)^{10}$, $(1s)^2$, $(3d)^7$ and $(3d)^3$, respectively. Both Co^{2+} and Cr^{3+} have unpaired electrons and thus their salts in aqueous solution will exhibit colour.

2. The reactions are:

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$4MnO_4^- + 6OH^- + 2HCHO \rightarrow 4MnO_4^{2-} + 4H_2O + 2HCOO^-$$

3. The complexes $[Cr(NH_3)_6]^{3+}(Cl^-)_3$ and $K_3[VF_6]$ are expected to be coloured as they contain 3 and 2 unpaired electrons, respectively.

4. The compounds formed by lanthanides are ionic.

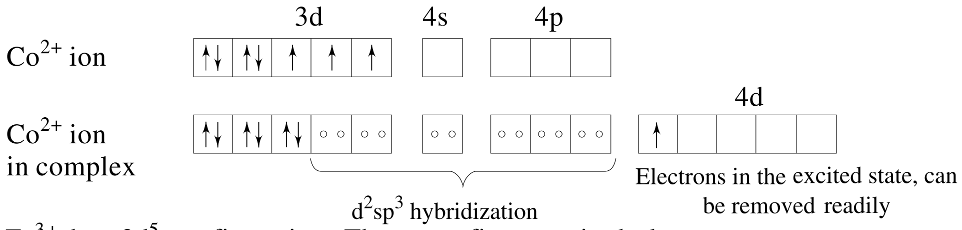
5. The complex formed is $[Ag(NH_3)_2]OH$

6. The species attached through secondary valencies in a complex are Lewis base.

8. (a) The correct configuration is $(3d)^5(4s)^1$ as half–filled d orbitals is more stable configuration.
(b) The electronic configuration of Zn^{2+} is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}$. It is diamagnetic as no unpaired electrons are present.
(c) Potassium ferrocyanide is diamagnetic (no unpaired electron) while potassium ferricyanide is paramagnetic (one unpaired electron).
(d) It is $(3d)^{10}(4s)^1$.

9. (b) It increases from Sc to Mn as there is increase in the unpaired electrons followed by decrease as there is decrease in the unpaired electrons.
(c) The electronic configuration of Cu(I) is $(3d)^{10}$ (no unpaired electrons) while that of Cu(II) is $(3d)^9$ (one unpaired electron).
(d) The electronic configuration of Fe^{2+} is $(3d)^6$ (four unpaired electrons) whereas that of Fe^{3+} is $(3d)^5$ (five unpaired electrons).

10. (a) The configuration of $[Co(NH_3)_6]^{2+}$ is



(b) Fe^{3+} has $3d^5$ configuration. There are five unpaired electrons.

(d) Near the end of transition series, an increase in atomic radii occurs.

11. (b) The number of unpaired electrons increases upto the middle of a particlar transition series and then decreases due to the pairing of electrons.

12. (a) The oxidation state of Cu in the complex is +I and thus its electronic configuration would be $3d^{10}4s^0$. There is no unpaired electrons. Hence, it is a colourless compound.

(b) The oxidation state of Ti in the complex is +IV and thus its electronic configuration is $(3d)^0(4s)^0$. There is no unpaired electrons. Hence, it is a colourless compound.

(c) The oxidation state of V in the complex is +III and thus its electronic configuration is $(3d)^2(4s)^0$. There are two unpaired electrons. Hence, it is a coloured compound.

CHAPTER 17

ORES/MINERALS AND EXTRACTIVE METALLURGY

Only a few metals such as gold, silver, copper and platinum occur in nature in the free or native state. Most of the metals occur in the form of their compounds such as oxides, carbonates, sulphides and silicates. Such naturally occurring sources are called *minerals*. A mineral from which a metal can be profitably extracted is called an *ore*. Thus, an ore is a mineral but a mineral may not be an ore. For example, iron pyrites, FeS_2, is a mineral but not an ore.

In this unit, we shall describe some commercially important ores of some metals and the principles involved in the extraction of the metals from their important ores.

IRON AND TIN

Iron occurs in the free state as meterorites which also contain 20 to 30% nickel.

In the combined state, iron occurs in the following minerals.

Magnetite, Fe_3O_4
Spathic iron ore, $FeCO_3$
Haematite, Fe_2O_3
Iron pyrites, FeS_2
Limonite, $3Fe_2O_3 \cdot 3H_2O$
Copper pyrites, $CuFeS_2$

Tin occurs scarcely in the free state but in the form of compounds it exists in a large number of minerals, e.g. pyrites ore of copper, iron and zinc. The most important source of tin is cassiterite or tin stone, SnO_2.

Both iron and tin are extracted by the *carbon reduction method.*

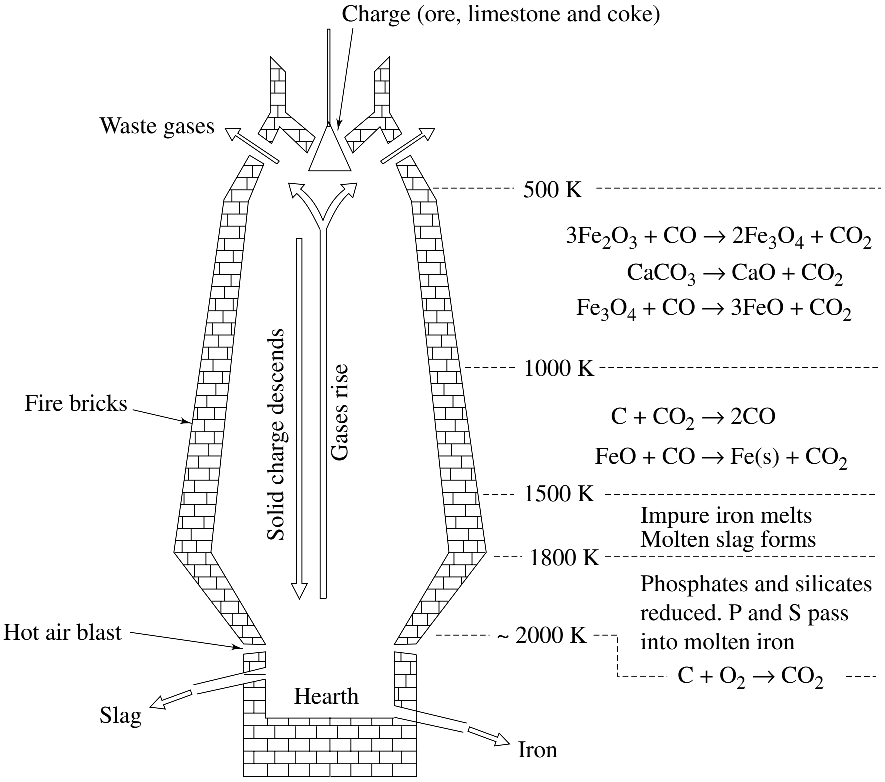


Fig. 17.1 Blast furnace

Extraction of Iron Iron is extracted from its principal ore, haematite. After the preliminary washing, concentration and roasting, the ore is smelted in the presence of coke and limestone in a blast furnace (Fig. 17.1).

Roasted ore (8 parts) with desulphurized coke (4 parts) and limestone pieces (1 part) is fed into the blast furnace from the top. Preheated air is blown in through water-jacketed pipes called tuyeres fixed in the lower part of the furnace. There is a temperature gradient as we move from the bottom (temperature about 2000 K) to the top (temperature about 500 K) of the blast furnace. The blast furnace may be broadly divided into three main parts as described in the following.

1. Zone of fusion The lower portion where coke burns and produce carbon dioxide and a lot of heating is known as zone of fusion :

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -406 \text{ kJ mol}^{-1}$$

Here the temperature is about 1775 K. A little above this, where temperature is about 1475 K – 1575K, iron coming from above melts.

2. Zone of heat absorption The middle portion (temperature 1075 K – 1275 K), CO_2 rising up is reduced to CO with the absorption of heat:

$$CO_2 + C \rightarrow 2CO \qquad \Delta H = 163 \text{ kJ mol}^{-1}$$

In this portion, limestone coming from above is decomposed and the resultant lime (CaO), which acts as flux, combines with silica (present as impurity-gangue) to form calcium silicate (fusible slag):

$$CaCO_3 \rightarrow CaO + CO_2; \qquad CaO + SiO_2 \rightarrow CaSiO_3$$

3. Zone of reduction The upper portion (675 K – 975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up the furnace:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

The reduction is believed to take place in stages:

$$3Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2; \qquad Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$FeO + CO \rightarrow Fe + CO_2$$

At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron from oxidation. These two can be removed from different holes (Fig. 17.1). Waste gases escaping at the top consists of about 30% CO, 10% CO_2 and the rest nitrogen.

Iron obtained from the blast furnace is known as pig iron.

Pig iron contains about 2–5% carbon as well as other impurities (usually Si, Mn, S and P). Pig iron is converted into cast iron by remelting in a vertical furnace heated by coke. Cast iron expands on solidification and is used for casting various articles. Wrought iron, which is the purest form of iron, can be obtained by heating cast iron in a reverberatory furnace lined with iron oxide. Wrought iron contains about 0.2% carbon.

Extraction of Tin Metallic tin is extracted from tin stone which contains about 10% of the metal as SnO_2, the rest being siliceous matter, tungstates of Fe, Cu and As. After crushing, the ore is concentrated by washing in a current of water (Gravity process to remove lighter gangue particles) and by magnetic separator to remove tungstates of Fe and Mn. The ore is roasted to remove S and As as their oxides. The ore then may be washed to remove sulphates of Cu and Fe. Finally, the ore is smelted in a reverberatory furnace or in a blast furnace at 1475–1575 K. The ore is mixed with one-fifth of its mass of powdered anthracite and little of lime or fluorspar which is used as flux. Tin oxide is reduced to tin:

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

The molten metal collected from the bottom of furnace contains impurities such as Fe, Pb, S and As. The metal may be purified electrolytically (electrolyte; tin sulphate, sulphuric acid and hydrofluosilicic acid. anode; impure tin and cathode; pure tin).

COPPER AND LEAD

Copper occurs in the native state as well as in the compound form. The natural ores of copper are

Copper pyrites, $CuFeS_2$	Malachite, $Cu(OH)_2 \cdot CuCO_3$	Cuprite or ruby copper, Cu_2O
	Azurite, $Cu(OH)_2 \cdot 2CuCO_3$	Copper glance, Cu_2S

Lead is widely distributed in nature. It is the stable end product of all natural radioactive elements. It occurs in traces in the native form. In the combined form, it occurs as

Galena, PbS	Cerussite, $PbCO_3$	Anglesite, $PbSO_4$
Wulfenite, $PbMnO_4$	Stolzite, $PbWO_4$	

Both Copper and lead may be extracted by *self-reduction method.*

Extraction of Copper Copper is mainly extracted from copper pyrites. After the concentration of its ore by froth flotation process, the ore is roasted in a current of air to remove arsenic, antimony and much of sulphur. The reactions occurring are

(i) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2\uparrow$ (major reaction)

(ii) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(iii) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ (minor reactions)

The ore is then mixed with a little coke and sand and smelted in a water-jacketed blast furnace. The minor reactions that occurred during roasting continue here. Ferrous oxide combines with sand to form a fusible slag. Cuprous oxide formed combines with ferrous sulphide to give ferrous oxide and cuprous sulphide. This is because iron has more affinity for oxygen than copper.

(iv) $FeO + SiO_2 \rightarrow FeSiO_3$

(v) $Cu_2O + FeS \rightarrow Cu_2S + FeO$

Molten mass collected from the bottom of furnace contains largely cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte.

The molten matte is finally transferred to Bessemer converter (Fig.17.2). A blast of sand and air is blown in the converter through tuyeres which are situated a little above the bottom. This causes removal of S and As as oxides and ferrous oxide as slag (reaction iv). At the same time Cu_2S is oxidized mostly into Cu_2O (reaction ii) and partly into CuO and $CuSO_4$. All these react with Cu_2S giving copper. The reactions are

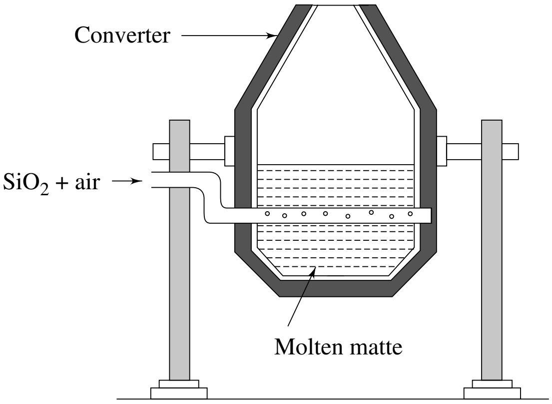


Fig. 17.2 Bessemer converter

(ii) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2\uparrow$

$2Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2\uparrow$

$Cu_2S + 2CuO \rightarrow 4Cu + SO_2\uparrow$

$2Cu_2S + 5O_2 \rightarrow 2CuSO_4 + 2CuO$

$CuSO_4 + Cu_2S \rightarrow 3Cu + 2SO_2\uparrow$

Finally, copper may be refined electrolytically (electrolyte; copper sulphate: anode; impure copper and cathode; pure copper).

Extraction of lead Lead is mainly extracted from galena. After the concentration of the ore by froth flotation process, the ore is roasted in a reverberatory furnace for about six hours at a moderate temperature in a current of air. Part of galena is converted into lead oxide and lead sulphate. After this, the supply of air is stopped and small quantities of carbon, quicklime and cheap iron ore are added along with increase of temperature. At this stage, unreacted sulphide reacts with the lead oxide and sulphate giving metallic lead :

$PbS + 2PbO \rightarrow 3Pb + 2SO_2$ $PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$

The obtained lead contains impurities such as Cu, Ag, Bi, Sb and Sn. Silver is removed by Parke's process where molten zinc is added to molten impure lead. The former is immiscible with the latter. Silver is more soluble in molten zinc than in molten lead. Zinc-silver alloy solidifies earlier than molten lead and thus can be separated. After this, crude lead is refined electrolytically (Electrolyte; lead silicofluoride, $PbSiF_6$ and hydrofluosilicic acid, H_2SiF_6 with a little gelatine, anode; curde lead and cathode; pure lead).

MAGNESIUM AND ALUMINIUM

Magnesium does not occur in the native state. Its important minerals are

Magnesite, $MgCO_3$ Dolomite, $MgCO_3 \cdot CaCO_3$

Carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$
Kiesserite, $MgSO_4 \cdot H_2O$
Schonite, $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$
Epsomite (epsom salt), $MgCO_3 \cdot 7H_2O$
Kainite, $MgSO_4 \cdot KCl \cdot 3H_2O$

Magnesium is widely distributed in nature in rocks, spring and seawater. In rocks and silicates it occurs in mineral like olivine (Mg_2SiO_4), spinel ($MgAl_2O_4$), talc ($Mg_3H_2(SiO_3)_4$), asbestos ($CaMg_3(SiO_3)_4$), etc.

Aluminium also does not occur free in nature. In the combined state, it occurs in the following forms.

Oxides: Corundum, Al_2O_3; diaspore, $Al_2O_3 \cdot H_2O$ and bauxite, $Al_2O_3 \cdot 2H_2O$.
Fluorides: Cryolite, Na_3AlF_6
Silicates: Feldspar, $KAlSi_3O_8$, mica ($KAlSi_3O_{10}(OH)_2$) and kaolinite ($Al(OH)_4$, Si_2O_5)
Basic Sulphates: Alunite or alumstone, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$
Basic Phosphates: Turquoise, $AlPO_4 \cdot Al(OH)_3 \cdot H_2O$.
Aluminates: Aluminates of Mg, Fe and Mn.

Aluminium is the third most abundant element of earth's crust.

Extraction of magnesium Magnesium is commonly obtained by the electrolysis of fused magnesium chloride containing a little sodium chloride and sodium fluoride at 700 °C in an air-tight iron pot which itself serves as the cathode, the anode being a graphite rod which dips into the electrolyte. The anode is surrounded by a perforated porcelain tube for the exit of chlorine. The electrolysis is carried out in the atmosphere of coal gas so as to prevent the attack of atmospheric oxygen and nitrogen on magnesium. Molten magnesium being lighter than the electrolyte, it floats over the fused electroyte and is withdrawn (Fig. 17.3).

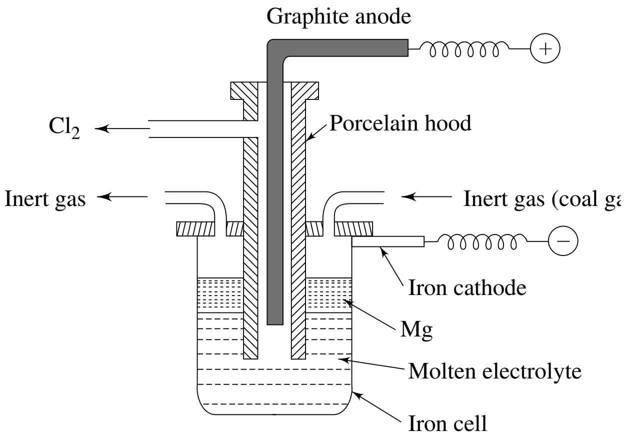


Fig. 17.3 Electrolytic cell for the production of magnesium

In *Dow Process*, magnesium is recovered from seawater as magnesium chloride which is then electrolysed using the cell described above (Fig. 17.3).

Anhydrous carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) may also be employed as the starting material of magnesium chloride. The cathode may be a layer of molten lead on the floor of the cell and anode may be graphite rods which are suspended above the molten lead. Magnesium liberated at the cathode dissolves in molten lead. The alloy of lead-magnesium is subjected to electrolysis to obtain pure magnesium (electrolyte: fused carnallite, anode- lead-magnesium alloy and cathode-steel rods).

Extraction of Aluminium Aluminium is isolated from the electrolysis of bauxite, $Al_2O_3 \cdot 2H_2O$. Since it is difficult to purify aluminium, bauxite ore is purified either by Baeyer's process (or Hall's process) or Serpek's process depending upon the impurity present in the ore.

If the bauxite contains iron oxide as the impurity, one can use Baeyer's or Hall's process as described below.

Baeyer's Process Finally ground ore is roasted to convert ferrous oxide to ferric oxide and then digested with concentrated caustic soda solution at 423 K. Al_2O_3 dissolves while Fe_2O_3 remains undissolved. The latter is filtered off and from the solution $Al(OH)_3$ is precipitated by adding a weak acid. The ignition of $Al(OH)_3$ gives Al_2O_3.

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow \underset{\text{aluminate ion dissolves}}{2Al(OH)_4^-} \qquad Al(OH)_4^- + H^+ \rightarrow \underset{\text{precipitates}}{Al(OH)_3} + H_2O$$

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3H_2O$$

Hall's Process In this process the ore is fused with sodium carbonate when soluble meta-aluminate ($NaAlO_2$) is produced. This is extracted with water leaving behind iron oxide. Carbon dioxide at 323-333 K is passed through water extract to get $Al(OH)_3$ which on heating gives Al_2O_3.

$$Al_2O_3 + Na_2CO_3 \xrightarrow{\text{fused}} \underset{\text{extracted with water}}{2NaAlO_2 + CO_2} \qquad 2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 + Na_2CO_3$$

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3H_2O.$$

If the impurity is silica, the Serpek's process is used to purify bauxite.

Serpek's Process The powdered ore is mixed with coke and heated to 2075 K in a current of nitrogen. Silica present is reduced to silicon which volatilizes off and alumina gives aluminium nitride. The hydrolysis of the latter gives $Al(OH)_3$, heating of which gives Al_2O_3.

$$SiO_2 + 2C \rightarrow Si\uparrow + 2CO_2\uparrow \qquad Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3 \qquad 2Al(OH)_3 \xrightarrow[\text{heat}]{} Al_2O_3 + 3H_2O$$

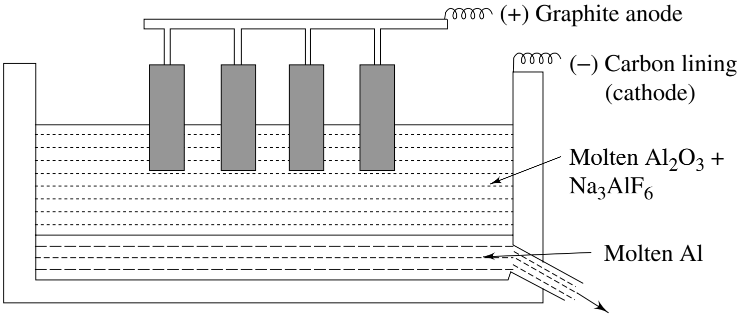
After obtaining pure Al_2O_3, it is dissolved in fused cryolite, Na_3AlF_6, with a little fluorspar, CaF_2, and is electrolysed in an iron tank lined with blocks of carbon which serve as the cathode. The anode consists of a number of graphite rods suspended vertically inside the tank (Fig. 17.4).

Aluminium gets settled at the bottom of the tank and can be removed. The reactions occurring at the electrodes are

Cathode $Al^{3+} + 3e^- \rightarrow Al$ *Anode* $2O_2^{2-} \rightarrow O_2 + 4e^-$

$C + O_2 \rightarrow CO_2$

Anode is replaced periodically because of its consumption.



At the cathode: $Al^{3+} + 3e^- \rightarrow Al$

At the anode: $C(s) + 2O^{2-} \rightarrow CO_2(g) + 4e^-$

Fig. 17.4 Electrolytic cell for the production of aluminium

SILVER

Silver in the native form is associated with copper and gold. The main ores of silver are

Argentite or silver glance, Ag_2S	Pyrargyrite, $3Ag_2S \cdot Sb_2S_3$
Proustite, $3Ag_2S \cdot As_2S_3$	Horn silver, AgCl

Extraction of Silver Silver is extracted from its ore by the cyanide process (MacArthur-Forrest process). After the preliminary crushing and concentration by froth floation process, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated by a current of air. Silver passes into solution as argentocyanide :

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

The air blown in remove Na_2S as $Na_2S_2O_3$ and Na_2SO_4 causing the above reaction to proceed to completion.

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH; \quad Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O$$

The solution obtained above is flitered and treated with scrap iron or zinc when silver gets precipitated :

$$2Ag(CN)_2^- + Zn \rightarrow Zn(CN)_4^{2-} + 2Ag$$

The obtained silver is purified electrolytically (electrolyte : silver nitrate solution containing 1% nitric acid, anode : impure silver and cathode : pure silver). The impurities like zinc and copper pass into the solution while gold falls down as anode mud.

Straight Objective Type

Carbon-Reduction Method (Iron and Tin)

1. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ions ends up in
(a) slag (b) gangue (c) metallic Ca (d) calcium carbonat (1982)

2. Which of the following minerals does not contain iron?
(a) Magnetite (b) Magnesite (c) Haematite (d) Limonite

3. The principal ore of iron is
(a) haematite (b) iron pyrites (c) copper pyrites (d) spathic iron

4. The principal reducing agent in the metallurgy of iron is
(a) carbon (b) carbon monoxide (c) carbnon dioxide (d) aluminium

5. The principal reaction in the zone of fusion of blast furnace employed in the metallurgy of iron is
(a) $C + O_2 \rightarrow CO_2$ (b) $2C + O_2 \rightarrow 2CO$
(c) $CO_2 + C \rightarrow CO$ (d) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

6. The principal reducing agent in the metallurgy of tin is
(a) carbon (b) carbon monoxide (c) carbon dioxide (d) aluminium (1982)

7. Iron is mainly extracted by
(a) carbon reduction method
(b) self-reduction method
(c) the method of electrolysis
(d) leaching with aqueous solution of NaCN followed by reduction

8. Which of the following sequences of carbon content is correct?
(a) steel < cast iron < wrought iron (b) steel < pig iron < wrought iron
(c) steel < wrought iron < cast iron (d) wrought iron < steel < cast iron

9. In the metallurgy of iron, the material obtained from the bottom of blast furnace is
(a) slag (b) pig iron (c) cast iron (d) wrought iron

10. The chemical processes in the production of steel from haematite ore involve
(a) reduction (b) oxidation
(c) reduction followed by oxidation (d) oxidation followed by reduction (2000)

11. In the manufacture of iron from haematite, the function of lime stone is as
(a) a reducing agent (b) slag (c) flux
(d) gangue (e) None of these (1978)

12. Extraction of zinc from zinc blende is achieved by
(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self-reduction (2007)

Self-Reduction Method (Copper and Lead)

13. Copper is mainly extracted from
(a) cuprite (b) azurite (c) copper pyrites (d) malachite

14. The composition of cuprite is
(a) Cu_2S (b) $CuFeS_2$ (c) $Cu(OH)_2 \cdot CuCO_3$ (d) Cu_2O

15. Copper is mainly extracted by
(a) carbon reduction method
(b) self-reduction method
(c) the method of electrolysis
(d) leaching with aqueous solution of NaCN followed by reduction

16. Which of the following is the mineral of lead?
(a) Malachite (b) Azurite (c) Galena (d) Carnallite

17. Lead is mainly extracted from
(a) cerussite (b) galena (c) anglesite (d) wulfenite

18. Lead is mainly extracted by
(a) carbon reduction method
(b) self-reduction method
(c) the method of electrolysis
(d) leaching with aqueous solution of NaCN followed by reduction

19. Desilverization of lead may be carried out by using
(a) MacArthur-Forrest process
(b) Parke's process
(c) Parting process
(d) cyanide process

20. In the metallurgy of copper, the material obtained from the bottom of blast furnace is
(a) slag (b) copper (c) matte (d) cuprous oxide

21. Copper can be extracted from
(a) Kupfernickel (b) Dolomite (c) Cinnabar
(d) Galena (e) Malachite (1978)

22. Among the following statements, the incorrect one is
(a) calamine and siderite are carbonates;
(b) argentite and cuprite are oxides;
(c) zinc blende and pyrites are sulphides;
(d) malachite and azurite are ores of copper. (1997)

23. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is
(a) Cu_2O + Fes (b) $FeSiO_3$ (c) $CuFeS_2$ (d) $Cu_2S + FeO$ (2001)

24. Lead and tin are, respectively, extracted from their chief ore by
(a) carbon reduction and self reduction
(b) carbon reduction and electrolytic reduction
(c) self reduction and carbon reduction
(d) electrolytic reduction and carbon reduction (2004)

25. Which of the following ores contains both iron and copper?
(a) Malachite (b) Azurite (c) Dolomite (d) Chalcopyrite (2005)

Electrolytic Reduction (Magnesium and Aluminium)

26. The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
(a) that of a catalyst
(b) to make the fused mixture very conducting
(c) to lower the temperature of the melt
(d) to decrease the rate of oxidation of carbon at the anode. (1993)

27. Which of the following is not the mineral of magnesium?
(a) Magnetite (b) Magnesite (c) Dolomite (d) Kainite

28. Magnesium is mainly extracted by
(a) carbon reduction method
(b) self-reduction method
(c) the method of electrolysis
(d) leaching with aqueous soslution of NaCN followed by reduction

29. In the electrolytic extraction of aluminium, the solvent is
(a) molten Al_2O_3 (b) water (c) Fe_2O_3 + Al (d) molten cryolite

30. Mineral that does not contain Al is
(a) feldspar (b) fluorspar (c) cryolite (d) mica

31. The main ore of aluminium is
(a) bauxite (b) alumina (c) potash alum (d) cryolite

32. Magnesium does not occur in
(a) the native state (b) seawater (c) rocks (d) the compounds form

33. Which of the following statements regarding the metallurgy of magnesium using electrolytic method is **not** correct?

(a) Electrolyte is magnesium chloride containing a little of NaCl and NaF
(b) Air tight iron pot acts as a cathode
(c) Electrolysis is done in the atmosphere of coal gas
(d) Molten magnesium is heavier than the electrolyte

34. Which of the following statements regarding the metallurgy of aluminium by electrolytic method is **not** correct?
(a) Electrolyte is Al_2O_3 dissolved in Na_3AlF_3 containing a little of CaF_2
(b) Anode consists of a number of graphite rods which are periodically replaced
(c) Aluminium being heavier than electrolyte floats over the surface of the latter
(d) Bauxite ore is purified before carrying out the electrolysis

35. Which of the following minerals contains both Mg and Ca?
(a) Dolomite (b) Gypsum (c) Epsomite (d) Talc

36. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(a) $Al(OH)_3$ in NaOH solution (b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of AlO(OH) and $Al(OH)_3$ (d) a molten mixture of Al_2O_3 and Na_3AlF_6 (1999)

37. 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 temperature
(d) in the presence of cryolite which forms a melt with higher melting point (2000)

38. Calcium is obtained by
(a) Electrolysis of molten $CaCl_2$ (b) Electrolysis of aqueous solution of $CaCl_2$
(c) Reduction of $CaCl_2$ with carbon (d) Roasting of lime stone (1980)

39. In the aluminothermite process, aluminium acts as
(a) an oxidizing agent (b) a flux (c) a reducing agent (d) a solder

40. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(a) $Al(OH)_3$ in NaOH solution (b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of Al_2O_3 and Na_3AlF_6 (d) a molten mixture of AlO(OH) and $Al(OH)_3$
(1999)

41. Which of the following processes is used in the extractive metallurgy of magnesium?
(a) fused salt electrolysis (b) self reduction
(c) aqueous solution electrolysis (d) thermite reduction (2002)

CYANIDE PROCESS

42. Silver is mainly extracted by
(a) carbon reduction method (b) self-reduction method
(c) the method of electrolysis (d) leaching with aqueous solution of NaCN followed by reduction

43. Cupellation is a process used for the refining of
(a) silver (b) lead (c) copper (d) iron

44. The anode mud in the electrolytic refining of silver contains
(a) Zn, Cu, Ag, Au (b) Zn, Ag, Au (c) Cu, Ag, Au (d) Au

45. In the extraction of silver, the reactions involved are

$$\text{Roasted silver ore} + CN^- + H_2O \xrightarrow{O_2} X + OH^-;$$
$$X + Zn \longrightarrow Y + Ag$$

The species X and Y, respectively, are
(a) $[Ag(CN)_2]^-$, $[Zn(CN)_4]^{2-}$ (b) $[Ag(CN)_2]^-$, $[Zn(CN)_6]^{2-}$
(c) $[Ag(CN)_4]^{3-}$, $[Zn(CN)_4]^{2-}$ (d) $[Ag(CN)_4]^-$, $[Zn(CN)_4]^{2-}$ (2003)

46. 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 (2008)

Multiple Correct Choice Type

1. In the electrolysis of alumina, cryolite is added to

(a) lower the melting point of alumina
(b) increase the electrical conductivity
(c) minimise the anode effect
(d) remove impurities from alumina (1986)

2. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are

(a) Ag (b) Mg (c) Cu (d) Al (1990)

3. The principal reaction(s) in the zone of heat absorption of blast furnace employed in the metallurgy of iron is/are

(a) $C + O_2 \longrightarrow CO_2$
(b) $2C + O_2 \longrightarrow CO$
(c) $CO_2 + C \longrightarrow 2CO$
(d) $CaCO_3 \xrightarrow{-CO_2} CaO \xrightarrow{-SiCO_2} CaSiO_3$

4. Which of the following minerals contain(s) iron?

(a) Magnetite (b) Magnesite (c) Siderite (d) Lemonite

5. Addition of high proportions of the manganese makes steel useful in making rails of railroads, because manganese

(a) gives hardness to steel.
(b) helps the formation of oxides of iron.
(c) can remove oxygen and sulphur.
(d) can show high oxidation state of +7.

6. Which of the following statements are **not** correct?

(a) A mineral is an ore but an ore may not be a mineral.
(b) In the blast furnace, temperature rises as one moves from bottom to top.
(c) In the blast furnace involving the reduction of ferric oxide, the main reaction occurring in the zone of fusion is $CO_2 + C \longrightarrow 2CO$.
(d) The zone of reduction in the blast furnace involving the metallurgy of iron lies in the middle portion of the furnace.

7. Which of the following statements are correct?

(a) Wrought iron is the purest form of iron.
(b) The composition of ruby copper is Cu_2S.
(c) Zinc-silver alloy solidifies earlier than molten lead.
(d) The epsom salt is $MgSO_4 \cdot H_2O$

8. Which of the following statements are correct?

(a) Magnesium can be extracted from seawater by the Dow process.
(b) The composition of argentite is $3Ag_2S \cdot Sb_2S_3$.
(c) Zinc can replace silver from the solution of $Na[Ag(CN)_2]$.
(d) Aluminum is extracted from bauxite by the process of electrolytic reduction.

9. Which of the following statements are **not** correct?

(a) Copper is extracted by carbon reduction method.
(b) The composition of limonite is Fe_2O_3.
(c) Lead is the stable end product of all natural radioactive elements.
(d) Copper is mainly extracted from copper pyrites.

10. Which of the following statements are correct?

(a) In extractive metallurgy of zinc partial fusion of ZnO with coke is called sintering and reduction of the ore to the molten metal is called smelting.
(b) A mineral from which a metal can be profitably extracted is known as ore.
(c) The principal ore of iron from which it is extracted is haematite.
(d) Air is blown in blast furnace through water-jacketed pipes called tuyers

11. Which of the following statements are correct?

(a) The principal reducing agent of Fe_2O_3 in the blast furnace is CO_2.
(b) The impurity silica present in the principal ore of iron is removed as calcium silicate in the blast furnace by the addition of limestone.
(c) Iron obtained from the blast furnace is known as cast iron.
(d) The purest form of iron is wrought iron.

12. Which of the following statements are correct?

(a) The carbon content of pig iron is about 2-5 per cent.
(b) The carbon content of wrought iron is about 0.2 per cent.

(c) A sulphide ore is concentrated by the froth floatation method.
(d) Tin is extracted from SnO_2.

13. Which of the following statements are correct?
(a) In the extraction of Sn, stannic oxide is reduced by aluminium.
(b) Copper is mainly extracted from the ore copper pyrites whose composition is CuS.
(c) Copper is extracted by using self-reduction method.
(d) Lead is mainly extracted from galena.

14. Which of the following statements are **not** correct?
(a) Lead is extracted by using carbon reduction method.
(b) Magnesium and aluminum are extracted by the self-reduction method.
(c) The third most abundant element of earth's crust is aluminium.
(d) Silver is extracted from its ore by the MacArthur-Forrest process.

15. Which of the following statements are **not** correct?
(a) The mineral $KCl \cdot MgCl_2 \cdot 6H_2O$ is known as carnallite.
(b) The chemical composition of magnesite is MgO.
(c) Cassiterite is an ore of tin.
(d) In the Hall's process of purifying aluminium ore, the concentrated ore is fused with CaO.

16. Which of the following statements are **not** correct?
(a) In the Baeyer's process of purifying aluminium ore, the roasted ore is treated with caustic soda solution.
(b) The chemical composition of haematite is FeO.
(c) The chemical composition of azurite is $CuCO_3 \cdot Cu(OH)_2$
(d) The chemical composition of wulfenite is $PbMnO_4$

17. Which of the following statements are **not** correct?
(a) The chemical composition of malachite is $Cu(OH)_2$.
(b) In the purification of lead electrolytically, the electrolytic solution contains $PbSiF_6$ and H_2SiF_6.
(c) Silver is less soluble in molten zinc than in molten lead.
(d) The chemical composition of dolomite is $MgCO_3 \cdot CaCO_3$.

18. Which of the following statements are correct?
(a) The chemical composition of cryolite is Na_3AlF_6.
(b) The chemical composition of horn silver is AgCl.
(c) In the cyanide process, the concentrated ore is leached with a dilute solution of NaCN kept agitated by a current of air.
(d) The chemical composition of iron pyrite is FeS.

Matching Type

1. Match the following extraction process with the appropriate metals listed below.

(a) Silver	(p) Fused-salt electrolysis
(b) Calcium	(q) Carbon reduction
(c) Zinc	(r) Carbon monoxide reduction
(d) Iron	(s) Amalgamation
(e) Copper	(t) Self reduction

(1979)

2. Write the matching pairs

(a) Bleaching agent	(p) Aluminium
(b) Smelting salt	(q) Carbon
(c) Cryolite	(r) Tin
(d) Bell metal	(s) Ammonium carbonate
(e) Fluorspar	(t) Ammonium phosphate
(f) Fertilizer	(u) Calcium
(g) Anthracite	(v) Chlorine

(1980)

3. Match the entries on the left with those given on the right.

(a) Welding	(p) Baeyer's process
(b) Production of ammonia	(q) Thermit

(c) Ore purification	(r) Ostwald process	
(d) Production of nitric acid	(s) Cyanamide	(1981)

4. Match the entries on the left with those given on the right

(a) Al	(p) Calamine	
(b) Cu	(q) Cryolite	
(c) Mg	(r) Malachite	
(d) Zn	(s) Carnallite	(1983)

5. Match the entries on the left with those given on the right

(a) Haber	(p) Activation energy	
(b) Graham	(q) Diffusion of gases	
(c) Arrhenius	(r) Oclet rule	
(d) Lewis	(s) Ammonia synthesis	(1983)

6. Match the entries on the left with those given on the right.

(a) Spinel	(p) $Mg\ Al_2O_4$	
(b) Felspar	(q) $PbCO_3$	
(c) Cerussite	(r) $KAlSi_2O_3$	
(d) Malachite	(s) $MgSO_4 \cdot H_2O$	
(e) Kisserite	(t) $Cu(OH)_2 \cdot CuCO_3$	(1985)

7. Match the entries on the left with those given on the right.

(a) Self reduction	(p) Copper extraction	
(b) Carbon reduction	(q) Lead extraction	
(c) Reduction by heating its trihalide	(r) Silver extraction	
(s) Complex formation followed by precipitation	(s) Boron extraction	(2006)

8. Match the conversions in Column I with the type(s) of reaction(s) given in Column II.

Column I	**Column II**	
(a) $PbS \longrightarrow PbO$	(p) roasting	
(b) $CaCO_3 \longrightarrow CaO$	(q) calcination	
(c) $ZnS \longrightarrow Zn$	(r) carbon reduction	
(d) $Cu_2S \longrightarrow Cu$	(s) self reduction	(2008)

Straight Objective Type

1. (a)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (a)
8. (d)	**9.** (b)	**10.** (d)	**11.** (c)	**12.** (b)	**13.** (c)	**14.** (d)
15. (b)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (c)	**21.** (c)
22. (b)	**23.** (b)	**24.** (c)	**25.** (d)	**26.** (c)	**27.** (a)	**28.** (c)
29. (d)	**30.** (b)	**31.** (a)	**32.** (a)	**33.** (d)	**34.** (c)	**35.** (a)
36. (d)	**37.** (c)	**38.** (a)	**39.** (c)	**40.** (c)	**41.** (a)	**42.** (d)
43. (a)	**44.** (d)	**45.** (a)	**46.** (b)			

ANSWERS

1. (a), (b)	**2.** (b), (d)	**3.** (c), (d)
4. (a), (c), (d)	**5.** (a), (c)	**6.** (a), (b), (c), (d)
7. (a), (c)	**8.** (a), (c), (d)	**9.** (a), (b)
10. (a), (b), (c), (d)	**11.** (b), (d)	**12.** (a), (b), (c), (d)
13. (c), (d)	**14.** (a), (b)	**15.** (b), (d)
16. (b), (c)	**17.** (a), (c)	**18.** (a), (b), (c)

Matching Type

1. (a)-(s); (b)-(p) (c)-(q); (d)-(r); (e)-(t)
2. (a)-(v); (b)-(s) (c)-(p); (d)-(r); (e)-(u); (f)-(t); (g)-(q)
3. (a)-(q); (b)-(s); (c)-(p); (d)-(r)
4. (a)-(q); (b)-(r); (c)-(s); (d)-(p)
5. (a)-(s); (b)-(q); (c)-(p); (d)-(r)
6. (a)-(p); (b)-(r); (c)-(q); (d)-(t); (e)-(s)
7. (a)-(p); (b)-(q); (c)-(s); (d)-(r)
8. (a)-(p); (b)-(q); (c)-(p), (r); (d)-(p), (s)

Straight Objective Type

10. Firstly, carbon which is added along with crushed haematite ore is oxidised to CO (and CO_2). The produced CO acts as chief reducing agent for the reduction of haematite to steel.

12. Zinc from zinc blende is achieved by roasting followed by reduction with carbon.

24. Lead is extracted by self-reduction method and tin by carbon-reduction method.

25. Chalcopyrite is $CuFeS_2$ Malachite is $Cu(OH)_2 \cdot CuCO_3$ Azurite is $Cu(OH)_2 \cdot 2CuCO_3$
Dolomite is $MgCO_3 \cdot CaCO_3$

45. The reactions involved are

$$4Ag + 8CN^- + 2H_2O + O_2 \longrightarrow \underset{(X)}{4[Ag(CN)_2]^-} + 4OH^-$$

$$2[Ag(CN)_2]^- + Zn \longrightarrow \underset{(Y)}{[Zn(CN)_4]^{2-}} + 2Ag$$

Multiple Correct Choice Type

6. (a) A mineral from which metal can be profitably extracted is called ore. Hence, an ore is mineral but a mineral may not be an ore.
(b) Temperature decreases as one moves from bottom to top.
(c) The main reaction occuring in the zone of fusion is $C + O_2 \longrightarrow CO_2$
(d) The top portion of the blast furnace is the zone of reduction.

7. (b) The composition is Cu_2O. (d) The epsom salt is $MgCO_3 \cdot 7H_2O$.

8. The composition of argentite is Ag_2S.

9. (a) Copper is extracted by self-reduction method. (b) The composition is $3Fe_2O_3 \cdot 3H_2O$.

CHAPTER 18

EXERCISES IN INORGANIC CHEMISTRY

This chapter deals with the exercises in inorganic chemistry. These include problems on identification of a compound based on its characteristic chemical reactions, increasing/decreasing characteristics, predicting chemical reactions, completing and balancing chemical equations and matching items.

I. PROBLEMS IN INORGANIC CHEMISTRY

The problems in inorganic chemistry mainly deal with the identification of inorganic element or compound based on the characteristic tests or reactions shown by it. A brief description of this is in order.

Action of Heat on a Salt

Many inorganic salts decompose on heating, liberating characteristic gases. A few such reactions are as follows.

$$\underset{\text{(red)}}{2HgO} \rightarrow \underset{\text{(silvery deposit)}}{2Hg} + O_2$$

$$\underset{\text{(red)}}{2Pb_3O_4} \rightarrow \underset{\text{(yellow)}}{6PbO} + O_2$$

$$\underset{\text{(brown)}}{2PbO_2} \rightarrow \underset{\text{(black}}{2PbO} + O_2$$

$$\underset{\text{(green)}}{CuCO_3} \rightarrow \underset{\text{(black)}}{CuO} + CO_2$$

$$\underset{\text{(white)}}{ZnCO_3} \rightarrow \underset{\substack{\text{yellow (hot)} \\ \text{white (cold)}}}{ZnO} + CO_2$$

$$\underset{\text{(blue)}}{CuSO_4 \cdot 5H_2O} \rightarrow \underset{\text{(white)}}{CuSO_4} + 5H_2O$$

$$CuSO_4 \rightarrow CuO + SO_3$$

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

$$\underset{\text{(white)}}{2Zn(NO_3)_2} \rightarrow \underset{\substack{\text{yellow(hot)} \\ \text{white(cold)}}}{2ZnO} + \underset{\text{(brown)}}{4NO_2} + O_2$$

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

$$2Cu(NO_3)_2 \rightarrow \underset{\text{(black)}}{2CuO} + \underset{\text{(brown)}}{4NO_2} + O_2$$

$$2Ag_2O \rightarrow 4Ag + O_2$$

$$2Ag_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2$$

$$\underset{\text{(white)}}{2Pb(NO_3)_2} \rightarrow \underset{\text{(yellow)}}{2PbO} + 4NO_2 + \underset{\text{(brown)}}{O_2}$$

$$\underset{\text{(orange)}}{(NH_4)_2Cr_2O_7} \rightarrow N_2 + \underset{\text{(green)}}{Cr_2O_3} + 4H_2O$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$

$$CaCO_3 \rightarrow CaO + CO_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

$$MgCO_3 \rightarrow MgO + CO_2$$

$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$$

$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$

$$2CaSO_4 \cdot 2H_2O \rightarrow \underset{\text{(plaster of paris)}}{2CaSO_4 \cdot H_2O} + 3H_2O$$

$$2AlCl_3.6H_2O \rightarrow Al_2O_3 + 6HCl + 3H_2O$$

$$2NH_3 \xrightarrow[\text{red heat}]{} N_2 + 3H_2$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

$$(COO)_2Fe \rightarrow \underset{\text{(black)}}{FeO} + CO + CO_2$$

Characteristic Tests of Anions

Carbonate Brisk effervescence with dilute sulphuric acid. CO_2 is released which can be tested with lime water.

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$$

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(milky)}}{CaCO_3} + H_2O; \quad CaCO_3 + H_2O + CO_2 \rightarrow \underset{\text{(soluble)}}{Ca(HCO_3)_2}$$

Sulphide With dilute H_2SO_4, H_2S is evolved which turns lead acetate paper black. With sodium nitroprusside, sulphide gives purple colour.

$$Pb(CH_3COO)_2 + H_2S \rightarrow \underset{\text{(black)}}{PbS} + 2CH_3COOH; \qquad Na_2[Fe(CN)_5NO] + Na_2S \rightarrow \underset{\text{(purple)}}{Na_4[Fe(CN)_5NOS]}$$

Sulphite With dilute H_2SO_4, SO_2 is released which turns potassium dichromate paper green.

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O$$

Nitrite With dilute H_2SO_4, nitric oxide is released which combines with atmospheric oxygen to give reddish-brown fumes. The nitric oxide turns ferrous sulphate solution brownish–black ($FeSO_4 \cdot NO$).

Chlorides With concentrated H_2SO_4, HCl gas is released which gives white fumes with ammonia. Silver nitrate solution gives white precipitate with Cl^- which is soluble in ammonia.

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow; \qquad AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

The characteristic test of Cl^- is chromyl chloride test:

$$K_2Cr_2O_7 + 4Cl^- + 6H_2SO_4 \rightarrow \underset{\text{(red vapours)}}{2CrO_2Cl_2} + 2KHSO_4 + 4HSO_4^- + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{(yellow soln)}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow \underset{\text{(yellow ppt)}}{PbCrO_4} + 2CH_3COONa$$

Bromides With concentrated H_2SO_4, brownish vapours of Br_2 are released. Silver nitrate solution gives yellow precipitate with Br^- which is soluble in excess of ammonium hydroxide.

The addition of Cl_2 water in a solution of bromide salt causes liberation of bromine. $2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$

Iodide With concentrated H_2SO_4, violet vapours of I_2 are released. Silver nitrate solution gives yellow precipitate with I^- which is insoluble in ammonium hydroxide.

The addition of Cl_2 water or bromine solution in a solution of iodide salt causes liberation of iodine.

$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2$$

Nitrate With concentrated H_2SO_4, brown vapours of NO_2 are released which turn ferrous sulphate black.

Sulphate Soluble sulphate salt gives white precipitate of $BaSO_4$ with $BaCl_2$ solution which is insoluble in concentrated HCl.

Thiosulphate With dilute sulphuric acid, it gives S and SO_2. With silver nitrate solution, white precipitate turning to brown and ultimately black is obtained.

$$S_2O_3^{2-} + 2Ag^+ \rightarrow \underset{\text{(white)}}{Ag_2S_2O_3}; \qquad Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{(black)}}{Ag_2S} + H_2SO_4$$

Oxalate With concentrated H_2SO_4, a mixture of CO and CO_2 is liberated.

$$C_2O_4^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + H_2C_2O_4; \qquad H_2C_2O_4 \xrightarrow[\Delta]{} CO + CO_2 + H_2O$$

With the addition of $CaCl_2$ in an aqueous solution of oxalate ion, a white precipitate of calcium oxalate is obtained. If $KMnO_4$ is added in the acidic solution of oxalate, the pink colour of MnO_4^- disappears due to its reduction to Mn^{2+}.

$$Ox^{2-} + Ca^{2+} \rightarrow \underset{\text{(white ppt)}}{CaOx\downarrow}; \qquad MnO_4^- + C_2O_4^{2-} + 8H^+ \rightarrow Mn^{2+} + 2CO_2 + 4H_2O$$

Fluoride With concentrated H_2SO_4, a flouride salt liberates HF. The latter on reacting with SiO_2 produces SiF_4.

$$2F^- + H_2SO_4 \rightarrow 2HF + SO_4^{2-}; \qquad SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Phosphate Heating of a phosphate salt to about 50–60 °C with concentrated HNO_3 and ammonium molybdate produces yellow precipitate of $(NH_4)_3PO_4 \cdot 12MoO_3$.

$$PO_4^{3-} + 3HNO_3 \rightarrow 3NO_3^- + H_3PO_4$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3[P(Mo_3O_{10})_4] + 12H_2O + 21NH_4NO_3$$

Borate Heating a borate salt in a test tube with concentrated H_2SO_4 and C_2H_5OH produces vapours of ethylborate which burns with green flame.

$$2BO_3^{3-} + 3H_2SO_4 \rightarrow 3SO_4^{2-} + 2H_3BO_3; \qquad H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{(Ethyl borate)}}{B(OC_2H_5)_3} + 3H_2O$$

Analysis of Cations

In a solution containing more than one cation, the scheme shown in Fig. 18.1 for the identification of cations may be adopted.

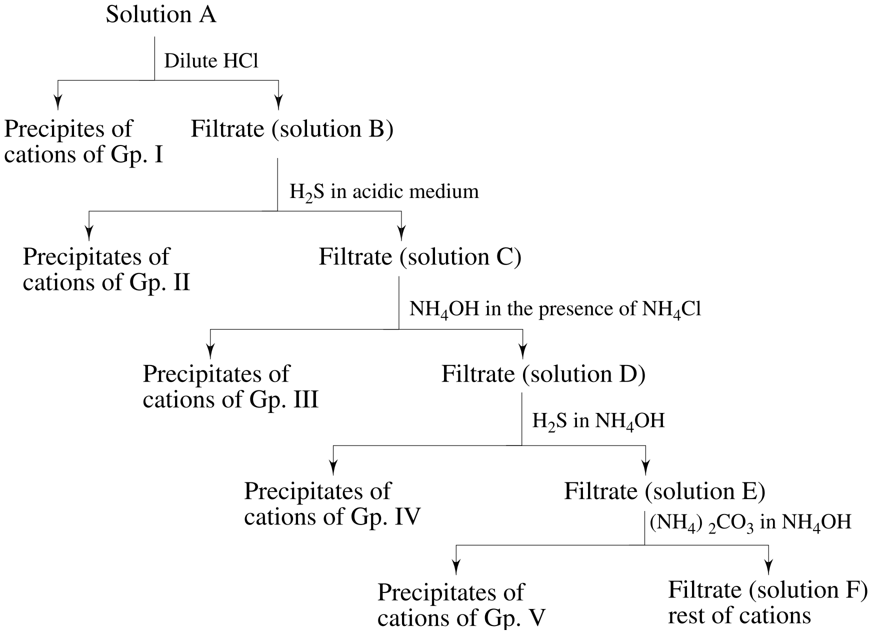


Fig. 18.1 Scheme for the analysis of cations

Details of Scheme

Cations of Group I These include the precipitates of AgCl, Hg_2Cl_2 and $PbCl_2$. From these $PbCl_2$ may be separated by boiling the precipitates with water and filtering the hot solution. In the fitrate, $PbCl_2$ may be tested by adding potassium chromate solution or potassium iodide:

$$PbCl_2(aq) + K_2CrO_4 \rightarrow \underset{\text{(yellow ppt.)}}{PbCrO_4} + 2KCl; \qquad PbCl_2(aq) + KI \rightarrow \underset{\text{(yellow ppt.)}}{PbI_2} + 2KCl$$

In the remaining precipitates, AgCl may be separated by additing ammonium hydroxide solution.

$$AgCl + 2NH_4OH \rightarrow \underset{\text{(soluble)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

Mercurous chloride forms black precipitates with NH_4OH.

$$Hg_2Cl_2 + 2NH_4OH \rightarrow \underset{\text{(black ppt.)}}{2[Hg(NH_3)]Cl} + 2H_2O$$

In solution, silver ions if present can be tested by adding KI solution:

$$[Ag(NH_3)_2]Cl + KI \rightarrow \underset{\text{(yellow ppt.)}}{AgI} + 2NH_3 + KCl$$

The black precipitates of $[Hg(NH_3)]Cl$ is soluble in aqua regia. To this solution, if $SnCl_2$ is added a white precipitate turning to black is obtained.

$$\underset{\text{(white ppt)}}{2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4}; \qquad \underset{\text{(black)}}{Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4}$$

Cations of Group II On passing H_2S gas through the acidified solution B (Fig. 18.1) the cations of Group II are precipitated as HgS (black), CuS (black), Bi_2S_3 (brown), CuS (black), CdS (yellow), As_2S_3 (yellow), Sb_2S_3 (orange-red) and SnS_2 (yellow). These sulphides may be separated into two groups by heating with ammonium polysulphide.

Cations of Group II A Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} and Cd^{2+}. The sulphides of these cations are insoluble.

Cations of Group IIB As^{3+}, Sb^{3+} and Sn^{2+}. The sulphide of these cations are soluble.

Identification of Cations of Group IIA These may be separated as shown in Fig. 18.2.

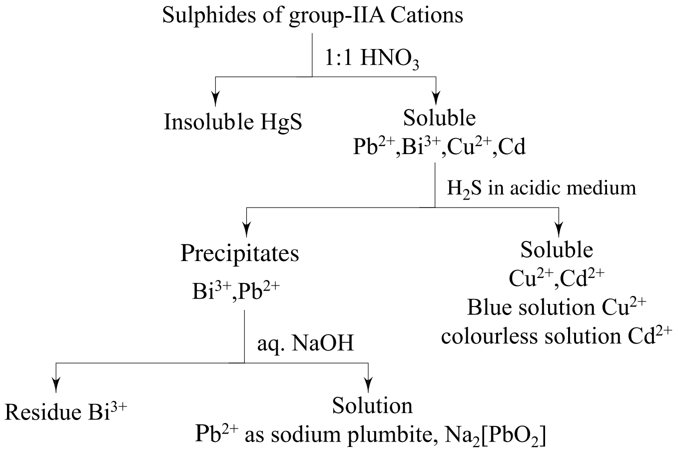


Fig. 18.2 Scheme of separating cations of GP. IIA

Specific Tests

1. HgS dissolves in aqua regia. The addition of $SnCl_2$ causes white precipitates turning to black

$$\underset{\text{(white ppt.)}}{2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4}; \qquad \underset{\text{(black)}}{Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4}$$

2. If dilute HCl is added to the residue of Bi^{3+}. It dissolves. To this solution, if excess of water is added white precipitate of $BiOCl_2$ is obtained. If sodium stannite is added, black precipitate is obtained.

$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$$

$$2BiCl_3 + 6NaOH + 3Na_2[SnO_2] \rightarrow \underset{\text{(black)}}{2Bi} + 3Na_2[SnO_3] + 3H_2O + 6NaCl$$

3. The solution containing Pb^{2+} ions may be tested as yellow precipitate by the addition of KI or K_2CrO_4 in acetic acid medium.
4. The solution containing Cu^{2+} ions is tested by adding $K_4Fe(CN)_6$ which gives chocolate-brown precipitate.

$$2Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow \underset{\text{(chocolate-brown precipitate)}}{Cu_2[Fe(CN)_6]}$$

5. To solution containing Cd^{2+} ions if H_2S is passed, yellow precipitate of CdS is obtained.

Identification of Cations of Group II B The sulphides of cations of Group II B are soluble in ammonium polysulphide forming $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. These are brought back to sulphides by treating with dilute HCl.

$$\underset{\text{ammonium thioarsenate}}{2(NH_4)_3AsS_4} + 6HCl \rightarrow As_2S_5 + 6NH_4Cl + 3H_2S$$

$$\underset{\text{ammonium thioantimonate}}{2(NH_4)_3SbS_4} + 6HCl \rightarrow Sb_2S_3 + 6NH_4Cl + 3H_2S + 2S$$

$$\underset{\text{ammonium thiostannate}}{(NH_4)_2SnS_3} + 2HCl \rightarrow SnS_2 + 2NH_4Cl + H_2S$$

When treated with concentrated HCl, the sulphides of Sb and Sn dissolve as chlorides.

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S; \qquad SnS_2 + 4HCl \rightarrow SnCl_4 + 2H_2S$$

The arsenic sulphide left behind is soluble in concentrated HNO_3.

$$3As_2S_5 + 10HNO_3 + 4H_2O \rightarrow 6H_3AsO_4 + 10NO + 15S$$

Specific Tests

1. The solution containing arsenic(V) is tested with ammonium molybdate.

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow \underset{\text{(yellow ppt.)}}{(NH_4)_3[As(Mo_3O_{10})_4]} + 21NH_4NO_3 + 12H_2O$$

2. To a solution containing chlorides of Sb and Sn, if ammonium hydroxide and oxalic acid is added, Sb^{3+} form unstable complex which on passing H_2S gives the precipitate of Sb_2S_3. The complex formed by Sn^{4+} is stable and is not decomposed by the passage of H_2S.

$$2NH_4OH + (COOH)_2 \rightarrow (NH_4)_2C_2O_4 + 2H_2O$$

$$SbCl_3 + 3(NH_4)_2C_2O_4 \rightarrow \underset{\text{(unstable)}}{(NH_4)_3[Sb(C_2O_4)_3]} + 3NH_4Cl$$

$$SnCl_4 + 4(NH_4)_2C_2O_4 \rightarrow \underset{\text{(stable)}}{(NH_4)_4[Sn(C_2O_4)_4]} + 4NH_4Cl$$

$$2(NH_4)_3[Sb(C_2O_4)_3] + 6H_2S \rightarrow \underset{\text{(orange ppt.)}}{Sb_2S_3} + 6H_2C_2O_4 + 3(NH_4)_2S$$

Cations of Group III The solution C (Fig. 18.1) is heated with a few drops to concentrated HNO_3 of oxidise Fe^{2+} ions (if present) to Fe^{3+} ions. To this solution, some solid NH_4Cl is added followed by the addition of NH_4OH. This causes the precipitation of $Fe(OH)_3$ (reddish brown), $Cr(OH)_3$ (green) and $Al(OH)_3$ (white gelatinous).

If these precipitates are treated with Na_2O_2 and NaOH solution, the hydroxides of Al^{3+} and Cr^{3+} dissolve as $NaAlO_2$ (colourless) and Na_2CrO_4 (yellow solution) while $Fe(OH)_3$ remains undissolved. If the latter is dissolved in dilute HCl followed by the addition of NH_4CNS, a red coloration of $Fe(CNS)_3$ is obtained.

To the solution containing $NaAlO_2$ and Na_2CrO_4 if solid NH_4Cl is added, white precipitate of $Al(OH)_3$ is obtained whereas Na_2CrO_4 remains in the solution.

Aluminium can be confirmed by carrying out the lake test. The precipitate of $Al(OH)_3$ is dissolved in dilute HCl and a few drops of litmust solution is added. This is followed by NH_4OH when blue coloured gelatinus precipitates are obtained.

To the solution containing Na_2CrO_4, the addition of lead acetate causes the precipitation of $PbCrO_4$ (yellow colour).

Cations of Group IV The cations of Group IV are Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}. These are precipitated as sulphides when H_2S is passed through the solution D (Fig. 18.1) after the addition of NH_4Cl and NH_4OH.

The addition of dilute HCl causes the dissolution of Mn^{2+} and Zn^{2+} sulphides while those of Co^{2+} and Ni^{2+} remain undissolved.

If the solution containing Mn^{2+} and Zn^{2+}, is heated with NaOH solution, Mn^{2+} is precipitated as $Mn(OH)_2$ while Zn^{2+} remains in the solution as Na_2ZnO_2 (sodium zincate).

Mn^{2+} can be tested by dissolving $Mn(OH)_2$ in concentrated HNO_3 and heating the resultant solution with PbO_2 (or sodium bismuthate) when purple colour of MnO_4^- is obtained.

$$5NaBiO_3 + 2Mn(NO_3)_2 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 2H_2O + 5Pb(NO_3)_2$$

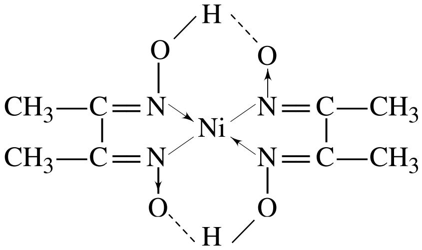
The zinc ions can be tested by acidfying sodium zincate solution followed by the addition of $K_4Fe(CN)_6$ when white precipitate of $Zn_2[Fe(CN)_6]$ is obtained.

The precipitates of Co^{2+} and Ni^{2+} (as sulphides) are heated to dryness with concentrated nitric acid. The residue is dissolved in water.

The cobaltic ions in the solution may be tested by adding $NaNO_2$ in acetic acid medium followed by the addition of a potassium salt. This causes the precipitation yellow precipitate of potassium cobaltinitrite.

$$Co^{3+} + 6NO_2^- \rightarrow [Co(NO_2)_6]^{3+}; \qquad 3K^+ + [Co(NO_2)_6]^{3+} \rightarrow K_3[Co(NO_2)_6]$$

The nickel ions in the solution is tested by adding dimethyl glyoxime and enough ammonia to make the solution ammoniacal. This gives red precipitate of nickel dimethylglyoxime:



Cations of Group V The addition of NH_4OH in solution E (Fig. 18.1) followed by the addition of $(NH_4)_2CO_3$ causes the precipitation of Ba^{2+}, Sr^{2+} and Ca^{2+} carbonates. These white carbonates are soluble in acetic acid.

The addition of K_2CrO_4 in the above solution causes the precipitation of $BaCrO_4$.

In the remaining solution, Sr^{2+} is precipitated as $SrSO_4$ with the addition of ammonium sulphate.

In the remaining solution, Ca^{2+} is tested with the addition of ammonium oxalate when a white precipitate of calcium oxalate is obtained.

Cations in the Solution F (*see* Fig. 18.1) This solution contains Mg^{2+} and K^+ ions if present in the mixture of salts.

Magnesium ions in the absence of ammonium salts are precipitated by ammonium carbonate solution as white gelatinous basic magnesium carbonate:

$$5Mg^{2+} + 6CO_3^{2-} + 7H_2O \rightarrow 4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O\downarrow + 2HCO_3^-$$

Magnesium ions are not precipitated in Group V of salt analysis because the presence of ammonium salts, the equilibrium

$$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$$

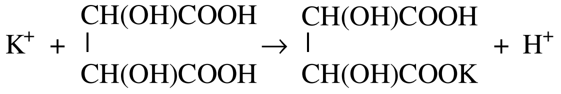
is shifted to right side and there is not enough CO_3^{2-} ions so as cause the precipitation of $MgCO_3$ ($K_{sp}^{\circ} = 1 \times 10^{-5}$).

Mg^{2+} ion is tested with the addition of sodium phosphate when white precipitate of $MgNH_4PO_4$ is obtained.

K^+ ion is tested as potassium cobaltinitrite with the addition of sodium nitrite, cobaltic nitrite and acetic acid

$$3K^+ + Na_3[Co(NO_2)_6] \rightarrow \underset{\text{(yellow ppt.)}}{K_3[Co(NO_2)_6]} + 3Na^+$$

K^+ ions also give white precipitate with a concentrated solution of tartaric acid.



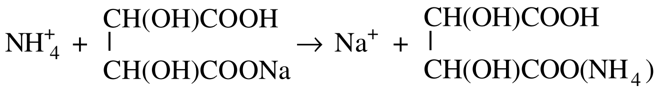
$$K^+ + \begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array} \rightarrow \begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOK\end{array} + H^+$$

(white ppt.)

Test of NH_4^+ This gives yellow precipitates with sodium cobaltinitrite:

$$3NH_4^+ + [Co(NO_2)_6]^{3-} \rightarrow (NH_4)_3[Co(NO_2)_6]$$

NH_4^+ ions also give white precipitate of ammonium tartrate:



$$NH_4^+ + \begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COONa\end{array} \rightarrow Na^+ + \begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COO(NH_4)\end{array}$$

(white ppt.)

With NaOH, ammonium salts liberate NH_3 gas which can be tested with Nessler's reagent:

$$K_2HgI_4 \rightarrow 2KI + HgI_2; \qquad HgI_2 + 2NH_3 \rightarrow IHgNH_2 + NH_4I$$

$$H_2NHgI + H_2NHgI + H_2O \rightarrow \underset{\text{(reddish brown ppt.)}}{H_2NHgOHgI} + NH_4I$$

Interfering Anions

The anions oxalate, phosphate, fluoride and borate interfere with the normal execution of separation of cations as given by the scheme shown in Fig. 18.1. If any of these ions is present, the cations of groups IV, V and VI are precipitated along with the cations of Group III. So, these anions should be removed before proceeding beyond Group II.

The anion oxalate is removed by heating the given mixture of salts to dryness with concentrated HNO_3. The oxalate is oxidized to CO_2 which escapes to atmosphere.

The anion borate and fluoride can be removed by heating the given mixture of salts with concentrated HCl. The borate and fluoride are converted into H_3BO_3 and HF, respectively, and these escape to atmosphere.

The above three anions may be removed from the filtrate obtained after the removal of cations of Group II.

The anion phosphate is removed from the filtrate obtained after the removal of cations of Group II. Added a few drops of concentrated HNO_3 in the filtrate (freed from the dissolved H_2S) and heat it. Dissolve about 0.5 g – 1.0 g solid NH_4Cl in the solution and start adding zirconium nitrate solution dropwise till no more precipitate of zirconium phosphate is obtained.

After the removal of these interferring anions, one can proceed beyond Group II according to the scheme shown in Fig. 18.1.

Characteristic Tests of Gases

Nitrogen Magnesium ribbon burns in a jar of nitrogen forming Mg_3N_2.

Oxygen It is absorbed by alkaline pyrogallol.

Carbon dioxide It turns lime water milky. The milkiness disappears by passing excess of CO_2.

Sulphur dioxide A pungent smelling gas which turns acidic dichromate solution green. It also turns lime water milky. The milkiness disappears by passing excess of SO_2.

Chlorine A greenish yellow gas which turns starch iodide paper blue.

Nitric oxide Turns brown in the presence of oxygen. It gives colour with ferrous sulphate solution.

Hydrogen chloride A pungent smelling gas. It produces white fumes with ammonium hydroxide.

Hydrogen sulphide It smells of rotten eggs. It turns lead acetate paper black.

Ammonia It produces white fumes with hydrogen chloride. It produces brown precipitate with Nessler's reagent.

Straight Objective Type

Action of Heat on a Salt

1. Which of the following compounds does not liberate O_2 on heating?
(a) HgO (b) NH_4NO_2 (c) $Pb(NO_3)_2$ (d) $NaNO_3$

2. Which of the following compounds liberate N_2 on heating?
(a) $(NH_4)_2Cr_2O_7$ (b) $Cu(NO_3)_2$ (c) $AgNO_3$ (d) NH_4NO_3

3. Which of the following compounds shows yellow appearance on heating and becomes white when cooled after heating?
(a) $CuCO_3$ (b) PbO_2 (c) $Pb(NO_3)_2$ (d) $ZnCO_3$

4. The gas released when NH_4NO_3 is heated is
(a) N_2 (b) NO (c) N_2O (d) NO_2

5. Which of the following salts liberates more than one gas on heating?
(a) $KMnO_4$ (b) $(COO)_2Fe$ (c) $NH_4Cr_2O_7$ (d) $NaNO_3$

6. Which of the following salts does not liberate more than one gas on heating?
(a) $FeSO_4$ (b) $Cu(NO_3)_2$ (c) Ag_2CO_3 (d) $K_2Cr_2O_7$

7. When $AgNO_3$ is heated strongly, the gas(es) evolved is/are
(a) NO_2 only (b) $NO_2 + O_2$ (c) O_2 only (d) NO + NO_2

8. When $FeSO_4$ is heated strongly, the gas(es) evolved is/are
(a) SO_2 only (b) SO_3 only
(c) mixture of SO_2 and SO_3 (d) mixture of SO_2 and O_2

9. Which of the following salts does not release a mixture of NO_2 and O_2 on strong heating?
(a) $AgNO_3$ (b) $Cu(NO_3)_2$ (c) $Zn(NO_3)_2$ (d) $NaNO_3$

10. NH_4NO_2 on heating produces a gas which can also be obtained on heating
(a) $AgNO_3$ (b) Ag_2CO_3 (c) $(NH_4)_2Cr_2O_7$ (d) NH_4NO_3 (2004)

Characteristics Tests of Anions

11. Chromyl chloride test is shown when the following compound is heated along the $K_2Cr_2O_7$ and conc. H_2SO_4?
(a) KCl (b) KNO_3 (c) Na_2SO_4 (d) CuO

12. Which of the following compounds gives white precipitate turning to brown and ultimately black when treated with silver nitrate solution?
(a) KNO_3 (b) K_2SO_4 (c) $Na_2S_2O_3$ (d) Na_2SO_3.

13. Which of the following anions interfere with the systematic scheme of testing cations?
(a) SO_4^{2-} (b) SO_3^{2-} (c) BO_3^{3-} (d) NO_3^-

14. Which of the following anions do not interfere with the systematic scheme of testing cations?
(a) Flouride (b) oxalate (c) phosphate (d) thiosulphate

15. Which of the following interfering anions can be removed from the solution of salts by adding zirconium nitrate in the ammoniacal solution?
(a) Fluoride (b) Oxalate (c) Borate (d) Phosphate

16. Heating of a phosphate salt to about 50 – 60°C with concentrated HNO_3 and ammonium molybdate produces yellow precipitate of
(a) $(NH_4)_3PO_4{\cdot}6MoO_3$ (b) $(NH_4)_3PO_4{\cdot}10MoO_3$
(c) $(NH_4)_3\ [P(Mo_3O_{10})_4]$ (d) $Mo_3(PO_4)_2$

17. Which of the following statements is correct?
(a) Cl_2 water liberates Br_2 from Br^-(aq) and I_2 from I^-(aq)
(b) Cl_2 water liberates Br_2 from Br^-(aq) but not I_2 from I^-(aq)
(c) Cl_2 water liberates I_2 from I^-(aq) but not Br_2 from I^-(aq)
(d) Cl_2 water does not liberates Br_2 from Br^-(aq) and I_2 from I^-(aq).

18. Which of the following statements is correct?
(a) Br_2 water liberates Cl_2(g) from Cl^-(aq) and I_2 from I^-(aq)
(b) Br_2 water liberates Cl_2(g) from Cl^-(aq) but not I_2 from I^-(aq)
(c) Br_2 water liberates I_2 from I^-(aq) but not Cl_2 from Cl^-(aq)
(d) Br_2 water does not liberate Cl_2(g) from Cl^-(aq) and I_2 from I^-(aq).

19. Sulphide ions gives purple colour with sodium nitroprusside. The purple colour is due to the formation of
(a) $Na_4[Fe(CN)_3(NOS)_3]$ (b) $Na_4[Fe(CN)_4(NOS)_2]$
(c) $Na_4[Fe(CN)_5(NOS)]$ (d) $Na_4[Fe(NOS)_6]$

20. Chloride gives white precipitate with silver nitrate. These white precipitates are soluble in ammonia due to the formation of
(a) $[Ag(NH_3)]\ Cl^-$ (b) $[Ag(NH_3)_2]\ Cl$
(c) $[Ag(NH_3)_4]\ Cl^-$ (d) $[Ag(NH_3)_6]\ Cl$

21. Chloride salt gives red vapour on heating with potassium dichromate. These red vapours are of
(a) $CrCl_3$ (b) Ag_2CrO_4 (c) CrO_2Cl_2 (d) $CrOCl_4$

22. Brown ring test is used for the detection of
(a) I^- (b) Br^- (c) NO_2^- (d) NO_3^-

23. White gelatinous precipitate is obtained when zirconium nitrate reagent is added to a solution containing PO_4^{3-} and 1 M hydrochloric acid. The white precipitate is of
(a) $ZrPO_4$ (b) $ZrO(HPO_4)]$ (c) $Zr_3(PO_4)_2$ (d) $Zr(HPO_4)_3$

24. Which of the following salts does not show chromyl-chloride test?
(a) KCl (b) $CuCl_2$ (c) $HgCl_2$ (d) $FeCl_3$

25. When borax is heated with concentrated H_2SO_4 and CH_3OH, the gas is released which imparts
(a) blue colour to the flame (b) green colour to the flame
(c) red colour to the flame (d) violet colour to the flame

26. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) $CrO(O_2)$ (1997)

27. From the following information
$X + H_2SO_4 \rightarrow Y$(a colourless and irritating gas); $Y + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ green solution
identify the pair X and Y from the list given below.
(a) Cl^-, HCl (b) S^{2-}, H_2S (c) CO_3^{2-}, CO_2 (d) SO_3^{2-}, SO_2 (2003)

Cation Analysis

28. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is

(a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+} (2007)

29. Which compound does dissolve in hot, dilute HNO_3?

(a) HgS (b) PbS (c) CuS (d) CdS (1996)

30. An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are:

(a) a colourless filtrate and a green residue (b) a yellow filtrate and a green residue

(c) a yellow filtrate and a brown residue (d) a green filtrate and a brown residue (1996)

31. The only cations present in a slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent that when added in excess to this solution would identify and separate Fe^{3+} in one step is

(a) 2 M HCl (b) 6 M NH_3 (c) 6 M NaOH (d) H_2S gas (1997)

32. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a

(a) Hg_2^{2+}salt (b) Cu^{2+} salt (c) Ag^+ salt (d) Pb^{2+} salt (2002)

33. A metallic nitrate gives black precipitates with KI solution. On adding excess of KI, an orange-coloured solution is obtained. The metallic ion in the metallic nitrate is

(a) Hg^{2+} (b) Sn^{2+} (c) Bi^{3+} (d) Pb^{2+} (2005)

34. A colourless aqueous solution on adding water and on heating gave a white precipitate. This precipitate when reacted with NH_4Cl and NH_4OH in excess resulted in dissolution of some of the precipitate and a gelatinous precipitate is obtained. The hydroxide formed in aqueous solution is

(a) $Zn(OH)_2$ (b) $Al(OH)_3$ (c) $Ca(OH)_2$ (d) $Mg(OH)_2$ (2006)

35. Heating an ammoniacal solution of $MgSO_4$ in the presence of NH_4Cl and Na_2HPO_4 causes the precipitation of

(a) $Mg(HPO_4)$ (b) $Mg(NH_4)PO_4$ (c) $MgCl_2$ (d) $Mg(NH_4)_4(PO_4)_2$ (2006)

36. Which of the following salt solution gives white precipitate turning to grey on adding $HgCl_2$ solution?

(a) $SnCl_2$ (b) $CuCl_2$ (c) $PbCl_2$ (d) $ZnCO_3$

37. Which of the following pairs of compounds are precipitated in different groups in the systematic analysis of cations?

(a) Bi^{3+}, As^{3+} (b) As^{3+}, Sn^{2+} (c) Cu^{2+}, Zn^{2+} (d) Ba^{2+}, Sr^{2+}

38. Which of the following sulphides is soluble in yellow ammonium sulphide?

(a) HgS (b) CuS (c) Bi_2S_3 (d) Sb_2S_3

39. Which of the following sulphides when dissolved in conc. HNO_3 will show positive test with ammonium molybdate?

(a) ZnS (b) CuS (c) As_2S_3 (d) SnS.

40. Which of the following cations will show red precipitate with dimethylglyoxime in ammoniacal solution?

(a) Ni^{2+} (b) Co^{2+} (c) Zn^{2+} (d) Cr^{3+}

41. Nessler's reagent is

(a) Ammoniacal solution of $K_2[HgI_4]$ (b) acidic solution of $K_2[HgI_4]$

(c) alkaline solution of $K_2[HgI_4]$ (d) aqueous solution of KI

42. Which of the following cations will form yellow precipitate with sodium cobaltinitrite?

(a) K^+ (b) Mg^{2+} (c) Ca^{2+} (d) Ba^{2+}

43. Which of the following compounds will form white precipitate with $K_4Fe(CN)_6$?

(a) Cu^{2+} (b) NH_4^+ (c) Zn^{2+} (d) Ca^{2+}

44. The composition of white precipitate when tartaric acid solution is added to a solution containing K^+ is

(a) $\begin{array}{l}\text{CH(OK)COOK}\\ |\\ \text{CH(OH)COOK}\end{array}$ (b) $\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOK}\end{array}$ (c) $\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OK)COOH}\end{array}$ (d) $\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOK}\end{array}$

45. The composition of yellow precipitate when a solution of ammonium molybdate is added to a hot solution of arsenic salt is

(a) $(NH_4)_3AsO_4 \cdot 12MoO_3$ (b) $(NH_4)_3AsO_4 \cdot 6MoO_3$ (c) $(NH_4)_3AsO_4 \cdot 4MoO_3$ (d) $(NH_4)_3AsO_4 \cdot MoO_3$

46. The precipitate of ZnS is

(a) white (b) black (c) red (d) yellow

47. If NH_4OH solution is added sparingly to a solution of $CuSO_4$, which of the following results is obtained?

(a) There is precipitation of $Cu(OH)_2$.
(b) There is precipitation of blue-coloured basic copper sulphate $Cu(OH)_2 \cdot CuSO_4$.
(c) There is precipitation of green-coloured basic copper sulphate $Cu(OH)_2 \cdot CuSO_4$.
(d) There is precipitation of $[Cu(NH_3)_4] \cdot SO_4$.

48. If potassium thiocyanate is added to a solution of $CuSO_4$, which of the following results is observed?

(a) There is precipitation of red-coloured $Cu(SCN)_2$.
(b) There is precipitation of blue-coloured $Cu(SCN)_2$.
(c) There is precipitation of black-coloured $Cu(SCN)_2$.
(d) There is no precipitation of $Cu(SCN)_2$.

49. If excess of sodium hydroxide is added to a solution of $CdSO_4$, which of the following results is observed?

(a) NaOH solution has no effect on $CdSO_4$ solution.
(b) There is formation of complex $Na_2[Cd(OH)_4]$.
(c) There is formation of green precipitates of $Cd(OH)_2$ which is soluble in excess of NaOH.
(d) There is formation of white precipitates of $Cd(OH)_2$ which is insoluble in excess of NaOH.

50. When excess of NH_4OH is added to the solutions of Cu^{2+} and Cd^{2+} ions, respectively, which of the following facts is observed?

(a) Solution containing Cu^{2+} is blue in colour while that containing Cd^{2+} is colourless.
(b) Solution containing Cd^{2+} is blue in colour while that containing Cu^{2+} is colourless.
(c) Both solutions are colourless.
(d) Both solutions are blue in colour.

51. In the Group II B of salt analysis, which of the following ions is not precipitated as sulphide in acidic medium?

(a) As^{3+} (b) Sb^{3+} (c) Sn^{2+} (d) Ni^{2+}

52. In the Group II B of salt analysis, arsenic sulphide is separated from other sulphides in this group by treating the sulphides with

(a) dilute hydrochloric acid solution (b) concentrated hydrochloric acid solution
(c) dilute nitric acid (d) concentrated nitric acid.

53. Phosphate and arsenate give yellow precipitates with ammonium molybdate solution in the presence of nitric acid. The experimental conditions for these two ions are

(a) gentle warming for arsenate and boiling for phosphate
(b) boiling for arsenate and gentle warming for phosphate
(c) gentle warming for both arsenate and phosphate
(d) boiling for both arsenate and phosphate.

54. Which of the ions of Group II in salt analysis produces orange-red precipitate with H_2S in acidic medium?

(a) As^{3+} (b) Sn^{2+} (c) Sb^{3+} (d) Bi^{3+}

55. A solution containing Sb^{3+} and Sn^{4+} is made just alkaline by 2M NH_3 solution. This is followed by the addition of oxalic acid and is boiled. $H_2S(g)$ is passed through this solution. Which of the following facts is observed?

(a) Sulphides of both Sb and Sn are precipitated out
(b) Sulphides of both Sb and Sn remains in solution
(c) Sulphide of Sn is precipitated out while that of Sb remains in solution
(d) Sulphide of Sb is precipitated out while that of Sn remains in solution

56. The addition of mercuric chloride to a solution results into the formation of white precipitate turning to grey. The solution contains

(a) Pb^{2+} ions (b) Sn^{2+} ions (c) Cu^{2+} ions (d) Cd^{2+} ions

57. Which of the following reagents does not convert Cr^{3+}(aq) into CrO_4^{2-}?
(a) 10% H_2O_2 in alkaline medium.
(b) Solid sodium perborate, $NaBO_3 \cdot 4H_2O$(s).
(c) Potassium peroxodisulphate in ammoniacal medium.
(d) FeO_2(s) in acidic medium.

58. Mn^{2+} ions in a solution free from hydrochloric acid and chloride ions can be converted into MnO_4^-(aq). Which of the following reagents is not able to carry out this conversion?
(a) Fe_2O_3 in dilute nitric acid medium.
(b) PbO_2 in concentrated nitric acid medium.
(c) $K_2S_2O_8$ in dilute sulphuric acid medium
(d) $NaBiO_3$ in dilute nitric acid medium.

59. The addition of potassium hexacyanoferrate(II) solution to a solution containing Zn^{2+} ions causes the formation of
(a) blue precipitate (b) green precipitate (c) white precipitate (d) red precipitate

60. With the addition of silver nitrate to the neutral solutions of sodium arsenite and sodium arsenate, which of the following results is observed?
(a) Yellow precipitates of both silver arsenite and silver arsenate.
(b) Brownish-red precipitates of both silver arsenite and silver arsenate.
(c) Yellow precipitates of silver arsenate and brownish-red precipitates of silver arsenite
(d) Yellow precipitates of silver arsenite and brownish-red precipitates of silver arsenate

61. With the addition of magnesia mixture solution (which contains $MgCl_2$, NH_4Cl and a little NH_3) or magnesium nitrate reagent (which contains $Mg(NO_3)_2$, NH_4NO_3, and a little NH_3) to the solution of sodium arsenite and sodium arsenate, which of the following results are observe?
(a) Both give white precipitates
(b) Both give no precipitates
(c) Sodium arsenite gives white precipitate of $Mg(NH_4)AsO_3$ while sodium arsenate gives no precipitate.
(d) Sodium arsenate gives white precipitate of $Mg(NH_4)AsO_4$ while sodium arsenite gives no precipitate.

62. Sb_2O_5 is
(a) acidic oxide (b) basic oxide (c) neutral oxide (d) amphoteric oxide

63. When ammonium thiocyanate solution is added to slightly acid solution of pure ferrous sulphate and pure ferric sulphate, which one of the following results is obtained?
(a) Both give red colouration
(b) Ferrous sulphate gives no colour while ferric sulphate gives red colouration
(c) Ferrous sulphate gives red colouration while ferric sulphate gives no colour
(d) Both give no colouration.

64. The addition of bismuth chloride into a large volume of water results into the formation of
(a) Bi_2O_3 (b) $Bi(OH)_3$ (c) BiOCl (d) $Bi(OH)Cl_2$

65. The addition of ammonium thiocyanate to a neutral or acid solution of cobalt(II) salt produces the species $[Co(SCN)_4]^{2-}$. The colour of this species is
(a) red (b) yellow (c) green (d) blue

66. The addition of acetic acid followed by potassium nitrite to a neutral solution cobalt(II) salt results into the formation of
(a) red-coloured $K_3[Co(NO_2)_6]$
(b) yellow-coloured $K_3[Co(NO_2)_6]$
(c) yellow-coloured $Co(NO_2)_3$
(d) red-coloured $Co(NO_2)_2$.

67. Nickel(II) salts solution with dimethylglyoxime produces
(a) red colouration provided the solution is acidic.
(b) red colouration provided the solution is just made alkaline with ammonia.
(c) red colouration provided the solution is neutral.
(d) yellow precipitate.

68. Which of the following ions produces brown colour or precipitate with Nessler reagent?
(a) Na^+ (b) NH_4^+ (c) Ca^{2+} (d) Mg^{2+}

69. Potassium compounds in non-luminous Bunsen flame produces
(a) red colouration (b) yellow colouration (c) violet colouration (d) green colouration.

70. In the presence of ammonium salts, magnesium ions with ammonium carbonate produces
(a) white precipitate of $MgCO_3$
(b) white precipitate of basic magnesium carbonate ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$)
(c) white precipitate of $Mg(OH)_2$
(d) no precipitate

71. Which of the following ions may appear in more than one group of salt analysis?
(a) Hg^{2+} (b) Pb^{2+} (c) Zn^{2+} (d) Ba^{2+}

72. In the presence of ammonium chloride and ammonium hydroxide, magnesium ion with disodium hydrogen phosphate form the white precipitate of
(a) $Mg(OH)_3$ (b) $Mg_3(PO_4)_2$ (c) $Mg(NH_4)PO_4$ (d) MgO

Multiple Correct Choice Type

1. Which of the following anions interfere in the systematic analysis of salt analysis?
(a) Sulphate (b) Phosphate (c) Borate (d) Thiosulphate

2. Which of the following anions form white precipitates with Ba^{2+} ions?
(a) Sulphite (b) Sulphate (c) Bromide (d) Fluoride

3. Which of the following cations give yellow precipitate with sodium cobaltinitrite?
(a) Ba^{2+} (b) Ca^{2+} (c) NH_4^+ (d) K^+

4. Which of the following cations are not analysed in Group 2A of salt analysis?
(a) Cu^{2+} (b) Sb^{3+} (c) Sn^{2+} (d) Bi^{3+}

5. Which of the following statements regarding Cu^{2+} and Co^{2+} ions are correct?
(a) Cu^{2+} is analysed in Group II A whereas Co^{2+} is analysed in Group IV of salt analysis
(b) Cu^{2+} is analysed in Group IV whereas Co^{2+} is analysed in Group IIA of salt analysis.
(c) K°_{sp} (CuS) < K°_{sp} (CoS)
(d) K°_{sp} (CuS) > K°_{sp} (CoS)

6. Oxygen is not released on heating the salts
(a) $CuSO_4$ (b) NH_4NO_3 (c) $Cu(NO_3)_2$ (d) Ag_2CO_3

7. Nitrogen is released on heating the salts
(a) NH_4NO_3 (b) NH_4NO_2 (c) $(NH_4)_2Cr_2O_7$ (d) $Cu(NO_3)_2$

8. Which of the following pairs compounds are precipitated in the same group of salt analysis?
(a) Pb^{2+}, Sb^{3+} (b) Fe^{3+}, Al^{3+} (c) Pb^{2+}, Cr^{3+} (d) Sr^{2+}, Mg^{2+}

9. Which of the following salts when treated with dilute sulphuric acid liberate a gas which turns lime water milky?
(a) $CaSO_3$ (b) $CaCO_3$ (c) $CaSO_4$ (d) Calcium oxalate

10. Which of the following salts are coloured?
(a) $PbCrO_4$ (b) $PbSO_4$ (c) PbI_2 (d) $PbCl_2$

11. Which of the following ions interfere with the ring test for NO_3^-?
(a) Cl^- (b) Br^- (c) I^- (d) CO_3^{2-}

12. Which of the sulphides of following ions are soluble in $(NH_4)_2S_x$?
(a) Bi^{3+} (b) Cd^{2+} (c) Sb^{3+} (d) Sn^{2+}

13. Which of the salts of following ions produce white precipitate when their solutions are poured in water?
(a) Bi^{3+} (b) Cd^{2+} (c) Sb^{3+} (d) As^{3+}

14. Which of the sulphides of Group IV of salt analysis is not white in colour?
(a) Co^{2+} (b) Ni^{2+} (c) Mn^{2+} (d) Zn^{2+}

15. Borax bead consists of
(a) $Na_2B_4O_7$ (b) H_3BO_3 (c) $NaBO_2$ (d) B_2O_3

16. Which of the sulphides of ions of Group IV of salt analysis dissolved in dilute hydrochloric acid?
(a) Co^{2+} (b) Ni^{2+} (c) Mn^{2+} (d) Zn^{2+}

17. Which of the following oxidizing agents are used to convert Mn^{2+} to MnO_4^-?
(a) Conc. HNO_3 (b) PbO_2 + Conc. HNO_3
(c) Sodium bismuthate ($NaBiO_3$) (d) BaO_2 + dil. HNO_3

18. Which of the following ions form white precipitate with saturated sodium hydrogen tartrate solution?
(a) NH_4^+ (b) K^+ (c) Na^+ (d) Mg^{2+}

19. Which of the following ions form white precipitate with silver nitrate solution?
(a) Cl^- (b) CN^- (c) OCN^- (d) SCN^-

20. Which of the following ions must be removed before proceeding to Group III of salt analysis?
(a) NO_3^- (b) F^- (c) Borate (d) SO_3^{2-}

21. Which of the following ions give yellow precipitate with hexachloroplatinic acid?
(a) Na^+ (b) K^+ (c) Mg^{2+} (d) NH_4^+

22. Which of the following ions form a precipitate with $K_4[Fe(CN)_6]$?
(a) Ca^{2+} (b) Zn^{2+} (c) Fe^{3+} (d) Fe^{2+}

23. Which of the following ions form a precipitate with Na_2HPO_4 in ammoniacal medium?
(a) Fe^{2+} (b) Mn^{2+} (c) Al^{3+} (d) Mg^{2+}

24. Which of the following statements regarding Ni^{2+}(aq) are correct?
(a) This gives green precipitate of $Ni(OH)_2$ with NaOH solution which is insoluble in excess of NaOH.
(b) This gives green precipitate of $Ni(OH)_2$ with NH_4OH which is solution in excess of ammonium hydroxide.
(c) This does not give green precipitate with NaOH in the presence of tartrate or citrate ions.
(d) This gives green precipitate $Ni(CN)_2$ with potassium cyanide solution which is soluble in excess of KCN giving complex $[Ni(CN)_4]^{2-}$.

25. Which of the following statements is correct for cobalt(II) nitrate solution?
(a) In excess of NaOH solution, pink precipitates of $Co(OH)_2$ appears
(b) With the excess of NH_4OH, blue coloured basic salt, $Co(OH)NO_3$, appears.
(c) With KCN, reddish-brown precipitates appear which is soluble in excess of KCN.
(d) With NH_4SCN, a red precipitates of $[Co(SCN)_4]^{2-}$.

Linked Comprehension Type

1. Given are the following observations:

$$\begin{tikzcd}
\mathrm{Bi^{3+}\,(aq)} \arrow[r, "I^-"] & \mathrm{Bi\,I_3}\downarrow \arrow[r, "\text{Excess } I^-"] \arrow[d, "\text{Water, heat}"] & {[\mathrm{Bi\,I_4}]^-} \arrow[l, bend left, "\text{Water}"] \\
 & \mathrm{BiOI}\downarrow &
\end{tikzcd}$$

Based on these observations, answer the following three questions?

(i) The colour of BiI_3 precipitates is
(a) orange (b) red (c) white (d) black

(ii) The colour the solution containing $[BiI_4]^-$ is
(a) orange (b) red (c) white (d) black

(iii) The colour of BiOI precipitates is
(a) orange (b) red (c) white (d) black

2. Given are the following observations.

$$Cu^{2+}(aq) \xrightarrow{CN^-} A\downarrow \xrightarrow{\text{on standing}} B\downarrow \xrightarrow[CN^-]{\text{excuss of}} C$$

Based on these observations, answer the following three questions.

(i) Which of the following facts is correct?
(a) A is $Cu(CN)_2$ and its colour is white
(b) A is $Cu(CN)_2$ and its colour is blue
(c) A is $Cu(CN)_2$ and its colour is yellow
(d) A is Cu_2CN_2 and its colour is white.

(ii) Which of the following facts is correct?
(a) B is CuCN and its colour is yellow
(b) B is CuCN and its colour is white
(c) B is Cu and its colour is red
(d) C is $Cu(CN)_2$ and its colour is white.

(iii) Which of the following facts is correct?
(a) C is Cu and its colour is red
(b) C is $[Cu(CN)]_3^-$ and its colour is red
(c) C is $[Cu(CN_4)]^{2-}$ and its colour is blue
(d) C is $[Cu(CN_4)]^{3-}$ and it is colourless.

3. Given are the following observations.

$$Cd^{2+}(aq) \xrightarrow{CN^-} A \xrightarrow{\text{excuss of } CN^-} B \xrightarrow{H_2S} C$$

Based on this fact, answer the following three questions.

(i) Which of the following facts is correct?
(a) A is $Cd(CN)_2$ soluble in water
(b) A is precipitates of $Cd(CN)_2$ and its colour is white
(c) A is precipitates of $Cd(CN)_2$ and its colour is yellow
(d) A is Cd^{2+} ions which shows no reaction with CN^- ions.

(ii) Which of the following facts is correct?
(a) B is $Cd(CN)_2$ and it is colourless
(b) B is a stable $[Cd(CN)_3]^{2-}$ complex
(c) B is a stable $[Cd(CN)_4]^{2-}$ complex and is not affected by the passage of $H_2S(g)$
(d) B is an unstable $[Cd(CN)_4]^{2-}$ complex and is decomposed on passing $H_2S(g)$.

(iii) Which of the following facts is correct?
(a) C is the same as B and B is not affected by the passage of H_2S
(b) C is the precipitated Cd(s)
(c) C is the precipitated CdS and its colour is yellow
(d) C is the same as the compound A.

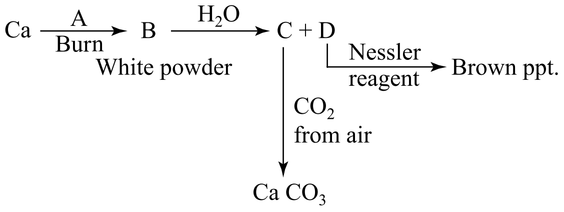
4. *p*-Amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate(II) leads to a brown coloration due to the formation of Z.

1. The compound X is
(a) $NaNO_3$ (b) NaCl (c) $NaSO_4$ (d) Na_2S

2. The compound Y is
(a) $MgCl_2$ (b) $FeCl_2$ (c) $FeCl_3$ (d) $ZnCl_2$

3. The compound Z is
(a) $Mg_2\,[Fe(CN)_6]$
(b) $Fe\,[Fe(CN)_6]$
(c) $Fe_4\,[Fe(CN)_6]_3$
(d) $K_2Zn_3\,[Fe(CN)_6]_2$ (2009)

5. Given are the following observations.



Based on these observations, answer the following three questions

(i) The substance A is

(a) N_2 (b) H_2 (c) O_2 (d) F_2

(ii) The substance B is

(a) CaH_2 (b) CaO (c) Ca_3N_2 (d) CaF_2

(iii) The substances C and D, respectively, are

(a) $Ca(OH)_2$, H_2O (b) $Ca(OH)_2$, NH_3 (c) $Ca(OH)_2$, NO_2 (d) $CaHCO_3$, HF

6. Potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III) are important reagents in analytical chemistry. These are used to characterize various cations in salt analysis. Based on their characteristic tests, answer the following three questions.

(i) With $AgNO_3$ solution, both hexacyanoferrate(II) and hexacyanoferrate(III) give precipitates whose characteristics respectively are

(a) white insoluble in NH_4OH and orange-red insoluble in NH_4OH

(b) white insoluble in NH_4OH and orange-red soluble in NH_4OH

(c) orange-red insoluble in NH_4OH and white soluble in NH_4OH

(d) orange-red soluble in NH_4OH and white insoluble in NH_4OH.

(ii) With copper sulphate solution, both hexacyanoferrate(II) and hexacyanoferrate(III) give precipitates whose colours, respectively, are

(a) brown and green (b) green and brown (c) brown and brown (d) green and green.

(iii) The addition of Fe^{2+} ions to $[Fe(CN)_6]^{4-}$ and Fe^{3+} ions to $[Fe(CN)_6]^{3-}$, respectively, show

(a) white precipitate and white precipitate (b) brown colouration and brown colouration

(c) white precipitate and brown colouration (d) brown colouration and white precipitate

(iv) The addition of Fe^{3+} ions to $[Fe(CN)_6]^{4-}$ and Fe^{2+} ions to $[Fe(CN)_6]^{3-}$, respectively, give which are formerly known as

(a) Prussian blue and Prussian red (b) Prussian blue and Turnbull's blue

(c) Turnbull's blue and Turnbull's blue (d) Turnbull's blue and Prussian blue

7. Both Cu^{2+} and Cd^{2+} ions are precipitated in Group II of salt analysis. The few characteristic reactions of these ions are mentioned in the following three questions. Answer these questions correctly.

(i) The addition of KCN in solutions of Cu^{2+} and Cd^{2+} ions causes the precipitation of $Cu(CN)_2$ and $Cd(CN)_2$, respectively. Which of the following facts is correct?

(a) $Cu(CN)_2$ is white while $Cd(CN)_2$ is yellow (b) $Cu(CN)_2$ is yellow while $Cd(CN)_2$ is white

(c) Both $Cu(CN)_2$ and $Cd(CN)_2$ are yellow (d) Both $Cu(CN)_2$ and $Cd(CN)_2$ are while.

(ii) When excess of KCN is added to solutions of Cu^{2+} and Cd^{2+} ions, the precipitation of $Cu(CN)_2$ and $Cd(CN)_2$ dissolves as the complex ions. Which of the following facts regarding the composition of complexes is correct?

(a) $[Cu(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ (b) $[Cu(CN)_4]^{2-}$ and $[Cd(CN)_4]^{3-}$

(c) $[Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$ (d) $[Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{3-}$

(iii) When H_2S is passed through solutions of Cu^{2+} and Cd^{2+} ions in the presence of excess of KCN, which of the following facts is correct?

(a) Precipitations of CuS and CdS

(b) No precipitations of CuS and CdS

(c) CuS is precipitated while CdS is not precipitated

(d) CdS is precipitated while CuS is not precipitated.

Assertion and Reason Type

Each of the following questions contain two statements. Answer these questions based on the following key:

(a) Both statements are correct and Statement–2 is correct explanation of Statement–1.

(b) Both Statements are correct and Statement–2 is not correct explanation of Statement–1.

(c) Statement–1 is correct and Statement–2 is incorrect.

(d) Statement–1 is incorrect and Statement–2 is correct.

	Statement–1	**Statement–2**
1.	A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing H_2S.	Solubility product of CdS is more than that of NiS. (1989)
2.	Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.	Ionic radius of Mg^{2+} is smaller than that of Ba^{2+} (1998)
3.	Magnesium ion is not precipitated in Group V of salt analysis.	Magnesium ion forms stable complex with NH_3.
4.	Cadmium ion in Group II of salt analysis is precipitated only if its acidic solution is dilute.	CdS is comparatively has lower solubility product as compared to sulphides of other cations in Group II of salt analysis.
5.	CoS and CuS are precipitated together in Group II of salt analysis.	$K_{sp}(CoS) > K_{sp}(CuS)$
6.	Potassium salt cannot be confirmed by sodium cobaltinitrite test in the presence of ammonium salt.	Both K^+ and NH_4^+ form yellow precipitates with sodium cobaltinitrite in acetic acid medium.
7.	Antimony and tin sulphides in Group II B cannot be separated from each other by chemical methods.	Precipitates of antimony and tin sulphides have different colours.
8.	Brown ring test of NO_3^- cannot be performed satisfactorily if the solution also contains Br^-/I^- ions.	Halogen (Br_2 or I_2) is released from halides Br^- or I^- when treated with concentrated H_2SO_4.
9.	Borates cannot be detected in the presence of copper or barium salt.	Copper or barium salts also imparts green colour to the flame.
10.	Sulphite in the presence of sulphate can be detected by treating with dilute hydrochloric acid.	Both sulphite and sulphate form white precipitate with barium chloride.
11.	$S_2O_3^{2-}$ ion gives dark-violet colouration with $FeCl_3$ solution, the colour disappears on standing.	Violet colour is due to the formation of $[Fe(S_2O_3)_2]^-$ which on reacting with Fe^{3+} gives Fe^{2+} and $S_4O_6^{2-}$.

Matrix Match Type

1. Column I lists some of elements whose salts give characteristics colour mentioned in Column II. Match each entry of Column I with those given in column II.

Column I	**Column II**
(a) Sodium	(p) Crimson flame
(b) Potassium	(q) Brick red flame
(c) Calcium	(r) Green flame
(d) Strontium	(s) Golden-yellow colour
	(t) Blue flame
	(u) Violet flame

2. Column I lists some of elements whose salts impart characteristics colour in oxidizing flame in the borax bead test. These are mentioned in Column II. Match the correct entries from columns I and II

Column I	**Column II**
(a) Cobalt	(p) Green (hot); Blue (cold)
(b) Copper	(q) Yellowish brown (hot); Yellow (cold)
(c) Iron	(r) Yellow (hot); Green (cold)
(d) Chromium	(s) Violet (hot); Reddish brown (cold)
	(t) Blue (hot); Blue (cold)
	(u) Yellow (hot); Colourless (cold)

3. Match the entries on the left with most appropriate choice(s) given on the right.

Column I	**Column II**
(a) $Bi_2O_3 \rightarrow BiO^+$	(p) Hydrolysis
(b) $AlO_2^- \rightarrow Al(OH)_3$	(q) Dilution with water
(c) $SiO_4^{4-} \rightarrow Si_2O_7^{2-}$	(r) Acidification
(d) $B4O_7^{2-} \rightarrow B(OH)_3$	(s) Heating

(2006)

4. Match the reactions given in Column I with nature of the reactions/type of the products given in Column II.

Column I	**Column II**
(a) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) redox reaction
(b) $CrO_4^{2-} + H^+ \rightarrow \cdots$	(q) one of the products has trigonal planar structure
(c) $MnO_4^- + NO_2^- + H^+ \rightarrow \cdots$ metal ion	(r) dimeric bridged tetrahedral
(d) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow \cdots$	(s) disproportionation

(2008)

5. Column II lists some of the gases evolved when the compounds mentioned in column I are heated. Match each entry of column I with those given in Column II.

Column I	**Column II**
(a) $Pb(NO_3)_2$	(p) N_2
(b) $Mg(NO_3)_2$	(q) O_2
(c) $(COO)_2Fe$	(r) CO_2
(d) $FeSO_4$	(s) NO_2
	(t) SO_2
	(u) CO

ANSWERS

Straight Objective Type

1. (b)	**2.** (a)	**3.** (d)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (b)
8. (c)	**9.** (d)	**10.** (c)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (d)
15. (d)	**16.** (c)	**17.** (a)	**18.** (c)	**19.** (c)	**20.** (b)	**21.** (c)
22. (d)	**23.** (b)	**24.** (c)	**25.** (b)	**26.** (b)	**27.** (d)	**28.** (b)
29. (a)	**30.** (c)	**31.** (b)	**32.** (d)	**33.** (c)	**34.** (b)	**35.** (b)
36. (a)	**37.** (c)	**38.** (b)	**39.** (c)	**40.** (a)	**41.** (c)	**42.** (a)
43. (c)	**44.** (b)	**45.** (a)	**46.** (a)	**47.** (b)	**48.** (c)	**49.** (d)
50. (a)	**51.** (d)	**52.** (b)	**53.** (b)	**54.** (c)	**55.** (d)	**56.** (b)
57. (d)	**58.** (a)	**59.** (c)	**60.** (d)	**61.** (d)	**62.** (d)	**63.** (b)
64. (c)	**65.** (d)	**66.** (b)	**67.** (b)	**68.** (b)	**69.** (c)	**70.** (d)
71. (b)	**72.** (c)					

Multiple Correct Choice Type

1. (b), (c)	**2.** (a), (b)	**3.** (c), (d)	**4.** (b), (c)
5. (a), (c)	**6.** (a), (b)	**7.** (b), (c)	**8.** (a), (b)
9. (a), (b)	**10.** (a), (c)	**11.** (b), (c)	**12.** (c), (d)
13. (a), (c)	**14.** (a), (b), (c)	**15.** (c), (d)	**16.** (c), (d)
17. (b), (c)	**18.** (a), (b)	**19.** (a), (b), (c), (d)	**20.** (b), (c)
21. (b), (d)	**22.** (a), (b), (c), (d)	**23.** (b), (c), (d)	**24.** (a), (b), (c)
25. (a), (c)			

Linked Comprehension Type

1. **(i)** (d) **(ii)** (a) **(iii)** (a)
2. **(i)** (c) **(ii)** (b) **(iii)** (d)
3. **(i)** (b) **(ii)** (d) **(iii)** (c)
4. **(i)** (d) **(ii)** (c) **(iii)** (b)
5. **(i)** (a) **(ii)** (c) **(iii)** (b)
6. **(i)** (b) **(ii)** (a) **(iii)** (c) **(iv)** (b)
7. **(i)** (b) **(ii)** (c) **(iii)** (d)

Assertion and Reason Type

1. (c) **2.** (b) **3.** (c) **4.** (c) **5.** (d) **6.** (a) **7.** (d)
8. (b) **9.** (d) **10.** (b) **11.** (a)

Matrix Match Type

1. (a)–(s); (b)–(u); (c)–(q); (d)–(p); **2.** (a)–(t); (b)–(p); (c)–(q); (d)–(r)
3. (a)–(p); (b)–(q); (c)–(s); (d)–(r); **4.** (a)–(p), (s); (b)–(r); (c)–(p), (q); (d)–(p)
5. (a)–(q), (s); (b)–(q), (s); (c)–(r), (u); (d)–(t);

Hints and Solutions

Straight Objective Type

1. NH_4NO_2 liberates N_2.
2. $(NH_4)_2Cr_2O_7$ liberates N_2. Other compounds liberate O_2.
3. $ZnCO_3$ gives ZnO which is yellow on heating and white when cooled.
4. NH_4NO_3 liberates N_2O.
5. $(COO)_2Fe$ liberates CO and CO_2.
6. $K_2Cr_2O_7$ liberates only O_2.
7. $AgNO_3$ liberates NO_2 and O_2.
8. $FeSO_4$ liberates SO_2 and SO_3.
9. $NaNO_3$ liberates only O_2.
10. NH_4NO_2 and $(NH_4)_2Cr_2O_7$ both liberate N_2.
11. Chromyl chloride test is for Cl^- ions.
12. $S_2O_3^{2-}$ gives white precipitate of $Ag_2S_2O_3$ which is ultimately decomposed to Ag_2S(black).
13. BO_3^{3-} interferes in the systematic analysis of salt analysis.
14. $S_2O_3^{2-}$ does not interfere.
15. PO_4^{3-} is removed by precipitating it as $ZrO(HPO_4)$ by adding zirconium nitrate in the ammonical solution. In fact the precipitate may have variable composition depending on the concentration of zirconium phosphate and H^+ ions. The species may have also $ZrO(H_2PO_4)_2$ and $ZrPO_4$.
16. The precipitate has formula $(NH_4)_3[P(Mo_3O_{10})_4]$. Each O^{2-} attached to Mo is replaced by $Mo_3O_{10}^{2-}$.
17. Cl_2 generates Br_2 and I_2 from Br^- and I^-, respectively.
18. Br_2 can generate I_2 from I^- and not Cl_2 from Cl^-.
19. The purpule colour is of $Na_4[Fe(CN)_5(NOS)]$.
20. AgCl goes in solution as $[Ag(NH_3)_2]Cl$.
21. The red vapours are due to chromyl chloride, CrO_2Cl_2.
22. Brown ring test is due to NO_3^- ions. NO gas combines with $FeSO_4$ to give $[Fe(NO)]^{2+}$. The test is unreliable in the presence of Br^-, I^-, NO_2^- and CrO_4^{2-}.
23. See Q. 15.
24. $HgCl_2$ is a covalent compound.
25. Green colour flame is due to methyl borate $B(OCH_3)_3$ vapours.
26. The green coloured powder is due to Cr_2O_3.
27. SO_3^{2-} gives SO_2 which is oxidized by $K_2Cr_2O_7$.
28. The reactions are $Hg^{2+} + 2I^- \rightarrow HgI_2$ (red precipitate)
$HgI_2 + 2KI \rightarrow K_2HgI_4$ (dissolves in solution).
$Hg^{2+} + Co^{2+} + 4SCN^- \rightarrow Co[Hg(SCN)_4]$ (blue precipitate)
29. HgS does not dissolved in dilute HNO_3. It is soluble in aqua regia.
30. Both Al^{3+} and Cr^{3+} goes into solution as $[Al(OH)_4]^-$ and CrO_4^{2-} (yellow solution). Fe^{2+} is precipitated as $Fe(OH)_2$. In air, $Fe(OH)_2$ is converted into $Fe(OH)_3$ (brown residue).

31. Both Zn^{2+} and Cu^{2+} go into solution as $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, respectively. Fe^{3+} is precipitated as $Fe(OH)_3$.

32. $PbCl_2$ is insoluble in cold, it is soluble in hot solution. PbS is black precipitate.

33. $Bi^{3+} + 3I^- \rightarrow BiI_3$ (black precipitate); $BiI_3 + I^-$ (excess) $\rightleftharpoons [BiI_4]^-$ (orange-coloured solution).

34. $Al(OH)_3$ shows the given characteristics.

35. The precipitation is of magnesium ammonium phosphate, $Mg(NH_4)PO_4$.

36. $Sn^{2+} + 2HgCl_2 \rightarrow \underset{\text{white}}{Hg_2Cl_2(s)} + Sn^{4+} + Cl^-$; $Hg_2Cl_2(s) + Sn^{2+} \rightarrow \underset{\text{grey}}{2Hg} + Sn^{4+} + Cl^-$

37. Cu^{2+} is precipitated in Group II while Zn^{2+} is precipitated in Group IV.
All other pairs are precipitated in the same group.

38. Sb_2S_3 which belongs to Group IIB is soluble in $(NH_4)_2S_x$ as SbS_4^{3-} (antimony thioantimonate).

39. As_2S_3 is soluble in conc. HNO_3. It gives yellow precipitates with ammonium molybdate $(NH_4)_2MoO_4$). The composition of precipitate is $(NH_4)_3[As(Mo_3O_{10})_4]$.

40. Ni^{2+} form red-coloured complex with dimethyl glyoxime in ammonical solution.

41. Nessler's reagent is alkaline solution of $K_2[HgI_4]$.

42. K^+ form yellow precipitate with sodium cobaltinitrite. The composition of precipitate is $K_3[Co(NO_2)_6]$.

43. Zn^{2+} form white precipitate of $K_2Zn_3[Fe(CN)_6]_2$. $3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \rightarrow K_2Zn_3[Fe(CN)_6]$

44. The white precipitate is due to the formation of $KHC_4H_4O_6$.

45. The composition is $(NH_4)_3[As(Mo_3O_{10})_4]$ which is $(NH_4)_3AsO_4 \cdot 12MoO_3$.

46. ZnS is white in colour.

47. Blue basic copper sulphate, $Cu(OH)_2 \cdot CuSO_4$ is precipitated.

48. With SCN^-, cupric ions form black-coloured $Cu(SCN)_2$ precipitates. These precipitates decompose slowly to give white coloured CuSCN.

49. $Cd(OH)_2$ is precipitated which is not soluble in excess of sodium hydroxide.

50. Cu^{2+} solution gives blue colour due to the formation of $[Cu(NH_3)_4]^{2+}$ species. Cd^{2+} solution gives colourless solution.

51. Ni^{2+} ions are precipitated in Group IV where sulphides are precipitated in ammoniacal solution.

52. As_2S_3 remains insoluble in concentrated hydrochloric acid while Sb_2S_3 and SnS are soluble.

53. Phosphate requires gentle warming while arsenate requires boiling of the solution.

54. Sb_2S_3 is orange-red precipitate. As_2S_3 and SnS_2 are yellow while Bi_2S_3 is black.

55. Both Sb^{3+} and Sn^{2+} form complex with oxalic acid. Antimony complex is dissociable with H_2S giving Sb_2S_3 precipitates. Tin complex is stable.

56. See Q. 36.

57. FeO in acidic medium is not able to convert $Cr^{3+}(aq)$ to CrO_4^{2-}.

58. Fe_2O_3 in dilute nitric acid is not able to convert Mn^{2+} to MnO_4^-.

59. White precipitate is due to $K_2Zn_3[Fe(CN)_6]_2$.

60. Arsenite gives yellow precipitates of Ag_3AsO_3 while arsenate gives brownish-red precipitate of Ag_3AsO_4.

61. Arsenite does not give any precipitate while arsenate forms precipitate of $Mg(NH_4)AsO_4$.

62. Sb_2O_5 is an amphoteric oxide. In acid medium, Sb^{3+} is stable while in alkaline medium, it exists as SbO^+.

63. Fe^{3+} ions gives red colouration while Fe^{2+} ions do not give coloration.

64. There is formation of white precipitates of $BiO \cdot Cl$.

65. Blue colouration appears due to the formation of $[Co(SCN)_4]^{2-}$.

66. Yellow coloured $K_3[Co(NO_2)_6]$ is formed.

67. Red colouration complex is formed in ammoniacal solution.

68. Brown precipitation or colouration is due to the formation of basic mercury(II) amido-iodine, $HgO \cdot Hg(NH_2)I$.

69. K^+ ions produce violet colour in non-luminous Bunsen flame.

70. There is suppression of CO_3^{2-} ions: $CO_3^{2-} + NH_4^+ \rightleftharpoons NH_3 + HCO_3^-$. Thus, no precipitation occurs.

71. Slight solubility of $PbCl_2$ in Group I results in the formation of PbS in Group II.

72. See Q. 35.

ANNEXURE

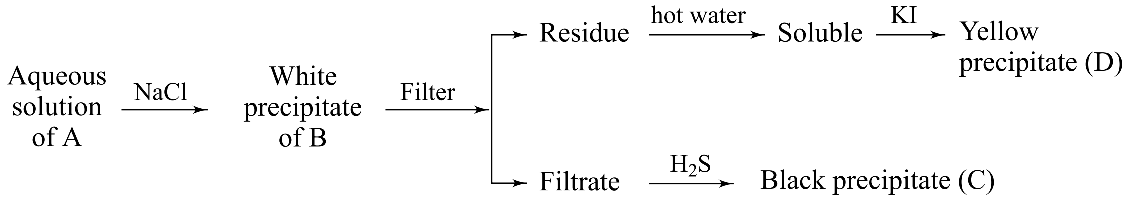
Additional Exercises For Practice

SOLVED PROBLEMS

1. An aqueous solution of salt A gives a white crystalline precipitate B with NaCl solution. The filtrate gives a black precipitate C when H_2S is passed through it. Compound B dissolves in hot water and the solution gives yellow precipitate D on treatment with potassium iodide and cooling. The compound A does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds A to D giving the involved equations. (1976)

Solution The given informations are as follows.

(a)



(b) $\text{No gas} \xleftarrow{\text{HCl}} \text{Salt} \xrightarrow[\text{heat}]{} \text{Brown coloured gas}$

From the information given in part (a), it may be concluded that the compound A is a lead salt. B is lead chloride as it is soluble in hot water. Yellow precipitate D is due to PbI_2. Black precipitate C is due to PbS. Lead chloride being spraingly soluble in water, a little of it remains in the filtrate which is subsequently precipitated as PbS.

From the information given in part (b), it may be concluded that anion associated with lead(II) is nitrate because lead nitrate dissociates on heating as

$$2Pb(NO_3)_2 \rightarrow 2PbO + \underset{\text{Brown coloured gas}}{4NO_2 + O_2}$$

Hence, A is $Pb(NO_3)_2$, B is $PbCl_2$, C is PbS and D is PbI_2.

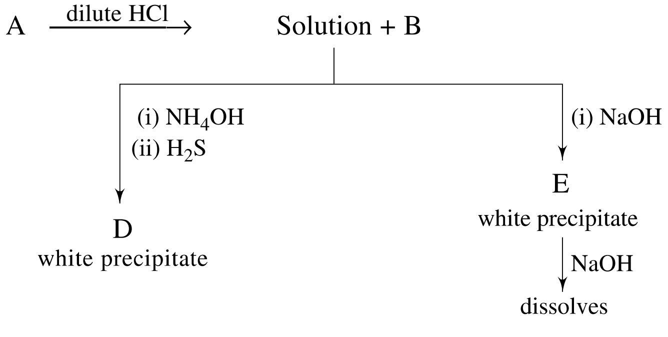
2. A white amorphous powder A when heated gives a colourless gas B, which turns lime water milky and the residue C which is yellow when hot but white when cold. The residue C dissolves in dilute HCl and the resulting solution gives a white precipitate on addition of potassium ferrocyanide solution. A dissolves in dilute HCl with the evolution of a gas which is identical in all respects with B. The solution of A as obtained above gives a white precipitate D on addition of excess of NH_4OH and on passing H_2S. Another portion of this solution gives initially a white precipitate E on addition of NaOH solution, which dissolves on further addition of the base. Identify the compounds A to E. (1979)

Solution The given information is as follows.

(a) $$\underset{\text{white powder}}{A} \xrightarrow{\text{heat}} \underset{\substack{\text{colourless gas}\\\text{turns lime water}\\\text{milky}}}{B} + \underset{\substack{\text{residue}\\\text{yellow when}\\\text{hot white when cold}}}{C}$$

(b) $C \xrightarrow{\text{dilute HCl}} \text{solution} \xrightarrow{K_4Fe(CN)_6} \text{white precipitate}$

(c)



From part (a), we conclude that B is CO_2 as it turns lime water milky: $\underset{\text{milky due to this}}{Ca(OH_2) + CO_2 \rightarrow CaCO_3 + H_2O}$

and C is ZnO as it becomes yellow on heating and is white in cold. Hence, the salt A must be $ZnCO_3$.

From part (b), it is confirmed that C is a salt of zinc(II) which dissolves in dilute HCl and white precipitate obtained after adding $K_4[Fe(CN)_6]$ is due to $Zn_2[Fe(CN)_6]$.

From part (c), it is again confirmed that A is $ZnCO_3$ as on adding dilute HCl, we get CO_2 and zinc(II) goes into solution. White precipitate is of ZnS which is precipitated in ammoniacal medium as its solubility product is not very low. White precipitate E is of $Zn(OH)_2$ which dissolves as zincate, in excess of NaOH. Hence, the given information is explained as follows.

(a) $\underset{(A)}{ZnCO_3} \xrightarrow{\text{heat}} \underset{(B)}{CO_2} + \underset{(C)}{ZnO}$ (b) $\underset{(C)}{ZnO} \xrightarrow{\text{dil H}} \underset{\text{solution}}{ZnCl_2} \xrightarrow{K_4Fe(CN)_6} \underset{\text{white precipitate}}{Zn_2[Fe(CN)_6]}$

(c) $ZnCO_3 \xrightarrow{\text{dil HCl}} \underset{\text{solution}}{ZnCl_2} + CO_2 + H_2O$ $ZnCl_2 + S^{2-} \rightarrow \underset{(D)}{ZnS \downarrow} + 2Cl^-$

$Zn^{2+} + 2OH^- \rightarrow \underset{(E)}{Zn(OH)_2}$ $Zn(OH)_2 + 2OH^- \rightarrow \underset{\text{dissolves}}{ZnO_2^{2-}} + 2H_2O$

3. Compound A is a light green crystalline solid. It gives the following tests.

(i) It dissolves in dilute sulphuric acid. No gas is produced.

(ii) A drop of $KMnO_4$ is added to the above solution. The pink colour disappears.

(iii) Compound A is heated strongly. Gases B and C with pungent smell came out. A brown residue D is left behind.

(iv) The gas mixture (B and C) is passed into a dichromate solution. The solution turns green.

(v) The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.

(vi) Residue D from (v) is heated on charcoal in reducing flame. It gives a magnetic substance.

Identify the compounds A to E. (1980)

Solution The given informations are as follows.

(a) $\underset{\text{light green}}{A} \xrightarrow{\text{dil. } H_2SO_4} \text{Solution of A} \xrightarrow{KMnO_4} \text{pink colour disappears}$

(b) $A \xrightarrow{\text{heat}} \underbrace{B + C}_{\text{pungent smelling gases}} + \underset{\text{brown residue}}{D}$

(c) $\underset{\text{solution}}{K_2Cr_2O_7} \xrightarrow{B + C} \text{green solution} \xrightarrow{Ba(NO_3)_2} \underset{\text{white precipitate}}{E}$

(d) $D \xrightarrow[\text{heat}]{\text{charcoal}} \text{magnetic substance}$

From (d), we conclude that D (hence also A) must be a salt of iron. Since A decolourises $KMnO_4$ solution, it may be a salt of iron(II). The reactions involved are

$$MnO_4 + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$$
$$\overline{MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

From (b) and (c), we conclude that A must be $FeSO_4$ as on heating it gives

$$\underset{(A)}{2FeSO_4} \rightarrow \underset{\substack{(D)\\(\text{brown})}}{Fe_2O_3} + \underbrace{\underset{(C)}{SO_2} + \underset{(D)}{SO_3}}_{\text{pungent smelling}}$$

SO_2 gas turns dichromate solution green due to the formation of chromium(III).

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \,]\times 3 \\ \hline Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O \end{array}$$

White precipitate E is of $BaSO_4$.

Hence, A is $FeSO_4$. B and C are SO_2 and SO_3. D is Fe_2O_3. E is $BaSO_4$.

4. An unknown solid mixture contains one or two of the following. $CaCO_3$, $BaCl_2$, $AgNO_3$, $ZnSO_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is formed which dissolves with further addition of the acid. What components is/are present in the solid? Give the involved chemical equations. (1981)

Solution As the mixture is completely soluble in water, $CaCO_3$ is excluded. As the water solution gives pink colour with phenolphthalein, the mixture contains NaOH.

It is given that Water solution of A $\xrightarrow{\text{HCl}}$ precipitate $\xrightarrow{\text{HCl}}$ dissolves

This fact excludes $BaCl_2$ and $AgNO_3$. Barium chloride does not give precipitate with dilute HCl. Silver nitrate does give precipitate of AgCl but it is not soluble in dilute HCl. However, the mixture contains $ZnSO_4$. On dissolving $ZnSO_4$ and NaOH in water, the former is present as zincate (ZnO_2^{2-}) ions. On adding HCl, NaOH is neutralized and ZnO_2^{2-} is converted into $Zn(OH)_2$ which being insoluble, precipitates out. This precipitate dissolves as more of HCl is added.

$$\underset{\text{precipitate}}{Zn(OH)_2} + 2HCl \rightarrow \underset{\text{dissolves}}{ZnCl_2} + 2H_2O$$

Hence, the mixture contains $ZnSO_4$ and NaOH.

5. When 16.8 g of white solid X was heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condenses to a colourless liquid. The solid Y that remained is dissolved in water to give an alkaline solution, with which excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X. (1984)

Solution The given facts may be summarized as follows.

(i) $\underset{16.8\text{ g}}{X} \xrightarrow[\text{heat}]{} \underset{4.4\text{g}}{A} + \underset{1.8\text{ g}}{B} + \underset{\text{solid}}{Y}$

(ii) $Y \xrightarrow{H_2O}$ alkaline solution $\xrightarrow{BaCl_2} \underset{\text{white ppt}}{Z} \xrightarrow{H^+} CO_2$ is released

Since Z on treatment with an acid gives CO_2 gas, Z must be a carbonate of barium, i.e. $BaCO_3$. Since $BaCO_3$ is obtained by adding $BaCl_2$ to an alkaline solution, Y must be a carbonate of an alkali metal. Let it be M_2CO_3. Now the gas A must be CO_2 as it turns lime water milky. With this, we conclude that X must be a bicarbonate of M as on heating it will be converted to carbonate with the release of CO_2 (i.e. A) and H_2O (i.e. B). Hence, we write

(i) $\underset{16.8\text{ g}}{2MHCO_3} \longrightarrow \underset{4.4\text{ g}}{CO_2} + \underset{1.8\text{ g}}{H_2O} + M_2CO_3$

Let M be the molar mass of M. We will have $2\left(\dfrac{M}{\text{mol}^{-1}} + 61\text{g}\right)$ of $MHCO_3$ liberates 44 g of CO_2.

Hence, from the given data, we get $\dfrac{2\left(\dfrac{M}{\text{mol}^{-1}} + 61\text{ g}\right)\text{of } MHCO_3}{44\text{ g } CO_2} \times 4.4\text{ g } CO_2 = 16.8\text{ g of } MHCO_3$

This gives, $M = 23\text{ g mol}^{-1}$

Thus, M must be soldium. The same conclusion is reached when M is determined from the given mass of H_2O formed. Hence, we have

X $NaHCO_3$; A CO_2 B H_2O; Y Na_2CO_3;

6. A mixture of two salts was treated as follows.

(i) The mixture was heated with MnO_2 and concentrated H_2SO_4 when yellowish-green gas was liberated.

(ii) The mixture on heating with NaOH solution gave a gas which turned red litmus blue.

(iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.

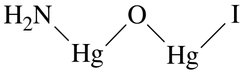
(iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate. Identify the two salts. Give ionic equations for the reactions involved. (1987)

Solution The reaction Mixture + $\underset{\text{(conc.)}}{MnO_2}$ + $H_2SO_4 \rightarrow$ yellowish-green gas indicates that the mixture contains Cl^- ion as the gas is Cl_2, i.e. $2Cl^- + MnO_2 + H_2SO_4 + 2H^+ \rightarrow MnSO_4 + 2H_2O + Cl_2$

The reactions; Mixture + NaOH $\longrightarrow$ Gas turns red litmus blue

$$\text{Mixture} + \text{KOH} \xrightarrow[\text{heat}]{\text{heat}} \text{Gas}; \qquad HgI_4^{2-} + \text{Gas} \longrightarrow \text{Brown precipitate}$$

indicate that the gas is NH_3. It is a basic gas so it turns red litmus to blue. With HgI_4^{2-}, the reaction is

$2HgI_4^{2-} + NH_3 + 3OH^- \rightarrow$  $+ 7I^- + 2H_2O$

iodide of Millon's base
(brown ppt)

From these facts, we conclude that the mixture contains NH_4^+ ions.

The reaction Mixture + $K_3[Fe(CN)_6] \rightarrow$ blue precipitate indicates that the mixture contains Fe^{2+} ions. i.e.

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \rightarrow \underset{\text{blue ppt.}}{Fe_3[Fe(CN)_6]_2}$$

The red coloration with NH_4CNS must be due to Fe^{3+} ions which is probably formed by aerial oxidation of Fe^{2+} ions, i.e. $Fe^{3+} + 3CNS^- \rightarrow \underset{\text{red}}{Fe(CNS)_3}$

Thus, the mixture contains NH_4^+, Fe^{2+} and Cl^- ions or NH_4Cl and $FeCl_2$ salts.

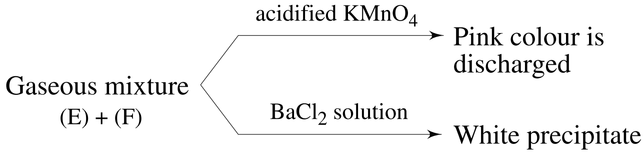
7. A hydrated metallic salt A, light green in colour, gives a white anhydrous residue B after being heated gradually. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue and a mixture of two gases E and F. The gaseous mixture, when passed through acidified permanganate, discharges the pink colour and when passed through acidified $BaCl_2$ solution, gives a white precipitate. Identify A, B, C, D, E and F. (1988)

Solution The given observations are as follows.

(i) $\underset{\text{(A)}}{\text{Hydrated metallic salt}} \xrightarrow[\text{heat}]{} \underset{\text{(B)}}{\text{white anhydrous residue}}$

(ii) Aqueous solution of B $\xrightarrow{\text{NO}}$ $\underset{\text{(C)}}{\text{dark brown compound}}$

(iii) Salt B $\xrightarrow[\text{heating}]{\text{strong}}$ $\underset{\text{(D)}}{\text{Brown residue}}$ + $\underset{\text{(E) + (F)}}{\text{Two gases}}$

(iv) 

The observation (ii) shows that B must be ferrous sulphate since with NO, it gives dark brown compound according to the reaction

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{dark brown}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Hence, the salt A must be $FeSO_4 \cdot 7H_2O$

The observation (iii) is $2FeSO_4 \rightarrow \underset{\substack{\text{(D)}\\ \text{brown}}}{Fe_2O_3} + \underbrace{SO_2 + SO_3}_{\text{(E) + (F)}}$

The gaseous mixture of SO_2 and SO_3 explains the observation (iv), namely,

$$\underset{\text{pink colour}}{2MnO_4^-} + 5SO_2 + 2H_2O \rightarrow \underset{\text{no colour}}{2Mn^{2+}} + 5SO_4^{2-} + 4H^+; \qquad 2H_2O + SO_2 + SO_3 \rightleftharpoons 4H^+ + SO_3^{2-} + SO_4^{2-}$$

$$Ba^{2+} + SO_3^{2-} \rightarrow \underset{\text{white ppt.}}{BaSO_3}; \qquad Ba^{2+} + SO_4^{2-} \rightarrow \underset{\text{white ppt.}}{BaSO_4}$$

Hence, the various compounds are

A	$FeSO_4 \cdot 7H_2O$	B	$FeSO_4$	C	$[Fe(H_2O)_5NO]SO_4$
D	Fe_2O_3	E and F	SO_2 and SO_3		

8. When 20.02 g of a white solid X is heated, 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue of mass 1.38 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z. (1989)

Solution We are given that

$$\underset{\substack{\text{white solid}\\(20.02\text{ g})}}{X} \rightarrow \underset{\substack{\text{gas}\\(4.4\text{ g})}}{A} + \underset{\substack{\text{gas}\\(1.8\text{ g})}}{B} + \underset{\substack{\text{residue}\\(13.8\text{ g})}}{Y}$$

As A turns lime water milky, it should be CO_2. The gas B is neutral and on condensing it gives a liquid which changes anhydrous copper sulphate blue, B should be H_2O.

Since Y gives a white precipitate with $BaCl_2$ and is also alkaline to litmus, the compound Y may be M_2CO_3 where M is an alkali metal. Now, CO_2, H_2O and M_2CO_3 could be obtained by heating $MHCO_3$ according to the equation

$$\underset{(X)}{2MHCO_3} \rightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{M_2CO_3}$$

Let the molar mass of M be *M*. We have

$$\underset{2\left(\frac{M}{\text{mol}^{-1}}+61\text{ g}\right)}{2MHCO_3} \rightarrow \underset{44\text{ g}}{CO_2} + \underset{18\text{ g}}{H_2O} + \underset{\left(\frac{2M}{\text{mol}^{-1}}+60\text{ g}\right)}{M_2CO_3}$$

It is given that 20.02 g of $MHCO_3$ produces 4.4 g of CO_2. From this data, we can determine the value of *M*.

$$\frac{20.02}{4.4} \times 44\text{ g} = 2\left(\frac{M}{\text{mol}^{-1}} + 61\text{ g}\right) \qquad \text{This gives} \qquad M = 39\text{ g mol}^{-1}$$

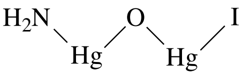
Thus, the element M is potassium. Hence X is $KHCO_3$ A is CO_2B is H_2O Y is K_2CO_3

9. The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in concentrated HCl. On heating the mixture with $K_2Cr_2O_7$ and concentrated H_2SO_4, red vapours A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the ions in the given mixture and write the balanced chemical equations for the formation of A and B. (1991)

Solution The observation

Mixture + NaOH →gas which gives reddish-brown precipitate with an alkaline solution of K_2HgI_4 indicates that the gas liberated is NH_3 and the mixture contains NH_4^+ ions.

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

$2HgI_4^{2-} + NH_3 + 3OH^- \rightarrow$  $+ 7I^- + 2H_2O$

iodide of Millon's base
(brown ppt.)

The white precipitate obtained by mixing $BaCl_2$ with aqueous solution of the mixture indicates the presence of SO_4^{2-} ions. This is also indicated by the fact that $BaSO_4$ is sparingly soluble in concentrated HCl.

On heating the mixture with $K_2Cr_2O_7$ and concentrated H_2SO_4, red vapours (A) are produced. This indicates the presence of Cl^- ions. The reactions involved are as follows.

$$\begin{array}{l}
K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O \\
Cl^- + H_2SO_4 \rightarrow HSO_4^- + HCl] \times 4 \\
2CrO_3 + 4HCl \rightarrow 2CrO_2Cl_2 + 2H_2O \\
\hline
K_2Cr_2O_7 + 4Cl^- + 6H_2SO_4 \rightarrow \underset{\text{red vapours}}{2CrO_2Cl_2} + 2KHSO_4 + 4HSO_4^- + 3H_2O
\end{array}$$

The reddish vapours are due to CrO_2Cl_2.

The deep blue colouration produced by mixing aqueous solution of the mixture and potassium ferricyanide solution indicates the presence of Fe^{2+} ions. The deep blue colouration is due to the formation of Turnbull's blue. In fact, because of the equilibrium $Fe^{2+} + Fe(CN)_6^{3-} \rightleftharpoons Fe^{3+} + Fe(CN)_6^{4-}$. The solution contains

$$\text{Chief products} \left[\begin{array}{l} \text{Ferric potassium ferrocyanide, } Fe\,K[Fe(CN)_6] \\ \text{Ferro ferricyanide, } Fe_3[Fe(CN)_6]_2 \end{array}\right.$$

$$\text{Minor products} \left[\begin{array}{l} \text{Ferric ferrocyanide, } Fe_4[Fe(CN)_6]_3 \\ \text{Ferro ferricyanide, } Fe_3[Fe(CN)_6]_2 \end{array}\right.$$

10. A light bluish green crystalline compound responds to the following tests.

(i) Its aqueous solution gives a brown precipitate or colouration with alkaline $K_2[HgI_4]$ solution.

(ii) Its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$ solution.

(iii) Its solution in hydrochloric acid gives a white precipitate with $BaCl_2$ solution. Identify the ions present and suggest the formula of the compound. (1992)

Solution

(i) Brown precipitate or colouration with alkaline $K_2[HgI_4]$ suggests the presence of NH_4^+ ions.

(ii) Blue colouration with $K_3Fe(CN)_6$ solution suggests the presence of Fe^{2+} ions.

(iii) White precipitate with acidified $BaCl_2$ solution suggests the presence of SO_4^{2-} ions.

The compound is Mohr's salt with molecular formula $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

11. An orange solid A on heating gave a green residue B, a colourless gas C and water vapour. The dry gas C on passing over heated Mg gave a white solid D. D on reaction with water gave a gas E which formed dense white fumes with HCl. Identify A to E and give the reactions involved. (1993)

Solution The compounds (A) to (E) along with the reactions involved are

$$\underset{\substack{\text{(A)} \\ \text{(orange solid} \\ \text{ammonium} \\ \text{dichromate)}}}{(NH_4)_2Cr_2O_7} \xrightarrow[\text{heat}]{} \underset{\substack{\text{(B)} \\ \text{(green} \\ \text{residue} \\ \text{chromic} \\ \text{oxide)}}}{Cr_2O_3} + \underset{\substack{\text{(C)} \\ \text{(colourless} \\ \text{gas} \\ \text{nitrogen)}}}{N_2} + \underset{\substack{\text{(water} \\ \text{vapours)}}}{4H_2O}$$

$$\underset{\text{(C)}}{N_2} + 3Mg \rightarrow \underset{\substack{\text{(D)} \\ \text{(white solid)}}}{Mg_3N_2}; \qquad \underset{\text{(D)}}{Mg_3N_2} + 6H_2O \rightarrow 3Mg(OH)_2 + \underset{\text{(E)}}{2NH_3}$$

$$\underset{\text{(E)}}{NH_3} + HCl \rightarrow \underset{\text{(white fumes)}}{NH_4Cl}$$

12. A is a binary compound of a univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B that forms a hydrated double salt, C with $Al_2(SO_4)_3$. Identify A, B and C. (1994)

Solution Since B forms a hydrated double salt with $Al_2(SO_4)_3$ the structure of double salt may be

$$M_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Hence, B may be a sulphate of univalent metal A. The reaction of A with sulphur may be written as

$$\underset{1.422\text{ g}}{A} + \underset{0.321\text{ g}}{S} \rightarrow \underset{1.743\text{ g}}{M_2SO_4}$$

Hence, the compound A must be M_2O_4, i.e. $2MO_2$. The metal M may be identified from the given data of masses of MO_2, S and M_2SO_4. If M is the molar mass of the metal M, we have

$$\text{Molar mass of } MO_2 = M + 2 \times 16 \text{ g mol}^{-1}$$

Now 0.321 g of S reacts with 1.422 g of MO_2. The mass of MO_2 that reacts with 32 g of S (= 1 molar mass of S) is

$$\frac{1.422\,\text{g}}{0.321\,\text{g}} \times 32 \text{ g} = 142.2 \text{ g}$$

This will be equal to the twice of molar mass of MO_2. Hence,

$$2(M + 2 \times 16 \text{ g mol}^{-1}) = 142.2 \text{ g mol}^{-1} \quad \text{or} \quad M = \left(\frac{142.2}{2} - 2\times16\right) \text{g mol}^{-1} = 39.1 \text{ g mol}^{-1}$$

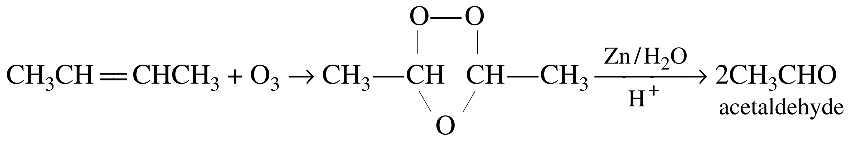
Thus, the metal M is potassium. Hence,

A is KO_2, potassium superoxide; B is K_2SO_4, potassium sulphate; and C is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, potash alum.

13. When the gas A is passed through dry KOH at low temperature, a deep red-coloured compound, B and a gas C are obtained. The gas A on reaction with but-2-ene, followd by treatment with Zn/H_2O yields acetaldehyde. Identify A, B and C. (1994)

Solution The given reactions are

$$2KOH + \underset{A}{5O_3} \rightarrow \underset{B}{2KO_3} + \underset{C}{5O_2} + H_2O$$

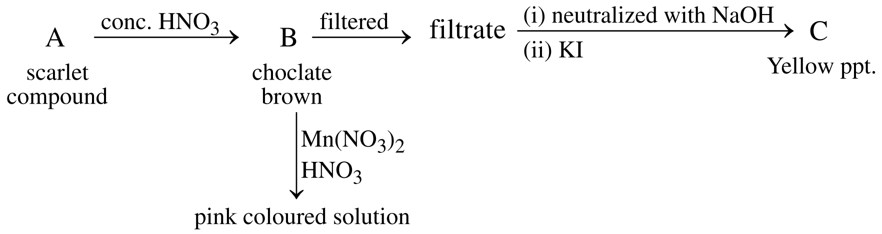


$$CH_3CH{=}CHCH_3 + O_3 \rightarrow CH_3\text{—}\underset{\text{(ozonide)}}{CH(O\text{—}O)(O)CH}\text{—}CH_3 \xrightarrow[H^+]{Zn/H_2O} \underset{\text{acetaldehyde}}{2CH_3CHO}$$

Hence, A is O_3, ozone; B is KO_3, potassium ozonide and C is O_2; oxygen

14. A scarlet compound A is treated with concentrated HNO_3 to give chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with concentrated HNO_3 in the presence of $Mn(NO_3)_2$ produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. (1995)

Solution The given reactions may be summarized as follows.



The compound B must be a powerful oxidizing agent which converts Mn^{2+} to the pink coloured MnO_4^- ion. Normally, PbO_2 is used for this purpose.

The compound C may be PbI_2 which is yellow in colour.

The given reactions may be explained as follows.

$$\underset{\substack{\text{(A)}\\ \text{scarlet}}}{Pb_3O_4} + 4HNO_3 \rightarrow \underset{\substack{\text{(B)}\\ \text{chocolate}\\ \text{brown ppt.}}}{PbO_2} + 2Pb(NO_3)_2 + 2H_2O; \qquad Pb(NO_3)_2 + 2KI \rightarrow \underset{\substack{\text{(C)}\\ \text{yellow ppt.}}}{PbI_2} + 2KNO_3$$

$$\underset{\text{(B)}}{5PbO_2} + 2Mn(NO_3)_2 + 4HNO_3 \rightarrow \underset{\substack{\text{(D)}\\ \text{pink coloured}}}{Pb(MnO_4)_2} + 4Pb(NO_3)_2 + 2H_2O$$

15. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. (1995)

Solution The involved reaction is $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$

Hence, 1 mol $H_2O_2 \equiv$ 1 mol I_2

$$\text{Amount of } I_2 \text{ liberated} = \frac{0.508\,\text{g}}{(2\times127)\,\text{g mol}^{-1}} = 2\times10^{-3}\ \text{mol}$$

Thus Amount of H_2O_2 in 5.0 cm^3 solution = 2×10^{-3} mol

$$\text{Molar concentration of } H_2O_2 = \frac{2\times10^{-3}\ \text{mol}}{5\times10^{-3}\ \text{L}} = 0.4\ \text{mol L}^{-1}$$

The volume strength of H_2O_2 is based on the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$

$$2\ \text{mol } H_2O_2 \equiv 1\ \text{mol } O_2 \equiv 22.4\,\text{L}\,O_2 \text{ at STP}$$

Now 2 molar solution of H_2O_2 has volume strength of 22.4

Hence, 0.4 molar solution of H_2O_2 has volume strength of $\dfrac{22.4}{2\,\text{M}} \times 0.4\ \text{M} = 4.48.$

16. An equal volume of a reducing agent is titrated separately with 1 M $KMnO_4$ in acid, neutral and alkaline media. The volumes of $KMnO_4$ required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equation for all the three half reactions. Find out the volume of 1 M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is titrated in an acid medium. (1989)

Solution Let N_1, N_2 and N_3 be the normalities of the same 1 M $KMnO_4$ solution in acidic, neutral and alkaline media, respectively. In a chemical reaction, the substances are consumed in equivalent amounts. Thus, (20 mL)$N_1 \equiv$ (33.4 mL)$N_2 \equiv$ (100 mL)N_3 (1)

In acidic medium, the chemical equation is $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^2 + 4H_2O$; i.e., 1 M $KMnO_4 \equiv$ 5 N $KMnO_4$

From Eq. (1), We can deduce $N_2 = \dfrac{20}{33.4}N_1 = \dfrac{20}{33.4}\times 5\ \text{N} = 3\ \text{N}$; $N_3 = \dfrac{20}{100}N_1 = \dfrac{20}{100}\times 5\ \text{N} = 1\ \text{N}$

Thus, the oxidation states of manganese in the reduction products are as under:

$$\overset{+7}{MnO_4^-} \xrightarrow[\text{acidic}]{5e^-} Mn^{2+}\ ;\quad \overset{+7}{MnO_4^-} \xrightarrow[\text{neutral}]{3e^-} Mn^{4+}\ ;\quad \overset{+7}{MnO_4^-} \xrightarrow[\text{alkaline}]{e^-} Mn^{6+}$$

Balanced equations for the three half-reactions are:

Acidic medium: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Neutral medium: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Alkaline medium: $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

The chemical equation of $Cr_2O_7^{2-}$ in acidic medium is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{i.e.,} \quad 1\ \text{M } Cr_2O_7^{2-} \equiv 6\ \text{N } Cr_2O_7^{2-}$$

The volume of 1 M $Cr_2O_7^{2-}$, if the same volume of the reducing agent is titrated, will be

$$V = \frac{(20\,\text{mL})N_1}{6\,\text{N}} = \frac{(20\,\text{mL})(5\,\text{N})}{6\,\text{N}} = 16.7\ \text{mL}$$

17. The composition of a sample of wüstite is $Fe_{0.93}O_{1.00}$. What percentage of the iron is present in the form of Fe(III)? (1994)

Solution The compound $Fe_{0.93}O_{1.00}$ is a non-stoichiometric where electrical neutrality is achieved by converting appropriate Fe^{2+} ions to Fe^{3+} ions. There are 7 Fe^{2+} ions missing out of the expected 100 Fe^{2+} ions. The missing 2 × 7 positive charge is compensated by the presence of Fe^{3+} ions. Replacement of one Fe^{2+} ion by Fe^{3+} ion increases one positive charge. Thus, 14 positive charge is compensated by the presence of 14 Fe^{3+} ions out of a total of 93 iron ions. Hence,

$$\text{Percent of } Fe^{3+} \text{ ions present} = \frac{14}{93} \times 100 = 15.05$$

18. 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. Identify the compounds A and B. (1996)

Solution The reactions are as follows.

$$3Ca + N_2 \rightarrow Ca_3N_2; \qquad Ca_3N_2 + 6H_2O \rightarrow \underset{\text{alkaline solution}}{3Ca(OH)_2} + \underset{\text{(A)}}{2NH_3}$$

$$Ca(OH)_2 + \underset{\text{from air}}{CO_2} \rightarrow \underset{\text{solid layer (B)}}{CaCO_3} + H_2O$$

19. A colourless inorganic salt (A) decomposes completely at about 250 °C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations of the reactions involved in the above process. (1966)

Solution It is given that

$$\underset{\substack{\text{colourless}\\\text{inorganic salt}}}{A} \rightarrow \underset{\substack{\text{neutral}\\\text{oxide}}}{B} + \underset{\substack{\text{liquid, oxide neutral}\\\text{to moist litmus paper}}}{C}$$

$$\underset{\text{Phosphorus}}{P} + B \rightarrow \text{Strong white dehydrating agent}$$

The reactions are explainable if A is taken to be NH_4NO_3.

$$\underset{\text{(A)}}{NH_4NO_3(s)} \rightarrow \underset{\text{(B)}}{N_2O} + \underset{\text{(C)}}{2H_2O}; \qquad P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$$

20. A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved. (1997).

Solution The liquid A is Br_2 and the two salts B and C are NaBr and $NaBrO_3$, respectively. The equations involved are

$$\underset{\text{(A)}}{3Br_2(1)} + 3Na_2CO_3 \rightarrow \underset{\text{(B)}}{5NaBr} + \underset{\text{(C)}}{NaBrO_3} + 3CO_2$$

$$5NaBr + NaBrO_3 + 3H_2SO_4 \rightarrow 3Br_2 + 3H_2O + 3Na_2SO_4$$

21. To a 25 mL H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution. (1997)

Solution The reactions involved are

(i) Oxidation of I^- by H_2O_2 in acidic medium

$$\begin{array}{c} H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \\ 2I^- \rightarrow I_2 + 2e^- \\ \hline H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2 \end{array} \qquad (1)$$

(ii) Reaction of I_2 with sodium thiosulphate $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ (2)

From Eq. (2), it follows that normality of $S_2O_3^{2-}$ = molarity of $S_2O_3^{2-}$

Also, from Eqs (1) and (2), it follows that $2 \text{ mol } S_2O_3^{2-} \equiv 1 \text{ mol } I_2 \equiv 1 \text{ mol } H_2O_2$ (3)

Now, Amolunt of $S_2O_3^{2-}$ consumed $= VM = (20 \times 10^{-3} \text{ L})(0.3 \text{ mol L}^{-1}) = 6 \times 10^{-3}$ mol

From Eq. (3), it follows that

$$6 \times 10^{-3} \text{ mol } S_2O_3^{2-} \equiv 3 \times 10^{-3} \text{ mol } H_2O_2$$

$$\text{Molarity of } H_2O_2 \text{ solution} = \frac{(3 \times 10^{-3} \text{ mol})}{25 \times 10^{-3} \text{ L}} = 0.12 \text{ mol L}^{-1}$$

From the reaction $2H_2O_2 \rightarrow H_2O + O_2$, it follows that 0.12 mol L^{-1} of H_2O_2 will liberate 0.06 mol of O_2 or 0.06×22.414 L of O_2 at 0 °C. Hence, the volume strength is $0.06 \times 22.414 = 1.345$.

22. 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. Identify A, B, C and D. (1997)

Solution

$$\underset{(A)}{3M} + N_2 \rightarrow \underset{(B)}{M_3N_2}; \qquad \underset{(B)}{M_3N_2} + 6H_2O \rightarrow \underset{(C)}{3M(OH)_2} + \underset{(D)}{2NH_3}$$

$$\underset{(C)}{M(OH)_2} + CO_2 \rightarrow \underset{(D)}{MCO_3} + H_2O$$

M is either Ca or Ba. Magnesium may be excluded due to very low solubility of $Mg(OH)_2$ in water.

23. A soluble compound of a poisonous element M, when heated with Zn/H_2SO_4 gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. (1997)

Solution The poisonous element M is arsenic. The given facts are as follows.

$$AsCl_3 + 6H \xrightarrow{Zn/H_2SO_4} \underset{(N)}{AsH_3} + 3HCl; \qquad 2AsH_3 \xrightarrow[\Delta]{} \underset{(M)}{2As} + 3H_2$$

24. 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. Give balance reactions involved in the formation of **Y** and its reaction with air. Draw the structure of **Y**. (2001)

Solution Since the hydride **Y** reacts with air forming boron trioxide, the compound **Y** must be an hydride of boron. From the given molecular composition of **Y**, we determine its empirical formula as shown in the following.

Given mass ratio is $B : H :: 78.28 : 21.72$

Its atomic ratio will be $B : H :: \dfrac{78.28}{11} : \dfrac{21.72}{1} :: 7.12 : 2.72 :: 1 : 3$

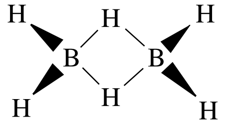
Hence, Empirical formula is BH_3.

Since boron forms two types of hydrides B_nH_{n+4} (nido-boranes) and B_nH_{n+6} (arachno-boranes), we conclude that Molecular formula of **Y** is B_2H_6.

Its formation from **X** and its reaction with O_2 are as follows.

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4]; \qquad B_2H_6 + 3O_2 \longrightarrow 2B_2O_3 + 3H_2O$$

Hence, the compound **X** must be a boron halide (BF_3 or BCl_3). The structure of borane is



Bridged B—H 133 pm
Terminal B—H 119 pm

The two bridging H atoms are in a plane perpendicular to the rest of the molecule.

25. A white substance **A** reacts with dilute H_2SO_4 to produce a colourless gas **B** and a colourless solution **C**. The reaction between **B** and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate **D**. The substance **D** burns in air to produce a gas **E** which reacts with **B** to yield **D** and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to **C** produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify **A, B, C, D** and **E**. Write the equations of the reactions involved. (2001)

Solution The given information are as follows.

1. $\underset{\text{white}}{\mathbf{A}} + \text{dil. } H_2SO_4 \rightarrow \underset{\text{colourless gas}}{\mathbf{B}} + \underset{\text{colourless solution}}{\mathbf{C}}$
2. $\mathbf{B} + \text{acidified } K_2Cr_2O_7 \rightarrow \text{green solution} + \underset{\text{Slightly coloured ppt.}}{D}$
3. $\mathbf{D} + \text{air} \rightarrow \underset{\text{gas}}{\mathbf{E}}$

4. **E** + **B** → **D** + colourless liquid, turns anhydrous $CuSO_4$ to blue
5. **C** + NH_3 or NaOH → precipitates dissolved in excess of NH_3 or NaOH.

The above informations are explainable if we identify A with ZnS. We have

1. $ZnS + \text{dil } H_2SO_4 \rightarrow \underset{\text{(B)}}{H_2S} + \underset{\text{(C)}}{ZnSO_4}$
2. $3H_2S + Cr_2O_7^{2-} + 8H^+ \rightarrow \underset{\substack{\text{green}\\\text{solution}}}{2Cr^{3+}} + \underset{\textbf{(D)}}{3S} + 7H_2O$
3. $\underset{\textbf{(D)}}{S} + O_2 \rightarrow \underset{\textbf{(E)}}{SO_2}$
4. $\underset{\textbf{(E)}}{SO_2} + \underset{\textbf{(B)}}{H_2S} \rightarrow \underset{\textbf{(D)}}{S} + \underset{\substack{\text{colourless liquid,}\\\text{turns anhydrous } CuSO_4 \text{ to blue}}}{H_2O}$
5. $\underset{\textbf{(C)}}{Zn^{2+}} + 2OH^- \rightarrow \underset{\text{ppt.}}{Zn(OH)_2} \xrightarrow{OH^-} \underset{\text{zincate ion}}{Zn(OH)_4^{2-}}$

26. When a white crystalline compound **X** is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas **A** is evolved. On passing **A** into caustic soda solution, a yellow coloured solution of **B** is obtained. Neutralizing the solution of **B** with acetic acid and on subsequent addition of lead acetate, a yellow precipitate **C** is obtained. When **X** is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitated **D** is formed. Identify **A, B, C, D** and **X,** Write the equations of reaction involved. (2002)

Solution The given reactions are as follows.

$$\underset{\text{(white)}}{X} + K_2Cr_2O_7 + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow[\Delta]{} \underset{\text{(reddish brown)}}{\text{Gas}} \qquad A + NaOH \rightarrow \underset{\text{(yellow coloured solution)}}{B}$$

$$B + CH_3COOH + Pb(CH_3COO)_2 \rightarrow \underset{\text{(yellow precipitate)}}{C} \qquad X + NaOH \xrightarrow[\Delta]{} \text{Colourless gas} \xrightarrow{K_2HgI_4} \underset{\substack{\text{(reddish brown}\\\text{precipitate)}}}{D}$$

The above reactions indicate that the compound X contains Cl^- and NH_4^+ Ions, hence the compound is NH_4Cl. The reactions shown above are as follows.

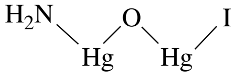
$$\underset{\text{(from } NH_4Cl)}{4Cl^-} + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow \underset{\text{(Gas A)}}{2CrO_2Cl_2} + 2KHSO_4 + 4HSO_4^- + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\substack{\text{(yellow solution)}\\\text{(B)}}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow \underset{\substack{\text{(yellow ppt.)}\\\text{(C)}}}{PbCrO_4} + 2CH_3COONa$$

$$\underset{\text{(from } NH_4Cl)}{NH_4^+} + NaOH \xrightarrow[\Delta]{} \underset{\text{(gas)}}{NH_3} + Na^+ + H_2O$$

$NH_3 + 2HgI_4^{2-} + H_2O \rightarrow$



$+ 7I^- + 3H^+$

(reddish brown precipitate)
(D)

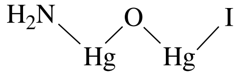
27. A mixture consists of A (yellow solid) and B (colourless solid) which gives lilac colour in flame

(a) Mixture gives black precipitate C on passing H_2S(g)
(b) C is soluble in aqua-regia and on evaporation of aqua-regia and adding $SnCl_2$ gives grayish black precipitate D.
(c) The salt solution with NH_4OH gives a brown precipitate.
(d) The sodium extract of the salt with $CCl_4/FeCl_3$ gives a violet layer.
(e) The sodium extract gives yellow precipitate with $AgNO_3$ which is insoluble in ammonia. Identify A and B, and the precipitates C and D. (2003)

Solution From the given information, it appears that A is HgI_2 and B is KI. The given reactions are as follows.

(a) $HgI_2 + H_2S \rightarrow \underset{\substack{\text{(C)}\\ \text{(black)}}}{HgS} + 2HI$

(b) $HgS \xrightarrow{\text{aqua regia}} HgCl_2$
$HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
$HgCl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

(c) $2HgI_4^{2-} + NH_3 + 3OH^- \rightarrow$  $+ 7I^- + 2H_2$

(iodide of Millon's base)

(d) I_2 is absorbed in CCl_4 giving violet colour. (e) $I^- + Ag^+ \rightarrow AgI\downarrow$ insoluble in NH_4OH.

28. There are two ores A_1 and A_2 of a metal M. (i) When the ore A_1 is calcined a black solid S is obtained alongwith the evolution of CO_2 and H_2O. (ii) The ore A_1 on treatment with HCI and KI gives a precipitate P and iodine is liberated. (iii) The ore A_2 on roasting gives a gas G and metal M is free. (iv) When the gas G is passed through $K_2Cr_2O_7$ it turns green. Identify M, A_1, A_2, S, P and G. (2004)

Solution Metal M is copper and its two ores are

A_1 : Malachite, $CuCO_3 \cdot Cu(OH)_2$ A_2 : Copper glance, Cu_2S

The given reactions are as follows.

(i) $\underset{(A_1)}{CuCO_3 \cdot Cu(OH)_2} \xrightarrow[\text{calcination}]{} \underset{\substack{\text{(S)}\\ \text{black}}}{2CuO} + CO_2 + H_2O$

(ii) $CuCO_3 \cdot Cu(OH)_2 + 4HCl \rightarrow 2CuCl_2 + CO_2 + 3H_2O$; $2CuCl_2 + 4KI \rightarrow \underset{\text{(P)}}{Cu_2I_2} + 4KCl + I_2$

(iii) $\underset{(A_2)}{2Cu_2S} + 3O_2 \xrightarrow[\text{roasting}]{} 2Cu_2O + \underset{\text{(G)}}{2SO_2}$; $Cu_2S + 2Cu_2O \rightarrow \underset{\text{(M)}}{6Cu} + SO_2$

(iv)
$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \times 3 \\ \hline Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O \end{array}$$

UNSOLVED PROBLEMS

1. One gram of an alloy of magnesium and aluminium reacts with excess of hydrochloric acid. The hydrogen collected was found to occupy a volume of 1.2 L at 699 mmHg and 273 K. Calculate the mass composition of the alloy.
2. When a mixture of sodium chloride and sodium bromide is repeatedly digested with sulphuric acid, sodium sulphate is formed. If the mass of sodium sulphate obtained is equal to the mass of the mixture, calculate the massper cents of NaBr and NaCl in the mixture.
3. 25.4 g of iodine and 14.2 g of chlorine are made to react completely to form a mixture of ICl and ICl_3. Calculate the masses of the products formed.
4. 1.0 g of a mixture of equal amounts (i.e. number of moles) of carbonates of two alkali metals required 44.4 mL of 0.5 M hydrochloric acid for complete reaction. The atomic mass of one of the metals is 7.0 amu. Find the atomic mass of the second metal. Calculate the masses of sulphates formed on quantitative conversion of 1.0 g of the mixture into sulphates.
5. 1.0 g of a moist sample of a mixture of potassium chlorate and potassium chloride was dissolved in water and made upto 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate and the excess of SO_2 was removed by boiling. The total chloride was precipitated as silver chloride whose mass was found to be 0.1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0.2 M solution of ferrous sulphate and the unreacted ferrous sulphate required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the mass per cents of chlorate and chloride in the given mixture. The reaction between ClO_3^- and Fe^{2+} is $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$

6. A solution of commercial H_2O_2 diluted to two-hundredth of its concentration was titrated against standard $KMnO_4$ solution. 25 mL of this dilute solution required 22.2 mL of 0.1 N $KMnO_4$. Calculate the concentration of H_2O_2 solution in g L^{-1} and in volume strength.

7. 5 g of bleaching powder was treated with excess of acetic acid. The chlorine was passed through excess of KI solution. The iodine liberated required 50 mL of M/5 hypo solution. Find per cent of available chlorine in the sample.

8. 0.1 g of a polyvalent metal of atomic mass 51.0 amu reacted with dilute sulphuric acid to give 43.9 mL of H_2 at STP. The solution, in the lower oxidation state, was found to require 58.8 mL of N/10 $KMnO_4$ solution for complete oxidation. Compute the valencies of the metal.

9. X is a potassium salt whose solution gave a characteristic precipitate or colour with Mohr's salt solution. An alkaline solution of H_2O_2 reduced a solution of X and pale yellow crystals of Y are obtained. When Y is heated with concentrated H_2SO_4, a gas Z is evolved which burns with a blue flame. Identify X, Y and Z giving the reactions involved.

10. A metal A burns in oxygen with a yellow flame to give a yellow powder B, which on treatment with water liberates O_2 giving a clear solution C. The solution C attacks aluminium liberating a gas D and forming a water soluble compound E. Identify A, B, C, D and E.

11. A 0.5201 g sample of impure As_2O_3 is dissolved and eventually secured in a solution of pH 8. The arsenic is titrated with 0.0946 M iodine, using starch as the indicator. At the end point 24.89 mL of iodine solution has been added. What is the per cent As_2O_3 in the impure material? Given: Molar mass of arsenic = 74.9 g mol^{-1}.

12. A mineral contains calcium oxide and inert substances. A 0.5689 g sample is dissolved in an appropriate medium, and the calcium is then precipitated under the best conditions as calcium oxalate. This precipitate is dissolved in dilute sulphuric acid and the resulting solution is titrated with 0.02081 M $KMnO_4$. The titration requires a total of 20.35 mL of $KMnO_4$ solution. What is the percentage of calcium in the mineral?

13. A sample of low grade solder is analyzed for lead. A 0.759 g sample is dissolved in acid resulting in a solution of Pb^{2+} . An excess of K_2CrO_4 is added and the lead precipitated as $PbCrO_4$. The precipitate is filtered off and washed and then dissolved in acid. This solution is treated with an excess of KI and the iodine liberated by the reaction of KI with CrO_4^{2-} is titrated with 0.051 M $Na_2S_2O_3$. The volume of hypo consumed at the end point is 11.22 mL. What is the percentage of lead in the solder? Molar mass of lead is 207.2 g mol^{-1}?

14. 1.0625 g of a material containing calcium carbonate and inert substances is treated with 50.0 mL of 0.10 M HCl. After treatment, the CO_2 is completely expelled. The excess acid is then titrated with 0.1055 M NaOH, 36.80 mL being required to reach a neutral red end point. Calculate the percentage of $CaCO_3$ in the mineral.

ANSWERS

1. 45.04% Mg, 54.96% Al

2. 59.24% NaCl, 40.76% NaBr

3. 16.25 g ICl and 23.35 g ICl_3

4. 22.89 g mol^{-1}, 1.4 g

5. 61.25% $KClO_3$, 37.25% KCl

6. 302 g L^{-1}, 99.5 volume

7. 7.1%

8. two and five

9. X is $K_3Fe(CN)_6$; Y is $K_4Fe(CN)_6$; Z is CO

The reactions are

(i) $$K_3[Fe(CN)_6] + Fe^{2+} \rightarrow \underset{\text{blue colour}}{KFe[Fe(CN)_6]} + 2K^+$$

(ii) $$[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{2-} + e^- \;] \times 2$$

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

$$2[Fe(CN)_6]^{3-} + H_2O_2 \rightarrow \underset{(Y)}{[Fe(CN)_6]^{2-}} + 2OH^-$$

(iii) $$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

10. A is Na, B is Na_2O_2, C is NaOH, D is H_2 and E is $NaAlO_2$

11. 44.77%

12. 7.43%

13. 5.20%

14. 5.27%

II. INCREASING/DECREASING CHARACTERISTICS

1.	Decreasing ionic size	Mg^{2+}, O^{2-} Na^+, F^-	(1985)
2.	Increasing acidic property	ZnO, Na_2O_2, P_2O_5, MgO	(1985)
3.	Increasing first ionization potential	Mg, Al, Si, Na	(1985)
4.	Increasing bond length	F_2, N_2, Cl_2, O_2	(1985)
5.	Increasing size	Cl^-, S^{2-}, Ca^{2+}, Ar	(1986)
6.	Increasing acid strength	$HClO_3$, $HClO_4$, $HClO_2$, $HClO$	(1986)
7.	Increasing bond strength	HCl, HBr, HF, HI	(1986)
8.	Increasing oxidation number of iodine	I_2, HI, HIO_4, ICl	(1986)
9.	Increasing thermal stability	HOCl, $HOClO_2$, $HOClO_3$, HOClO	(1988)
10.	Increasing bond enthalpy	N_2, O_2, F_2, Cl_2	(1988)
11.	Increasing acidic character	CO_2, N_2O_5, SiO_2, SO_3	(1988)
12.	Increasing ionic size	N^{3-}, Na^+, F^-, O^{2-}, Mg^{2+}	(1991)
13.	Increasing basic character	MgO, SrO, K_2O, NiO, Cs_2O	(1991)
14.	Increasing extent of hydrolysis	CCl_4, $MgCl_2$, $AlCl_3$, PCl_5, $SiCl_4$	(1991)
15.	Increasing strength of hydrogen bonding $(X \cdots H - X)$	O, S, F, Cl, N	(1991)
16.	Increasing ionic radii in water	Li^+, Na^+, K^+, Rb^+, Cs^+	
17.	Increasing molar conductivity in water	Li^+, Na^+, K^+, Rb^+, Cs^+	
18.	Increasing reactivity with water	Li, Na, K, Rb, Cs	
19.	Increasing reactivity with hydrogen	Li, Na, K, Rb, Cs	
20.	Increasing melting point	Li, Na, K, Rb, Cs	
21.	Increasing basic nature of hydroxides	LiOH, NaOH, KOH, RbOH, CsOH	
22.	Increasing thermal stability of hydroxides	LiOH, NaOH, KOH, RbOH, CsOH	
23.	Inreasing covalent character	LiCl, LiBr, LiI	
24.	Increasing ionic character	$CaCl_2$, $BeCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$	
25.	Increasing solubility	$BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$	
26.	Increasing solubility	BeF_2, MgF_2, CaF_2, BaF_2	
27.	Increasing solubility	$Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$	
28.	Increasing basicity	$Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$	
29.	Increasing hydration of ions	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	
30.	Increasing reactivity with water	Be, Mg, Ca, Sr, Ba	
31.	Increasing reactivity towards air	Be, Mg, Ca, Sr, Ba	
32.	Increasing solubility	$BeSO_4$, $MgSO_4$, $CaSO_4$, $SrSO_4$, $BaSO_4$	
33.	Increasing ionic character	BCl_3, $AlCl_3$, $GaCl_3$	
34.	Increasing strength of Lewis acid	BF_3, BCl_3, BBr_3	
35.	Increasing strength of Lewis acid	$AlCl_3$, $GaCl_3$, $InCl_3$	
36.	Increasing reducing power	$GeCl_2$, $SnCl_2$, $PbCl_2$	
37.	Increasing oxidizing power	$GeCl_4$, $SnCl_4$, $PbCl_4$	
38.	Increasing number of hybrid orbitals of	C, Si, Sn	
39.	Increasing basic character	NH_3, AsH_3, SbH_3, PH_3	
40.	Increasing thermal stability	NH_3, AsH_3, SbH_3, PH_3	
41.	Increasing acidic strength	HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4	
42.	Increasing solubility in water	HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4	
43.	Increasing order of +5 oxidation state	N, P, As, Sb and Bi	
44.	Increasing extent of hydrolysis	NCl_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$	
45.	Increasing stability of hydrides	H_2O, H_2S, H_2Se, H_2Te	
46.	Increasing poisonous nature	H_2S, H_2Se, H_2Te, H_2Po	
47.	Increasing acidic strength	H_2O, H_2S, H_2Se, H_2Te	

48.	Increasing strength of oxoacids	H_2SO_3, H_2SeO_3, H_2TeO_3
49.	Increasing stability of oxoacids	H_2SO_3, H_2SeO_3, H_2TeO_3
50.	Increasing strength of oxoacids	H_2SO_4, H_2SeO_4, H_2TeO_4
51.	Increasing stability of oxoacids	H_2SO_4, H_2SeO_4, H_2TeO_4
52.	Increasing electron affinity	F, Cl, Br, I
53.	Increasing reducing power	HF, HCl, HBr, HI
54.	Increasing affinity for hydrogen	F_2, Cl_2, Br_2, I_2
55.	Increasing acidity	HF, HCl, HBr, HI
56.	Increasing melting point	HF, HCl, HBr, HI
57.	Increasing boiling point	HF, HCl, HBr, HI
58.	Increasing stability	HFO_3, $HClO_3$, $HBrO_3$, HIO_3
59.	Increasing covalent character	$TiCl_2$, $TiCl_3$, $TiCl_4$
60.	Increasing magnetic moment	Ti^{3+}, Ni^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}
61.	Increasing ionic character	VCl_2, VCl_3, VCl_4
62.	Increasing electropositivity	Fe, Na, Cu, Li
63.	Increasing density	Fe, Pb, Al, Au
64.	Increasing basic characteristics	Li_2O, BeO, B_2O_3, CO_2
65.	Increasing electronegativity	As, P, S, Cl
66.	Increasing ionization energy	N, O, F
67.	Increasing atomic size	S, O, Se, C
68.	Increasing acidity	HOCl, HOBr, HOI
69.	Increasing density	H_2S, O_2, CO_2, NH_3, H_2
70.	Increasing thermal stability	HF, HCl, HBr, HI
71.	Increasing bond enthalpy	N_2, O_2, F_2, Cl_2
72.	Increasing melting point	CaF_2, $CaCl_2$, $CaBr_2$, CaI_2
73.	Increasing oxidizing power	O, S, Se, Te
74.	Increasing oxidizing power	F, Cl, Br, I
75.	Increasing size	B, Be, Li, Na
76.	Increasing single bond strength	N—N, O—O, F—F
77.	Increasing stability of hydrides	LiH, NaH, KH, CsH
78.	Decreasing pH of aqueous solution of	LiCl, $BeCl_2$, $MgCl_2$, $AlCl_3$
79.	Increasing acidic oxide	Al_2O_3, MgO, SiO_2, P_4O_{10}
80.	Increasing basicity	F^-, Cl^-, Br^-, I^-
81.	Increasing basic strength	F^-, OH^-, NH_2^-, CH_3^-
82.	Increasing boiling point	NH_3, PH_3, AsH_3, SbH_3
83.	Increasing ionization energy	B, C, N, O
84.	Increasing thermal stability	$BeCO_3$, $MgCO_3$, $CaCO_3$, $BgCO_3$
85.	Increasing paramagnetism	Ca, Al, N, O
86.	Increasing ionic character	LiBr, NaBr, KBr, RbBr, CsBr
87.	Increasing hydration energy	Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}
88.	Increasing bond angle	NH_3, PH_3, AsH_3
89.	Increasing bond angle	NF_3, PH_3, AsF_3
90.	Increasing bond angle	H_2O, H_2S, H_2Se
91.	Increasing bond angle	NF_3, NCl_3
92.	Increasing bond angle	NO_2^+, NO_2, NO_2^-
93.	Increasing bond angle	NH_3, NF_3
94.	Increasing bond angle	PH_3, PF_3
95.	Increasing electronegativity	O^+, O, O^-
96.	Increasing basicity	H_2O, OH^-, CH_3OH, CH_3O^-

ANSWERS

1. $O_2^- > F^- > Na^+ > Mg^{2+}$

   All the four species are isoelectronic ($1s^2 2s^2 2p^6$). The number of positive charges in the nucleus decreases in the order ${}_{12}Mg > {}_{11}Na > {}_{9}F > {}_{8}O$. Hence, O^{2-} involved minimum nucleus-electrons attraction and maximum electron-electron repulsion while Mg^{2+} involves maximum nucleus-electrons attraction and minimum electron-electron repulsion. These factors make the size of anion greater than the corresponding neutral atom and that of cation lesser than the corresponding atom.

2. $Na_2O_2 < MgO < ZnO < P_2O_5$

   Oxides of electropositive elements are alkaline while those of electronegative elements are acidic. Alkaline property will increase with increase in electropositive character of metal and acidic characteristics increase with increase in electronegative characteristics of nonmetals. Since the electronegativity increases in the order Na < Mg < Zn < P, the acidic character of oxide will also increase in the same order.

3. Na < Al < Mg < Si

   The electronic configurations of given elements are

${}_{11}Na$	$(1s)^2(2s)^2(2p)^6(3s)^1$	${}_{13}Al$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$
${}_{12}Mg$	$(1s)^2(2s)^2(2p)^6(3s)^2$	${}_{14}Si$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$

   Aluminium will have lower ionization potential than magnesium as the removal of one electron leads to the formation of stable completely filled orbital configuration. So it is loosely held and can be removed more easily than to remove electron from filled 3s orbital of magnesium atom.

4. $N_2 < O_2 < F_2 < Cl_2$

   Nitrogen contains triple bond, oxygen contains double bond and fluorine and chlorine contain a single bond each. Chlorine involves bonding of 3p orbitals while fluorine involves 2p orbitals.

5. $Ca^{2+} < Cl^- < S^{2-} < Ar$

   The given species are isoelectronic. The size of cation will be the smallest. The mononegative anion will have smaller size than the dinegative anion. The size of the noble gas Ar will be maximum.

6. $HClO < HClO_2 < HClO_3 < HClO_4$

   These acids are better represented as Cl—OH, OCl—OH, O_2Cl—OH, O_3Cl—OH.

   The larger the number of oxygen atoms attached to chlorine, greater the electron pull towards oxygen, hence, more easy to remove hydrogen from the acid.

7. HI < HBr < HCl < HF

   As the size of the halogen atom increases, the strength of HX bond decreases. Besides this, decreasing per cent ionic character from HF to HI makes the bond less stable.

8. $HI < I_2 < ICl < HIO_4$

   The oxidation states of iodine in HI, I_2, ICl and HIO_4 are –1, 0 +1 and +7, respectively.

9. $HOCl < HOClO < HOClO_2 < HOClO_3$

   The stability is explained by the increasing number of electrons involved in the formation of σ and π bonds in going from HOCl to $HOClO_3$. In ClO_4^- ion all the valence orbitals and electrons of chlorine are involved in the formation of bonds.

10. $F_2 < Cl_2 < O_2 < N_2$

    N_2 involves a triple bond, O_2 involves a double bond, F_2 and Cl_2 involve a single bond each. F_2 has a lower bond enthalpy than Cl_2. This is due to more repulsion of nonbonding electrons in F_2. Besides this, there is a possibility of multiple bonding in Cl_2 involving d orbitals.

11. $SiO_2 < CO_2 < N_2O_5 < SO_3$

    Increasing electronegativity of an element makes its oxide more acidic.

12. $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$ See Q. 1.

13. $NiO < MgO < SrO < K_2O < Cs_2O$

    Increasing electropositive nature of the element makes its oxide more basic.

14. $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$

In covalent halides, hydrolysis occurs as a result of coordination of a water molecule to the less electronegative element. CCl_4 does not undergo hydrolysis as carbon cannot expand its octet to accommodate water molecules.

15. $S < Cl < N < O < F$

The negative charge on X in HX increases with increasing electronegativity of X. This makes the hydrogen bonding more strong.

16. $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$

The ions in solution are present as hydrated ions. The smaller the size of the ion, the greater the extent of hydration. So the size of hydrated ions becomes larger for smaller sized ion and vice versa.

17. $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Li^+ ion being heavily hydrated has the lowest mobility and Cs^+ ion being less hydrated has the highest mobility.

18. Li < Na < K < Rb < Cs The reactivity increases on descending the Group 1.

19. Cs < Rb < K < Na < Li. The ease of formation of hydrides decreases on descending the Group 1.

20. Cs < Rb < K < Na < Li The melting (or boiling) point decreases on descending the group.

21. LiOH < NaOH < KOH < RbOH < CsOH

The basic nature of hydroxides of elements of Group 1 increases on descending the group.

22. LiOH < NaOH < KOH < RbOH < CsOH

Thermal stability of hydroxides increases on descending the group.

23. LiCl < LiBr < LiI

The smaller sized Li^+ ions polarizes the larger anion more predominantly giving larger covalent character.

24. $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2 < SrCl_2$

25. $BaCO_3 < CaCO_3 < MgCO_3 < BeCO_3$

On moving down the group, the lattice energies of carbonates do not decrease much while the degree of hydration of the metal ions decreases significantly leading to decreased solubility.

26. $BeF_2 < MgF_2 < CaF_2 < BaF_2$

Lattice energy variation is more dominating than the variation in hydration energy.

27. $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Ba(OH)_2$ Same as Q. 26.

28. $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Ba(OH)_2$

29. $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$

The extent of hydration of ion decreases with increase in ionic size.

30. Be < Mg < Ca < Sr < Ba

The reaction of alkaline-earth metals becomes increasingly vigorous with increasing atomic number.

31. Be < Mg < Ca < Sr < Ba

32. $BaSO_4 < SrSO_4 < CaSO_4 < MgSO_4 < BeSO_4$

Hydration of ion plays a dominating role as compared to lattice energy.

33. $BCl_3 < AlCl_3 < GaCl_3$

Increase in the electropositivity of element increases its ionic character.

34. $BF_3 < BCl_3 < BBr_3$

Besides σ bond between boron and halogen atoms, there exist additional pπ-pπ bond between the two atoms resulting from back-donation of electrons from fluorine to boron (back bonding).

The tendency to form pπ-pπ bond is maximum in BF_3 (2pπ—2pπ back bonding) and falls rapidly on passing to BCl_3 (2pπ—3pπ back bonding) and BBr_3 (2pπ—4pπ back bonding). The tendency to accept electron pair, therefore, increases from BF_3 to BBr_3.

35. $InCl_3 < GaCl_3 < AlCl_3$

With increase in size of elements of Group 13, the tendency to accept electron pair is decreased.

36. $PbCl_2 < SnCl_2 < GeCl_2$.

The stability of element in +II oxidation state increases on ascending the Group 14. This is due to inert-pair effect.

37. $GeCl_4 < SnCl_4 < PbCl_4$

The stability of element in +IV oxidation state decreases on ascending the Group 14. This is due to inert pair effect.

38. $Sn < Si < C$

The number of hybrid orbitals and ease with which these are formed decreases from carbon to lead.

39. $SbH_3 < AsH_3 < PH_3 < NH_3$

The decrease in electronegativity and increase in size of element cause the decrease in tendency to accept proton.

40. $SbH_3 < AsH_3 < PH_3 < NH_3$

41. $H_3SbO_4 < H_3AsO_4 < H_3AsO_3 < HNO_3$

42. $H_3SbO_4 < H_3AsO_4 < H_3AsO_3 < HNO_3$

43. $Bi < Sb < As < P < N$

44. $NCl_3 < PCl_3 < AsCl_3 < SbCl_3 < BiCl_3$

45. $H_2Te < H_2Se < H_2S < H_2O$

46. $H_2S < H_2Se < H_2Te < H_2Po$

47. $H_2O < H_2S < H_2Se < H_2Te$

Larger the size of X (= O, S, Se, Te) weaker its bonds with hydrogen and more easily H^+ gets lost in aqueous solution.

48. $H_2TeO_3 < H_2SeO_3 < H_2SO_3$

Decreasing size and increasing electronegativity from Te to S withdraws electrons from O—H bond towards itself, thus, facilitating the release of proton.

49. $H_2TeO_3 < H_2SeO_3 < H_2SO_3$

50. $H_2TeO_4 < H_2SeO_4 < H_2SO_4$

51. $H_2TeO_4 < H_2SeO_4 < H_2SO_4$

52. $Cl > F > Br > I$

53. $HF < HCl < HBr < HI$

54. $I_2 < Br_2 < Cl_2 < F_2$

55. $HF < HCl < HBr < HI$

56. $HCl < HBr < HF < HI$ Anomalous behaviour of HF is due to hydrogen bonding.

57. $HCl < HBr < HI < HF$ Anomalous behavour of HF is due to hydrogen bonding.

58. $HFO_3 < HClO_3 < HBrO_3 < HIO_3$

Ions of these acids are stabilized due to strong pπ-dπ bonding between full 2p orbitals on oxygen and empty orbitals on the halogen atom. Fluorine has no d orbitals and cannot form pπ-dπ bonds. Thus oxoacids of fluorine are not known.

59. $TiCl_2 < TiCl_3 < TiCl_4$

Increasing oxidation state of Ti increases charge density on the metal leading to increase in the polarization of the anionic charge clound and thus covalency increases.

60. $Zn^{2+} < Ti^{3+} < Ni^{2+} < Co^{2+} < Cr^{2+}$

Increasing number of unpaired electrons increases magnetic moment. The number of unpaired electrons in the given species are as follows.

Ti^{3+} one, Ni^{2+} two, Co^{2+} three, Cr^{2+} four and Zn^{2+} zero.

61. $VCl_4 < VCl_3 < VCl_2$

Decreasing oxidation state of element increases the ionic character.

62. $Hg < Cu < Na < Li$

63. $Al < Fe < Pb < Au$

64. $CO_2 < B_2O_3 < BeO < Li_2O$

65. $As < P < S < Cl$

66. $O < N < F$

67. $O < C < S < Se$

68. $HOI < HOBr < HOCl$

69. $H_2 < NH_3 < O_2 < H_2S < CO_2$ Increasing molecular mass increases the density.

70. $HI < HBr < HCl < HF$

71. $F_2 < Cl_2 < O_2 < N_2$

72. $CaI_2 < CaBr_2 < CaCl_2 < CaF_2$

Increasing size of anion increases its polarization by the cation making the compound more covalent.

73. Te < Se < S < O

74. I < Br < Cl < F

75. B < Be < Li < Na

76. N—N < O—O < F—F

77. CsH < KH < NaH < LiH

78. LiCl > $MgCl_2$ > $BeCl_2$ > $AlCl_3$
Hydrolysis of cations depends on two factors; larger charge and smaller size favour more hydrolysis, hence more free H^+ (i.e. lesser pH).

79. MgO < Al_2O_3 < SiO_2 < P_4O_{10}

80. I^- < Br^- < Cl^- < F^- Stronger the acid, weaker its the conjugate base.

81. F^- < OH^- < NH_2^- < CH_3^-
More electronegative the atom, lesser its tendency to give a lone pair of electrons.

82. PH_3 < AsH_3 < NH_3 < SbH_3
Boiling point increases with increase of molecular mass with the exception of NH_3 which exhibits hydrogen bonding

83. B < C < O < N
Nitrogen has extra stability due to half-filled p orbitals.

84. $BeCO_3$ < $MgCO_3$ < $CaCO_3$ < $BaCO_3$
Increasing size of cation decreases its polarizing ability towards carbonate making the compound more stable.

85. Ca < Al < O < N
Paramagnetism increases with increase of number of unpaired electrons.

86. LiBr < NaBr < KBr < RbBr < CsBr
The larger the difference between the electronegativities, greater the ionic character.

87. Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}
The smaller the size, more the hydration energy.

88. AsH_3 < PH_3 < NH_3
The increasing size and lower electronegativity of the central atom permit the bonding electrons to be drawn out further, thus decreasing repulsion between bonding pairs.

89. AsF_3 < PH_3 < NH_3

90. H_2Se < H_2S < H_2O

91. NF_3 < NCl_3 The bonding pair repulsion in NF_3 is less than that in NCl_3

92. NO_2^+ < NO_2 < NO_2^-
There is maximum repulsion between free electron(s) on nitrogen and bonding pairs.

93. NF_3 < NH_3 There is lesser repulsion in bonding pairs in NF_3.

94. PH_3 < PF_3
The multiple bonding in P—F bond due to back bonding (involving filled p orbital on F and empty d orbital on P) increases the electron density and electronic repulsion among the bonding electron

95. O^- < O < O^+
The positive charge on atom increases its electronegativity while negative charge decreases its electronegativity.

96. The increasing basicity is H_2O < CH_3OH < OH^- < CH_3O^-

III. PREDICTING CHEMICAL REACTIONS

Write the balanced chemical equations of the following:

1. White phosphorus (P_4) is boiled with a strong solution of sodium hydroxide in an inert atmosphere. (1982) (1987)

2. Sodium iodate is treated with sodium bisulphite solution. (1982)

3. Sulphur dioxide gas is bubbled through an aqueous solution of copper sulphate in presence of potassium thiocyanate. (1982)

4. An alkaline solution of potassium ferricyanide is reacted with hydrogen peroxide. (1982) (1989)

5. Propene is bubbled through a hot aqueous solution of potassium permanganate. (1982)
6. Mixing of aqueous solution of ferric sulphate and potassium iodide. (1984)
7. Aqueous solution of potassium manganate and acid. (1984)
8. Aqueous solution of potassium chromate and acid. (1984)
9. A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. (1985)
10. Potassium permanganate reacts with manganese dioxide in presence of potassium hydroxide. (1985)
11. Calcium phosphate is heated with a mixture of sand and carbon. (1985)
12. Potassium ferrocyanide is heated with concentrated sulphuric acid. (1985)
13. Ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. (1985)
14. Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide. (1985)
15. Aqueous ammonia is added drop-wise to a solution of copper sulphate till it is in excess. (1985)
16. Tin is heated with concentrated nitric acid. (1985)
17. $CrCl_3$ solution is treated with sodium hydroxide and then with hydrogen peroxide. (1985)
18. Pb_3O_4 is treated with nitric acid. (1985)
19. Chlorine gas is bubbled through a solution of ferrous bromide. (1986)
20. Zinc oxide is treated with excess of sodium hydroxide solution. (1986)
21. Iodine is added to a solution of stannous chloride. (1986)
22. Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. (1986)
23. Dilute nitric acid is slowly reacted with metallic tin. (1987)
24. Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. (1987)
25. Gold is dissolved in aqua regia. (1987)
26. Iodate ion reacts with bisulphite ion to liberate iodine. (1988)
27. Extraction of silver from silver glance by cyanide process. (1988)
28. Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. (1988)
29. Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (1988)
30. Hypophosphorus acid is heated. (1989)
31. Sodium bromate reacts with fluorine in the presence of an alkali. (1989)
32. Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. (1989)
33. Cobalt(II) solution reacts with KNO_2 in acetic acid medium. (1989)
34. Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. (1989)
35. A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4. (1990)
36. An aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution. (1990)
37. Sodium iodate is added to a solution of sodium bisulphite. (1990)
38. Iron reacts with cold dilute nitric acid. (1990)
39. Potassium permanganate is added to a hot solution of manganous sulphate. (1990)
40. Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. (1991)
41. Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. (1991)
42. Elemental phosphorus reacts with concentrated HNO_3 to give phosphoric acid. (1991)
43. Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. (1991)
44. Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. (1991)
45. Carbon dioxide is passed through a suspension of lime stone in water. (1991)
46. Copper reacts with HNO_3 to give NO and NO_2 in molar ratio of 2:1. (1992)
47. Sodium carbonate is added to a solution of copper sulphate. (1992)
48. Red phosphorus is reacted with iodine in presence of water. (1992)
49. Anhydrous potassium nitrate is heated with excess of metallic potassium. (1992)
50. Potassium dichromate and concentrated hydrochloric acid are heated together. (1992)
51. Heating sodium azide with sodium nitrite.
52. Aqueous solution of sodium carbonate is saturated with SO_2 gas.

53. Sodium thiosulphate added to AgBr.
54. Sodium thiosulphate added to silver nitrate.
55. To cupric chloride, sodium thiosulphate is added slowly till it is in excess.
56. Sodium thiosulphate is added slowly to auric chloride solution.
57. Carbon dioxide is passed through a suspension of calcium sulphate in aqueous ammonia.
58. Magnesium is treated with dilute nitric acid.
59. Sulphur dioxide is passed through colemanite ($Ca_2B_6O_{11}$) in boiling water.
60. Passing $SiCl_4$ vapour over molten aluminium.
61. Heating a fluoride salt with sand in the presence of concentrated sulphuric acid followed by exposure of the vapours to water.
62. Stannous chloride is added to mercuric chloride.
63. Iodine is treated with cold caustic soda solution.
64. Iodine is treated with hot caustic soda solution.
65. Chlorine is passed through hot milk of lime.
66. Iodine treated with concentrated nitric acid.
67. Iodine is treated with hot concentrated $KClO_3$ solution.
68. Chromium chloride treated with an alkaline solution of hypochlorous acid followed by the addition of acetic acid and lead acetate.
69. Ferrous sulphate is added to potassium ferricyanide.
70. Ferric sulphate is added to potassium ferrocyanide.
71. Red lead is treated with concentrated sulphuric acid.
72. Red lead is treated with concentrated hydrochloric acid.
73. Ammonia is treated with excess of chlorine.
74. Nitric oxide is passed through cold solution of ferrous sulphate followed by heating.
75. Nitric oxide is passed through acidified potassium permanganate.
76. Dilute nitric acid is added to zinc.
77. Heating of hydrated aluminium chloride.
78. Heating of lead nitrate.
79. Heating of hydrated ferrous sulphate.
80. Heating of potassium permanganate.
81. Chloride is passed through sodium thiosulphate solution.
82. Carbon monoxide is passed through sodium hydroxide solution.
83. Fluorine is passed through dilute sodium hydroxide solution.
84. Fluorine is passed through concentrated sodium hydroxide solution.
85. Bromine is added to sodium thiosulphate solution.
86. Ozone is passed through potassium ferrocyanide solution.
87. Magnesium is burnt in the atmosphere of ammonia.
88. Carbon dioxide is passed over heated potassium superoxide.
89. Sodium nitrite is added to acidified potassium permanganate solution.
90. A mixture of nitric oxide and oxygen is passed through sodium carbonate solution.
91. Phosphorous acid is added to silver nitrate solution.
92. Concentrated nitric acid is mixed with concentrated sulphuric acid.
93. Silver oxide is added to hydrogen peroxide solution.
94. Copper is treated with concentrated hydrochloric acid.
95. Stannous sulphite is treated with sodium hydroxide solution.
96. Aluminium oxide is heated with amorphous carbon.
97. Potassium iodide is added to $Na_3[Ag(S_2O_3)_2]$ solution.
98. Heating of $ZnCl_2 \cdot 2H_2O$.
99. Mercuric chloride is treated with phosphorous acid.
100. Ozone is passed through potassium ferrocyanide solution.

ANSWERS

1. $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

2. This is a redox reaction where HSO_3^- is a reducing agent and IO_3^- is an oxidizing agent.

$$\begin{array}{l} HSO_3^- + H_2O \rightarrow HSO_4^- + 2H^+ + 2e^-] \times 3 \\ 2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O \\ HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^-] \times 2 \\ \hline 5HSO_3^- + 2IO_3^- \rightarrow 3HSO_4^- + 2SO_4^{2-} + I_2 + H_2O \end{array}$$

The third reaction namely the oxidation of HSO_3^- to SO_4^{2-} is written so as to have no H^+ in the final reaction. Molecular reaction may be derived either from the above expression or as follows.

$$\begin{array}{l} NaIO_3 + NaHSO_3 \rightarrow Na_2SO_3 + HIO_3] \times 2 \\ 2HIO_3 \rightarrow I_2 + H_2O + 5O \\ NaHSO_3 + O \rightarrow NaHSO_4] \times 3 \\ Na_2SO_3 + O \rightarrow Na_2SO_4\ ] \times 2 \\ \hline 5NaHSO_3 + 2NaIO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2 \end{array}$$

3. This is a composite reaction, where SO_2 reduces copper(II) to copper(I) followed by the formation of CuSCN.

$$\begin{array}{l} SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \\ Cu^{2+} + e^- \rightarrow Cu^+\ ] \times 2 \\ Cu^+ + SCN^- \rightarrow CuSCN] \times 2 \\ \hline SO_2 + 2H_2O + 2Cu^{2+} + 2SCN^- \rightarrow SO_4^{2-} + 4H^+ + 2CuSCN \end{array}$$

or $SO_2 + 2H_2O + 2CuSO_4 + 2KSCN \rightarrow K_2SO_4 + 2H_2SO_4 + 2CuSCN$

4. This is redox reaction where H_2O_2 acts as a reducing agent. It reduces ferricyanide to ferrocyanide. Since the reaction is carried out in alkaline medium, we write

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ as $H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$

Hence, the reactions occurring are

$$\begin{array}{l} H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^- \\ [Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}\ \} \times 2 \\ \hline H_2O_2 + 2OH^- + 2[Fe(CN)_6]^{3-} \rightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2 \end{array}$$

or $H_2O_2 + 2KOH + 2K_3[Fe(CN)_6] \rightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$

5. Since the reaction is carried out in hot aqueous medium, permanganate oxidizes propene to propanoic acid and itself is reduced to MnO_2.

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 10 \\ CH_3CH{=}CH_2 + 10OH^- \rightarrow CH_3COOH + CO_2 + 6H_2O + 6e^-\ ] \times 3 \\ \hline 10MnO_4^- + 3CH_3CH{=}CH_2 + 2H_2O \rightarrow 10MnO_2 + 3CH_3COOH + 10OH^- + 3CO_2 \end{array}$$

6. This is redox reaction where ferric oxidizes I^- to I_2

$$\begin{array}{l} Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2 \\ 2I^- \rightarrow I_2 + 2e^- \\ \hline 2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \end{array}$$

or $Fe_2(SO_4)_3 + 2KI \rightarrow 2FeSO_4 + I_2 + K_2SO_4$

7.

$$\begin{array}{l} MnO_4^{2-} \rightarrow MnO_4^- + e^-] \times 2 \\ MnO_4^{2-} + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O \\ \hline 3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O \end{array}$$

8. In acidic medium, CrO_4^{2-} is transformed to $Cr_2O_7^{2-}$, as the reaction

$$2CrO_4^{2-} + 2H^+ \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$$

proceeds to the forward direction. Thus, the reaction is

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O \quad \text{or} \quad 2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

9. In this reaction, chlorate ion oxidizes oxalic acid to CO_2 and itself is reduced to ClO_2.

$$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O] \times 2$$
$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$$
$$\overline{2ClO_3^- + H_2C_2O_4 + 2H^+ \rightarrow 2ClO_2 + 2CO_2 + 2H_2O}$$

or $\quad 2KClO_3 + H_2C_2O_4 + H_2SO_4 \rightarrow 2ClO_2 + K_2SO_4 + 2CO_2 + 2H_2O$

10. In this reaction, permanganate oxidizes MnO_2 to manganate and itself is reduced to manganate.

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}] \times 2$$
$$MnO_2 + 4OH^- \rightarrow MnO_4^{2-} + 2H_2O + 2e^-$$
$$\overline{2MnO_4^- + MnO_2 + 4OH^- \rightarrow 3MnO_4^{2-} + 2H_2O}$$

or $\quad 2KMnO_4 + MnO_2 + 4KOH \rightarrow 3K_2MnO_4 + 2H_2O$

11. In this reaction, phosphorus is obtained.

$$2Ca_3(PO_4)_2 + 10C \rightarrow 6CaO + 10CO + P_4$$
$$CaO + SiO_2 \rightarrow CaSiO_3] \times 6$$
$$\overline{2Ca_3(PO_4)_2 + 10C + 6SiO_2 \rightarrow 6CaSiO_3 + 10CO + P_4}$$

12. $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$

13. $(NH_4)_2SO_4 + NO + NO_2 \rightarrow H_2SO_4 + 3H_2O + 2N_2$

14. Hydrogen sulphide reduces SO_2 to S and itself is oxidized to S. There is a formation of colliodal sulphur.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

15. There is first formation of green precipitate of $Cu(OH)_2$ which dissolves in excess of NH_3 forming blue tetraminecopper complex.

$$CuSO_4 + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$
$$Cu(OH)_2 + 4NH_3 \rightarrow \underset{\text{deep blue colour}}{[Cu(NH_3)_4]^{2+}} + 2OH^-$$

16. With concentrated nitric acid, hydrated stannic oxide (metastannic acid) is formed.

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O] \times 4$$
$$Sn + 3H_2O \rightarrow H_2SnO_3 + 4H^+ + 4e^-$$
$$\overline{Sn + 4NO_3^- + 4H^+ \rightarrow H_2SnO_3 + 4NO_2 + H_2O}$$

The exact formula of metastannic acid is $(SnO_2 \cdot H_2O)_5$.

17. With NaOH, green coloured precipitates of $Cr(OH)_3$ are formed which are dissolved as chromate due to the oxidation by H_2O_2.

(i) $CrCl_3 + 3NaOH \rightarrow Cr(OH)_3 + 3NaCl$

(ii) $Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-] \times 2$

$$H_2O_2 + 2e^- \rightarrow 2OH^-] \times 3$$
$$\overline{2Cr(OH)_3 + 3H_2O_2 + 4OH^- \rightarrow 2CrO_4^{2-} + 8H_2O}$$

18. Pb_3O_4 is a mixed oxide, $2PbO \cdot PbO_2$. With nitric acid, PbO is converted to $Pb(NO_3)_2$ while PbO_2 remains as such. $\quad Pb_3O_4 + 4HNO_3 \rightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$

19. Chlorine displaces bromide as bromine and it is reduced to Cl^-

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2 \quad \text{or} \quad Cl_2 + FeBr_2 \rightarrow Br_2 + FeCl_2$$

20. ZnO is dissolved as zincate ion. $\quad ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

21.

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$
$$I_2 + 2e^- \rightarrow 2I^-$$
$$\overline{Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-}$$

22. The products are sodium sulphate and HCl.

$$\begin{array}{l} SO_2 + H_2O \rightarrow H^+ + HSO_3^- \,] \times 2 \\ 2HSO_3^- + O_2 \rightarrow 2HSO_4^{2-} \\ 2NaCl + H^+ + HSO_4^- \rightarrow Na_2SO_4 + 2HCl] \times 2 \\ \hline 2SO_2 + 2H_2O + O_2 + 2NaCl \rightarrow 2Na_2SO_4 + 4HCl \end{array}$$

23. Tin reduces nitric acid (dilute) to ammonia.

$$\begin{array}{l} Sn \rightarrow Sn^{2+} + 2e^-] \times 4 \\ NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O \\ \hline 4Sn + NO_3^- + 10H^+ \rightarrow 4Sn^{2+} + NH_4^+ + 3H_2O \end{array}$$

24. MnO_4^- oxidizes oxalic acid to carbon dioxide.

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2 \\ (COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^-] \times 5 \\ \hline 2MnO_4^- + 6H^+ + 5(COOH)_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \end{array}$$

or $2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

25. Gold dissolves in aqua regia as $HAuCl_4$.

$$\begin{array}{l} Au + 3HCl + HNO_3 \rightarrow AuCl_3 + NO + 2H_2O \\ AuCl_3 + HCl \rightarrow HAuCl_4 \\ 2HNO_3 + NO \rightarrow 3NO_2 + H_2O \\ \hline Au + 4HCl + 3HNO_3 \rightarrow HAuCl_4 + 3NO_2 + 3H_2O \end{array}$$

26. Same as reaction (2).

27. After the concentration of ore, it is treated with dilute solution of sodium cyanide.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

A current of air is simultaneously passed through the solution so as to oxidize Na_2S to $Na_2S_2O_3$ and Na_2SO_4, thus the reaction proceeds to completion. The addition of Zn replaces Ag from the complex.

$$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag$$

28.

$$\begin{array}{l} 2HNO_3 \rightarrow H_2O + 2NO + 3O] \times 2.5 \\ 2HNO_3 \rightarrow H_2O + 2NO_2 + O] \times 2.5 \\ P_4 + 6H_2O + 10\ O \rightarrow 4H_3PO_4 \\ \hline P_4 + 10HNO_3 + H_2O \rightarrow 4H_3PO_4 + 5NO + 5NO_2 \end{array}$$

29. $NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl$

30. $2H_3PO_2 \xrightarrow[\text{heat}]{} H_3PO_4 + PH_3$

31.

$$\begin{array}{l} F_2 + 2e^- \rightarrow 2F^- \\ BrO_3^- + 2OH^- \rightarrow BrO_4^- + H_2O + 2e^- \\ \hline BrO_3^- + 2OH^- + F_2 \rightarrow BrO_4^- + 2F^- + H_2O \end{array}$$

or $NaBrO_3 + 2NaOH + F_2 \rightarrow NaBrO_4 + 2NaF + H_2O$

32. $AgCl + 2NaCN \rightleftharpoons Na[Ag(CN)_2] + NaCl$

$2Na[Ag(CN)_2] + Zn + 4NaOH \rightarrow Na_2ZnO_2 + 2Ag + 4NaCN + 2H_2O$

33. $Co^{2+} + 3K^+ + 7NO_2^- + 2CH_3COOH \rightarrow \underset{\text{yellow precipitate}}{K_3[Co(NO_2)_6]} + NO + H_2O + 2CH_3COO^-$

34. $2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2NaHSO_4 + 2ClO_2$

35. This produces chromyl chloride.

$$\begin{array}{l} K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O \\ NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4 \\ 2CrO_3 + 4HCl \rightarrow 2CrO_2Cl_2 + 2H_2O \\ \hline K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2KHSO_4 + 3H_2O + 4NaHSO_4 \end{array}$$

36. Nitrate is reduced to ammonia. $NaNO_3 + 4Zn + 7NaOH \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$

37. Same as reaction (2).

38. With cold dilute acid, iron produces ferrous nitrate and ammonium nitrate.

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

39. MnO_4^- oxidizes Mn^{2+} to MnO_2 and is itself reduced to MnO_2.

$$\begin{array}{l} MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O] \times 2 \\ Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-] \times 3 \\ \hline 2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \end{array}$$

or $2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

40.

$$\begin{array}{l} NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \\ Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH \\ NaOH + HNO_2 \rightarrow NaNO_2 + H_2O \\ NaHCO_3 + HNO_2 \rightarrow NaNO_2 + CO_2 + H_2O \\ \hline Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2 \end{array}$$

41.

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2 \\ 2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \\ \hline 2MnO_4^- + 2NH_3 \rightarrow 2MnO_2 + 2OH^- + 2H_2O + N_2 \end{array}$$

or $2KMnO_4 + 2NH_3 \rightarrow 2MnO_2 + 2KOH + 2H_2O + N_2$

42.

$$\begin{array}{l} NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O] \times 20 \\ P_4 + 10H_2O \rightarrow 2P_2O_5 + 20H^+ + 20e^- \\ P_2O_5 + 3H_2O \rightarrow 2H_3PO_4] \times 2 \\ \hline 20NO_3^- + 20H^+ + P_4 \rightarrow 20NO_2 + 4H_2O + 4H_3PO_4 \end{array}$$

43.

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2 \\ C_2H_4 + 2OH^- \rightarrow HOCH_2CH_2OH + 2e^-] \times 3 \\ \hline 2MnO_4^- + 3C_2H_4 + 4H_2O \rightarrow 2MnO_2 + 2OH^- + 3HOCH_2CH_2OH \end{array}$$

44.

$$\begin{array}{l} 2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2 \\ SO_2 + 2H_2S \rightarrow 3S + 2H_2O \\ \hline 2NaHSO_3 + 2H_2S \rightarrow Na_2SO_3 + 3H_2O + 3S \end{array}$$

45. $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

46.

$$\begin{array}{l} Cu \rightarrow Cu^{2+} + 2e^-] \times 7 \\ HNO_3 + H^+ + 2e^- \rightarrow NO_2 + H_2O] \times 2 \\ HNO_3 + 3H^+ + 3e^- \rightarrow 2H_2O + NO] \times 4 \\ \hline 7Cu + 6HNO_3 + 14H^+ \rightarrow 7Cu^{2+} + 2NO_2 + 4NO + 10H_2O \end{array}$$

or $7Cu + 20HNO_3 \rightarrow 7Cu(NO_3)_2 + 2NO_2 + 4NO + 10\ H_2O$

47. On adding Na_2CO_3 to copper sulphate solution, the solution becomes alkaline and thus $Cu(OH)_2$ is precipitated. The net reaction is

$$CuSO_4 + Na_2CO_3 + H_2O \rightarrow Cu(OH)_2 + Na_2SO_4 + CO_2$$

48. $2P + 3I_2 + 6H_2O \rightarrow 2H_3PO_3 + 6HI$

49. $2KNO_3(s) + 10K(s) \rightarrow 6K_2O(s) + N_2$

50.

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ 2HCl \rightarrow Cl_2 + 2H^+ + 2e^-] \times 3 \\ \hline Cr_2O_7^{2-} + 6HCl + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2 \end{array}$$

or $K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

51. $3NaN_3 + NaNO_2 \rightarrow 2Na_2O + 5N_2$

52. $Na_2CO_3 + H_2O + 2SO_2 \rightarrow 2NaHSO_3 + CO_2$

53. AgBr dissolves in dilute solution of sodium thiosulphate. $AgBr + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$

54. White precipitate changes to yellow, brown and finally becomes black

$$S_2O_3^{2-} + 2Ag^+ \rightarrow \underset{\text{white}}{Ag_2S_2O_3}; \qquad Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{black}}{Ag_2S} + H_2SO_4$$

55. Sodium thiosulphate reduces Cu(II) to Cu(I). A precipitate of cuprous chloride is obtained which dissolves in excess of thiosulphate.

$$2CuCl_2 + 2Na_2S_2O_3 \rightarrow 2CuCl + Na_2S_4O_6 + 2NaCl$$

$$2CuCl + S_2O_3^{2-} \rightarrow Cu_2S_2O_3 + 2Cl^-$$

$$3Cu_2S_2O_3 + 2S_2O_3^{2-} \rightarrow [Cu_6(S_2O_3)_5]^{4-}$$

56. Sodium thiosulphate reduces auric salt to aurous salt which forms complex with excess of sodium thiosulphate.

$$AuCl_3 + 2S_2O_3^{2-} \rightarrow AuCl + S_4O_6^{2-} + 2Cl^-$$

$$AuCl + 2S_2O_3^{2-} \rightarrow [Au(S_2O_3)_2]^{2-} + Cl^-$$

57. $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$

$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$$

58. Nitric acid is reduced to ammonia by magnesium.

$$\begin{array}{l} Mg \rightarrow Mg^{2+} + 2e^-] \times 4 \\ HNO_3 + 8H^+ + 8e^- \rightarrow NH_3 + 3H_2O \\ \hline 4Mg + HNO_3 + 8H^+ \rightarrow 4Mg^{2+} + NH_3 + 3H_2O \end{array}$$

or $4Mg + 9HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_3 + 3H_2O$

Ammonia is converted into ammonium nitrate: $NH_3 + HNO_3 \rightarrow NH_4NO_3$

So, the net reaction is $4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

59. This is the method to prepare boric acid.

$$\begin{array}{l} Ca_2B_6O_{11} + 4H_2O + 4SO_2 \rightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11} \\ H_4B_6O_{11} + 7H_2O \rightarrow 6H_3BO_3 \\ \hline Ca_2B_6O_{11} + 4SO_2 + 11H_2O \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3 \end{array}$$

60. This is the method to prepare crystalline silicon.

$$3SiCl_4 + 4Al \rightarrow 4AlCl_3 + 3Si$$

Aluminium being volatile passes over, while liberated Si dissolves in molten aluminium and separates out as crystalline silicon.

61. Heating of a fluoride with silica in the presence of concentrated sulphuric acid forms silicon tetrafluoride which hydrolyses to give silicic acid.

$$SiO_2 + 2CaF_2 + 2H_2SO_4 \rightarrow SiF_4 + 2CaSO_4 + 2H_2O$$

$$3SiF_4 + 4H_2O \rightarrow \underset{\text{milky}}{Si(OH)_4} + 2H_2SiF_6$$

62. Stannous chloride reduces Hg_2Cl_2 to $HgCl_2$ followed by reduction of Hg_2Cl_2 to black mercury.

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4; \qquad Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$

63. Iodine with cold alkaline gives iodide and hypoiodous acid.

$$\begin{array}{l} 2NaOH + I_2 \rightarrow NaI + NaIO + H_2O \\ NaIO + H_2O \rightarrow HIO + NaOH \\ \hline NaOH + I_2 \rightarrow NaI + HIO \end{array}$$

64. Iodine with hot alkalis gives iodide and iodate salts.

$$\begin{array}{l} 2NaOH + I_2 \rightarrow NaI + NaIO + H_2O] \times 3 \\ 3NaIO \rightarrow NaIO_3 + 2NaI \\ \hline 6NaOH + 3I_2 \rightarrow 5NaI + NaIO_3 + 3H_2O \end{array}$$

65. The reaction is $6Ca(OH)_2 + 6Cl_2 \rightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$

66. The reaction is $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

67. The reaction is $3I_2 + 5KClO_3 + 3H_2O \rightarrow 6HIO_3 + 5KCl$

68. The reactions are

(i) $CrCl_3 + 3NaOH \rightarrow Cr(OH)_3 + 3NaCl$

(ii) $HClO + NaOH \rightarrow NaClO + H_2O$

(iii)
$$\begin{array}{l} NaClO + H_2O + 2e^- \rightarrow NaCl + 2OH^-] \times 3 \\ Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-] \times 2 \\ \hline 3NaCl + 2Cr(OH)_3 + 4OH^- \rightarrow 3NaCl + 2CrO_4^{2-} + 5H_2O \end{array}$$

(iv) $CrO_4^{2-} + Pb^{2+} \rightarrow \underset{\text{yellow ppt.}}{PbCrO_4}$

69. Blue colour is obtained $Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow Fe_3[Fe(CN)_6]_2$

70. Blue colour or precipitate of prussian blue is obtained. $Fe^{3+} + [Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]$

71. Red lead on treating with concentrated sulphuric acid liberates oxygen.

$$2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$$

72. Red lead oxidizes HCl to Cl_2. $Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$

73. An explosive nitrogen trichloride is formed. $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

74. With cold ferrous sulphate, a dark brown nitrosyl complex ion is formed which decomposes on heating

$$[Fe(H_2O)_6]^{2+} + NO \underset{\text{hot}}{\overset{\text{cold}}{\rightleftharpoons}} [Fe(NO)(H_2O)_5]^{2+} + H_2O$$

75. Acidified $KMnO_4$ oxidizes nitric oxide to nitrate ion.

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 3 \\ NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-] \times 5 \\ \hline 3MnO_4^- + 4H^+ + 5NO \rightarrow 3Mn^{2+} + 5NO_3^- + 2H_2O \end{array}$$

76. Zinc reduces HNO_3 to N_2O.

$$\begin{array}{l} Zn \rightarrow Zn^{2+} + 2e^-] \times 4 \\ 2HNO_3 + 8H^+ + 8e^- \rightarrow N_2O + 5H_2O \\ \hline 4Zn + 2HNO_3 + 8H^+ \rightarrow N_2O + 5H_2O + 4Zn^{2+} \end{array}$$

or $4Zn + 10HNO_3 \rightarrow N_2O + 5H_2O + 4Zn(NO_3)_2$

77. $2AlCl_3 \cdot 6H_2O \xrightarrow[\text{heat}]{} Al_2O_3 + 6HCl + 9H_2O$

78. $2Pb(NO_3)_2 \xrightarrow[\text{heat}]{} 2PbO + 4NO_2 + O_2$

79. $2FeSO_4 \cdot 7H_2O \xrightarrow[\text{heat}]{} Fe_2O_3 + SO_2 + SO_3 + 14H_2O$

80. $2KMnO_4 \xrightarrow[\text{heat}]{} K_2MnO_4 + MnO_2 + O_2$

81. $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaCl + 2H_2SO_4 + 6HCl$

82. $CO + NaOH \rightarrow HCOONa$

83. $F_2 + 2NaOH \xrightarrow[\text{(dilute)}]{} F_2O + 2NaF + H_2O$

84. $2F_2 + 4NaOH \xrightarrow[\text{(conc.)}]{} 4NaF + 2H_2O + O_2$

85. $Br_2 + Na_2S_2O_3 + H_2O \rightarrow Na_2SO_4 + 2HBr + S$

86. $O_3 + 2K_4Fe(CN)_6 + H_2O \rightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$

87. $3Mg + 2NH_3 \xrightarrow[\text{heat}]{} Mg_3N_2 + 3H_2$

88. $4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2$

89. $5NaNO_2 + 3H_2SO_4 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$

90. $Na_2CO_3 + 2NO + O_2 \rightarrow NaNO_3 + NaNO_2 + CO_2$

91. $2AgNO_3 + H_3PO_3 + H_2O \rightarrow 2Ag + 2HNO_3 + H_3PO_4$

92. $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

93. $Ag_2O + H_2O_2 \rightarrow 2Ag + O_2 + H_2O$

94. $2Cu + 6HCl \rightarrow 2H_2[CuCl_3] + H_2$

95. $3SnS_2 + 6NaOH \rightarrow 2Na_2SnS_3 + Na_2SnO_3 + 3H_2O$

96. $2Al_2O_3 + 9C \xrightarrow[\text{heat}]{} Al_4C_3 + 6CO$

97. $[Ag(S_2O_3)_2]^{3-} + I^- \rightarrow AgI(s) + 2S_2O_3^{2-}$

98. $ZnCl_2 \cdot 2H_2O \xrightarrow[\text{heat}]{} Zn(Cl)(OH) + HCl + H_2O$

99. $2HgCl_2 + H_3PO_3 + H_2O \rightarrow Hg_2Cl_2 + H_3PO_4 + 2HCl$

100. $2K_4Fe(CN)_6 + O_3 + H_2O \rightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$

IV. COMPLETING AND BALANCING CHEMICAL EQUATIONS

Complete and balance the following equations:

1. $SO_2 + MnO_4^- + \_\_\_ \rightarrow SO_4^{2-} + Mn^{2+} + \_\_\_$ (1981)

2. $HCO_3^- + Al^{3+} \rightarrow Al(OH)_3 + \_\_\_$ (1981)

3. $AlBr_3 + K_2Cr_2O_7 + H_3PO_4 \rightarrow K_3PO_4 + AlPO_4 + H_2O + \_\_\_ + \_\_\_$ (1981)

4. $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + H_2O + \_\_\_$ (1981)

5. $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + \_\_\_$ (1981)

6. $C_2H_5OH + I_2 + OH^- \rightarrow HCO_2^- + I^- + H_2O + \_\_\_$ (1981)

7. $Zn + NO_3^- + \_\_\_ \rightarrow Zn^{2+} + NH_4^+ + \_\_\_$ (1983)

8. $Cr_2O_7^{2-} + C_2H_4O + \_\_\_ \rightarrow C_2H_4O_2 + Cr^{3+} + \_\_\_$ (1983)

9. $HNO_3 + HCl \rightarrow NO + Cl_2 + \_\_\_$ (1983)

10. $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$ (1983)

11. $Cl_2 + OH^- \rightarrow Cl^- + ClO^- + \_\_\_$ (1983)

12. $NH_3 + NaOCl \rightarrow \_\_\_ + \_\_\_ + \_\_\_$ (1993)

13. $AgBr + Na_2S_2O_3 \rightarrow \_\_\_ + \_\_\_$ (1993)

14. $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \rightarrow \_\_\_ + \_\_\_ + \_\_\_$ (1993)

15. $[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \rightarrow \_\_\_ + [Fe(H_2O)_6]^{3+} + H_2O$

$Fe(H_2O)_6^{2+} + \_\_\_ \rightarrow \_\_\_ + H_2O$ (1993)

16. $Na + NH_3(l) \xrightarrow[\text{heat}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

17. $NaNO_2(s) + Na(s) \xrightarrow[\text{fused}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

18. $Na_2CO_3 + SO_2 + H_2O \rightarrow NaHSO_3 + \underline{\hspace{1cm}}$
19. $NaHSO_3 + Na_2CO_3 \rightarrow Na_2SO_3 + \underline{\hspace{1cm}}$
20. $Al + \text{conc. } H_2SO_4 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
21. $[Al(OH)_4]^- + CO_2 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
22. $Al_2O_3 + C + N_2 \xrightarrow[\text{heat}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

23. $Pb + O_2 + H_2O \rightarrow \underline{\hspace{1cm}}$
24. $Pb + KOH \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
25. $PbO_2 + HCl \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
26. $Pb_3O_4 + \text{dil. } H_2SO_4 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
27. $Fe^{3+} + SO_2 + H_2O \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
28. $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow NO + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
29. $CuSO_4 + KI \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
30. $CuSO_4 \xrightarrow[\text{heat}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

31. $Zn + [Ag(CN)_2]^- \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
32. $Zn + OH^- + H_2O \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
33. $Zn + Fe_2(SO_4)_3 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
34. $Ag + O_2 + CN^- + H_2O \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
35. $AgBr(s) + S_2O_3^{2-} \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
36. $NH_3 + Cl_2 \rightarrow \underline{\hspace{1cm}} + HCl$
37. $NaNO_3 + (NH_4)_2SO_4 \xrightarrow[\text{heat}]{} Na_2SO_4 + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

38. $NaNO_2 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NaHSO_4 + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
39. $NO + SO_2 + H_2O \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
40. $MnO_4^- + H^+ + NO \rightarrow Mn^{2+} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
41. $As_2O_3 + HNO_3 + H_2O \rightarrow \underline{\hspace{1cm}} + H_3AsO_3$
42. $FeCl_2 + HNO_2 + HCl \rightarrow FeCl_3 + H_2O + \underline{\hspace{1cm}}$
43. $NO + H_2S \rightarrow S + \underline{\hspace{1cm}} + H_2O$
44. $P_4 + N_2O \rightarrow P_4O_{10} + \underline{\hspace{1cm}}$
45. $S + \text{conc. } HNO_3 + \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + H_2O$
46. $C + \text{conc. } HNO_3 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + H_2O$
47. $P_4 + \text{conc. } HNO_3 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

48. $NH_4NO_3 \xrightarrow[\text{above } 300°C]{\text{heat}} \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

49. $SO_2 + HNO_3 + H_2O \rightarrow \underline{\hspace{1cm}} + NO$
50. $P_4O_{10} + 4HNO_3 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
51. $I_2 + O_3 + \underline{\hspace{1cm}} \rightarrow HIO_3 + \underline{\hspace{1cm}}$
52. $MnO_4^- + H_2S + \underline{\hspace{1cm}} \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
53. $I_2 + SO_2 + H_2O \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
54. $C + SiO_2 \xrightarrow[\text{heat}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

55. $CaC_2 + N_2 \xrightarrow[\text{heat}]{} \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

56. $MnO_2 + HCl \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$
57. $P_4O_{10} + HCl \rightarrow POCl_3 + \underline{\hspace{1cm}}$

58. $KClO_3 + HCl \rightarrow KCl + Cl_2 + \text{———} + \text{———}$

59. $3HClO_3 \xrightarrow[\text{sunlight}]{} HClO_4 + \text{———} + \text{———}$

60. $2AgClO_3 + Cl_2 \rightarrow \text{———} + ClO_2 + O_2$

61. $MnO_4^{2-} + H^+ \longrightarrow \text{———} + MnO_4^- + H_2O$

62. $Ca_5(PO_4)_3F + H_2SO_4 + H_2O \xrightarrow{\text{heat}} \text{———} + 5CaSO_5\cdot 2H_2O + \text{———}$

63. $SO_2(aq) + Cr_2O_7^{2-} + 2H^+ \rightarrow \text{———} + \text{———} + \text{———}$

64. $Sn + 2KOH + 4H_2O \rightarrow \text{———} + \text{———}$

ANSWERS

1. $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$:

2. $3HCO_3^- + Al^{3+} \rightarrow Al(OH)_3 + 3CO_2$

3. $3K_2Cr_2O_7 + 6AlBr_3 + 14H_3PO_4 \rightarrow 6CrPO_4 + 6AlPO_4 + 2K_3PO_4 + 21H_2O + 9Br_2$

4. $3Cu_2O + 14H^+ + 2NO_3^- \rightarrow 6Cu^{2+} + 7H_2O + 2NO$

5. $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

6. $C_2H_5OH + 4I_2 + 6OH^- \rightarrow HCO_2^- + 5I^- + 5H_2O + CHI_3$

7. $4Zn + NO_3^- + 10H^+ \rightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

8. $Cr_2O_7^{2-} + 3C_2H_4O + 8H^+ \rightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

9. $2HNO_3 + 6HCl \rightarrow 2NO + 3Cl_2 + 4H_2O$

10. $2Ce^{3+} + S_2O_8^{2-} \rightarrow 2Ce^{4+} + 2SO_4^{2-}$

11. $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

12. $2NH_3 + NaOCl \rightarrow H_2NNH_2 + NaCl + H_2O$

13. $AgBr + 2Na_2S_2O_3 + Na_3[Ag(S_2O_3)_2] + NaBr$

14. $(NH_4)_2S_2O_8 + 2H_2O + MnSO_4 \rightarrow (NH_4)_2SO_4 + MnO_2 + 2H_2SO_4$

15. $3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \rightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$
$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

16. $2Na + 2NH_3(l) \xrightarrow[\text{heat}]{} 2NaNH_2 + H_2$

17. $2NaNO_2 + 6Na \xrightarrow[\text{fuse}]{} 4Na_2O + N_2$

18. $Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$

19. $NaHSO_3 + Na_2CO_3 \rightarrow Na_2SO_3 + NaHCO_3$

20. $2Al + \text{conc. } 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$

21. $2[Al(OH)_4]^- + CO_2 \rightarrow 2Al(OH)_3 + CO_3^{2-} + H_2O$

22. $Al_2O_3 + 3C + N_2 \xrightarrow[\text{heat}]{} 2AlN + 3CO$

23. $2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$

24. $Pb + 2KOH \rightarrow K_2PbO_2 + H_2$

25. $PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$

26. $Pb_3O_4 + \text{dilute } 2H_2SO_4 \rightarrow 2PbSO_4 + PbO_2 + 2H_2O$

27. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

28. $6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

29. $2CuSO_4 + 4KI \rightarrow 2CuI + I_2 + 2K_2SO_4$

30. $CuSO_4 \xrightarrow[\text{heat}]{} CuO + SO_3$

31. $Zn + 2[Ag(CN)_2]^- \rightarrow 2Ag + [Zn(CN)_4]^{2-}$

32. $Zn + 2OH^- + 2H_2O \rightarrow [Zn(OH)_4]^{2-} + H_2$

33. $Zn + Fe_2(SO_4)_3 \rightarrow ZnSO_4 + 2FeSO_4$

34. $4Ag + O_2 + 8CN^- + 2H_2O \rightarrow 4[Ag(CN)_2]^- + 4OH^-$

35. $AgBr(s) + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$

36. $2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$

37. $2NaNO_3 + (NH_4)_2SO_4 \xrightarrow[\text{heat}]{} Na_2SO_4 + 2N_2O + 4H_2O$

38. $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$

39. $2NO + SO_2 + H_2O \rightarrow H_2SO_4 + N_2O$

40. $3MnO_4^- + 4H^+ + 5NO \rightarrow 3Mn^{2+} + 5NO_3^- + 2H_2O$

41. $As_2O_3 + 2HNO_3 + 2H_2O \rightarrow N_2O_3 + 2H_3AsO_4$

42. $FeCl_2 + HNO_2 + HCl \rightarrow FeCl_3 + H_2O + NO$

43. $2NO + H_2S \rightarrow S + N_2O + H_2O$

44. $P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$

45. $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$

46. $C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + H_2O$

47. $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

48. $2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O$

49. $3SO_2 + 2HNO_3 + 2H_2O \rightarrow 3H_2SO_4 + 2NO$

50. $P_4O_{10} + 4HNO_3 \rightarrow 2N_2O_5 + 4HPO_3$

51. $I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$

52. $2MnO_4^- + 5H_2S + 6H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$

53. $I_2 + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2I^- + 4H^+$

54. $3C + SiO_2 \xrightarrow[\text{heat}]{} SiC + 2CO$

55. $CaC_2 + N_2 \xrightarrow[\text{heat}]{} CaCN_2 + C$

56. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

57. $P_4O_{10} + 3HCl \rightarrow POCl_3 + 3HPO_3$

58. $2KClO_3 + 4HCl \rightarrow 2KCl + Cl_2 + 2ClO_2 + 2H_2O$

59. $3HClO_3 \xrightarrow[\text{sunlight}]{} HClO_4 + 2ClO_2 + H_2O$

60. $2AgClO_3 + Cl_2 \rightarrow 2AgCl + 2ClO_2 + O_2$

61. $3MnO_4^{2-} + 4H^+ \xrightarrow[\text{heat}]{} MnO_2 + 2MnO_4^- + 2H_2O$

62. $Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \xrightarrow{\text{heat}} 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF$

63. $3SO_2(aq) + Cr_2O_7^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

64. $Sn + 2KOH + 4H_2O \rightarrow K_2Sn(OH)_6 + 2H_2$

ORGANIC CHEMISTRY

CHAPTER 19

HYBRIDIZATION, ISOMERISM AND NOMENCLATURE

CONCEPT OF HYBRIDIZATION

Carbon (atomic number 6 and electronic configuration $1s^2 2s^2 2p^2$) forms a large number of compounds. From its electronic configuration, carbon is expected to be bivalent, but in all its compounds, it exhibits tetravalency. The bonding between a carbon atom and another atom (may be carbon or any other atom) may involve pure p orbital or a hybrid orbital. The latter is obtained as a result of mixing of two or more pure atomic orbitals centred on the same atom. This process is known as *hybridization*. The number of hybrid orbitals obtained is equal to the number of atomic orbitals mixed and these are completely identical in sizes, shapes, orientations and energies.

Carbon in its compounds exhibits three types of hybridization described in the following.

sp hybridization This involves mixing of 2s and one of the 2p orbitals to provide two sp hybrid orbitals oriented at an angle of 180° with respect to each other. This hybridization is also known as *diagonal* or *linear hybridization*. One of the examples illustrating sp hybridization of carbon is acetylene (Fig. 19.1).

sp^2 hybridization This involves mixing of 2s and two 2p orbitals to provide three sp^2 hybrid orbitals oriented at angle of 120° with respect to each other and point towards the three corners of an equilateral triangle. This hybridization is also known as *trigonal hybridization*. One of the common examples illustrating sp^2 hybridization of carbon is ethylene (Fig. 19.2).

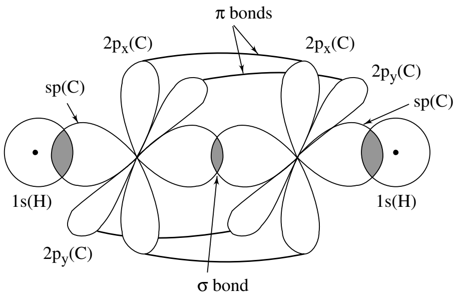


Fig. 19.1 Structure of acetylene $H{-}C{\equiv}C{-}H$

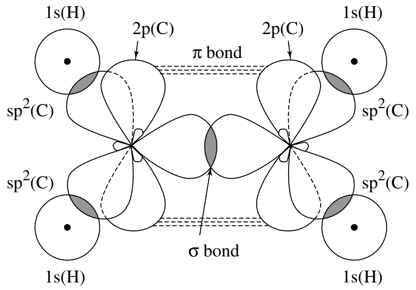
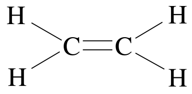


Fig. 19.2 Strucutre of ethylene



sp^3 hybridization This involves mixing of 2s and three 2p orbitals to provide four sp^3 hybrid orbitals oriented at angle of 109°28′ with respect to each other and point towards the four corners of a regular tetrahedron. This hybridization is also known as *tetrahedral hybridization*. One of the common examples illustrating sp^3 hybridization of carbon is methane (Fig. 19.3).

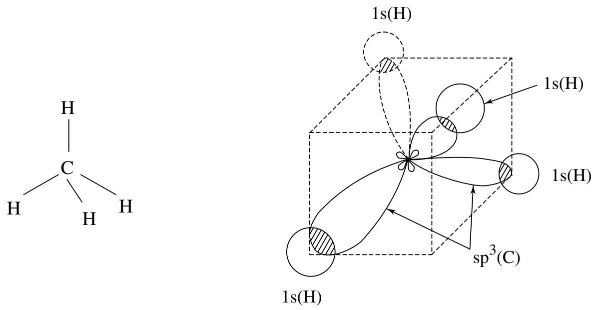


Fig. 19.3 Structure of methane

Comparison of sp, sp^2 and sp^3 hybrid orbitals of carbon

The per cent of s (or p) orbital in a hybrid orbital is given as

$$\text{Per cent of s (or p) contribution} = \frac{\text{Number of s (or p) orbitals mixed}}{\text{Total number of orbitals mixed}}$$

Thus, we have

sp orbital : 50% contribution from each of s and p orbitals.
sp^2 orbital : 33.33% contribution from s orbital and 66.67 from p orbitals.
sp^3 orbital : 25% contribution from s orbital and 75% from p orbitals.

Since s orbital in an atom is more near to the nucleus as compared to p orbital, we may expect the following relative characteristics of hybrid orbitals.

1. *Size of orbitals* Size of a hybrid orbital increases with decrease (or increase) of s (or p) contribution in it. Hence, the relative sizes of hybrid orbitals follows the order $sp^3 > sp^2 > sp$
2. *Eletronegativity of Orbitals* The electronegativity of an orbital increases with increase (or decrease) of s (or p) contribution in it. Hence, the electronegativity of hybrid orbitals follows the order $sp > sp^2 > sp^3$

SIGMA AND PI BOND

A covalent bond between two atoms is formed by overlapping of two atomic orbitals–one from each atom. Head-to-head overlap of atomic orbitals results in the formation of sigma (σ) bond and side-to-side overlap results into the formation of pi(π) bond. This is illustrated in Fig. 19.4.

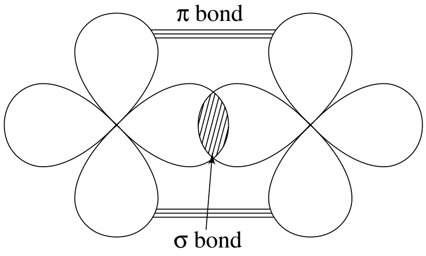


Fig. 19.4 Illustration of σ and π bonds

The overlapping of two atomic orbitals between the two atoms produces a new orbital, known as localized molecular orbital, which embraces both atoms. The overlapping involving the same sign of orbitals results into the formation of *bonding molecular orbital* as it creates more electron density between the atoms. The overlapping involving the different sign results into the formation of *antibonding molecular orbital* as it creates a node (a point where electron density is zero) between the atoms. The bonding orbital has lower energy than the individual atomic orbitals whereas antibonding molecular orbital has a higher energy. This is depicted in Fig. 19.5.

The C—C in C_2H_6 is a σ–bond, C=C bond in C_2H_4 (Fig. 19.2) involves one σ and one π bond, and C≡C bond in C_2H_2 (Fig. 19.1) involves one σ and two π bonds.

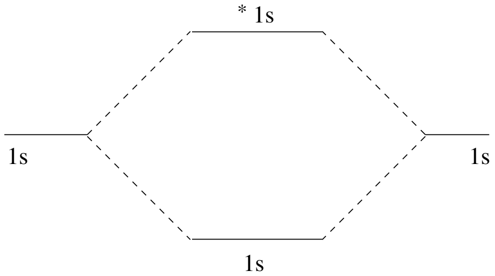


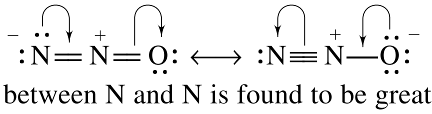
Fig. 19.5 Energies of bonding and antibonding orbitals relative to atomic orbitals

Bond Lengths The bond length decreases with increase in the number of bonds between the two carbon atoms. For example, the C—C bond length is 154 pm, C=C is 134 pm and C≡C is 121 pm. The C—H bond length decreases with increase in the electronegativity of hybrid orbital of carbon atom. For example

Molecule	CH_4		C_2H_4		C_2H_2
Order of electronegativity of hybrid orbital of C	sp^3	$<$	sp^2	$<$	sp
Bond length	110 pm		108 pm		106 pm

RESONANCE

For some molecules, more than one Lewis structures having fixed arrangement of atomic nuclei and differing in the arrangement of electrons can be written. Such a molecule is said to possess different *resonating* or *canonical structures*. None of the individual structures explains adequately the characteristics of the molecule. The resonance theory postulates that the actual state of the molecule is hybrid of all canonical structures. For example, for dinitrogen oxide, we can write



$$\overset{-}{:\ddot{N}}=\overset{+}{N}=\ddot{\underset{\cdot\cdot}{O}}: \longleftrightarrow :N\equiv\overset{+}{N}-\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}:$$

The observed bond length of 112 pm between N and N is found to be greater than the calculated triple bond length (110 pm) and smaller than double bond length (120 pm). The same is the situation between N and O atoms. The observed value is 119 pm, calculated double and single bond lengths are 115 pm and 147 pm, respectively. These observations indicate that the resonance hybrid has some double-bond character between N and O and some triple-bond character between N and N.

The energy of the hybrid is always less than the calculated energy of any canonical structure. The *resonance energy* is defined as the difference between the enthalpy of formation of the molecule and that of resonating structure having the lowest energy (obtained theoretically). The resonance energy depends on the two main factors listed below.

1. Number of resonating structures
2. Energies of resonating structures

In organic molecules, benzene constitutes an excellent example of resonance. The canonical structures of benzene are shown in Fig. 19.6.

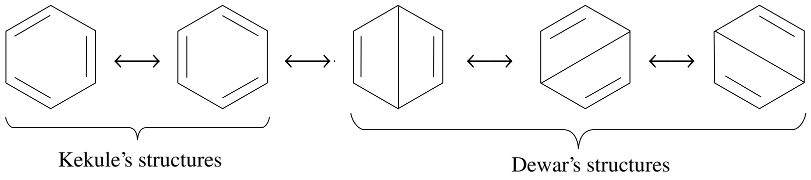


Fig. 19.6

The actual molecule of benzene involves 39% contribution from each of Kekule's structure and 7.3% from each of Dewar's structures. All the C and C bond lengths are identical and have bond length equal to 139 pm. This value is greater than C═C bond length (134 pm) and smaller than C—C bond length (154 pm).

Hyperconjugation π-Orbitals can overlap with other π-orbitals to produce conjugation. π-Orbitals, however, can also overlap to certain extent with the adjacent σ-orbitals to form extended orbitals. This phenomenon, known as hyperconjugation, is displayed by methyl group attached to an unsaturated carbon atom; as shown in Fig. 19.7.

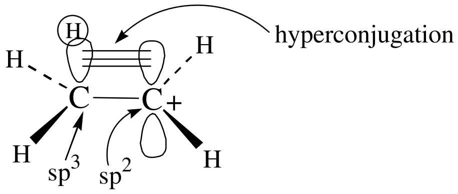


Fig. 19.7

The effect of hyperconjugation is to increase ionic character of the C—H bond, the electrons of which become partially delocalised through conjugation. Hyperconjugation is also known as no bond resonance.

HOMOLOGOUS SERIES

In organic chemistry, a series of compounds having same functionìal group but differing in CH_2 group can be written. Such a series is known as homologous series and the members of such a series is known as homologues. The physical properties of the members of a homologous series exhibit gradual variation with increase in the molecular mass.

ISOMERISM

In organic chemistry, two or more compounds may have the same molecular formula but different structural formulae. Such compounds are known as isomers and this phenomenon is known as isomerism. Since the compounds have different structural formulae, they differ in both physical and chemical properties.

There are two main types of isomerism. These are described in the following.

1. *Structural Isomerism* This is due to the different arrangement of atoms within the molecule.
2. *Stereoisomerism* This is due to the different spatial arrangement of atoms or groups around a particular atom in the molecule.

The structural isomerism may be classified into five categories. These are:

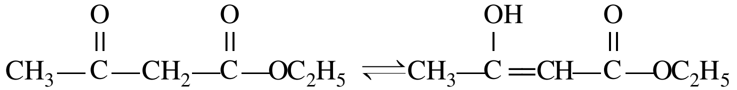
(a) *Chain isomerism* Differ in the order in which carbon atoms are linked in the molecule.

(b) *Position isomerism* Differ in the placement of a functional group on the carbon chain or placement of multiple bond.

(c) *Functional isomerism* Differ in functional groups.

(d) *Metamerism* Differ in the groups attached to a functional group.

(e) *Tautomerism* Migration of a proton from carbon atom to the adjacent atom; the two forms are in dynamic equilibrium with each other. One of the examples exhibiting keto–enol tautomerism is ethyl acetoacetate :

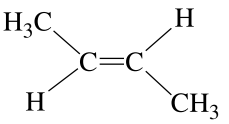


$$\underset{\text{keto form}}{CH_3—\overset{\overset{O}{||}}{C}—CH_2—\overset{\overset{O}{||}}{C}—OC_2H_5} \rightleftharpoons \underset{\text{enol form}}{CH_3—\overset{\overset{OH}{|}}{C}=CH—\overset{\overset{O}{||}}{C}—OC_2H_5}$$

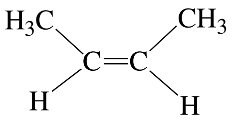
This compound shows the properties of both keto and enol groups. For example, it forms oxime with hydroxylamine and phenylhydrazone with phenylhydrazine which are characteristics of a keto group; it also decolorises bromine water indicating unsaturation and also gives violet colour with neutral ferric chloride—a test for enol group.

The stereoisomerism has been classified into two main categories. These are:

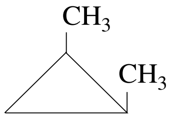
(a) *Geometrical isomerism* Due to the restricted motion within the molecule. For examples, 2-butene and 1, 2-dimethylcyclopropane.



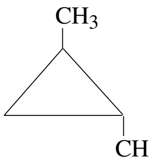
trans-2-butene



cis-2-butene



cis-1, 2-dimethylcyclopropane



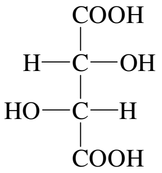
trans-1, 2-dimethylcyclopropane

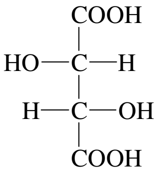
In *cis* form, similar groups are on the same side whereas in *trans* from, they are on the opposite side.

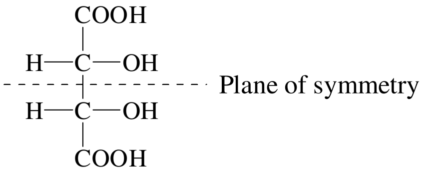
(b) *Optical isomerism* Differ in the capacity to rotate the plane polarized light in the opposite directions.

The following terms are used to describe isomers.

1. *Optically active molecule* A molecule that cannot be superimposed on its mirror image. It is also called chiral molecule.
2. *Asymmetric or chiral carbon* A carbon atom that is bonded to four different groups.
3. *Enantiomers* The optical isomers which are mirror images of each other.
4. *Dextrorotatory isomer* or (+)-*isomer* An isomer which rotates the plane of polarized light to the right (clockwise direction).
5. *Laevorotatory isomer* or (–)-*isomer* An isomer which rotates the plane of polarized light to the left (anticlockwise direction).
6. *Racemic mixture* An equimolar mixture of the two isomers. Since the optical rotatory powers of two isomers are equal in magnitude but opposite in sign, the racemic mixture does not rotate the plane of polarized light. The two isomers in a racemic mixture cannot be separated by ordinary laboratory methods as the two isomers resemble each other closely in all properties except optical. They can, however, be separated if they are made to combine with another optically active compound.
7. *Diastereomers* The optical isomers that are not mirror images. Diastereomers are observed if the molecule contains more than one chiral carbon atom. The two isomers have the same configuration with respect to one chiral carbon atom and will have different configurations with respect to the rest of molecules. Taking the example of tartaric acid, we have


(+)-tartatic acid


(–)-tartaric acid



mesotartaric acid

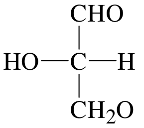
Here, (+)-tartaric acid and (–)-tartaric acid are enantiomers whereas (+)-tartaric acid or (–)-tartaric acid and mesotartaric acid are diastereoisomers.

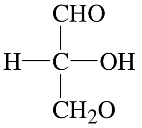
8. *Meso-compound* A compound which has more than one chiral carbon atom and it is superimposable on its mirror image. In this compound, optical rotation caused by one chiral carbon is cancelled by that of the other, consequently the *meso*-compounds are optically inactive. The molecule of a meso-compound has a plane of symmetry dividing it midway between the two chiral atoms.
9. *Racemisation* The phenomenon of conversion of one enantiomer into the other such that a mixture containing 50% of each is formed is known as racemisation.
10. *Resolution* The separation of a racemic mixture into its two optically active components is known as resolution.

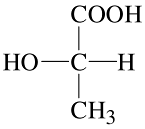
Absolute Configuration of an Optical Isomer The specification of exact spatial orientation of all four substituents around the central chiral carbon atom provides the absolute configuration of the optical isomer.

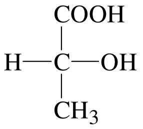
Polarimetric studies provide only the dextrorotatory and laevorotatory forms of the optical isomer but nothing about the absolute configuration of the molecule.

Traditionally, the absolute configuration of the molecule is done on the basis of arrangement of hydrogen atom attached to the chiral carbon atom. By convention, a hydrogen atom is shown on the horizontal line in the *Fischer projection** of the molecule. The arrangement having hydrogen atom right to the chiral carbon atom is termed as L form while that having hydrogen atom to the left is termed as D form. For example, we have


L-(–)-Glyceraldehyde


D-(+)-Glyceraldehyde


L-(+)-Lactic acid


D-(–)-Lactic acid

Thus, a dextrorotatory isomer may have D form or L form depending upon its absolute configuration.

A newer and more general system designates isomers as the *R* form or *S* form (see p.19.14).

Number of Optical Isomers The number of optically-active and optically-inactive isomers of a compound containing *n* chiral carbons may be computed from the expressions given below.

1. If the molecule is not divisible into two equal and similar halves.

$$N = \underset{\text{(optically active)}}{2^n} + \underset{\text{(optically inactive)}}{0} = 2^n$$

Example: $OHC\overset{*}{C}H(OH)\overset{*}{C}H(OH)CH_2OH$; $N = 2^2 = 4$.

2. If *n* is even and the molecule is divisible into two equal and similar halves

$$N = \underset{\text{(optically active)}}{2^{(n-1)}} + \underset{\text{(optically inactive)}}{2^{(n-2)/2}}$$

Example: $HO_2C\overset{*}{C}H(OH)^{*}CH(OH)CO_2H$; $N = 2^{(2-1)} + 2^{(2-2)/2} = 3$

3. If *n* is odd and the molecule is divisible into two equal and similar halves via the central atom

$$N = \underset{\text{(optically active)}}{[2^{(n-1)} - 2^{(n-1)/2}]} + \underset{\text{(optically inactive)}}{2^{(n-1)/2}}$$

Example: $HO_2C\overset{*}{C}H(OH)\overset{*}{C}H(OH)\overset{*}{C}H(OH)CO_2H$; $N = [2^{(3-1)} - 2^{(3-1)/2}] + 2^{(3-1)/2} = 4$

4. If the molecule contains a double bond and the chiral atom is away from the terminal carbon of the double bond.

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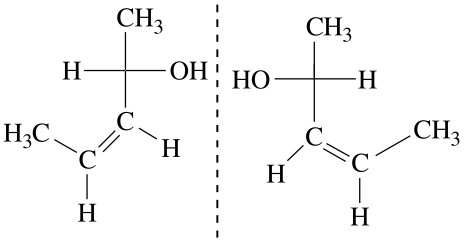
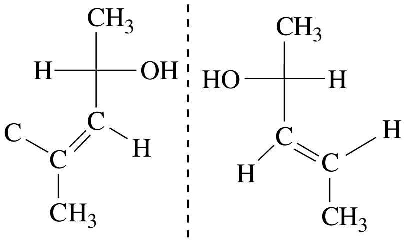
* In the Fischer projection, the horizontal line represents bonds coming out of the page, and the vertical line represents bond going into the page (see supplementary material of this chapter).

The total number of stereoisomers will be double the number of optical isomers computed from the above expressions.

Example: $H_3C\overset{*}{C}H(OH)CH{=\!=}CHCH_3$; $N = 2 * 2^1 = 4$. These are



cis(±)–isomers



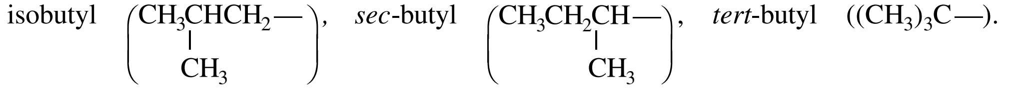
trans(±)–isomers

IUPAC System of Nomenclature of Organic Compounds

International Union of Pure and Applied Chemistry (IUPAC) has suggested a scheme for giving systematic names to organic compounds on the basis of structure. A brief description of this is given here.

1. Nomenclature of alkanes The first four members are known by their common names; methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). The higher members start from Greek prefix that indicate the number of carbon atoms in the molecules and end with 'ane'—the last three letters in alkane; pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}) and so on.

The alkyl group is obtained by removing one hydrogen atom from an alkane; methyl (CH_3), ethyl (C_2H_5), propyl (C_3H_7) and so on. Some simpler substituents with branced chains are often given common names;

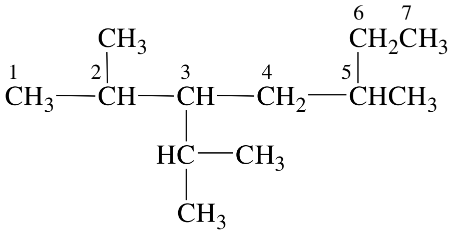


isobutyl $\left(\begin{array}{c}CH_3\underset{|}{C}HCH_2—\\ \;\;CH_3\end{array}\right)$, *sec*-butyl $\left(\begin{array}{c}CH_3CH_2\underset{|}{C}H—\\ \;\;\;\;CH_3\end{array}\right)$, *tert*-butyl ($(CH_3)_3C$—).

The following rules are followed while naming other alkanes.

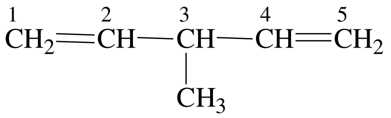
- (a) *Longest chain rule* The longest chain of carbon is chosen and the compound is named as a derivative of this alkane.
- (b) *Lowest number rule* The numbering (in arabic numerals) of the chain is started from the end where branching gets the lowest number.
- (c) *Preference to the substituent with the least number of carbon atoms* The numbering is started from the end which is nearest to the branch with the least number of carbon atoms.
- (d) *Preference to the greater number of substituents* The end of the chain which is nearest to the large number of substituents is taken to be the first carbon.
- (e) *Alphabetical order of alkyl group* The substituents are named in the alphabetical order irrespective of their placements. The names methyl, dimethyl, trimethyl, etc. are all considered to start with alphabet m.
- (f) *Proper way of writing* A numeral and letter are separated by a hypen, and numeral from numeral by a coma. The entire name is written as one complete word.

For example, the name of the compound



is 2, 5-dimethyl-3- isopropylheptane.

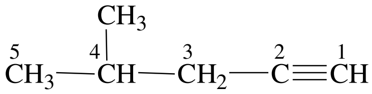
2. Nomenclature of alkenes The IUPAC name is obtained by replacing the suffix '-ane' of the corresponding alkane by '-ene'. The double bond gets the smallest number in the longest carbon chain. More than one double bond is indicated by ending the name with diene, triene, etc. The position of double bond may be placed between the suffix ene and the rest of the name. For example, the name of the compound



$$\overset{1}{C}H_2=\overset{2}{C}H-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{4}{C}H=\overset{5}{C}H_2$$

is 3-methylpent-1,4-diene.

3. **Nomenclature of alkynes** Here, the suffix '-ane' is replaced by '-yne'. For example, the compound

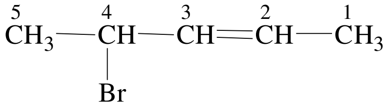


$$\overset{5}{C}H_3-\overset{\displaystyle CH_3}{\overset{4}{C}H}-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$$

is 4-methylpent-1-yne.

4. **Nomenclature of halogen derivatives**

The compound is named as haloalkane, haloalkene, and haloalkyne depending upon the nature of the carbon chain. For example, the compound

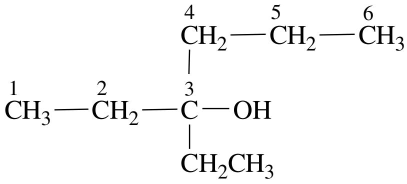


$$\overset{5}{C}H_3-\underset{\displaystyle Br}{\overset{4}{C}H}-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$$

is 4-bromopent-2-ene.

5. **Nomenclature of alcohols**

Here, the suffix '-ol' replaces the '-e' of the alkane to indicate the OH group. For example, the compound

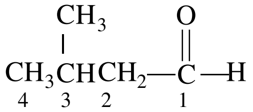


$$\overset{1}{C}H_3-\overset{2}{C}H_2-\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle \overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3}{\overset{3}{C}}}-OH$$

is 3–ethyl-3-hexanol.

6. **Nomenclature of aldehydes**

Here, the suffix '-al' replaces the '-e' of the alkane. The numbering of carbon atoms is always done starting from —CHO group. For example, the compound

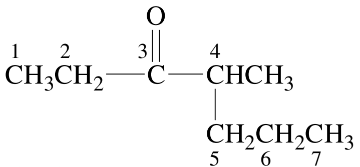


$$\underset{4}{C}H_3\underset{3}{\overset{\displaystyle CH_3}{C}H}\underset{2}{C}H_2-\underset{1}{\overset{\displaystyle O}{\overset{\|}{C}}}-H$$

is 3-methylbutanal.

7. **Nomenclature of ketones**

Here, the suffix '-one' replaces the '-e' of the alkane. For example the compound

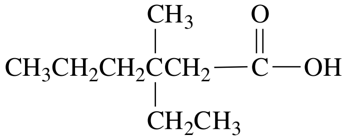


$$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{\displaystyle O}{\overset{\|}{\overset{3}{C}}}-\underset{\displaystyle \underset{5}{C}H_2\underset{6}{C}H_2\underset{7}{C}H_3}{\overset{4}{C}HCH_3}$$

is 4-methyl-3-heptanone.

8. **Nomenclature of carboxylic acid**

Here, the suffix '-oic' acid replaces '-e' of the alkane. The numbering of carbon atoms is always done starting from —COOH group. For example, the compound



$$CH_3CH_2CH_2\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle CH_3}{C}}CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

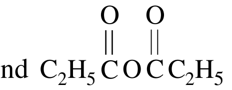
is 3-ethyl-3-methylhexanoic acid.

9. Nomenclature of carboxylic acid derivatives

(a) *Acid chlorides* These are named by changing the ending '-ic acid' of the corresponding carboxylic acid to '-yl chloride'. For example, CH_2CH_2COCl is propanoyl chloride.

(b) *Esters* These are named by writing first the alkyl group attached to oxygen atom followed by the word derived from carboxylic acid with the replacement of '-ic acid' to '-ate'. For example, $CH_3COOC_2H_5$ is ethyl ethanoate.

(c) *Anhydrides* These are named by changing the word 'acid' of the parent carboxyìlic acid to 'anhydride'

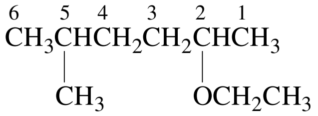


For example, the compound $C_2H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C_2H_5$ is propanoic anhydride.

(d) *Amides* These are named by replacing the ending '-oic acid' of the corresponding carboxylic acid with the ending '-amide'. For example, CH_3CONH_2 is ethanamide.

10. Nomenclature of ethers

These compounds are named as alkoxyalkanes. The smaller alkyl group along with the oxygen atom is known as alkoxy group. For example, the compound

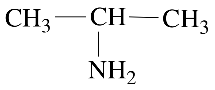


$$\overset{6}{CH_3}\underset{CH_3}{\underset{|}{\overset{5}{C}H}}\overset{4}{CH_2}\overset{3}{CH_2}\underset{OCH_2CH_3}{\underset{|}{\overset{2}{C}H}}\overset{1}{CH_3}$$

is 2-ethoxy-5-methylhexane.

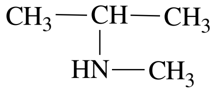
11. Nomenclature of amines

Primary amines are named by replacing the ending '-e' of the parent alkane by '-amine'. The position of —NH_2 is indicated by the number. Secondary and tertiary amines are names as *N*-substituted derivatives of primary amines. For example,



$$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3$$

2-propanamine



$$CH_3-\underset{HN-CH_3}{\underset{|}{CH}}-CH_3$$

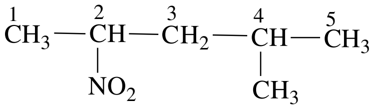
N-methyl-2-propanamine

12. Nomenclature of cyanides or nitriles

These are named as alkanenitriles. Numebring includes the nitrile carbon atom. For example, $\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CN}$ is butanenitrile.

13. Nomenclature of nitro compounds

These are named by adding prefix 'nitro-' to the parent alkane. For example,

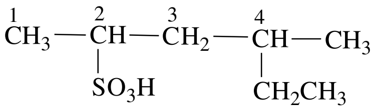


$$\overset{1}{CH_3}-\underset{NO_2}{\underset{|}{\overset{2}{C}H}}-\overset{3}{CH_2}-\underset{CH_3}{\underset{|}{\overset{4}{C}H}}-\overset{5}{CH_3}$$

is 4-methyl-2-nitropentane.

14. Nomenclature of sulphonic acids

These are named by adding suffix '-sulphonic acid' to the alkane name. For example,



$$\overset{1}{CH_3}-\underset{SO_3H}{\underset{|}{\overset{2}{C}H}}-\overset{3}{CH_2}-\underset{CH_2CH_3}{\underset{|}{\overset{4}{C}H}}-CH_3$$

is 4-methyl-2-hexanesulphonic acid.

15. Nomenclature of polyfunctional groups

In such compounds, one functional group is taken as the principal functional group and others are treated as substituents. The order of preference of principal functional group is as follows.

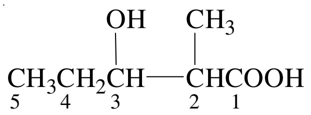
Carboxylic acid, sulphonic acid, ester, acid, halide, amide, nitrile, aldehyde, ketone, alcohol, amine, ether, alkene.

The compounds containing both double and triple bonds are called enynes (and not ynenes).

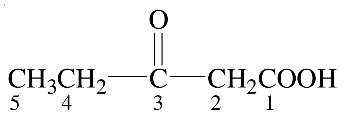
The prefixes used for the substituents are as follows.

—Cl ,	—Br ,	—I ,	—R ,	—OR ,	—OH ,	—NH_2 ,	—CO— ,	—NO_2 ,	—NO ,	—CN
chloro	bromo	iodo	alkyl	alkoxy	hydroxy	amino	oxo	nitro	nitroso	cyano

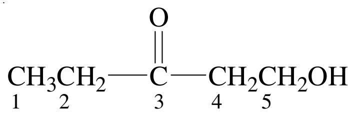
A few examples of compounds containing more than one functional group are given in the following.

1. 
$\underset{5}{CH_3}\underset{4}{CH_2}\underset{3}{\overset{OH}{\overset{|}{C}H}}-\underset{2}{\overset{CH_3}{\overset{|}{C}H}}\underset{1}{COOH}$

3-hydroxy-2-methylpentanoic acid

2. 
$\underset{5}{CH_3}\underset{4}{CH_2}-\underset{3}{\overset{O}{\overset{\|}{C}}}-\underset{2}{CH_2}\underset{1}{COOH}$

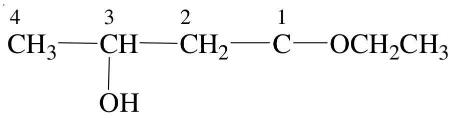
3-oxopentanoic acid

3. 
$\underset{1}{CH_3}\underset{2}{CH_2}-\underset{3}{\overset{O}{\overset{\|}{C}}}-\underset{4}{CH_2}\underset{5}{CH_2OH}$

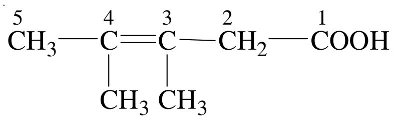
5-hydroxy-3-pentanone

4. $\underset{1}{CH_3}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{C}\equiv\underset{5}{CH}$

2-penten-4-yne

5. 
$\overset{4}{CH_3}-\overset{3}{\underset{\underset{OH}{|}}{CH}}-\overset{2}{CH_2}-\overset{1}{C}-OCH_2CH_3$

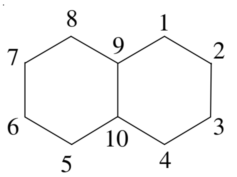
ethyl-3-hydroxybytanoate

6. 
$\overset{5}{CH_3}-\overset{4}{\underset{\underset{CH_3}{|}}{C}}=\overset{3}{\underset{\underset{CH_3}{|}}{C}}-\overset{2}{CH_2}-\overset{1}{COOH}$

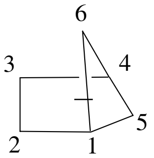
3, 4-dimethylpent-3-penten-1-yne

16. Nomenclature of polycyclic rings of carbon atoms

The prefix 'bicyclo-' is combined with a pair of brackets enclosing numbers separated by periods, which is followed by the name of the alkane whose number of C's equals to the numbers of C's in the rings. The bracketed numbers show the number of carbon atoms in each cycle and are cited in decreasing order. For example,

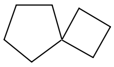


Bicyclo[4.4.0]decane



Bicyclo[2.1.1] hexane

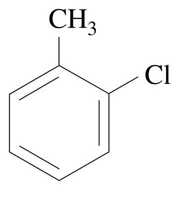
The numbering of bicycles start at one bridgehead C and move along the longest chain to the next bridgehead C. This is continued to the next longest chain to return to the first bridgehead C. The shortest ring is numbered in the last. For decalines, the numbering starts with C next to bridgehead and is so chosen to have the lowest number to the substituent, polycyclic that share only one C is called spirane. For example,

 is spiro[4.3]octane.

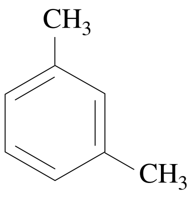
17. Nomenclature of benzene derivatives

Three different schemes are used in naming benzene derivatives. These are

(a) *When substitution is in the benzene ring* These are considered as benzene derivatives. For example,

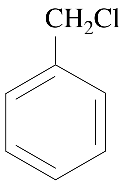


1-chloro-2-methylbenzene

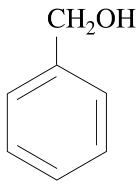


1, 3-dimethylbenzene

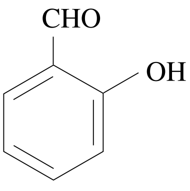
(b) *When substitution is in one or more carbon attached to the ring* These are considered as phenyl substituted aliphatic compounds. For example,



phenylchloromethane

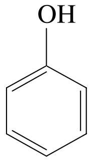


phenylmethanol

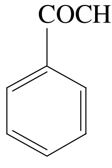


2-hydroxyphenyl-methanal

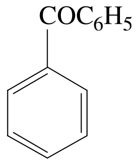
(c) *Some derivatives are named as per their common names.* For example,



phenol



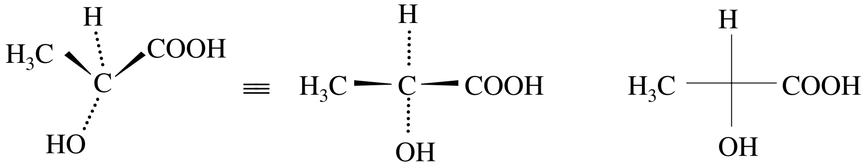
acetophenone



benzophenone

SUPPLEMENTARY MATERIAL

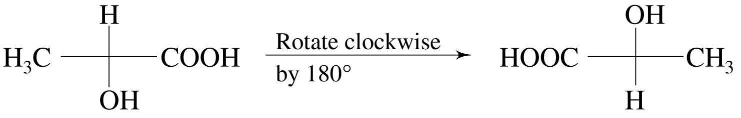
Fischer Projections Fischer projection is a standard method to depict a three-dimensional arrangement of atoms on a flat page. In this method, a tetrahedral carbon is represented by two crossed lines. The horizontal lines represent bonds coming out of the page, and the vertical lines represent bonds going into the page. For example,



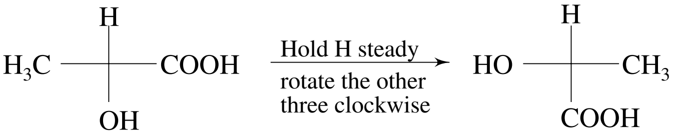
(+)-Lactic acid

Many different Fischer projections can be drawn for a given molecule. Quite often, it is necessary to compare two different projections to see if they represent the same or different enantiomers. To test this, a Fischer projection may be moved in the following two ways without changing the meaning of the projection.

1. Rotating the Fischer projection by 180° (and not by 90° or 270°).



2. Hold any one group steady and rotate the other three in either a clockwise or a counterclockwise direction.



Sawhorse Projections In a sawhorse projection, C—C bond in the two adjacent carbon atoms is displayed by a larger diagonal line which is taken to be the plane of the paper and the substituents attached to these carbon atoms are projected above and below the plane by small lines. For example, the sawhorse projection of $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3$ is shown in Fig. 19.8a

Since there is a free rotation about $\overset{2}{C}—\overset{3}{C}$ bond, one can draw other conformations of the molecule by rotating the substituents of one of the carbon atoms clockwise or anticlockwise. The conformation shown in Fig. 19.8a is the staggered form of butane, its eclipsed form will be represented as shown in Fig. 19.8b.

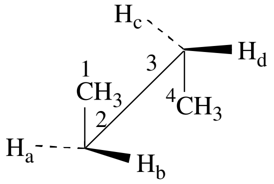


Fig. 19.8a

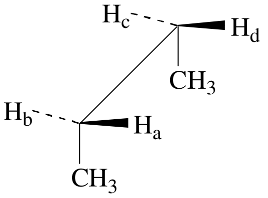


Fig. 19.8b

Newman Projections In a Newman projection, the two C atoms in the molecule CH_3—CH_3 (or a molecule in which H atom(s) is(are) replaced by any other substituent(s)) are represented by the superimposed circles (in fact, only one of the circles will be visible). The centre of the circle represent the front carbon atom and the circumference of the circle represents the back carbon atom. The substituents attached to these carbon atoms are projected into a vertical plane, the bonds thus appear as the spokes of a wheel at angles of 120° for each carbon, the spokes for the rear carbon being displaced by an angle of 60° with respect to the bonds on the front carbon. Thus, the molecule CH_3—CH_3 is represented as shown in Fig. 19.9a.

Since there is a free rotation about C—C bond, one can draw other conformations by rotating spokes of each carbon atom clockwise or anticlockwise. The conformation shown in Fig. 19.9a is the staggered form of ethane, its clipsed form will be represented as shown in Figs. 19.9b.

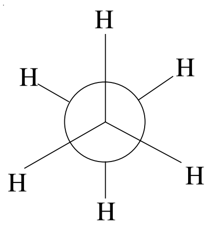


Fig. 19.9a

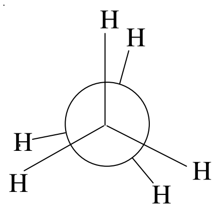
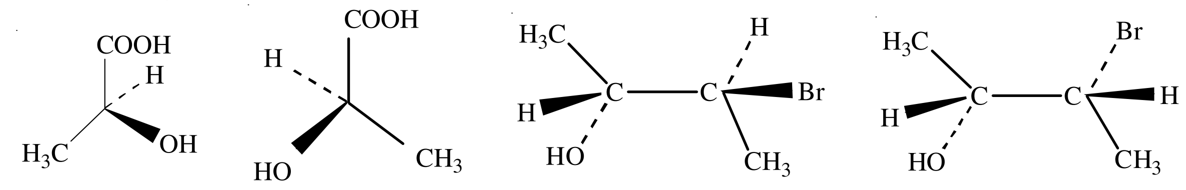


Fig. 19.9b

Flying Wedge Projection In a flying wedge projection, two bonds of a carbon atom are shown in the plane of the paper, third and fourth bonds are shown as the projections in front and back of the paper, respectively. The bonds in the plane of paper are shown by ordinary lines (——), the bond above the plane is projected as solid cone (▬) and the bond below the plane is projected as broken line (----). The flying-wedge projections of lactic acid and 3-bromobutan-2-ol are shown in Fig. 19.10.



(+)–Lactic acid (–)–Lactic acid

Fig. 19.10

Inter-Conversion of Projections

Fischer to Sawhorse to Newman and Vice Versa The conversion of Fischer projection to Sawhorse projection gives the eclipsed form of the latter. The last carbon atom in Fischer projection (counted from the top) becomes the front carbon in Sawhorse projection. The conversion of Sawhorse to Newman projection is straightforward and is shown in Fig. 19.11.

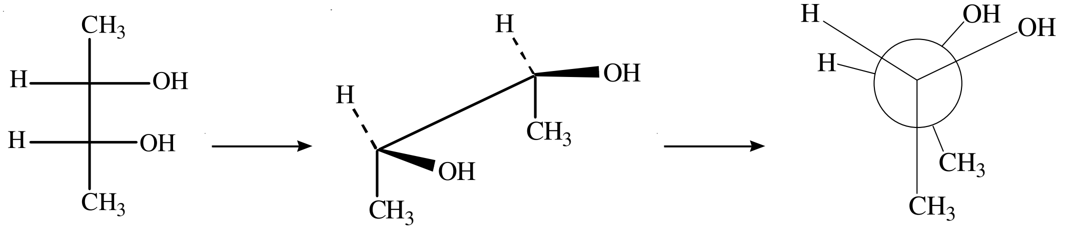
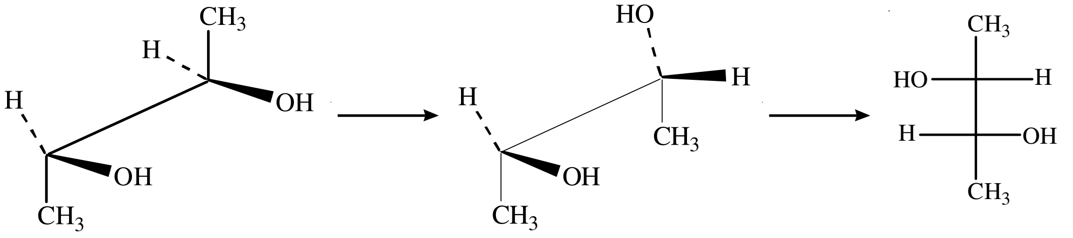


Fig. 19.11

To convert staggered form of Sawhorse (or Newman) projection to Fisher projection involves firstly the conversion of staggered form of Sawhorse or Newman) projection to its eclipsed form and then to Fischer projection. This conversion is shown in Fig. 19.12.



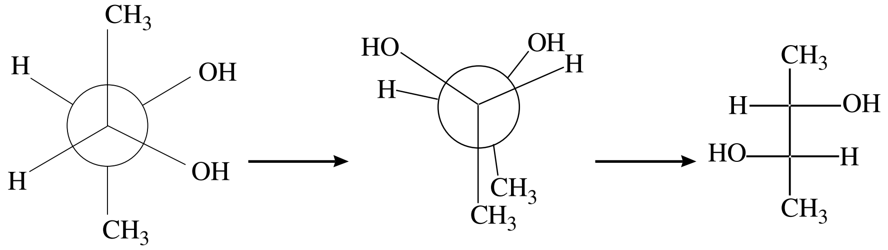


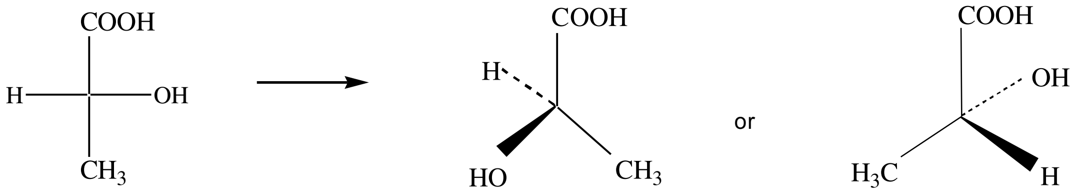
Fig. 19.12

Note: Whether the rotation is carried on the front or rear carbon, both lead to the same configuration of Fischer projection.

Comment on the Eclipsed Form of Newmann Projection If the like substituents occupy eclipsed positions then the conformation represents *meso* compound.

Fischer Projection to Flying Wedge Projection and Vice Versa

In this conversion, the vertical bonds in Fischer projection are considered to be in the plane of the paper and the horizontal bonds are projected in front and back of the paper. One of the vertical bond is bent on the right (or left) side and the horizontal bond on the same side is projected in front of the paper and the other on the back of the paper. For example, the conversion of (–) lactic acid is shown in Fig. 19.13.



bending of C—CH_3 bond to the right, C—OH bond is projected in front of the paper

bending of C—CH_3 bond to the left, C—H bond is projected in front of the paper

Fig. 19.13

In the reverse conversion (i.e. flying wedge projection to Fischer projection), the bent bond in the plane of the paper is made vertical by bending it to left (or right) and the bonds in front and back of the plane are made horizontal projected to right (or left) and left (or right), respectively.

SEQUENCE RULES FOR SPECIFYING *R* AND *S* CONFIGURATIONS

To specify the configuration of chiral carbon, Cahn-Ingold-Prelog sequence rules are used. These are as follows:

1. Rank the atoms directly attached to the chiral centre in order of decreasing atomic number. The group with highest atomic number is ranked first; the group with lowest atomic number is ranked fourth.
2. If a decision about priority cannot be reached by applying rule 1, work outward to the first point of difference.
3. Multiple-bonded atoms are considered as if they were an equivalent number of single-bonded atoms.

In the stereochemical configuration around the chiral carbon, the molecule is oriented so as to have the group of lowest priority directly back, away from the viewer. On looking at the three remaining substituents, the configuration is assigned as follows:

1. If the direction of travel from highest to second-highest to third-highest substituent ($1 \rightarrow 2 \rightarrow 3$) is **clockwise**, the chiral carbon has ***R* configuration**.

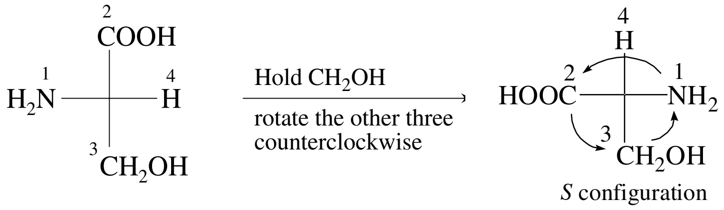
2. If the direction of travel from highest to second-highest to third-highest substituent ($1 \rightarrow 2 \rightarrow 3$) is **counterclockwise**, the chiral carbon has ***S* configuration**. The prefixes *R* and *S* are Latin words: *R* from *rectus* (right) and *S* from *sinister* (left).

Assignment of *R*, *S* Configurations to Fischer Projections

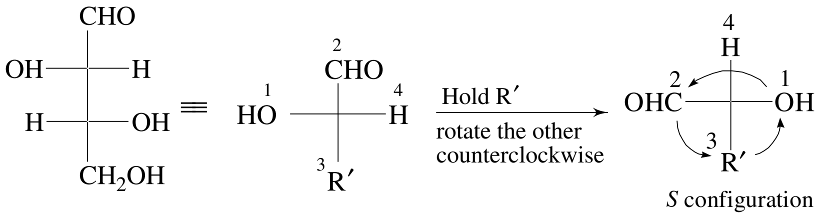
R, *S* designation to Fischer projections can be carried out using the following three steps:

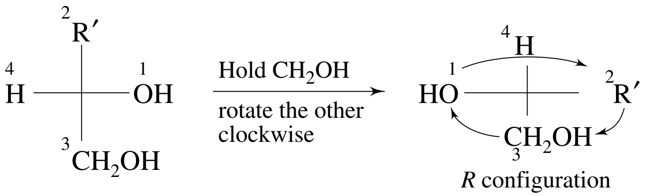
1. Assign priorities to the four substituents.
2. Perform one of the allowed motions to place the group of lowest (fourth) priority at the top (or bottom) of the Fischer projection.

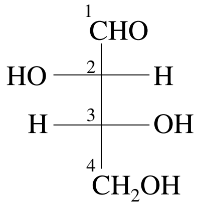
3. Determine the direction of rotation in going from priority 1 to 2 to 3 and assign *R* or *S* configuration. For example.



For a molecule containing more than one chiral carbon atoms, the above procedure may be applied to each chiral atom one by one. For example,





Thus, the molecule  is (2*S*,3*R*)-2,3,4-trihydroxybutanal.

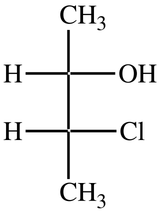
The relationships between enantiomers and diastereomers are as follows:

- Enantiomers have opposite configurations around all chiral centres.
- Diastereomers have the same configurations at one or more, but opposite configurations at the other chiral centres.

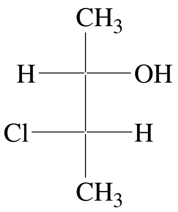
The above relationship is illustrated in the Table below for molecules having two chiral carbon atoms:

Stereoisomer	*Enantiomer*	*Diastereomers*
(2*R*, 3*R*)	(2*S*, 3*S*)	(2*R*, 3*S*); (2*S*, 3*R*)
(2*S*, 3*S*)	(2*R*, 3*R*)	(2*R*, 3*S*); (2*S*, 3*R*)
(2*R*, 3*S*)	(2*S*, 3*R*)	(2*R*, 3*R*); (2*S*, 3*S*)
(2*S*, 3*R*)	(2*R*, 3*S*)	(2*R*, 3*R*); (2*S*, 3*S*)

Erythro and Threo Configurations The terms *erythro* and *threo* are used to describe diastereomers of two adjacent chiral C's when both C's have two sets of identical ligands. If the third different ligands are on the same side of Fischer projection, they are said to have *erythro* configuration. If they are on different side, the configuration is said to be threo configuration.



erythro

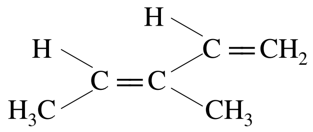


threo

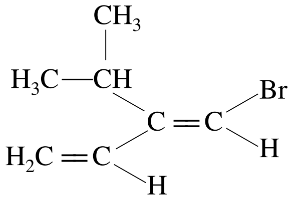
Sequence Rules for *E*, *Z* Designation of an Alkene

To denote the geometry of trisubstituted and tetasubstituted double bonds, *E*, *Z* system of nomenclature has been proposed.

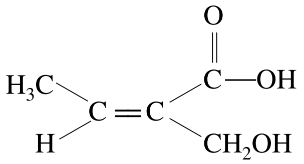
The substitutents attached to each carbon of double bond are ranked according to the Cahn-Ingold-Prelog sequence rules. If the groups of higher priority in the two alkene carbons are on the same side of the double bond, the alkene is designated as *Z* (from German word *Zusammen*, 'together'). If the higher-priority groups are on opposite sides, the alkene is designated *E* (from German word *entgegen*, 'opposite'). A few examples are.



(*E*) -3-methyl-1, 3-pentadiene



(*E*) -1-bromo-2-isopropyl-1, 3-butadiene



(*Z*) -2-hydroxymethyl-2-butenoic acid

Straight Objective Type

Bond Length

1. Molecule in which the distance between the two adjacent carbon atoms is largest is
(a) ethane (b) ethene (c) ethyne (d) benzene (1981)

2. The compound with no dipole moment is
(a) methyl chloride (c) carbon tetrachloride (c) methylene chloride (c) chloroform (1982)

3. The C—H bond distance is the longest in
(a) C_2H_2 (b) C_2H_4 (c) C_2H_6 (d) $C_2H_2Br_2$ (1989)

4. The number of sigma and pi bonds in 1-butene-3-yne are
(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi (c) 8 sigma and 2 pi (d) 6 sigma and 4 pi (1989)

5. Which of the following orders regarding the C—H bond distance in CH_4, C_2H_4 and C_2H_2 is correct?
(a) $CH_4 > C_2H_4 > C_2H_2$ (b) $CH_4 < C_2H_4 < C_2H_2$ (c) $CH_4 > C_2H_4 < C_2H_2$ (c) $CH_4 < C_2H_4 > C_2H_2$

Resonance

6. Which of the following statements regarding the concept of resonance is **not** correct?
(a) The different resonating structures of a molecule have fixed arrangement of atomic nuclei
(b) The different resonating structures differ in the arrangement of electrons
(c) None of the individual resonating structures explains the various characteristics of the molecule
(d) The hybrid structure has equal contribution from all the resonating structures

7. Which of the following statements is **not** correct?
(a) The energy of hybrid structure is always less than that of any resonating structure
(b) The resonance energy is the difference between the enthalpies of formation of the molecule and the resonating structure having maxium energy
(c) Kekule's structures have larger contribution than Dewar's structures in the hybrid structure of benzene
(d) All the C—C bond distances in benzene are equal to 139 pm

Hybridization

8. The compound 1,2-butadiene has
(a) only sp hybridized carbon atoms (b) only sp^2 hybridized carbon atoms
(c) both sp and sp^2 hybridized carbon atoms (d) sp, sp^2 and sp^3 hybridized carbon atoms (1983)

9. The bond between carbon atom (1) and carbon atom (2) in compound $N{\equiv}\underset{1}{C}{-}\underset{2}{CH}{=}CH_2$ involves respectively the hybrid orbitals
(a) sp^2 and sp^2 (b) sp^3 and sp (c) sp and sp^2 (d) sp and sp (1987)

10. The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane, respectively, will be about
(a) 120° and 109.5° (b) 109.5° and 90° (c) 90° and 109.5° (d) 109.5° and 120° (1988)

11. The compound in which $\dot{C}$ uses its sp^3 hybrid orbitals for bond formation is
(a) $H\dot{C}OOH$ (b) $(H_2N)_2\dot{C}O$ (c) $(CH_3)_3\dot{C}OH$ (d) $CH_3\dot{C}HO$ (1989)

12. The hybridization of carbon atoms in C—C single bond in $HC{\equiv}C{-}CH{=}CH_2$ is
(a) sp^3–sp^3 (c) sp^2–sp^3 (c) sp–sp^2 (d) sp^3–sp (1991)

13. Which of the following orders regarding the size of hybrid orbital of carbon is correct?
(a) $sp > sp^2 > sp^3$ (b) $sp < sp^2 < sp^3$ (c) $sp > sp^2 < sp^3$ (d) $sp < sp^2 > sp^3$

14. Which of the following orders regarding the electronegativity of hybrid orbital of carbon is correct?
(a) $sp > sp^2 > sp^3$ (b) $sp < sp^2 < sp^3$ (c) $sp > sp^2 < sp^3$ (d) $sp < sp^2 > sp^3$

15. Which of the following statements regarding the molecule $CH_2{=}C{=}CH_2$ is not correct?
(a) Both the two π-bonds are present in the same plane
(b) The central carbon atom is sp hybridized while the terminal atoms are sp^2 hybridized
(c) The molecule is linear
(d) The molecule contains six σ bonds and two π bonds

16. In the compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the $\overset{2}{C}-\overset{3}{C}$ bond is of the type
(a) sp-sp^2 (b) sp^3-sp^3 (c) sp-sp^3 (d) sp^2-sp^3 (1999)

17. Which of the following molecules represents the hybridization sp^2, sp^2, sp, sp from left to right atoms?
(a) $H_2C{=}CH{-}C{\equiv}CH$ (b) $HC{\equiv}C{-}C{\equiv}CH$
(c) $H_3C{-}CH{=}CH{-}CH_3$ (d) $H_2C{=}CH{-}CH{=}CH_2$ (2003)

Isomerism

18. The compound which is not isomeric with diethyl ether is
(a) *n*-propyl methyl ether (b) 1-butanol (c) 2-methyl-2-propanol (d) butanone (1981)

19. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is
(a) 2 (b) 3 (c) 4 (c) 5 (1982)

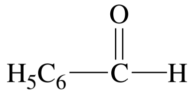
20. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?
(a) 2-Butene (b) 2-Butyne (c) 2-Butanol (d) Butanal (1983)

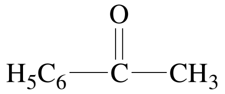
21. If two compounds have the same empirical formula but different molecular formulae they must have
(a) different percentage composition (c) different molar mass
(c) same viscosity (d) same vapour density (1987)

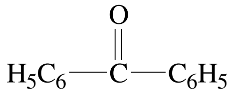
22. The number of isomers of C_6H_{14} is
(a) 4 (b) 5 (c) 6 (d) 7 (1987)

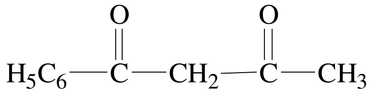
23. The number of structural and configurational isomers of a bromo compound C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively, are
(a) 1 and 2 (b) 2 and 4 (c) 4 and 2 (d) 2 and 1 (1988)

24. Keto-enol tautomerism is observed in

(a) 
$H_5C_6-\overset{O}{\overset{\|}{C}}-H$

(b) 
$H_5C_6-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 
$H_5C_6-\overset{O}{\overset{\|}{C}}-C_6H_5$

(d) 
$H_5C_6-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (1988)

25. The number of isomers for the compound with molecular formula $C_2BrClFI$ is
(a) 3 (b) 4 (c) 5 (d) 6 (2001)

26. The enolic form of acetone contains
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs (b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(c) 10 sigma bonds, 1 pi bond and 1 lone pair (d) 9 sigma bonds, 2 pi bonds and 1 lone pair
(1990)

27. Isomers which can be interconverted through rotation around a single bond are
(a) conformers (b) diastereomers (c) enantiomers (d) positional isomers
(1992)

28. 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 (2003)

29. Monochlorination of 2-methylbutane produces
(a) no optically active isomers (b) two optically active isomers
(c) four optically active isomers (d) six optically active isomers (2004)

30. The number of stereoisomers obtained by bromination of *trans*-2-butene is
(a) 1 (b) 2 (c) 3 (d) 4 (2007)

31. The number of structural isomers for C_6H_{14} is
(a) 3 (b) 4 (c) 5 (d) 6 (2007)

32. Isomers are the compounds having the
(a) same molecular formula but different structural formulae
(b) same structural formula but different molecular formulae
(c) same chemical properties but different physical properties
(d) same physical properties but different chemical properties

33. The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol^{-1}) is
(a) two (b) three (c) four (d) six

34. 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 are optically inactive
(c) A *meso* compound has molecules which are superimposable on their mirror images even though they contain chiral centres
(d) A *meso* compound is optically inactive because the rotation caused by any molecule is cancelled by an equal and opposite rotation caused by another molecule that is the mirror image of the first

35. The terms stereoisomers, enantiomers and diastereomers will refer
(a) only to configurational isomers including geometric isomers
(b) only to conformational isomers
(c) to both configurational as well as conformational isomers
(d) to neither configuration nor conformational isomers

36. The two enantiomers of a compound can be separated by
(a) fractional distillation (c) fractional crystallization
(c) chromatographic techniques (d) the use of a suitable optically active reagent

37. The two enantiomers of a compound have
(a) different direction of rotation but the same amount of rotation
(b) same direction of rotation but different amount of rotation
(c) same direction of rotation as well same amount of rotation
(d) different direction of rotation as well as different amount of rotation

38. Which of the following statements is correct?
(a) The two enantiomers of a compound are diastereomers
(b) The two diastereomers of a compound are enantiomers
(c) The two diastereomers have identical physical properties
(d) The two diastereomers have similar chemical properties but may differ in the rates of reaction

39. The compound 2, 3–dichlorobutane has
(a) four stereoisomers
(b) two pairs of enantiomers
(c) one pair of enantiomers and one *meso* compound
(d) one pair of enantiomers and two *meso* compounds

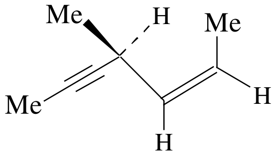
40. Which of the following compounds shows optical isomerism?
(a) $CH_3CHOHCOOH$ (b) $CH_3CH(CH_3)COOH$ (c) $CH_3CH(CH_3)CH_2OH$ (d) $CH_3CH(CH_3)CH_2Cl$

41. Mesotartaric acid and d-tartaric acid are
(a) position isomers (b) enantiomers (c) diastereomers (c) racemic mixture

42. Mesotartaric acid has
(a) a centre of symmetry (b) a plane of symmetry
(c) an axis of symmetry (d) an angle of symmetry

43. Racemic tartaric acid is optically inactive due to
(a) internal compensation (b) external compensation
(c) loss of asymmetric centre (d) a steric hindrance

44. Which of the following statements is **not** correct?
(a) Molecules that are superimposable on their mirror images are chiral
(b) Molecule that are not superimposable on their mirror images are chiral
(c) A compound whose molecules are chiral can exist as enantiomers
(d) A compound whose molecules are achiral cannot exist as enantiomers

45. Hydrogenation of the compound  in the presence of poisoned palladium catalyst gives

(a) an optically active compound (b) an optically inactive compound
(c) a racemic mixture (d) a diastereomeric mixture (2001)

46. Which of the following compounds exhibits stereoisomerism?
(a) 2-methylbutene-1 (b) 3-methylbutyne-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid (2002)

47. For an optically active compound, which of the following requirements is necessary?
(a) A double bond (b) Presence of one chiral atom
(c) Presence of two chiral atoms (d) Presence of plane of symmetry

48. A molecule is said to be chiral if it
(a) contains a centre of symmetry (b) contains a plane of symmetry
(c) cannot be superimposed on its mirror images (d) exists as *cis* and *trans*-forms

49. Which of the following compounds is optically active?
(a) 1-Bromobutane (b) 2-Bromobutane
(c) 1-Bromo-2-methylpropane (d) 2-Bromo-2-methylpropane

50. The number of isomers of C_7H_{16} is
(a) 5 (b) 7 (c) 9 (d) 11

51. The compounds $CH_3—CH{=}CH—CH_3$ and $CH_3—CH_2—CH{=}CH_2$
(a) are tautomers
(b) are position isomers
(c) contain same number of $sp^3–sp^3$, $sp^3–sp^2$ and $sp^2–sp^2$ carbon-carbon bonds
(d) exist together in dynamic equilibrium

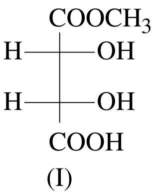
52. The number of different substitution products possible when ethane is allowed to react with bromine in sunlight is
(a) 7 (b) 8 (c) 9 (d) 10

53. The number of isomers of $C_3H_5Br_3$ is
(a) 2 (b) 3 (c) 4 (d) 5

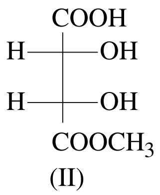
54. The number of optically active compounds in the isomers of $C_3H_5Br_3$ is
(a) 1 (b) 2 (c) 3 (d) 4

55. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is
(a) 2 (b) 3 (c) 4 (d) 1 (1997)

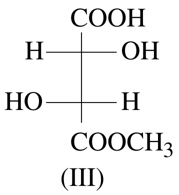
56. The correct statements about the compounds I, II and III



(I)



(II)



(III)

is

(a) I and II are identical (b) I and II are diastereomers
(c) I and III are enantiomers (d) I and II are enantiomers (1997)

57. How many optically active stereoisomers are possible for butane-2, 3-diol?
(a) 1 (b) 2 (c) 3 (d) 4 (1997)

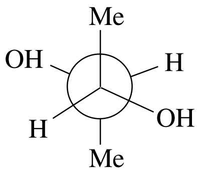
58. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive
(a) optical rotation and is derived from D-glucose
(b) pH in organic solvent
(c) optical rotation is derived from D-(+)-glyceraldehyde
(d) optical rotation when substituted by deuterium (1999)

59. A solution of (+)-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 (1999)

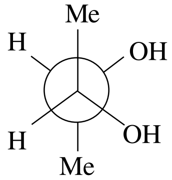
60. Which of the following compounds will exhibit geometrical isomerism?
(a) 1-Phenyl-2-butene (b) 3-Phenyl-1-butene (c) 2-Phenyl-1-butene (d) 1,1-Diphenyl-1-propene (2000)

61. The compounds $CH_2{=}CHOH$ and CH_3CHO are
(a) metamers (b) chain isomers (c) tautomers (d) functional isomers

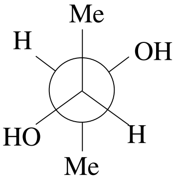
62. Given are the four Newmann projections of 2, 3-butandiol.



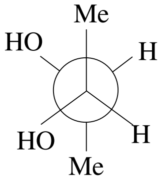
(I)



(II)



(III)



(IV)

Amongst these projections, the structures representing meso-2, 3-butanediol is/are
(a) (I) and (II) (b) (I) and (III) (c) (II) and (III) (d) (II) and (IV)

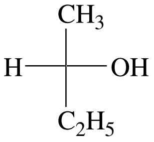
63. The number of stereoisomers of methylcyclopropane is
(a) zero (b) one (c) two (d) three

64. The number of stereoisomers of 1,2-dimethylcyclopropane is
(a) one (b) two (c) three (d) four

Supplementary Materials

65. The correct decreasing priority of ligands —$CH(OH)CH_3$, —OH, —COOH and—CH_2OH in absolute configuration of an enantiomer is
(a) $CH(OH)CH_3 > OH > COOH > CH_2OH$ (b) $OH > CH(OH)CH_3 > CH_2OH > COOH$
(c) $OH > COOH > CH(OH)CH_3 > CH_2OH$ (d) $COOH > OH > CH(OH)CH_3 > CH_2OH$

66. The correct decreasing priority of ligands —NO_2, —C≡N, —NH_2 and —CH_2NH_2 in absolute configuration of an enantiomer is
(a) $NO_2 > NH_2 > C{\equiv}N > CH_2NH_2$ (b) $NO_2 > C{\equiv}N > NH_2 > CH_2NH_2$
(c) $NH_2 > NO_2 > C{\equiv}N > CH_2NH_2$ (d) $NH_2 > NO_2 > CH_2NH_2 > C{\equiv}N$

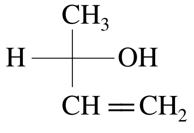
67. Which of the following operations on the Fischer formula  $H-\overset{CH_3}{\underset{C_2H_5}{C}}-OH$ does not change its absolute configuration?
(a) Exchanging ligands across the horizontal bond
(b) Exchanging ligands across the vertical bond
(c) Exchanging ligands across the horizontal bond and also across the vertical bond
(d) Exchanging a vertical and horizontal ligand.

68. Which of the following switching ligands or rotating Fischer structures changes its absolute configuration?
(a) An even number of switches
(b) An odd number of switches

(c) Rotating the Fischer projection by 180° in the plane of the paper
(d) Exchange ligands across the horizontal bond as well as those across the vertical bond

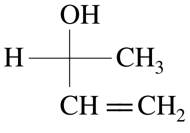
69. Which of the following rotating Fischer structure is allowed?
(a) A 180° horizontal rotation outside of the plane of the paper
(b) A 180° vertical rotation outside of the plane of the paper
(c) A 90° rotation in the plane of paper
(d) A 180° rotation in the plane of paper.

70. Which of the following combinations amongst the four Fischer projections represents the same absolute configuration?



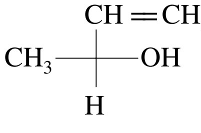
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(I)



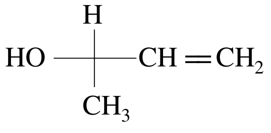
$$\begin{array}{ccc} & \mathrm{OH} & \\ \mathrm{H} & + & \mathrm{CH_3} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(II)



$$\begin{array}{ccc} & \mathrm{CH{=}CH_2} & \\ \mathrm{CH_3} & + & \mathrm{OH} \\ & \mathrm{H} & \end{array}$$

(III)

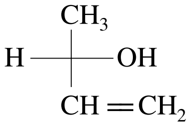


$$\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{HO} & + & \mathrm{CH{=}CH_2} \\ & \mathrm{CH_3} & \end{array}$$

(IV)

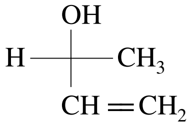
(a) (I) and (II) (b) (I) and (III) (c) (I) and (IV) (d) (II) and (III)

71. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?



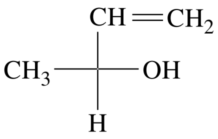
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(I)

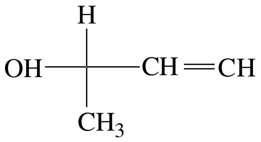


$$\begin{array}{ccc} & \mathrm{OH} & \\ \mathrm{H} & + & \mathrm{CH_3} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(II)



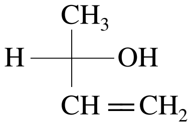
$$\begin{array}{ccc} & \mathrm{CH{=}CH_2} & \\ \mathrm{CH_3} & + & \mathrm{OH} \\ & \mathrm{H} & \end{array}$$



$$\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{OH} & + & \mathrm{CH{=}CH} \\ & \mathrm{CH_3} & \end{array}$$

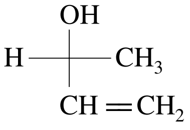
(a) (II) and (III) (b) (I) and (IV) (c) (II) and (IV) (d) (III) and (IV)

72. Which of the following combinations amongst the four Fischer projections represents the enantiomers?



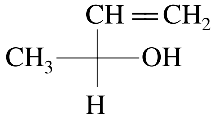
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(I)



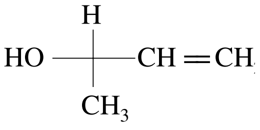
$$\begin{array}{ccc} & \mathrm{OH} & \\ \mathrm{H} & + & \mathrm{CH_3} \\ & \mathrm{CH{=}CH_2} & \end{array}$$

(II)



$$\begin{array}{ccc} & \mathrm{CH{=}CH_2} & \\ \mathrm{CH_3} & + & \mathrm{OH} \\ & \mathrm{H} & \end{array}$$

(III)



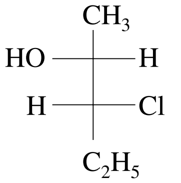
$$\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{HO} & + & \mathrm{CH{=}CH} \\ & \mathrm{CH_3} & \end{array}$$

(IV)

(a) (I) and (II) (b) (I) and (III) (c) (II) and (IV) (d) none

73. The number of pairs of enantiomers for the compound 3-chloro-2-pentanol is
(a) 1 (b) 2 (c) 3 (d) 4

74. The full name of the compound



$$\begin{array}{ccc} & \mathrm{CH_3} & \\ \mathrm{HO} & + & \mathrm{H} \\ \mathrm{H} & + & \mathrm{Cl} \\ & \mathrm{C_2H_5} & \end{array}$$

is

(a) (2*R*,3*R*)-3-chloro-2-pentanol (b) (2*R*,3*S*)-3-chloro-2-pentanol
(c) (2*S*,3*R*)-3-chloro-2-pentanol (d) (2*S*,3*S*)-3-chloro-2-pentanol

75. The number of stereoisomers for a compound having four different chiral centres is
(a) 2 (b) 4 (c) 8 (d) 16

76. The two enantiomers differ in
(a) their boiling and melting points. (b) their chemical properties towards achiral reagents
(c) their optical activities (d) their solubilities in a solvent.

77. The number of stereoisomers of 2,3-butanediol is
(a) 2 (b) 3 (c) 4 (d) 8

78. Which of the following statements for a *meso* compound is not correct?
(a) The *meso* compound has either a plane or a point of symmetry.
(b) The *meso* compound has at least one pair of similar stereocenters.
(c) The *meso* compound is achiral
(d) The *meso* compound is formed when equal amounts of two enantiomers are mixed.

79. The free radical monochlorination of butane gives

(a) (*R*)-2-chlorobutane only (b) (*S*)-2-chlorobutane only

(c) *meso*-2-chlorobutane only (d) *racemic*-2-chlorobutane

80. The free radical monochlorination of (*S*)-2-chlorobutane gives

(a) (*S*)-1,2-dichlorobutane (b) (*R*)-1,2-dichlorobutane

(c) (*R*)-1,3-dichlorobutane (d) (2*R*,3*R*)-2,3-dichlorobutane

81. Which of the following reactions involves the inversion of configuration?

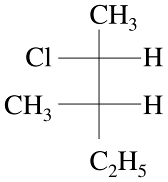
(a) $CH_3CH_2CH(OH)CH_2Br + OH^- \rightarrow CH_3CH_2CH(OH)CH_2OH + Br^-$

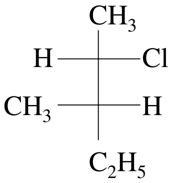
(b) $CH_3CH_2CH(OH)CH(CH_3)_2 + CH_3COCl \rightarrow CH_3CH_2CH(OCOCH_3)CH(CH_3)_2 + HCl$

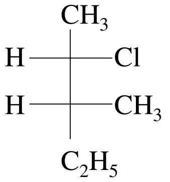
(c) $CH_3CH(NH_2)COOH + NaOH \rightarrow CH_3CH(NH_2)COO^-Na^+ + H_2O$

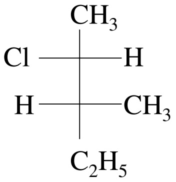
(d) $CH_3CH_2CH_2CH(Cl)CH_3 + OH^- \rightarrow CH_3CH_2CH_2CH(OH)CH_3 + Cl^-$

82. The structure of (2*S*,3*S*)-$CH_3CHClCH(CH_3)C_2H_5$ is

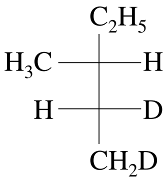
(a)


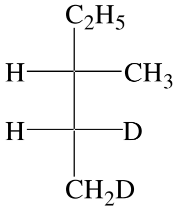
(b)


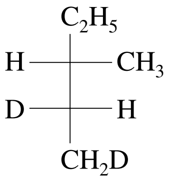
(c)


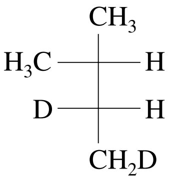
(d)


83. The structure of (2*R*,3*R*)-$C_2H_5CH(CH_3)CH(D)CH_2D$ is

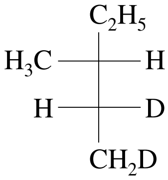
(a)


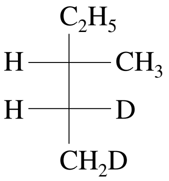
7 (b)


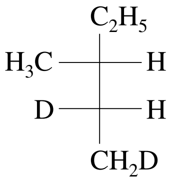
(c)


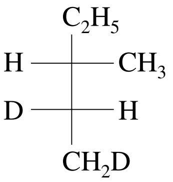
(d)


84. The structure of (2*R*,3*S*)-$C_2H_5CH(CH_3)CH(D)CH_2D$ is

(a)


(b)


(c)


(d)


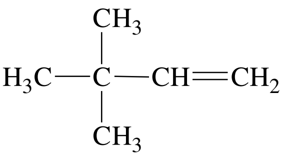
85. The number of stereoisomers formed when (*R*)-2-methyl-3-chlorobutane is further monochloriated is

(a) 2 (b) 3 (c) 4 (d) 5

86. The number of *meso* diastereomers of $C_6H_{12}Cl_2$ is

(a) 2 (b) 3 (c) 4 (d) 5

Nomenclature

87. The IUPAC name of the compound

$H_3C-C(CH_3)_2-CH{=}CH_2$
is

(a) 3, 3, 3–trimethyl–1–propene (b) 1, 1, 1–trimethyl–2–propene

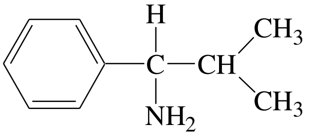
(c) 3,3–dimethyl–1–butene (d) 2,2–dimethyl–3–butene (1984)

88. The IUPAC name of the compound $CH_2{=}CH-CH(CH_3)_2$ is

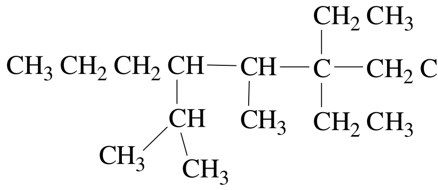
(a) 1, 1–dimethyl-2-propene (b) 2-vinylpropane

(c) 3-methyl-1-butene (d) 1-isopropylethene (1987)

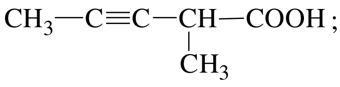
89. The compound which has one isopropyl group is
(a) 2, 2, 3, 3-tetramethylpentane (b) 2, 2-dimethylpentane
(c) 2, 2, 3-trimethylpentane (d) 2-methylpentane (1989)

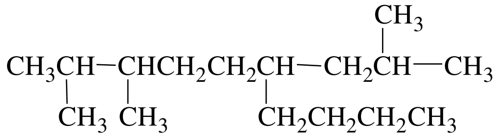
90. The IUPAC name of the compound  is

(a) 1-amino-1-phenyl-2-methylpropane (b) 1-amino-2-methyl-1-phenylpropane
(c) 2-methyl-1-amino-1-phenylpropane (d) 1-isopropyl-1-phenylmethyl amine

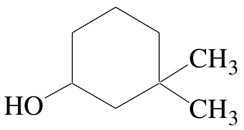
91. The IUPAC name of the compound  $CH_3CH_2CH_2\underset{\underset{CH_3\quad CH_3}{CH}}{CH}-\underset{CH_3}{CH}-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-CH_2CH_3$ is

(a) 3, 3,-diethyl-4-methyl-5-isopropyloctane (b) 3, 3-diethyl-5-isopropyl-4-methyloctane
(c) 4-isopropyl-5-methyl-6, 6-diethyloctane (c) 6, 6-diethyl-4-isopropyl-5-methyloctane

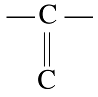
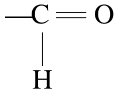
92. Which of the following compounds is wrongly named?
(a) $CH_3CH_2CH_2CH(CI)COOH$; 2-chloropentanoic acid
(b)  $CH_3-C\equiv C-\underset{CH_3}{CH}-COOH$; 2-methylhex-3-enoic acid
(c) $CH_3CH_2CH=CHCOCH_3$; Hex-3-en-2-one
(d) $CH_3CH(CH_3)CH_2CH_2CHO$; 4-methylpentanal

93. The IUPAC name of the compound  $CH_3\underset{CH_3}{CH}-\underset{CH_3}{CH}CH_2CH_2\underset{CH_2CH_2CH_2CH_3}{CH}-CH_2\overset{CH_3}{CH}-CH_3$ is

(a) 2,3,8-trimethyl-6-butylnonane (b) 6-butyl-2,3,8-trimetylnonane
(c) 2,3-dimethyl-6-(2-methylpropyl)decane (d) 5-(2-methylpropyl)-8,9-dimethyldecane

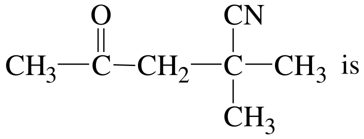
94. The IUPAC name of the compound  is
(a) 1, 1-dimethyl-3-hydroxycyclohexane (b) 3, 3-dimethyl-1-hydroxycyclohexane
(c) 2,2-dimethyl-1-cyclohexanol (d) 1, 1-dimethyl-3-cyclohexanol

95. Which of the following compounds represents 2,2,3-trimethylhexane?
(a) $CH_3C(CH_3)_2CH_2CH_2CH(CH_3)_2$ (b) $CH_3C(CH_3)_2CH_2CH(CH_3)CH_2CH_3$
(c) $CH_3C(CH_3)_2CH(CH_3)CH_2CH_2CH_3$ (d) $CH_3C(CH_3)_2CH_2C(CH_3)_2CH_3$

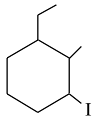
96. Which of the following is regarded as the principal functional group?
(a) $-C\equiv C-$ (b) $-OH$ (c)  $-\underset{\underset{C}{\|}}{C}-$ (d)  $-\underset{H}{C}=O$

97. Which of the following represents neopentyl alcohol?
(a) $CH_3CH(CH_3)CH_2CH_2OH$ (b) $(CH_3)_3CCH_2OH$
(c) $CH_3(CH_2)_3OH$ (d) $CH_3CH_2CH(OH)CH_3$

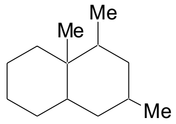
98. The IUPAC name of the compound $CH_3CH{=}CHCH{=}CHC{\equiv}CCH_3$ is
(a) 4, 6 - octadien - 2 - yne (b) 2, 4 - octadien - 6 - yne
(c) 2 - octyn - 4, 6 - diene (d) 6 - octyn - 2, 4 - diene

99. The IUPAC name of the compound  $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}}-CH_3$ is
(a) 4–cyano–4–methyl–2–oxopentane (b) 2–cyano–2–methyl–4–oxopentane
(c) 2, 2–dimethyl–4–oxopentanenitrile (d) 4–cyano–4–methyl–2–pentanone

100. The IUPAC name of $(C_2H_5)_2NCH_2CHClCOOH$ is
(a) 2–chloro–4–*N*–ethylpentanoic acid (b) 2–chloro–3–(*N*, *N*–diethylaminopropanoic acid)
(c) 2–chloro–2–oxodiethylamine (d) 2–chloro–2–carboxy–*N*–ethylethane

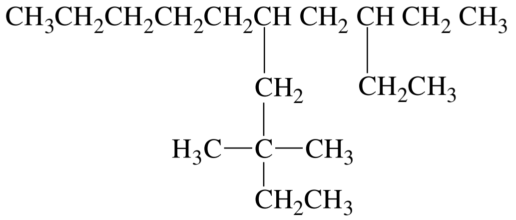
101. The IUPAC name of the compound  is

(a) 1-Iode-2-methyl-3-ethylcyclohexane (b) 1-methyl-2-ethyl-6-iodocyclohexane
(c) 1-Ethyl-2-methyl-3-iodocyclohexane (d) 1-Iodo-2-methyl-1-ethylcyclohexane

102. The IUPAC name of the compound  is

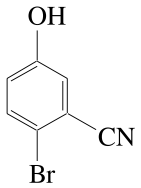
(a) 1,2,3-Trimethylbicyclo [4.4.0] decane (b) 1,8,10-Trimethylbicyclo [4.4.0] decane
(c) 1,3,9-Trimethylbicyclo [4.4.0] decane (d) 1,3,10-Trimethylbicyclo[4.4.0]decane

103. The IUPAC name of the compound



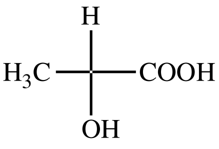
(a) 5-(2-ethylbutyl)-3,3-dimethyldecane (b) 5-(2,2-dimethylbutyl)-3-3-ethyldecane
(c) 6-(2,2-dimethylbutyl)-8-ethyldecane (d) 3,3-dimethyl-5-(2-ethylbutyl)decane

104. The IUPAC name of C_6H_5COCl is
(a) Benzal chloride (b) Benzyl chloride
(c) Benzoyl chloride (d) Phenylchloro ketone (2006)

105. The IUPAC name of the compound  is

(a) 4-Bromo-3-cyanophenol (b) 2-Bromo-5-hydroxybenzonitrile
(c) 2-cyano-4-hydroxybromobenzene (d) 6-Bromo-3-hydroxybenzonitrile (2009)

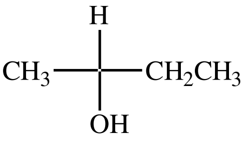
Multiple Correct Choice Type

1. Three dimensional structure of (+)-lactic acid is represented as  . In this structure

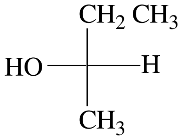
(a) CH_3 and COOH groups are coming out of the page.
(b) H and OH groups are coming out of the page.

(c) CH_3 and COOH groups are going into the page.
(d) H and OH groups are going into the page.

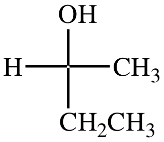
2. Amongst the following structures


$\begin{array}{c} H \\ CH_3 - C - CH_2CH_3 \\ OH \end{array}$

(I)


$\begin{array}{c} CH_2\,CH_3 \\ HO - C - H \\ CH_3 \end{array}$

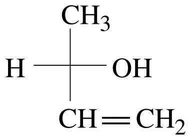
(II)


$\begin{array}{c} OH \\ H - C - CH_3 \\ CH_2CH_3 \end{array}$

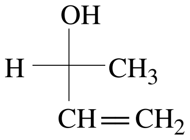
(III)

(a) the structures I and II are identical
(b) the structures I and II are different.
(c) the structures I and III are identical.
(d) the structures I and III are different.

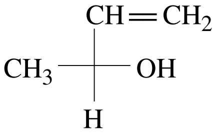
3. Which of the following statements for the structures


$\begin{array}{c} CH_3 \\ H - C - OH \\ CH{=}CH_2 \end{array}$

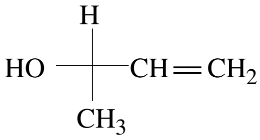
(A)


$\begin{array}{c} OH \\ H - C - CH_3 \\ CH{=}CH_2 \end{array}$

(B)


$\begin{array}{c} CH{=}CH_2 \\ CH_3 - C - OH \\ H \end{array}$

(C)


$\begin{array}{c} H \\ HO - C - CH{=}CH_2 \\ CH_3 \end{array}$

(D)

is/are correct?

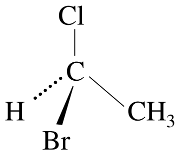
(a) The structures A and B are enantiomers.
(b) The structures A and C are identical.
(c) The structures A and D are enantiomers.
(d) The structures B and D are identical.

4. Which of the following statements is/are **not** correct?

(a) A compound with *S* configuration is the (–) enantiomer.
(b) An achiral compound can have chiral centres.
(c) An optically inactive a substance must be achiral.
(d) In chemical reactions the change from an *S* reactant to an *R* product always signals an inversion of configuration.

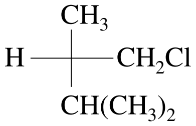
5. Which of the following statements are correct?

(a) The absolute configuration of the enantimomer



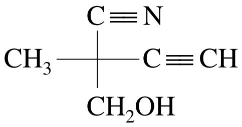
is *R*.

(b) The absolute configuration of the enantiomer


$\begin{array}{c} CH_3 \\ H - C - CH_2Cl \\ CH(CH_3)_2 \end{array}$

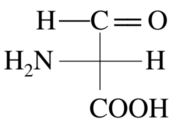
is *R*.

(c) The absolute configuration of the enantiomer


$\begin{array}{c} C{\equiv}N \\ CH_3 - C - C{\equiv}CH \\ CH_2OH \end{array}$

is *S*.

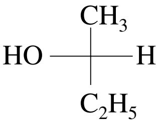
(d) The absolute configuration of the enantiomer


$\begin{array}{c} H{-}C{=}O \\ H_2N - C - H \\ COOH \end{array}$

is *S*.

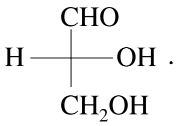
6. Which of the following statements are correct?

(a) The Fischer structure of (*R*)-2-butanol is


$\begin{array}{c} CH_3 \\ HO - C - H \\ C_2H_5 \end{array}$

.

(b) The Fischer sructure of (*S*)-glyceraldehyde is

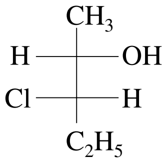

$\begin{array}{c} CHO \\ H - C - OH \\ CH_2OH \end{array}$

.

(c) The *R* configuration of an enantiomer is always dextrorotatory.
(d) The *R* and *S* configurations of a chiral molecule are enantiomers.

7. Which of the following statements are correct?

(a) The full name of the compound

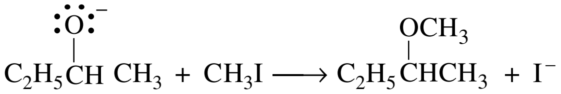


is (2*S*, 3*R*)-3-chloro-2-pentanol.

(b) The *cis*-1, 2-dimethylcyclopropane is a *meso* compound.
(c) The *trans*-1, 2-dimethylcyclopropane exists as a pair of enantiomers.
(d) The optically active 2-iodobutane is eventually converted into racemic mixture in the presence of I^-.

8. Which of the following staements are correct?

(a) The *R*/*S* designation of the product in the reaction



$$C_2H_5\overset{\overset{\cdot\cdot}{:O:}^-}{\overset{|}{C}}H\,CH_3 + CH_3I \longrightarrow C_2H_5\overset{OCH_3}{\overset{|}{C}}HCH_3 + I^-$$

is the same as that of the reactant.

(b) The *R*/*S* designation of the product in the reaction

$$C_3H_7CH(OH)CH{=\!=}CH_2 + H_2 \xrightarrow{Pt} C_3H_7CH(OH)CH_2CH_3$$

is the same as that of the reactant.

(c) If the replacement of I with ^{137}I in the reaction (*R*)-$CH_3CHIC_2H_5$ + $\xrightarrow{^{137}I^-}$ $CH_3CHIC_2H_5$
$\alpha_{obs} = -15.90°$ $\alpha_{obs} = -15.26°$
does not change the sign or value of the rotation, the percentage of the molecules which undergo inversion is about 2%.

(d) An optically inactive substance must be achiral.

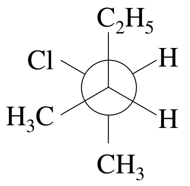
9. Which of the following statements are **not** correct?

(a) A compound with the *S* configuration is the (–) enantiomer.
(b) The number of enantiomer pairs in 2,3-butanediol is two.
(c) The number of stereoisomers of 2,3,4-trihydroxypentane is eight.
(d) The number of stereoisomers of 2,3,4,5-tetrahydroxyhexane is sixteen.

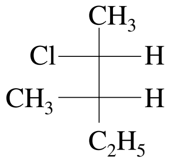
10. Which of the following statements are correct?

(a) The number of stereoisomers obtained by the free radical mono chlorination of (*R*)-2-methyl-3-chlorobutane is five.

(b) The Fischer structure of the Newman structure

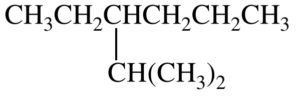


is



.

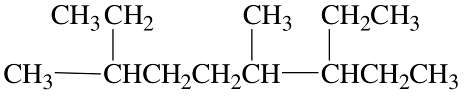
(c) The IUPAC name of



$$CH_3CH_2\underset{\underset{CH(CH_3)_2}{|}}{C}HCH_2CH_2CH_3$$

is 3-ethyl-2-methyhexane.

(d) The IUPAC name of the compound



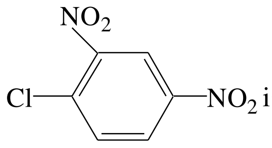
$$CH_3\text{—}\overset{\overset{CH_3CH_2}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}H\text{—}\overset{\overset{CH_2CH_3}{|}}{C}HCH_2CH_3$$

is 2,6-diethyl-5-methyloctane.

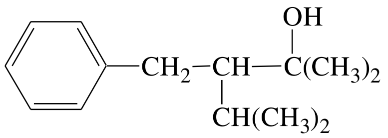
11. Which of the following statements are correct?

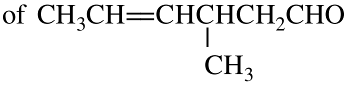
(a) The IUPAC name of the compound $CH_3CH{=}CHCH{=}CHC{\equiv}CCH_3$ is 2,4-octadien-6-yne.

(b) The IUPAC name of



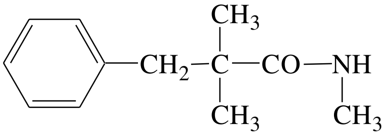
is 1-chloro-2,4-dinitrobenzane.

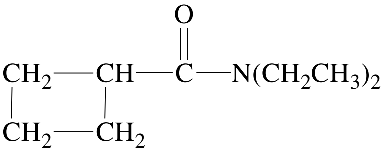
(c) The IUPAC name of  is 3-benzyl-2,4-dimethyl-2-pentanol.

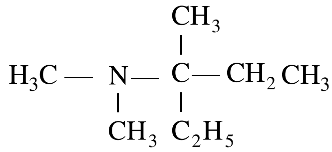
(d) The IUPAC name of  $CH_3CH{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CHO$ is 3-methyl-4-hexenal.

12. Which of the following statements are correct?

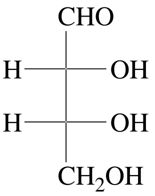
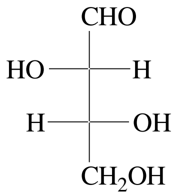
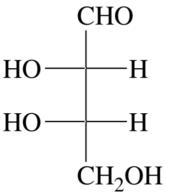
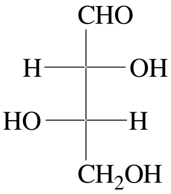
(a) The IUPAC name of $CH_3CH{=}CHCH{=}CHCOOH$ is 2,4-hexadienoic acid.

(b) The IUPAC name of the compound  is *N*-methyl-2,2-dimethyl-3-phenylpropanamide.

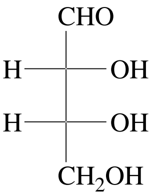
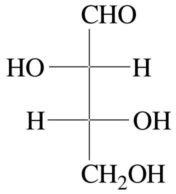
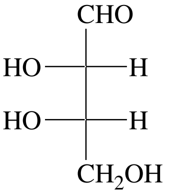
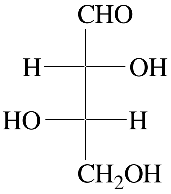
(c) The IUPAC name of the compound  is *N-N*-diethylcyclobutanecarboxamide.

(d) The IUPAC name of the compound  $H_3C-\underset{\displaystyle CH_3}{\underset{|}{N}}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle C_2H_5}{\underset{|}{C}}}}-CH_2CH_3$ is (*N*,*N*-dimethyl amino)-3-ethylbutane.

13. Which of the following structures represent *erythro* configurations?

(a) 
(b) 
(c) 
(d) 

14. Which of the following structures represent *threo* configurations?

(a) 
(b) 
(c) 
(d) 

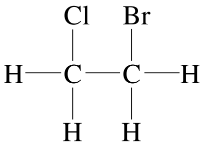
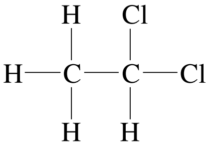
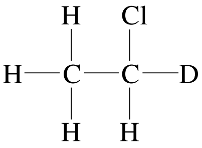
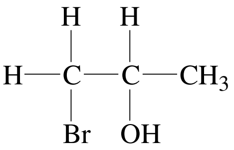
15. Resonating structure of a molecule should have

(a) identical arrangement of atoms (b) nearly the same energy content
(c) the same number of paired electrons (d) identical bonding (1984)

16. Only two isomeric monochloro derivatives are possible for

(a) *n*-butane (b) 2, 2-dimethylpentane
(c) benzene (d) 2-methylpropane (1986)

17. Which of the following have asymmetric carbon atom?

(a) 
(b) 
(c) 
(d) 

18. Which of the following statements is/are **not** correct for D-(+)-glyceraldehyde?
- (a) The symbol D indicates the dextrorotatory nature of the compound
- (b) The sign (+) indicates the dextrorotatory nature of the compound
- (c) The symbol D indicates that hydrogen atom lies left to the chiral centre in the Fischer projection diagram
- (d) The symbol D indicates that hydrogen atom lies right to the chiral centre in the Fisher projection diagram

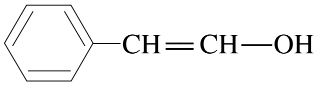
19. Which of the following statements is/are **not** correct?
- (a) A compound whose molecule has D configuration will always be dextrorotatory
- (b) A compound whose molecule has D configuration may be dextrotatory or laevorotatory
- (c) A compound whose molecule has L configuration will always be laevorotatory
- (d) A compound whose molecule has L configuration may be dextrorotatory or laevorotatory

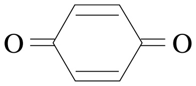
20. Which of the following compounds will show geometrical isomerism?

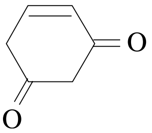
(a) 2-Butene (b) Propene (c) 1-Phenylpropene (d) 2-Methyl-2-butene

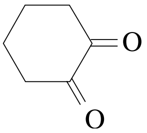
(1998)

21. Tautomerism is exhibited by

(a) 

(b) 

(c) 

(d) 

(1998)

22. Which of the following statements is/are **not** correct?
- (a) Metamerism belongs to the category of structural isomerism
- (b) Tautomeric structures are the resonating structures of a molecule
- (c) The violet colouration produced by a molecule with neutral ferric chloride solution indicates the presence of enolic group in the molecule
- (d) Geometrical isomerism is shown only by alkenes

23. Which of the following statements regarding diastereomers is/are **not** correct?
- (a) They have different physical properties.
- (b) They cannot be separated from each other by fractional crystallization.
- (c) They can be separated from each other by chromatographic methods.
- (d) They have identical chemical properties towards both chiral and achiral reagents.

24. Which of the following statements are correct?
- (a) sp hybrid orbital is more electronegative than sp^2 hybrid orbital.
- (b) The size of sp^3 hybrid orbital of carbon is smaller than that of sp hybrid orbital.
- (c) Amongst CH_4, C_2H_4 and C_2H_2, the carbon-hydrogen bond length is maximum in methane.
- (d) The resonating structures differ in the number of unpaired electrons.

25. Which of the following statements are correct?
- (a) The resonance energy is defined as the difference between the enthalpy of formation of the molecule and that of resonating structure having the largest energy.
- (b) Benzene has about 78 per cent contribution from Kekule’s structures.
- (c) Metamerism is due to the different arrangement of groups attached to a functional group.
- (d) Tautomers of a compound are in equilibrium with each other.

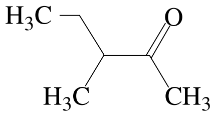
26. Which of the following statements are **not** correct?
- (a) *Cis*- and *trans*- structures can be written for the substituted cyclopropane.
- (b) Diastereomers are observed in a molecule containing one chiral carbon atom
- (c) Mesotartaric acid has a centre of symmetry.
- (d) In the compound D-(+)-glyceraldehyde, D stands for the dextrorotatory nature of the molecule.

27. Which of the following statements are correct?
- (a) Chain isomers are possible for alkanes having four or more carbon atoms.
- (b) Enantiomorphs possess the same physical properties.
- (c) Maleic acid has zero dipole moment.
- (d) Only organic molecules can be optically active.

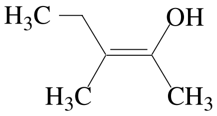
28. Which of the following statements are correct?
- (a) A racemic mixture contains equal masses of the two enantiomers.
- (b) A racemic mixture contains equal masses of the two diastereoisomers.
- (c) Of ethane, ethene and ethyne, the ethynic hydrogens are most acidic.
- (d) Propandiene has both sp and sp^2 hybrid carbon atoms.

29. Which of the following statements are correct?
- (a) Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity.
- (b) The specific rotation of a pure enantiomer is +12°. It is isolated from a reaction with 20% racemisation and 80% retention. Its observed angle of rotation will be +10.6°.
- (c) The specific rotation of a pure enantiomer is +12°. It is isolated from a reaction with 80% racemisation and 20% inversion. Its observed angle of rotation will be – 2.4°.
- (d) The specific rotation of a pure enantiomer is +12°. The percentage composition of this isomer in a mixture having rotation of – 9° is 15%.

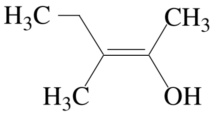
30. The correct statement(s) concerning the structures **E**, **F** and **G** is (are)



(E)



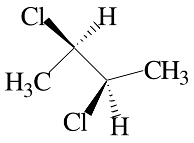
(F)



(G)

- (a) **E**, **F** and **G** are resonance structures
- (b) **E**, **F** and **E, G** are tautomers
- (c) **F** and **G** are geometrical isomers
- (d) **F** and **G** are diastereomers (2008)

31. The correct statement(s) about the compound given below is(are)



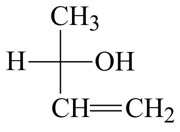
- (a) The compound is optically active
- (b) The compound possesses centre of symmetry
- (c) The compound possesses plane of symmetry
- (d) The compound possesses axis of symmetry (2008)

32. The correct statement(s) about the compound X, $H_3C(HO)HC{=}CH{-}CH{-}CH(OH)CH_3$, is(are)
- (a) The total number of stereoisomers possible for X is 6.
- (b) The total number of diastereomers possible for X is 3.
- (c) If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4.
- (d) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2.

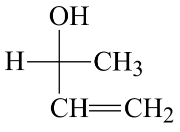
(2009)

Linked Comprehension Type

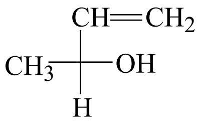
1. Given are the following isomers.



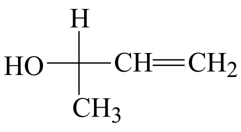
(A)



(B)



(C)



(D)

Based on these isomers, answer the following three questions.

(i) The structures having configuration S is/are
- (a) A and B
- (b) A and C
- (c) A and D
- (d) B and D

(ii) The structures having configuration R is/are
- (a) A and B
- (b) A and C
- (c) A and D
- (d) B and D

(iii) The compounds which are enantiomeric is/are

(a) A and B (b) A and C (c) A and D (d) B and D

2. Given is the compound $HO_2CCH(OH)CH(OH)CH(OH)CO_2H$. Based on this compound, answer the following three questions.

(i) The total number of optical isomers of this compound is

(a) 2 (b) 3 (c) 4 (d) 5

(ii) Which of the following facts is correct?

(a) The compound has one dl pair and one *meso* isomers.
(b) The compound has two dl pair of isomers only.
(c) The compound has one dl pair and two *meso* isomers.
(d) The compound has one dl pair and three *meso* isomers.

(iii) the total number of pair of diastereomers is

(a) two (b) three (c) four (d) five

3. Given is the organic compound C_4H_7Br. Based on this compound, answer the following three questions.

(i) The number of isomers including geometrical isomers of this compound is

(a) 2 (b) 3 (c) 4 (d) 6

(ii) The compound C_4H_7Br undergoes hydrogenation. If all isomers of C_4H_7Br are present, the number of hydrogenated products obtained are

(a) 2 (b) 3 (c) 4 (d) 6

(iii) In the hydrogenated products, the number of optical isomers including enantiomer and diastereomers is

(a) 2 (b) 3 (c) 4 (d) 6

4. Substituted cycloalkene show geometrical isomerism due to the fact that the ring is rigid and the rotation around the ring C— C is not possible. Based on this fact, answer the following three questions based on the geometrical isomers of trisubstituted cyclohexane.

(i) The number of geometrical isomers shown by 1, 3, 5-trimethylcyclohexane is

(a) 2 (b) 3 (c) 4 (d) 6

(ii) The number of geometrical isomers shown by 1, 2, 4-trimethylcyclohexane is

(a) 2 (b) 3 (c) 4 (d) 6

(iii) The number of geometrical isomers shown by 1, 2, 3-trimethylcyclohexane is

(a) 2 (b) 3 (c) 4 (d) 6

Assertion and Reason Type

Given below are two statements. Based on the following key, answer each question.

(a) Both Statements 1 and 2 are correct and Statement-2 is the correct explanation of Statement-1.
(b) Both Statements 1 and 2 are correct and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	2, 3-Pentadiene is a chiral molecules with two stereocentres but has no chiral centres	Molecule is chiral due to the two adjacent π-bonds perpendicular to each other.
2.	Monosubstituted carbocyclic compound do not have stereoisomers.	No isomers is due to the existence of a plane of symmetry in the molecule.
3.	All *cis*-disubstituted cycloalkanes with the same ligands not attached to the opposite ends of the ring exist as *meso* compound.	The molecules have no asymmetric carbon atom.
4.	All *cis*-disubstituted cycloalkanes with the same ligands not attached to the opposite ends of the ring exist as *meso* compound.	The molecules have asymmetric carbon atom.
5.	All *trans*-disubstituted cycloalkanes with the same ligands not attached to the opposite ends of a ring with an even number of carbon atoms exist as a pair of enantiomers.	The molecules do not have the plane of symmetry with no symmetric carbon atom.

6.	A compound with the *S* configuration is the (–) enantiomer.	The sign of rotation is not related to the configuration.
7.	An achiral compound can have chiral centres.	A *meso* compound is an achiral compound.
8.	An optical active substance must be achiral.	A substance existing in two enantiomers with equal amounts is an optically inactive.
9.	In chemical reactions the change from an *S* reactant to an *R* product always signals an inversion of configuration.	The change in priority sequence of ligands may also results into the change in the stereochemistry.
10.	A D enantiomer rotates the plane of polarized light to the right and L enantiomer to the left.	The terms D and L do not refer to the sign of rotation.
11.	There is no exception to the general rule that the maximum number of possible stereoisomers for a compound with *n* stereocentres is 2^n.	The rule of 2^n stereoisomers is not applicable if the molecule can be divided into two equal and similar halves.
12.	All D and L stereoisomers are enantiomers.	All D and L stereoisomers may or may not be enantiomers except when the molecule contains one chiral atom.
13.	Compounds having only one chiral centre can exist in two enantiomers.	Diastereomers may or may not be chiral molecule.
14.	Disubstituted cycloalkanes display geometric isomerism.	The geometric isomerism is due to rigid structure of cycloalkanes.

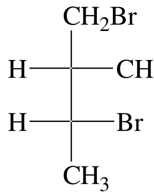
Matrix Match Type

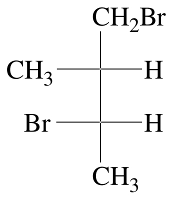
1. Column I includes four organic compounds and Column II lists the number of optically active and inactive isomers. Match each entry of Column I with those given in Column II.

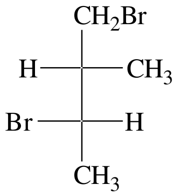
Column I	**Column II**
(a) $HO_2CCHOHCO_2H$	(p) No optically inactive isomers
(b) $HO_2C(CHOH)_2CO_2H$	(q) One optically inactive isomers
(c) $HO_2C(CHOH)_3CO_2H$	(r) two optically inactive isomers
(d) $HO_2C(CHOH)_4CO_2H$	(s) two optically active isomers
	(t) four optically active isomers
	(u) eight optically active isomers

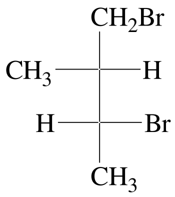
2. Column I includes the Fischer projections of 1,3-dibromo-2-methylbutane and Column II lists their absolute configurations. Match the correct entries of Column I and Column II.

Column I **Column II**

(a)


(b)


(c)


(d)


(p) (2*R*, 3*R*)

(q) (2*S*, 3*S*)

(r) (2*R*, 3*S*)

(s) (2*S*, 3*R*)

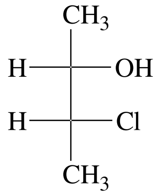
3. Column I lists the products of radical monochlorination of (*S*)-2-chlorobutane and Column II lists some of their characteristics. Identify the correct matchings.

Column I	**Column II**
(a) 1,2-Dichlorobutane	(p) *R* configuration, optical active
(b) 2,2-Dichlorobutane	(q) *S* configuration, optical active
(c) 2,3-Dichlorobutane	(r) optically inactive
(d) 1,3-Dichlorobutane	(s) (2*S*, 3*S*) configuration, optical active
	(t) (2*S*, 3*R*) configuration, optical inactive
	(u) (2*S*, 3*R*) configuration, optical active

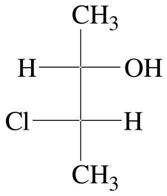
4. Column I lists the isomers of 3-chloro-3-butanol and Column II lists some of their characteristics. Identify the correct matching.

Column I

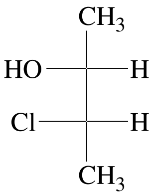
(a)



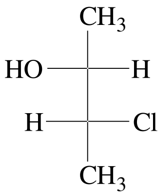
(b)



(c)



(d)



Column II

(p) erythro configuration

(q) threo configuration

(r) *RR* configuration

(s) *RS* configuration

(t) *SR* configuration

(u) *SS* configuration.

ANSWERS

Straight Objective Type

1. (a)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (b)
8. (d)	**9.** (c)	**10.** (a)	**11.** (c)	**12.** (c)	**13.** (b)	**14.** (a)
15. (a)	**16.** (d)	**17.** (a)	**18.** (d)	**19.** (c)	**20.** (a)	**21.** (b)
22. (b)	**23.** (b)	**24.** (d)	**25.** (d)	**26.** (a)	**27.** (a)	**28.** (a)
29. (c)	**30.** (a)	**31.** (c)	**32.** (a)	**33.** (b)	**34.** (b)	**35.** (a)
36. (d)	**37.** (a)	**38.** (d)	**39.** (c)	**40.** (a)	**41.** (c)	**42.** (b)
43. (b)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (b)	**48.** (c)	**49.** (b)
50. (c)	**51.** (b)	**52.** (c)	**53.** (d)	**54.** (a)	**55.** (a)	**56.** (d)
57. (b)	**58.** (c)	**59.** (d)	**60.** (a)	**61.** (c)	**62.** (b)	**63.** (b)
64. (c)	**65.** (c)	**66.** (a)	**67.** (c)	**68.** (b)	**69.** (d)	**70.** (b)
71. (c)	**72.** (a)	**73.** (b)	**74.** (a)	**75.** (d)	**76.** (c)	**77.** (b)
78. (d)	**79.** (d)	**80.** (b)	**81.** (d)	**82.** (b)	**83.** (a)	**84.** (c)
85. (c)	**86.** (b)	**87.** (c)	**88.** (c)	**89.** (d)	**90.** (b)	**91.** (b)
92. (b)	**93.** (c)	**94.** (c)	**95.** (c)	**96.** (d)	**97.** (b)	**98.** (b)
99. (c)	**100.** (b)	**101.** (d)	**102.** (c)	**103.** (a)	**104.** (c)	**105.** (b)

Multiple Correct Choice Type

1. (a), (d)	**2.** (a), (c)	**3.** (a), (b), (c), (d)	**4.** (a), (c), (d)
5. (a), (c)	**6.** (a), (d)	**7.** (b), (c), (d)	**8.** (a), (c)

9. (a), (b), (c), (d) **10.** (a), (c) **11.** (a), (b), (c), (d) **12.** (a), (b), (c)
13. (a), (c) **14.** (b), (d) **15.** (a), (b), (c) **16.** (a), (d)
17. (c), (d) **18.** (a), (d) **19.** (a), (c) **20.** (a), (c)
21. (a), (c), (d) **22.** (b), (d) **23.** (b), (d) **24.** (a), (c)
25. (b), (c), (d) **26.** (b), (c), (d) **27.** (a), (b) **28.** (a), (c), (d)
29. (a), (c) **30.** (b), (c), (d) **31.** (a), (d) **32.** (a), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (d) **(iii)** (a)
2. **(i)** (c) **(ii)** (c) **(iii)** (d)
3. **(i)** (c) **(ii)** (b) **(iii)** (a)
4. **(i)** (a) **(ii)** (c) **(iii)** (b)

Assertion and Reason Type

1. (a) **2.** (a) **3.** (c) **4.** (b) **5.** (c) **6.** (d) **7.** (b)
8. (d) **9.** (d) **10.** (d) **11.** (d) **12.** (d) **13.** (b) **14**. (a)

Matrix Match Type

1. (a)-(p), (s); (b)-(q), (s); (c)-(r), (s); (d)-(r), (u)
2. (a)-(s); (b)-(r); (c)-(q); (d)-(p)
3. (a)-(p); (b)-(r); (c)-(s), (t); (d)-(q)
4. (a)-(p), (t); (b)-(q), (u); (c)-(p), (s); (d)-(q), (r)

Hints and Solutions

Straight Objective Type

1. A single C— C bond has the largest bond distance.
2. Carbon tetrachloride has no dipole moment.
3. The C— H bond length increases with decrease in the electronegativity of hybrid orbital of carbon atom. Hence, the bond length C—H will be largest in C_2H_6.
4. The structural formula is 1-butene-3-yne is $H_2C{=}CH{-}C{\equiv}CH$
It has 7 sigma (4 C—H and 3 C—C) and 3 pi bonds (one in double and two in triple bond).
5. The larger the contribution of s orbital, shorter the C—H bond length. Hence, we have $CH_4 > C_2H_4 > C_2H_2$.
6. The hybrid structure may not have equal contributions from all resonating structure.
7. The resonance energy is defined as the difference between the enthalpy of formation of the molecule and that of resonating structure having the lowest energy (obtained theoretically).
8. 1, 2-Butadiene is $\underset{sp^2}{CH_2}{=}\underset{sp}{C}{=}\underset{sp^2}{CH}{-}\underset{sp^3}{CH_3}$. It has sp, sp^2 and sp^3 carbon atoms.
9. C–1 is sp hybridized and C–2 is sp^2 hybridized
10. C in 1,1,1,2-tetrachloroethene is sp^2 hybridized. The angle Cl—C—Cl is expected to be 120°.
C in tetrachloromethane is sp^3 hybridized. The angle Cl—C—Cl is expected to be 109.5°.
11. $H\dot{C}OOH$ involves sp^2; $(H_2N)_2\dot{C}O$ involves sp^2; $(CH_3)_3\dot{C}OH$ involves sp^3 and $CH_3\dot{C}HO$ involves sp^2 $\dot{C}$ atom.
12. We have $HC{\equiv}\underset{sp}{C}{-}\underset{sp^2}{CH}{-}CH_2$.
13. The larger contribution of s orbital decreases the size of hybrid orbital. Hence, we have $sp < sp^2 < sp^3$.
14. The larger contribution of s orbital increases the electronegativity of hybrid orbital. Hence, we have $sp > sp^2 > sp^3$.
15. The two π-bonds are present in two different planes perpendicular to each other.

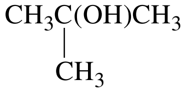
16. The numbering in the given compound goes as follows.

$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH_2}{-}\overset{4}{CH_2}{-}\overset{5}{C}{\equiv}\overset{6}{CH}$$

The C^2—C^3 bond is sp^2–sp^3 type.

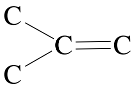
17. The molecule $H_2{=}CH{-}C{\equiv}CH$ involves sp^2,sp^2,sp and sp carbons from left to right of the molecule.

18. Diethyl ether is $C_2H_5OC_2H_5$ (molecular formula $C_4H_{10}O$). The formulae of the given compounds are as follows.

n-Propylmethyl ether	$CH_3CH_2CH_2OCH_3$	$C_4H_{10}O$
1-Butanol	$CH_3CH_2CH_2CH_2OH$	$C_4H_{10}O$
2-Methyl-2-propanol	 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}(OH)CH_3$	$C_4H_{10}O$
Butanone	$CH_3COCH_2CH_3$	C_3H_8O

Butanone is not isomer of diethyl ether.

19. The skeletons of C_4H_8 are: C— C—C=C; C—C=C—C; *cis* and *trans*



There are four isomers.

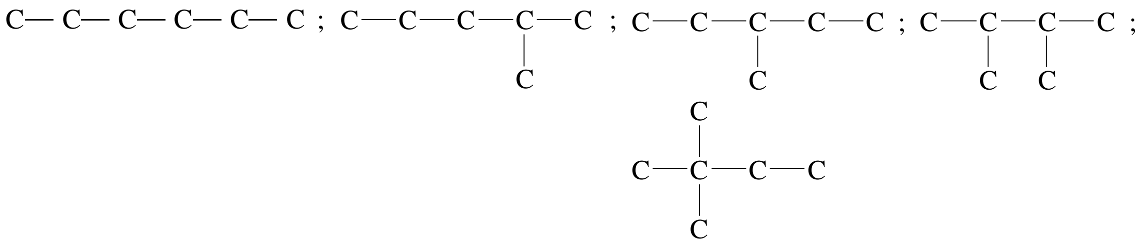
20. The structure of given compounds are

2-Butene	$CH_3{-}CH{=}CH{-}CH_3$	2-Butanol	$CH_3CH_2CH(OH)CH_3$
2-Butyne	$CH_3{-}C{\equiv}C{-}CH_3$	Butanal	$CH_3CH_2CH_2CHO$

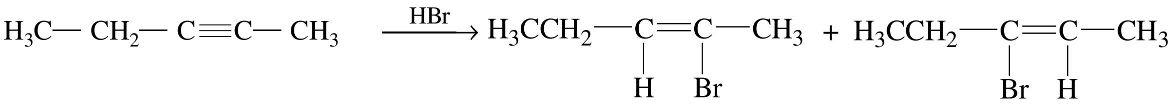
Only 2-Butene shows *cis-trans* isomerism.

21. Different formulae implies different molar masses.

22. The skeletons of carbon in C_6H_{14} are as follows



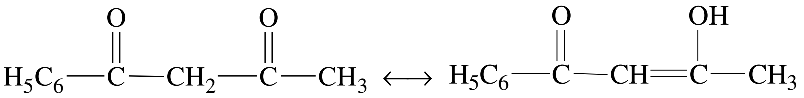
23.



$$H_3C{-}CH_2{-}C{\equiv}C{-}CH_3 \xrightarrow{HBr} H_3CCH_2{-}\underset{H}{\underset{\vert}{C}}{=}\underset{Br}{\underset{\vert}{C}}{-}CH_3 + H_3CCH_2{-}\underset{Br}{\underset{\vert}{C}}{=}\underset{H}{\underset{\vert}{C}}{-}CH_3$$

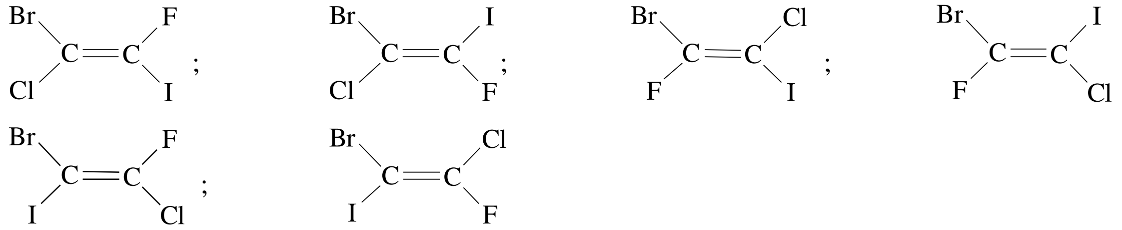
There will be 2 structural isomers and 4 configurational (*cis-trans*) isomers.

24.

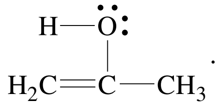


$$H_5C_6{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3 \longleftrightarrow H_5C_6{-}\overset{O}{\overset{\Vert}{C}}{-}CH{=}\overset{OH}{\overset{\vert}{C}}{-}CH_3$$

25. The six compounds will be



26. The enolic form of acetone is

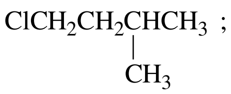


$$H_2C{=}\overset{H-\ddot{O}:}{\overset{\vert}{C}}{-}CH_3$$

. It contains 9 sigma bonds, 1 pi bond and two lone pairs of electron on oxygen.

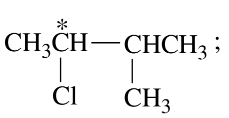
27. Isomers which can be interconverted through rotation around a single bond are known as conformers.

29. The possible products are



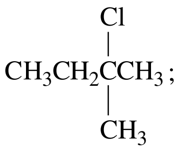
$$\mathrm{ClCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3}\ ;$$

(Optically inactive)



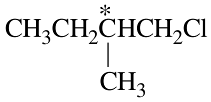
$$\mathrm{CH_3\overset{*}{\underset{\underset{Cl}{|}}{C}}H—\underset{\underset{CH_3}{|}}{C}HCH_3}\ ;$$

(Optically active)
(Two isomers)



$$\mathrm{CH_3CH_2\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3}\ ;$$

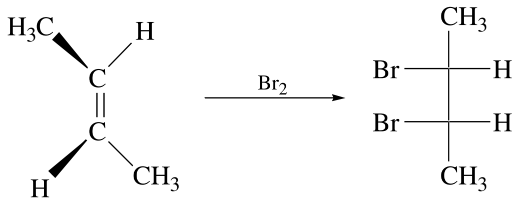
(Optically inactive)



$$\mathrm{CH_3CH_2\overset{*}{\underset{\underset{CH_3}{|}}{C}}HCH_2Cl}$$

(Optically inactive)
(Two isomers)

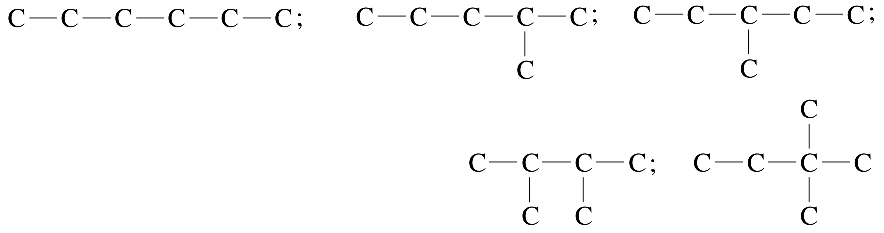
30. The addition of Br_2 across a double bond involves the formation of a bromonium ion intermediate followed by the *anti* addition of Br^-. For *trans*-2-butene, the reaction proceeds so as to form *meso*-2, 3-dibromobutane.



meso-2, 3-dibromobutane

Thus, only, one stereoisomer is obtained.

31. The molecule C_6H_{14} is an alkane. It can have the following carbon skeletons



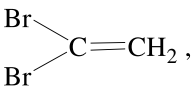
$$\mathrm{C—C—C—C—C—C;\quad C—C—C—\underset{\underset{C}{|}}{C}—C;\quad C—C—\underset{\underset{C}{|}}{C}—C—C;}$$

$$\mathrm{C—\underset{\underset{C}{|}}{C}—\underset{\underset{C}{|}}{C}—C;\quad C—C—\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}—C}$$

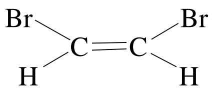
Thus, the molecule C_6H_{14} can have 5 structure isomers.

32. Isomers are the compounds having the same molecular formula but different structural formulae.

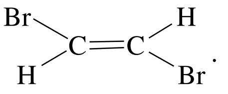
33. The alkene is $C_2H_2Br_2$. It has three isomers



,



and



.

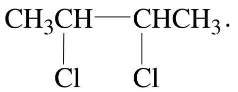
34. A *meso* compound has more than one chiral carbon atom and it is superimposable on its mirror image. In this compound, optical rotation caused by one chiral carbon is cancelled by that of the other, consequently the *meso* compound is optically inactive.

35. The terms stereoisomers, enantiomers and diastereomers will refer only to configurational isomers including geometric isomers.

36. The two enantiomers of a compound can be separated by chromatographic techniques.

37. The two enantiomers of a compound have different direction of rotation but same amount of rotation.

38. The two diaseteromers have more than one chiral carbon atoms. The two isomers have the same configuration with respect to one chiral carbon atom and have different configurations with respect to the rest of molecules. They have similar chemical properties but differ in the rates of reaction.

39. The compound is  $\mathrm{CH_3\underset{\underset{Cl}{|}}{C}H—\underset{\underset{Cl}{|}}{C}HCH_3}$. It has one pair of enantiomers and one *meso* compound.

40. Only the compound $CH_3CHOHCOOH$ has chiral carbon atom. It shows optical isomerism.

41. Mesotartaric acid and d-tartaric acid are diastereoisomers.

42. Mesotartaric has a plane of symmetry.

43. Racemic tartaric acid is optically inactive due to external compensation.

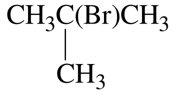
44. Molecules that are not superimposable on their mirror images are chiral.

46. Only 2-methylbutanoic acid has chiral carbon.

47. Presence of at least one chiral atom is necessary.

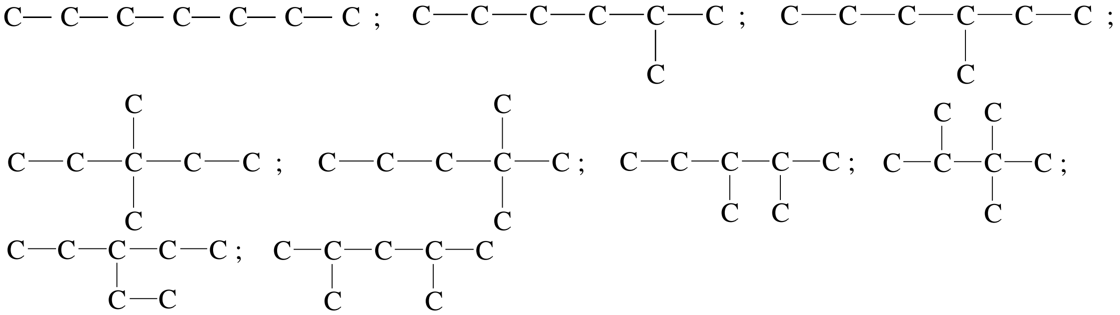
48. A molecule is said to be chiral if it cannot be superimposed on its mirror image.

49. The given compounds are

1-bromobutane	$BrCH_2CH_2CH_2CH_3$	1-bromo-2-methylpropane	$BrCH_2CH(CH_3)CH_3$
2-bromobutane	$CH_3CH(Br)CH_2CH_3$	2-bromo-2-methylpropane	 $CH_3\underset{\mid \atop CH_3}{C}(Br)CH_3$

Only 2-bromobutane contains a chiral carbon atom. It is thus an optically active compound.

50. The carbon skeleton of C_7H_{16} are as follows:



$C-C-C-C-C-C-C$; $C-C-C-C-\underset{\mid \atop C}{C}-C$; $C-C-C-\underset{\mid \atop C}{C}-C-C$;

$C-C-\overset{C \atop \mid}{\underset{\mid \atop C}{C}}-C-C$; $C-C-C-\overset{C \atop \mid}{\underset{\mid \atop C}{C}}-C$; $C-C-\underset{\mid \atop C}{C}-\underset{\mid \atop C}{C}-C$; $C-\overset{C \atop \mid}{C}-\overset{C \atop \mid}{\underset{\mid \atop C}{C}}-C$;

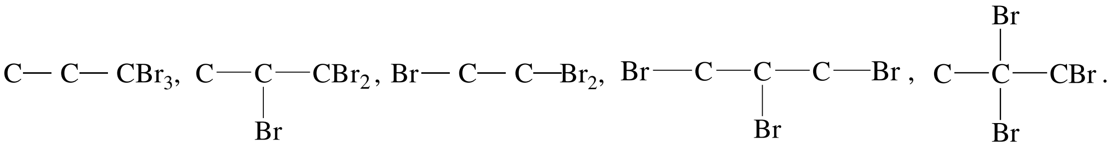
$C-C-\underset{\mid \atop C-C}{C}-C-C$; $C-\underset{\mid \atop C}{C}-C-\underset{\mid \atop C}{C}-C$

There are nine isomers.

51. The compounds $CH_3CH{=}CHCH_3$ and $CH_3CH_2CH{=}CH_2$ are position isomers.

52. There are nine isomers; CH_3CH_2Br, CH_3CHBr_2, $BrCH_2CH_2Br$, CH_3CBr_3, $BrCH_2CHBr_2$, $BrCH_2CBr_3$, $Br_2CHCHBr_2$, Br_2CHCBr_3, Br_3CCBr_3.

53. There are five isomers. The skeleton of these compounds are



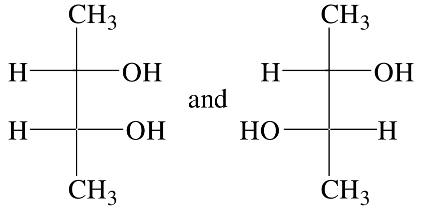
$C-C-CBr_3$, $C-\underset{\mid \atop Br}{C}-CBr_2$, $Br-C-C-Br_2$, $Br-C-\underset{\mid \atop Br}{C}-C-Br$, $C-\overset{Br \atop \mid}{\underset{\mid \atop Br}{C}}-CBr$.

54. Only one optically active compound $H_3CCH(Br)CHBr_2$ is possible.

55. There are two possible enantiomeric pairs, one each for $ClCH_2\overset{*}{C}(CH_3)CH_2CH_3$ and $CH_3CH(CH_3)\overset{*}{C}H(Cl)CH_3$.

56. The compounds I and II are enantiomers. Rotation of compound II by 180° produces mirror image of compound I.

57. For the compound $CH_3CH(OH)CH(OH)CH_3$, two optically active seteroisomers are possible.



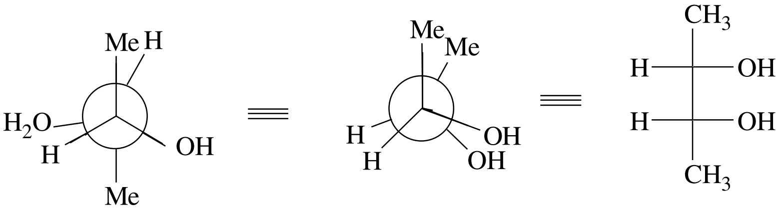
58. D-(+) tartaric acid has a positive optical rotation and is derived from D-(+)-glyceraldehyde.

59. A solution (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of carbocation.

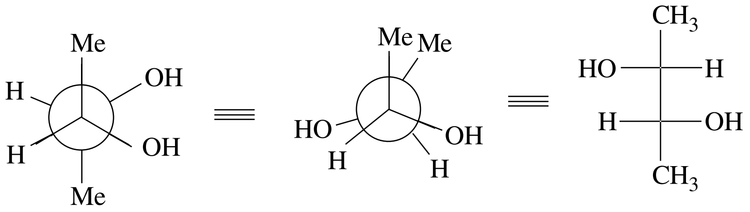
60. The compound 1-phenyl-2-butene ($C_6H_5CH_2CH{=}CHCH_3$) will exhibit geometrical isomerism.

61. The compounds $CH_2{=}CHOH$ and CH_3CHO are tautomers: $CH_3CHO \leftrightarrow CH_2{=}CHOH$

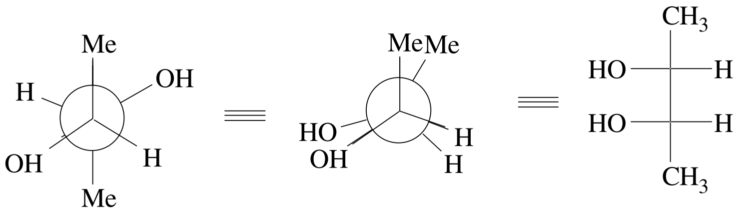
62. (I)



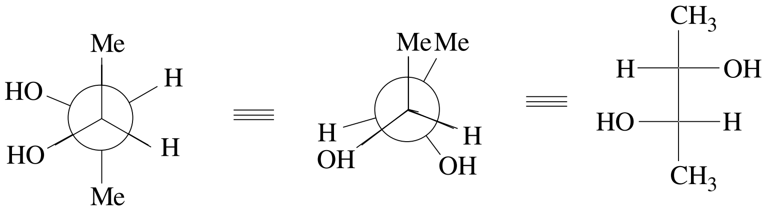
(II)



(III)



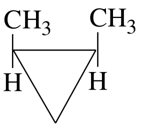
(IV)



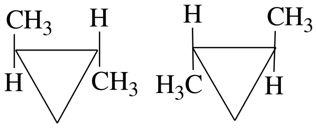
Rotate about the C— C bond until a staggered conformer with one of the substituent is in an eclipsed form. If all substituents are in eclipsed form, the conformation is a *meso* compound. The structures (I) and (III) satisfy this requirement.

63. There exists a plane of symmetry in methylcyclopropane. Hence, only one stereoisomer exists for this compound.

64. There are three isomers. *cis*-1,2 are *meso*, and *trans*-1,2 exists as pair of enantiomers.



cis(*meso*)



trans(racemate)

65. Rank the atoms directly attached to the chiral centre in order of decreasing atomic number. The group with highest atomic number is ranked first; the group with lowest atomic number is ranked fourth. Continue working outward to the first point of difference. The correct order of decreasing priority of given ligands are —OH > —COOH > $CH(OH)CH_3$ > CH_2OH.

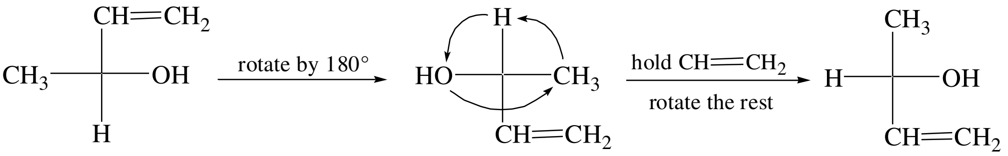
66. The correct decreasing priority is $—NO_2 > —NH_2 > —C{\equiv}N > —CH_2NH_2$.

67. Exchanging ligands across the horizontal bond and also across the vertical bond (which is equivalent to rotation by 180°) does not change its absolute configuration.

68. An odd number of switches changes its absolute configuration.

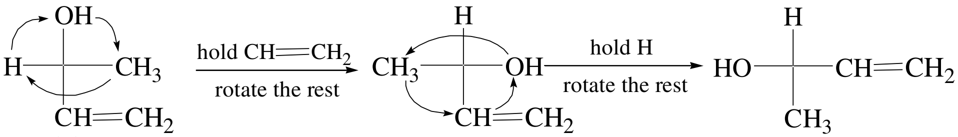
69. A 180° rotation in the plane of paper is allowed.

70. The structures (I) and (III) represent the same absolute configuration.



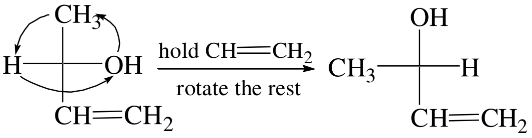
(III) (I)

71. The structures (II) and (IV) represent the same absolute configuration.



(II) (IV)

72. The structures (I) and (II) represent enantiomers.

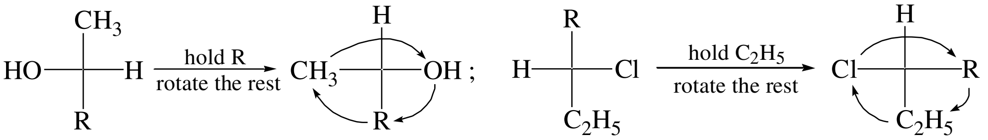


(I)

enantiomer of (II)

73. The compound 3-chloro-2-pentanol has two asymmetric carbon atoms. it will have two pairs of enantiomers.

74. We have

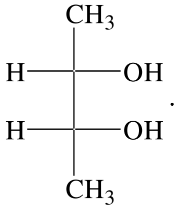


(*R* configuration) (*R* configuration)

The compound is named as (2$R_1$3R)-3-chloro-2-pentanol.

75. The number of stereoisomers will be 16 (= 2^4).

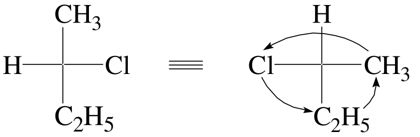
76. The two enantiomers differ in their optical activities.

77. The compound is  . It has two identical chiral carbon atoms. The number of stereoisomers will be equal to $2^2 - 1 = 3$.

78. The *meso* compound is not formed when equal amounts of two enantiomers are mixed.

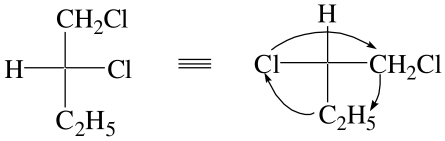
79. The free radical monochlorination of butane would produce *racemic*-2-chlorobutane.

80. (*S*)-2-Chlorobutane is



(*S*-configuration)

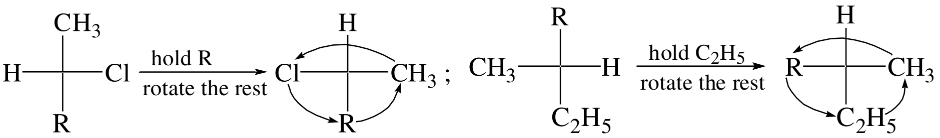
Monochlorination would give



(*R*-configuration)

81. The reaction $CH_3CH_2CH_2CH(Cl)CH_3 \xrightarrow{OH^-} CH_3CH_2CH_2CH(OH)CH_3 + Cl^-$ proceeds via S_N2 mechanism. This involves inversion of configuration.

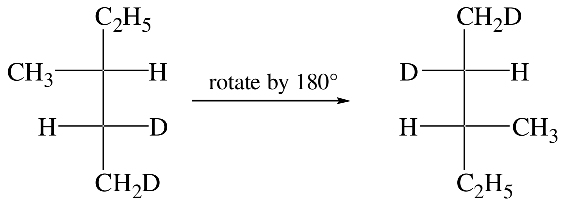
82. We have

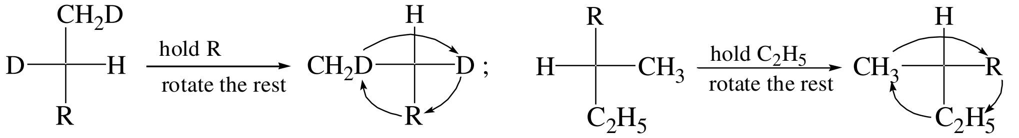


(*S*-configuration) (*S*-configuration)

Choice (b) represents (2*S*, 3*S*)-$CH_3CHClCH(CH_3)C_2H_5$.

83. We have



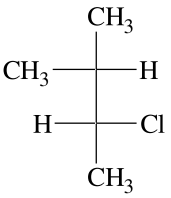


(*R* configuration) (*R* configuration)

Choice (a) represents (2*R*, 3*R*)–$C_2H_5CH(CH_3)CH(D)CH_2D$

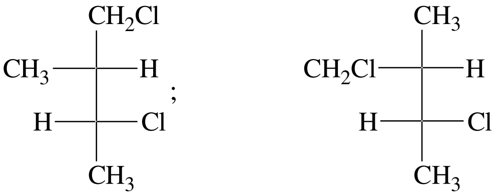
84. Choice (c) represents (2*R*, 3*S*)—$C_2H_5CH(CH_3)CH(D)CH_2D$.

85. (R)-2-methyl-3-chlorobutane is



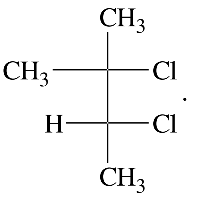
Four structural isomers are as follows.

1. Chlorination at $^{(1)}C$ creates a new chiral centre at $^{(2)}C$. Since this C can be R or S, two diastereomers are formed. (These are 2R, 3R and 2S, 3R)



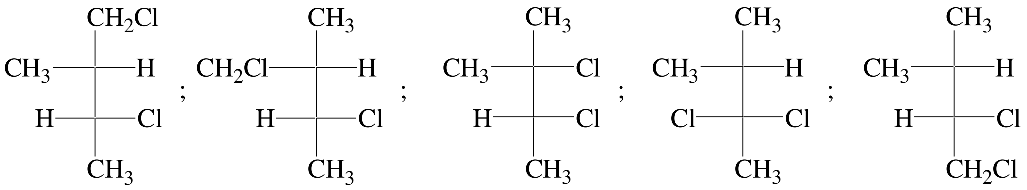
(2R, 3R) (2S, 3R)

2. Chloriation at $^{(2)}C$ gives



3. Chlorination at $^{(3)}C$ results in the loss of chirality.
4. Chlorination at ^4C results into S as the priority sequence is changed, though its configuration remains the same.

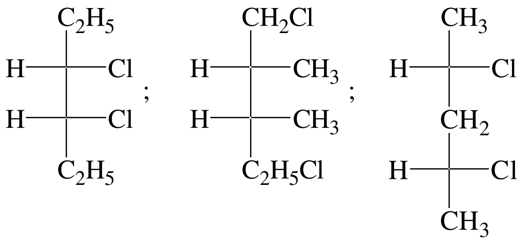
Thus, the possible products are



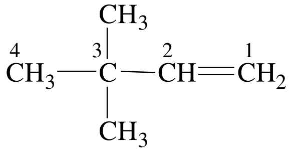
(2*R*, 3*R*) (2*S*, 3*R*) (*R*) Achiral (*S*)

Thus, four stereoisomers are possible.

86. A *meso* compound has a plane of symmetry. We can draw three such structures.

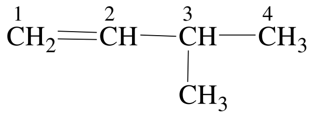


87. The IUPAC name of the compound



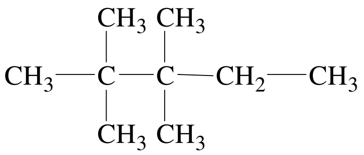
$\overset{4}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{3}{C}}}-\overset{2}{CH}=\overset{1}{CH_2}$ is 3, 3-dimethyl-1-butene.

88. The IUPAC name of the compound



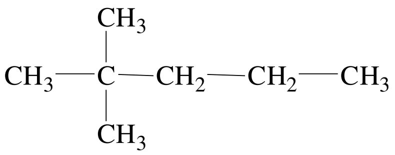
$\overset{1}{CH_2}=\overset{2}{CH}-\underset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_3}$ is 3-methyl-1-butene.

89. The structural formulae are



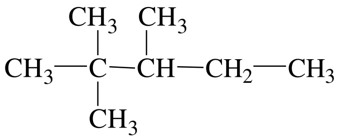
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

2, 2, 3, 3-tetramethaylpentane



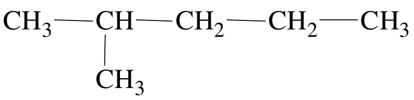
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-CH_3$

2, 2-dimethylpentane



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2-CH_3$

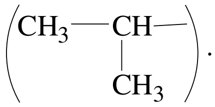
2, 2, 3-trimethylpentane



$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-CH_3$

2-methylpentane

Only 2-methylpentane has one isopropyl group



$\left(CH_3-\underset{CH_3}{CH}-\right)$.

90. The IUPAC name is 1-amino-2-methyl-1-phenylpropane.

91. The IUPAC name is 3,3-diethyl-5-isopropyl-4-methyloctane.

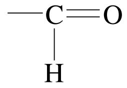
92. The IUPAC name of $CH_3C\equiv CCH(CH_3)COOH$ is 2-methylpent-3-enoic acid.

93. The IUPAC name is 2,3-dimethyl-6-(2-methylpropyl) decane.

94. The IUPAC name is 2,2-dimethyl-1-cyclohexanol

95. The structure of 2,2,3-trimethylhexane is $CH_3C(CH_3)_2CH(CH_3)CH_2CH_2CH_3$.

96.



$-\underset{H}{C}=O$ is the principal functional group.

97. Neopentyl alcohol is $(CH_3)_3CCH_2OH$.

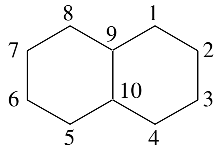
98. The preference goes to a triple bond, but counting is done from the double bond end. The correct name is 2,4-octadien-6-yne.

99. The compound is name as nitrile. The correct name is 2,2-dimethyl-4-oxopentanenitrile.

100. The IUPAC name of $(C_2H_5)_2N\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{C}OOH$ is 2-choloro-3-(N, N-diethylamino)propanoic acid.

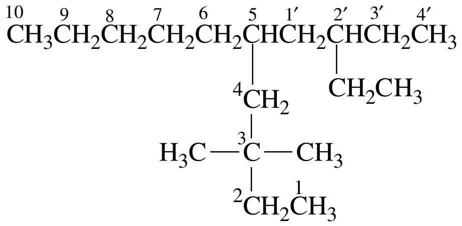
101. Substituted cycloalkanes are named in the same way as alkanes. The name of the given compound is 3-Iodo-2-methyl-1-ethylcyclohexane.

102. The numbering in the given compound goes as follows:



The name of the given compound is 1,3,9-trimethylbycyclo[4.4.0]decane. The numbers within the brackets indicate number of carbon in each cycle. They are inserted in decreasing order.

103. The numbering goes as follows.



Its IUPAC name is 5-(2-ethylbutyl)-3, 3-dimethyldecane.

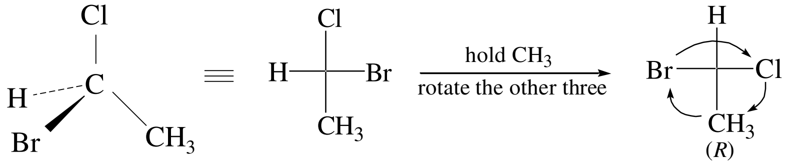
105. The order of preference of principal functional group is as follows.

Carboyxlic acid, sulphonic acid, ester, acid halide, amide, nitrile, aldehyde, ketone, alcohol, amine, ether, alkene.

The given compound contains —OH, —CN and —Br groups. Of these, —CN group gets the preference and thus the compound is named as nitrile. Hence, its name is 2-Bromo-5-hydroxybenzonitrile.

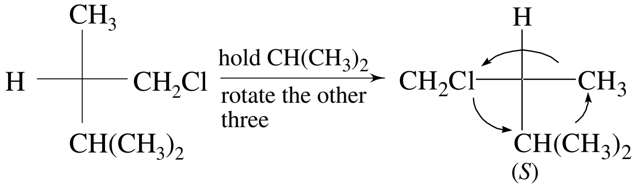
Multiple Correct Choice Type

5. (a) In the given molecule, the priority sequence is Br > Cl > CH_3 > H. The given molecule is to be visualised as under:

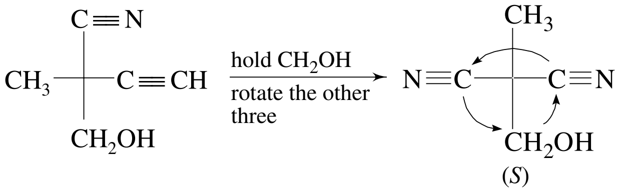


Since the priority sequence follows clockwise, the molecule is designated as *R*.

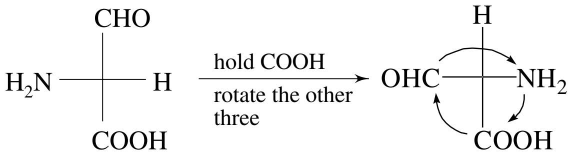
(b) The priority order is CH_2Cl > $CH(CH_3)_2$ > CH_3 > H. The molecule may be visualised as follows:



(c) The priority order is CH_2OH > CN > C≡CH > CH_3.

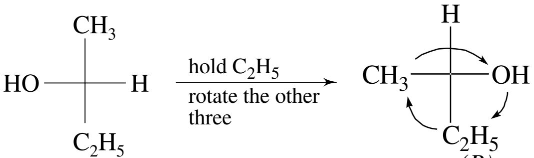


(d) The priority order is $NH_2 > COOH > CHO > H$.



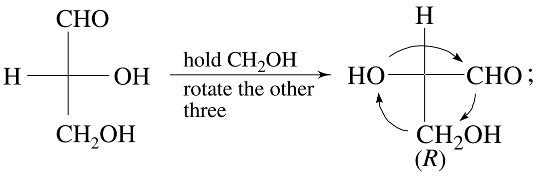
(*R*)

6. (a) The priority order is $OH > C_2H_5 > CH_3 > H$



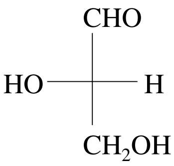
(*R*)

(b) The priority order is $OH > CHO > CH_2OH > H$



(*R*)

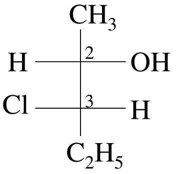
; The correct structure is



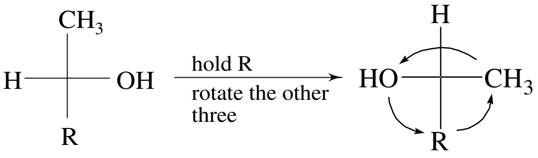
.

(c) The absolute configuration is in no way related to the sign of rotation.

7. (a) The given compound is

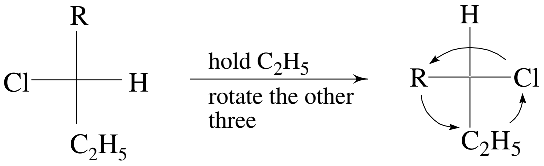


The priority order of ligands at C^2 is $OH > CH(Cl)C_2H_5 > CH_3 > H$
At C^2, the molecule may be visualised as



(*S*)

The priority order of ligands at C^3 is $Cl > CH(OH)CH_3 > C_2H_5 > H$
At C^3, the molecule may be visualised as



Hence, the correct name of the compound is (2*S*,3*S*)-3-chloro-2-pentanol.

(d) Optically active RI reacts with I^- with inversion at C^* and eventually is racemised.

8. (a) The configuration is unchanged because the bonds with the chiral C are not disturbed and also the priority order of the ligands is not changed.

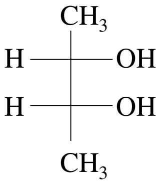
(b) Though the bonds to the chiral C are not disturbed but the priority sequence changes. The reactant has *S* configuration while the product has *R* configuration.

(c) If x is the fraction of molecules which have undergone inversion, then
$(1 - x)(-15.9°) + (x)(15.9°) = -15.26°$ or $(31.8°)(x) = 0.64°$ or $x = 0.64/31.8 \simeq 0.02$
Hence, the percentage of molecules undergone inversion is about 2%.

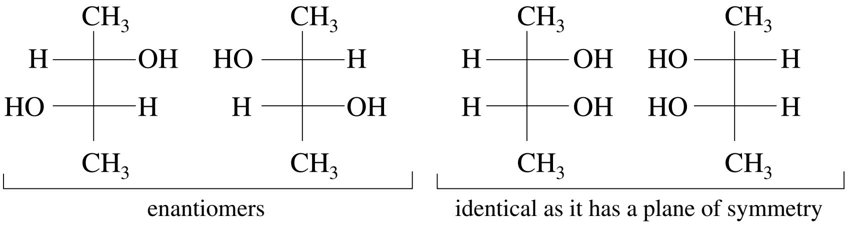
(d) An optically active substance may be racemic mixture.

9. (a) The absolute configuration is in no way related to the sign of rotation.

(b) The structure of 2,3-butanediol is

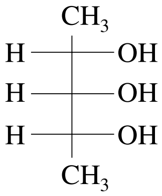


It has two chiral carbon atoms. The total number of expected stereoisomers is $2^2 = 4$. These are



Thus, number of enantiomer pairs is one.

(c) The structure of 2,3,4-trihydroxypentane is



It has three chiral carbon atoms. The number of expected stereoisomers is $2^3 = 8$. Amongst these, a few will have identical configurations as one pair carbon atoms (C^2 and C^4) are similar. The expected eight stereoisomers are

1. (*RRR*) 2. (*RRS*) 3. (*RSR*) 4. (*SRR*) 5. (*RSS*) 6. (*SRS*) 7. (*SSR*) 8. (*SSS*)

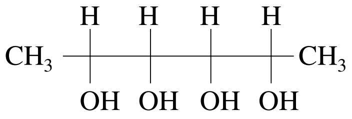
Of these, the configurations (*RRS*) and (*SRR*) as well as (*SSR*) and (*RSS*) are identical. Hence, the actual configurations are

(RRR), (SSS)]
(RRS), (SSR)] Two pairs of enantiomers

(*RSR*), (*SRS*)] Two *meso* compounds.

Thus, it has six stereoisomers.

(d) The structure of 2,3,4,5-tetrahydroxyhexane is



There are four chiral carbon atoms. Of these, the pairs (C^2 and C^5) and (C^3 and C^4) are similar. Therefore, the number of stereoisomers will not be equal to $2^4 = 16$.

The expected sixteen configurations are

1. *RRRR* 2. *RRRS* 3. *RRSR* 4. *RSRR* 5. *SRRR* 6. *RRSS* 7. *RSRS* 8. *RSSR*
9. *SRRS* 10. *SRSR* 11. *SSRR* 12. *RSSS* 13. *SRSS* 14. *SSRS* 15. *SSSR* 16. *SSSS*

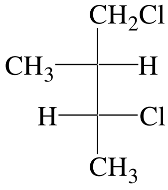
Of these sixteen configurations, the following pairs are identical

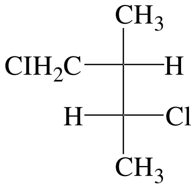
(*RRRS*) and (*SRRR*); (*RSRS*) and (*SRSR*); (*RSRR*) and (*RRSR*); (*SSSR*) and (*RSSS*);
(*RRSS*) and (*SSRR*); (*SSRS*) and (*SRSS*);

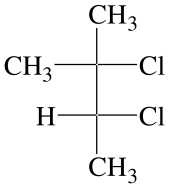
Thus, the ten distinct configurations are:

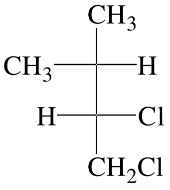
Four enantiomeric pairs (*RRRR*) and (*SSSS*); (*RRRS*) and (*SSSR*); (*RRSR*) and (*SSRS*); (*RSSR*) and (*SRRS*);
Two *meso* diastereomers (RSRS) and (RRSS)

10. (a) The five structures are

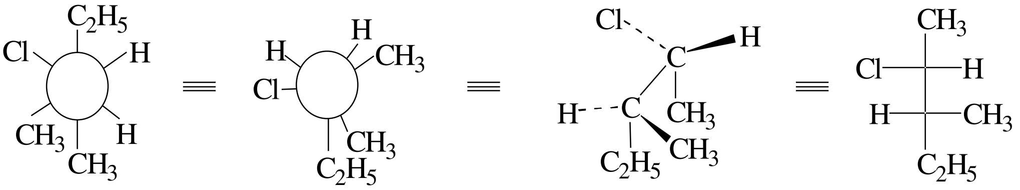

(2*R*, 3*R*)


(2*S*, 3*R*)


Optically inactive


(*S*)

(b)



(d) The correct name is 3-ethyl-4, 7-dimethylnonane

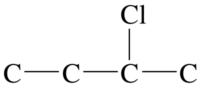
12. (d) The correct name is 3-(N, N-dimethylamino)-3-methyl-pentane

13. The *erythro* configurations have two like groups on the chiral atoms of a molecule on the same side in its Fischer projection.

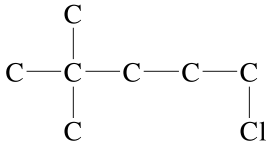
14. The *threo* configurations have two like groups on the chiral atoms of a molecule on the opposite sides in its Fischer projection.

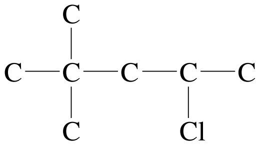
15. Resonance structures have identical arrangement of atoms, nearly the same energy content and the same number of unpaired electrons.

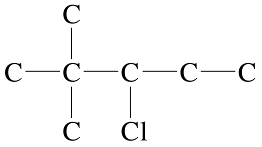
16. *n*-Butane: C— C— C— C— Cl ;


$C-C-\overset{Cl}{\overset{|}{C}}-C$

2, 2-Dimethylpentane:


$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-C-\underset{\underset{Cl}{|}}{C}$;

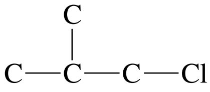

$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\underset{\underset{Cl}{|}}{C}-C$;

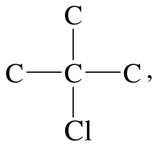

$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{Cl}{|}}{C}-C-C$

and so on.

Benzene: C_6H_5Cl

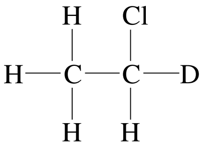
2-Methylpropane:


$C-\overset{\overset{C}{|}}{C}-C-Cl$;

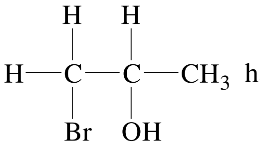

$C-\underset{\underset{Cl}{|}}{\overset{\overset{C}{|}}{C}}-C$,

Compounds *n*-butane and 2-methylpropane have two monochloro derivatives.

17. The compounds


$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-D$

and


$H-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$

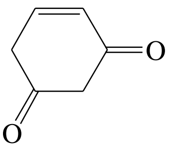
have asymmetric carbon atom.

18. The symbol D does not stand for dextrorotatory but for the configuration in which hydrogen atom at the chiral carbon lies left in the Fischer projection diagram.

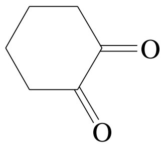
19. A compound whose molecule has D or L configuration may be dextrorotatory or laevorotatory.

20. The compound 2-butene ($CH_3CH{=}CHCH_3$) and 1-phenylpropene ($C_6H_5CH{=}CHCH_3$) will show geometrical isomerism.

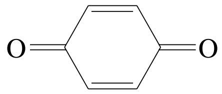
21. The compound $C_6H_5CH{=}CH{-}OH$,



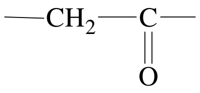
and



will show tautomerism. The compound



does not contain


$-CH_2-\underset{\underset{O}{\|}}{C}-$

group.

22. Tautomeric structure are not the resonating structures of a molecule. Geometrical isomerism is shown by many other molecules.

24. (b) The larger the contribution of p orbital, greater the size.

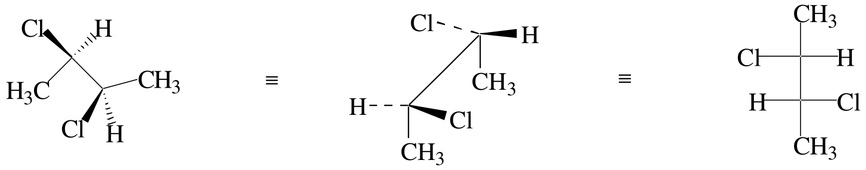
25. (a) It is the difference between the enthalpy of formation of the molecule and the resonating structure having lowest energy.
(b) There is 78% contribution from Kekule's structures and 22% contribution from Dewar's structures.

26. (a) Diastereomers are observed if the molecule contains more than one chiral carbon atom.
(c) It has a plane of symmetry.
(d) The symbol D stands for the absolute configuration.

29. (a) There occurs breaking and making of C— I bond. This results into two enantiomers which form racemic mixture.
(b) The isolated mixture will contain 90% of this isomer (10% from the racemised mixture and 80% due to its retention) and 10% of its inversion. Hence, the observed bond angle would be
$\alpha = (0.90)\,(+12°) + (0.10)\,(-12°) = +9.6°$
(c) The isolated mixture will contain 40% of this isomer (from 80% racemic mixture) and a total of 60% of its inversion. Hence $\alpha = (0.40)\,(+\,12°) + (0.60)\,(-12°) = -\,2.4°$
(d) if x is the fraction of the given isomer in the racemic mixture, we would have
$(x)\,(+12°) + (1 - x)\,(-12°) = -\,9°$
This gives $x = 1/8$. Hence, the mixture contains 12.5% of this isomer.

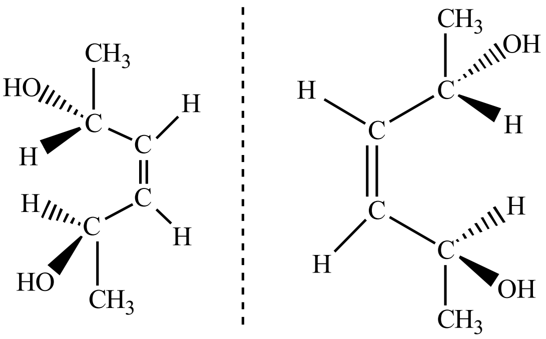
30. **E** and **F**, and **E** and **G** involve the migration of a proton from carbon atom to the adjacent atom. These are keto-enol tautomers.
F and G are *cis-* and *trans-* isomers and thus constitute geometrical isomers.
F and G are diastereomers. These are optical isomers that are not mirror images.

31. The given compound is

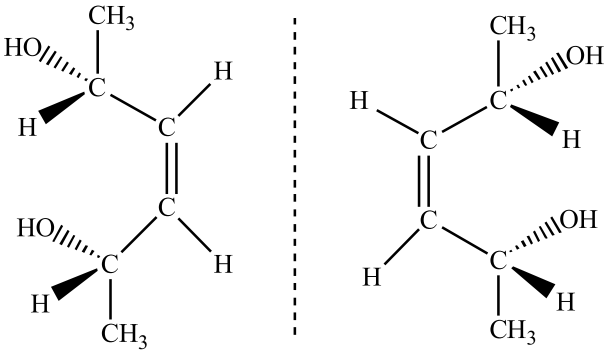


The compound is optically active and has diad axis of symmetry.
Therefore, the choices (A) and (D) are correct.

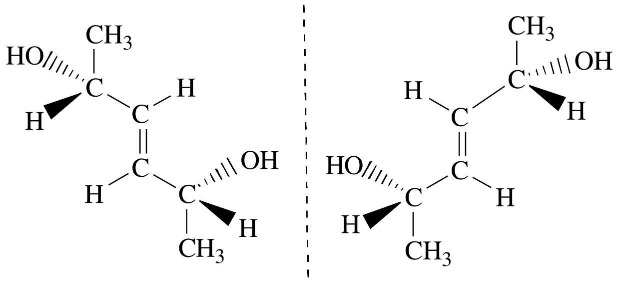
32. The configurations of the given compounds are as follows.



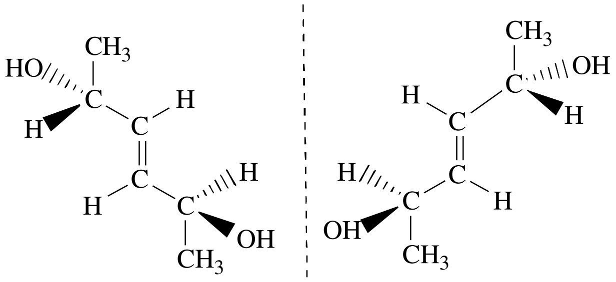
Enantiomers



Plane of symmetry
Identical Configurations



Enantiomers



Centre of symmetry
Identical Configurations

CHAPTER 20

INDUCTIVE AND RESONANCE EFFECTS

INDUCTIVE EFFECT

The inductive effect implies the atom's ability to cause bond polarization. This is due to the different electronegativity values of the two involved atoms. The σ electrons lie more near to the more electronegative atom and hence this atom acquires a partial negative charge. The other atom acquires an equal and opposite partial positive charge. This polarization can be expressed in terms of a physical quantity, known as *bond moment*. It is defined as

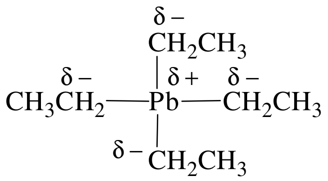
$$p = (\delta q)(d)$$

where δq is the partial charge on either atom and d is the distance between the two atoms. In Chemistry, it is customary to show the bond moment by an arrow pointing towards the electron pull. The dipole moment of the molecule is obtained by the vector addition of its bond moments.

The electronegativities of carbon and hydrogen are 2.5 and 2.2, respectively. Because of the small difference, C—H bonds are taken to be relatively nonpolar. Elements lying right to carbon in the periodic table, such as oxygen, fluorine, and chlorine, are more electronegative and hence attract electrons more strongly than carbon. Thus, when carbon bonds to one of these elements, carbon acquires partial positive charge and the other atom acquires partial negative charge as shown in the following example

$$\mathrm{CH_3—\overset{\delta+}{CH_2}—\overset{\delta-}{OH}}$$

On the other hand, elements lying left to carbon in the periodic table are less electronegative than carbon and attract electrons less strongly. Thus, when carbon bonds to one of these elements, the bond is polarized so that carbon bears a partial negative charge and the other atom bears a partial positive charge. This is shown in the following example.



$$\begin{array}{ccc} & \overset{\delta-}{\mathrm{CH_2CH_3}} & \\ & | & \\ \overset{\delta-}{\mathrm{CH_3CH_2}}— & \overset{\delta+}{\mathrm{Pb}} & —\overset{\delta-}{\mathrm{CH_2CH_3}} \\ & | & \\ & \overset{\delta-}{\mathrm{CH_2CH_3}} & \end{array}$$

+*I* and –*I* Groups Atoms or groups which push electrons towards carbon atom are said to have +*I* effect whereas those pushing away from carbon atom are said to have – *I* effect. +*I* effect is exhibited by electron-releasing groups and –*I* effect is exhibited by electron-attracting groups.

A few examples of +*I* and –*I* groups are given below.

+*I* Group: $—CH_3$, $—CH_2CH_3$, $—CH(CH_3)_2$, $—C(CH_3)_3$

–*I* Group: $—C_6H_5$, —OH, $—OCH_3$, —Cl, —Br, —COOH, —CN, $—NO_2$

RESONANCE EFFECT

The resonance effect implies the dispersion of electrical charges over several atomic centres caused by the movement of delocalized electrons. This effect makes the species more stable. For example, carbanion shown in Fig. 20.1 gets stabilised due to resonance effect.

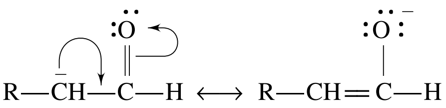


Fig. 20.1 Resonance stabilisation of a carbanion

The groups —OH and —NH_2 are electron releasing groups in aromatic compounds (Fig. 20.2). This is due to resonance effect and operates via p–orbital overlap with the aromatic-ring pi electrons. Both oxygen and nitrogen also exhibit inductive effect. However, the resonance electron-donating effect far outweighs the inductive electron-withdrawal effect for these substituents.

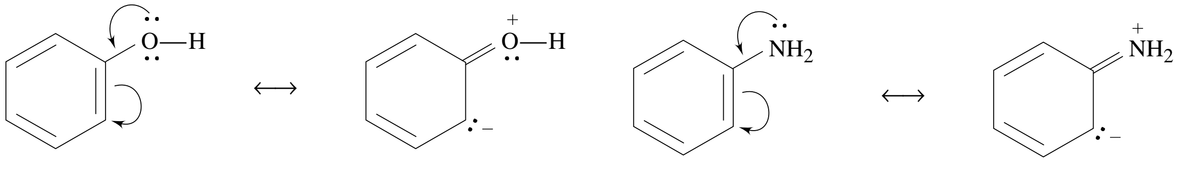


Fig. 20.2 Resonance donation of pi electrons

ACIDS AND BASES

According to the Bronsted-Lowry definition, an acid is a substance that donates a proton (H^+), and a base is a substance that accepts a proton. Transfer of a proton from acid to base is represented as

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{base}}}{A^-} + \underset{\substack{\text{conjugate}\\ \text{acid}}}{HB^+} \qquad (1)$$

A strong acid HA produces weak conjugate base and vice versa.

To chemists, the Lewis definition of acids and bases is more useful. A Lewis acid is a substance that accepts an electron pair and a Lewis base is a substance that donates an electron pair. All Lewis acids have vacant, low-energy orbitals that can accept electron pairs. The common examples in organic chemistry are BF_3, $AlCl_3$, $FeCl_3$ and $ZnCl_2$. Most organic compounds containing oxygen and nitrogen are good Lewis bases.

Strengths of acids In aqueous solution, transfer of proton from an acid to water (base) is represented as

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

This equilibrium is expressed as $K_a = K_{eq}[H_2O] = \dfrac{[A^-][H_3O^+]}{[HA]}$

The values of K_a are conveniently expressed as

$$pK_a^\circ = -\log K_a^\circ$$

Stronger acids have larger values of K_a (or lesser values of pK_a°) whereas weaker acids have smaller values of K_a (or larger values of pK_a°).

The relative strength of some common acids and their conjugate bases are as follows.

Acids	HCl >	HNO_3 >	HF >	CH_3COOH >	HCN >	H_2O >	C_2H_5OH
pK_a°'s	–7.0	–1.3	3.2	4.72	9.2	15.74	16.00
Conjugate bases	Cl^- <	NO_3^- <	F^- <	CH_3COO^- <	CN^- <	OH^- <	$C_2H_5O^-$

Since the dissociation of a carboxylic acid (which is a weaker acid) is an equilibrium process (such as $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$), any factor that stabilises carboxylate anion relative to undissociated carboxylic acid increases the acidity of the acid. Conversely, any factor that destabilises carboxylate anion relative to undissociated acid should result in decreased acidity.

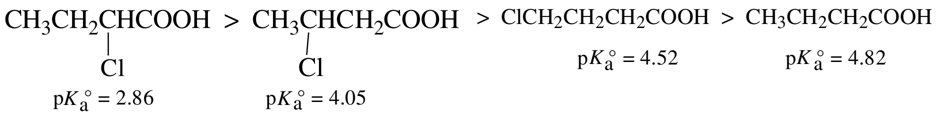
Electron-withdrawing group (i.e. – *I* group) attached to the carboxyl group withdraws electron density inductively and hence stabilises the carboxylate anion and increases acidity of acid. On the other hand, the electron-releasing group (i.e. +*I* group) have exactly the opposite effect by destabilising the carboxylate anion and hence decreases acidity.

A few examples are as follows.

$$-I \text{ Groups:} \quad \underset{pK_a^\circ = 0.64}{Cl_3CCOOH} > \underset{pK_a^\circ = 1.26}{Cl_2CHCOOH} > \underset{pK_a^\circ = 2.85}{ClCH_2COOH} > \underset{pK_a^\circ = 4.72}{CH_3COOH}$$

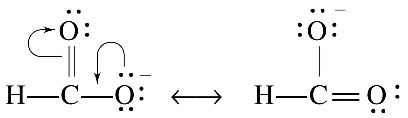
$$+I \text{ Groups:} \quad CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$$

Inductive effects are strongly dependent on the distance. For example, the strength of halogen substituted carboxylic acids decreases as the distance of halogen is increased from carboxylic group:



$$\underset{pK_a^\circ = 2.86}{CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH} > \underset{pK_a^\circ = 4.05}{CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2COOH} > \underset{pK_a^\circ = 4.52}{ClCH_2CH_2CH_2COOH} > \underset{pK_a^\circ = 4.82}{CH_3CH_2CH_2COOH}$$

Another factor which also contributes to acid strength is the extra stability of the resultant anion due to the resonance. For example, formate anion gets stabilised by resonance and hence formic acid is comparatively a stronger acid than acetic acid:



HOMOLYTIC AND HETEROLYTIC CLEAVAGES

The breaking of a bond in an organic reaction can take place in the two different ways.

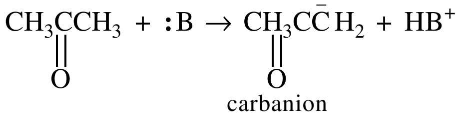
1. Homolytic Cleavage In this cleavage, the bonding electrons are equally divided into the two atoms resulting in the formation of free radicals.

$$A : B \rightarrow A^{\cdot} + {}^{\cdot}B$$

Free radicals are electrically neutral species and contain one unpaired electrons. These are extremely reactive species and thus the reactions involving these usually proceed with very fast speed.

2. Heterolytic Cleavage In this cleavage, both the bonding electrons go to the more electronegative atom resulting into the formation of positively and negatively charged species. Depending upon the atom or group attached to carbon, this cleavage results in the formation of either carbonium ion or carbocation (carbon carrying positive charge) or carbanion (carbon carrying negative charge):

$$(CH_3)_3CBr \rightarrow \underset{\text{carbocation}}{(CH_3)_3C^+} + :Br^-$$



$$CH_3\underset{\displaystyle O}{\underset{\|}{C}}CH_3 + :B \rightarrow \underset{\text{carbanion}}{CH_3\underset{\displaystyle O}{\underset{\|}{C}}\bar{C}H_2} + HB^+$$

The reactions involving heterolytic cleavage of bonds proceed via polar or ionic mechanism.

Stability of carbocation and carbanion A carbocation or carbanion may be stabilised through inductive and resonance effects. From the inductive effect viewpoint, any substitutent which helps spreading positive (or negative) charge on carbon over the entire species makes carbocation (or carbanion) more stable. Hence,

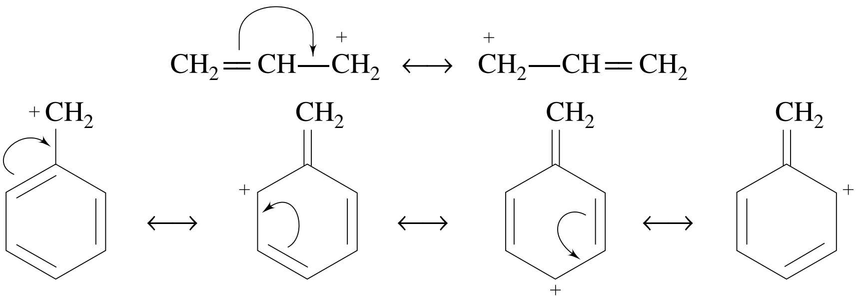
Electron-releasing group (+*I* group) stabilises carbocation and destabilises carbanion
Electron-withdrawing group (–*I* group) destabilises carbocation and stabalises carbanion.

For example, the stability of carbocations follow the order given below.

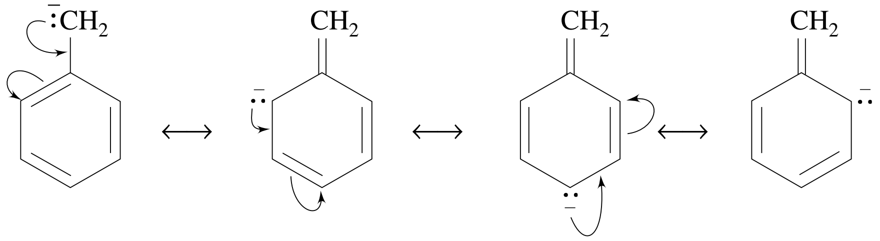
$$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$$

$$Cl_3C^+ < Cl_2CH^+ < ClCH_2^+ < CH_3^+$$

Resonance effect also influences the stability of carbocation and carbanion. For example, allyl and benzyl carbocations are much more stable than propyl carbonium ion:



Similarly, benzyl carbanion is more stable than propyl carbanion:



Classification of Carbonium ion The carbonium ion has been classified into primary (or 1°), secondary (or 2°) and tertiary (or 3°) depending upon one, two and three carbon atoms to which C^+ is attached with. For example,

$CH_3\overset{+}{C}H_2$	$(CH_3)_2C^+H$	$(CH_3)_3\overset{+}{C}$
primary (or 1°)	secondary (or 2°)	tertiary (or 3°)

Classification of Reagents Two types of reagents may be distinguished on the basis of their centre of attack. These are given below.

Electrophiles or Electrophilic Reagents The reagents which attack region of high electron density (negative centres) are knwon as electrophiles (meaning electron loving). These include positive ions (such as carbonium ion) and neutral molecules with electron-deficient centres. Examples are

$$H^+,\ Cl^+,\ Br^+,\ I^+,\ NO_2^+,\ R_3C^+,\ RN_2^+,\ AlCl_3,\ BF_3,\ ZnCl_2,\ FeCl_3,\ ICl,\ NOCl$$

Nucleophiles or Nucleophilic Reagents The reagents which attack region of high positive charge density are known as nucleophiles (meaning nucleus loving). These include negative ions (such as carbanion) and neutral molecules with free electron pairs. Examples are

$$Cl^-,\ Br^-,\ I^-,\ CN^-,\ OH^-,\ R\overset{-}{C}H_2,\ NH_3,\ H_2O,\ ROH$$

TYPES OF ORGANIC REACTIONS

The common organic reactions may be classified into three categories, viz., substitution reactions, addition reactions and elimination reactions. A brief description of these is in order.

1. Substitution Reactions In these reactions, an atom attached to carbon atom of a molecule is replaced by another atom. These reactions may be initiated by free radical, electrophile or nucleophile.

Free-radical substitution One of the common examples is the reaction between CH_4 and Cl_2. The reaction is initiated by the homolytic cleavage of Cl_2 by sunlight. The mechanism of the reaction is as follows.

(a) *Initiation step*

$$Cl : Cl \rightarrow 2\,{}^{\bullet}Cl$$

(b) *Propagation steps*

$$CH_4 + {}^{\bullet}Cl \rightarrow CH_3^{\bullet} + HCl$$
$$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$$

……………… ………………

……………… ………………

(c) *Termination steps*

$$Cl^{\bullet} + {}^{\bullet}Cl \rightarrow Cl_2$$
$$CH_3^{\bullet} + {}^{\bullet}Cl \rightarrow CH_3Cl$$

The reactivity of X_2 (=F_2, Cl_2, Br_2, I_2) with CH_4 decreases from F_2 to I_2. Though initiation step is endothermic, the rate of reaction is not determined by this step but seems to be decided by the first reaction in the propagation step as the activation energy increases from F_2 to I_2. This energy which decides the fraction of collisions of sufficient energy for the reaction to proceed in the forward direction.

Electrophilic Substitution Reactions The reaction initiated by an electrophile is known as electrophilic substitution reaction. Aromatic substitution reactions are the examples of this type of reaction. For example,

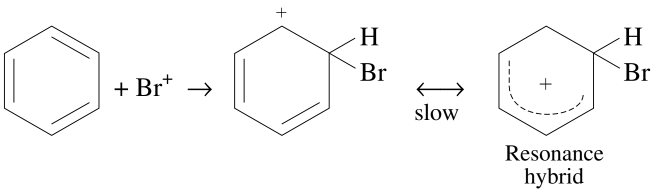
$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$

The mechanism of this reaction is as follows.

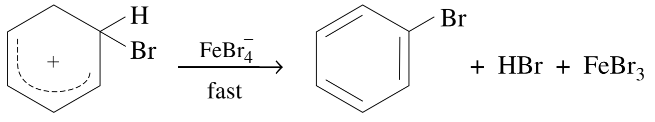
(a) *Formation of an electrophile*

$$Br : Br + \underset{\text{lewis acid}}{FeBr_3} \rightarrow \underset{\text{electrophile}}{Br^+} + FeBr_4^-$$

(b) *Electrophilic attack*



(c) *Elimination of proton*



Nucleophilic Substitution Reactions The reaction involves an attack by a nucleophile. The reaction can proceed either via S_N1 or S_N2 mechanism.

In S_N1 mechanism, rate determining step involves only one molecule. For example, the reaction

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

proceeds as follows.

(a) Formation of carbonium ion $(CH_3)_3CBr \xrightarrow[\text{step}]{\text{rate determining}} \underset{\text{carbonium ion}}{(CH_3)_3C^+ + Br^-}$

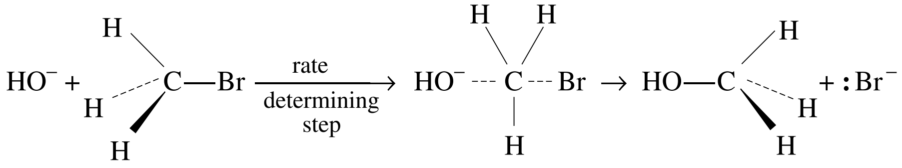
(b) Attack by the nucleophile $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$

The stability of carbonium ion is the controlling factor for this mechanism. The formation of 3° carbonium ion as an intermediate proceeds via this mechanism. In an optically active compound, substitution at chiral atom via S_N1 produces racemic mixture.

In S_N2 mechanism, rate determining step involves two species. For example, the reaction

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

proceeds via this mechanism which may be represented as follows.



transition state

Since 1° carbonium ion is less stable than the transition state formed above, the reaction involving primary alkyl halides proceed via S_N2 mechanism. During the reaction, configuration of carbon is inverted. This is known as Walden inversion.

Secondary alkyl halides may undergo hydrolysis by either S_N1 or S_N2 mechanism depending upon the comparative stability of 2° carbonium ion and the transition state. In general, S_N2 mechansim is strongly inhibited by increasing steric bulk of the reagents. In such a case, S_N1 is favoured.

The order of reactivity of nucleophiles in a nucleophilic substitution reaction decreases as the base strength of the leaving group increases, i.e. the weaker the Brönsted basicity of X^- in RX, the better leaving group is X^- and the more reactive is RX.

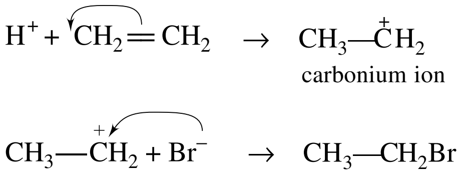
2. Addition Reactions In these reactions, atoms or groups of atoms are simply added to a double or triple bond. The addition may be initiated by an electrophile or nucleophile.

Electrophilic addition reaction The reaction

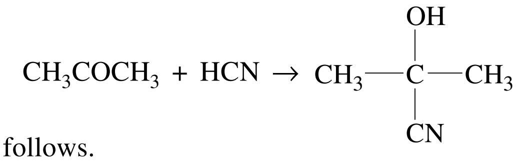
$$CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$$

involves an initial attack by the electrophile H^+ to the double bond followed by the addition of Br^-. The mechanism may be formulated as follows.

$$H{-}Br \rightarrow \underset{\text{electrophile}}{H^+} + \underset{\text{nucleophile}}{Br^-}$$



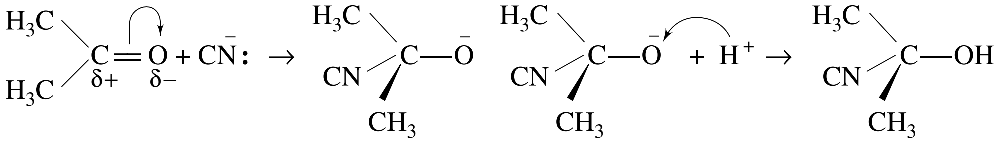
Nucleophilic addition reaction In this reaction, an initial attack of a nucleophile takes place. The addition of species across $>C{=}O$ (carbon-oxygen) double bond proceeds via this mechansim. For example, the reaction



$$CH_3COCH_3 + HCN \rightarrow CH_3{-}\underset{CN}{\overset{OH}{C}}{-}CH_3$$

proceeds as follows.

$$H{-}CN \rightarrow H^+ + CN{:}^-$$



3. Elimination Reactions In these reactions, atoms or group of atoms attached to adjacent carbon atoms are eliminated to generate double or triple bond. For example

$$R{-}CH_2{-}CH_2{-}X \xrightarrow{\text{KOH (alc.)}} R{-}CH_2{=}CH_2$$

The reaction may proceed via E1 or E2 mechanism.

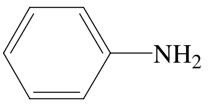
Straight Objective Type

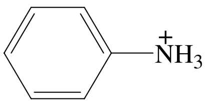
Inductive and Resonance Effects

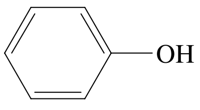
1. The inductive effect
   (a) implies the atom's ability to cause bond polarization
   (b) increases with increase in distance
   (c) implies the transfer of lone pair of electrons from more electronegative atom to lesser electronegative atom in a molecule
   (d) implies the transfer of lone pair of electrons from lesser electronegative atom to more electronegative atom in a molecule
2. Which of the following belongs to +*I* group?
   (a) —OH (b) $-OCH_3$ (c) —COOH (d) $-CH_3$
3. Which of the following belongs to –*I* group?
   (a) $-C_6H_5$ (b) $-CH_3$ (c) $-CH_2CH_3$ (d) $-C(CH_3)_3$

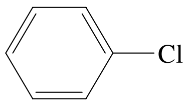
4. The oxygen atom in phenol
 (a) exhibits only inductive effect
 (b) exhibits only resonance effect
 (c) has more dominating resonance effect than inductive effect
 (d) has more dominating inductive effect than the resonance effect

5. In which of the following molecules, the resonance effect is not present?

(a) 

(b) 

(c) 

(d) 

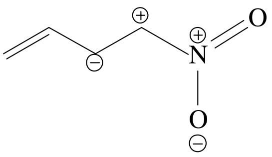
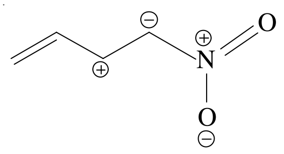
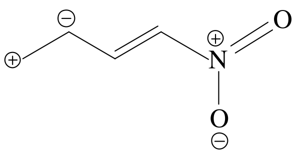
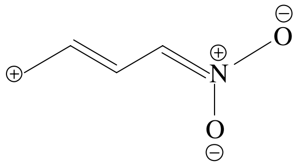
6. Which of the following orders is correct regarding the –*I* effect of the substituents?
 (a) $-NR_2 > -OR > -F$ (b) $-NR_2 < -OR < -F$
 (c) $-NR_2 > -OR < -F$ (d) $-NH_2 < -OR > -F$

7. 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) $-SR < -OR < -\overset{+}{O}R_2$

8. The number of resonating structures of allyl radical is
 (a) 1 (b) 2 (c) 3 (d) 4

9. For 1-methoxy-1, 3-butadiene, which of the following resonating structures is the least stable?
 (a) $H_2C{=}C{-}\overset{\oplus}{C}H{-}\overset{\ominus}{C}H{-}O{-}CH_3$ (b) $H_2C{=}CH{-}\overset{\ominus}{C}H{-}CH{=}\overset{\oplus}{O}{-}CH_3$
 (c) $H_2\overset{\ominus}{C}{-}\overset{\oplus}{C}H{-}CH{=}CH{-}O{-}CH_3$ (d) $H_2\overset{\ominus}{C}{-}CH{=}CH{-}CH{=}\overset{\oplus}{O}{-}CH_3$ (2005)

10. Among the following, the least stable resonance structure is

(a) 
(b) 
(c) 
(d) 
(2007)

11. The correct stability order of the resonance structures

$$\underset{\text{(I)}}{H_2C{=}\overset{+}{N}{=}\underset{\cdot\cdot}{\overset{-}{N}}\colon} \quad \underset{\text{(II)}}{H_2\overset{+}{C}{-}\overset{\cdot\cdot}{N}{=}\underset{\cdot\cdot}{\overset{-}{N}}\colon} \quad \underset{\text{(III)}}{H_2\overset{-}{\overset{\cdot\cdot}{C}}{-}\overset{+}{N}{\equiv}N\colon} \quad \underset{\text{(IV)}}{H_2\overset{-}{\overset{\cdot\cdot}{C}}{-}\overset{\cdot\cdot}{N}{=}\overset{+}{N}\colon}$$

is
 (a) (I) > (II) > (IV) > (III) (b) (I) > (III) > (II) > (IV)
 (c) (II) > (I) > (III) > (IV) (d) (III) > (I) > (IV) > (II) (2009)

12. Hyperconjugation involves overlap of the following orbitals
 (a) $\sigma - \sigma$ (b) $\sigma - p$ (c) p – p (d) $\pi - \pi$ (2008)

13. Which of the following statements regarding resonance is **not** correct?
 (a) The different resonating structures of a molcule have fixed arrangement of atoms
 (b) The different resonating structures differ in the arrangement of electrons.
 (c) All resonating structures are equally probable
 (d) The characteristics of a molecule exhibiting resonance cannot be explained on the basis of one resonating structure

Strengths of Acids and Bases

14. Which of the following orders of relative strength of acids is correct?
 (a) $CH_3COOH > HCN > H_2O > C_2H_5OH$ (b) $CH_3COOH < HCN < H_2O < C_2H_5OH$
 (c) $CH_3COOH > HCN < H_2O < C_2H_5OH$ (d) $CH_3COOH < HCN < H_2O > C_2H_5OH$

15. Which of the following orders of relative strength of bases is correct?

(a) $CH_3COO^- > CN^- > OH^- > C_2H_5O^-$ (b) $CH_3COO^- < CN^- < OH^- < C_2H_5O^-$

(c) $CH_3COO^- > CN^- < OH^- < C_2H_5O^-$ (d) $CH_3COO^- < CN^- < OH^- > C_2H_5O^-$

16. Which of the following orders is true regarding the acidic nature of COOH?

(a) Formic acid > Acetic acid > Propanoic acid (b) Formic acid > Acetic acid < Propanoic acid

(c) Formic acid < Acetic acid > Propanoic acid (d) Formic acid < Acetic acid < Propanoic acid

17. Which of the following orders is correct regarding the basicity of NH_2 group?

(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$ (b) $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

(c) $CH_3NH_2 > (CH_3)_2NH < (CH_3)_3N$ (d) $CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$

18. 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) $CH_3CH_2CH(Cl)COOH < CH_3CH(Cl)CH_2COOH > ClCH_2CH_2CH_2COOH$

19. Which of the following orders is correct regarding the acidity of carboxylic acid?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$ (b) $Cl_3CCOOH > Cl_2CHCOOH < ClCH_2COOH$

(c) $Cl_3CCOOH < Cl_2CHCOOH > ClCH_2COOH$ (d) $Cl_3CCOOH < Cl_2CHCOOH < ClCH_2COOH$

20. Which of the following orders is correct regarding the acidity of carboxylic acids?

(a) $(CH_3)_3CCOOH > (CH_3)_2CHCOOH > CH_3CH_2COOH$

(b) $(CH_3)_3CCOOH > (CH_3)_2CHCOOH < CH_3CH_2COOH$

(c) $(CH_3)_3CCOOH < (CH_3)_2CHCOOH > CH_3CH_2COOH$

(d) $(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3CH_2COOH$

21. From the following reaction

$$RONa + H_2O \rightleftharpoons ROH + NaOH$$

$$ROH + NaNH_2 \rightleftharpoons RONa + NH_3$$

predict which of the following sequences regarding acid strength is correct?

(a) $H_2O > NH_3 > ROH$ (b) $H_2O > ROH > NH_3$ (c) $NH_3 > H_2O > ROH$ (d) $ROH > NH_3 > H_2O$

22. From the following reaction

$$RONa + H_2O \rightleftharpoons ROH + NaOH$$

$$ROH + NaNH_2 \rightleftharpoons RONa + NH_3$$

predict which of the following orders regarding base strength is correct?

(a) $OH^- < NH_2^- > RO^-$ (b) $NH_2^- < OH^- < RO$ (c) $OH^- < RO^- < NH_2^-$ (d) $RO^- > NH_2^- > OH$

23. Which of the following statements is not correct?

(a) NH_3 is a stronger base than PH_3. (b) SH^- is a weaker base than OH^-

(c) CH_3COO^- is a weaker base than CH_3O^- (d) $CH_3SO_3^-$ is a stronger base than $CH_3SeO_3^-$

24. The pK_a° values of four acids are given below. Which one will correspond to the weakest acid?

(a) –1.3 (b) 4.72 (c) 9.2 (d) 16.0

25. The correct order of base strength amongst NH_3, CH_3NH_3 and NF_3 is

(a) $NH_3 > CH_3NH_3 > NF_3$ (b) $CH_3NH_3 > NH_3 > NF_3$

(c) $CH_3NH_3 > NF_3 > NH_3$ (d) $NF_3 > CH_3NH_3 > NH_3$

Stability of Carbocations, Carbanions and Radicals

26. Which of the following is **not** a nucleophile?

(a) BF_3 (b) CN^- (c) OH^- (d) NH_3

27. Which of the following is an electrophile?

(a) BF_3 (b) CO_2 (c) H_2O (d) NH_3

28. Which of the following is the most stable carbocation?

(a) $\overset{+}{C}H_3$ (b) $R\overset{+}{C}H_2$ (c) $R_2\overset{+}{C}H$ (d) $R_3\overset{+}{C}$

29. An electrophilic reagent must have

(a) a vacant orbital (b) an orbital containing one electron

(c) an orbital containing two electrons (d) all completely filled atomic orbitals

30. Which of the following is an electrophile?

(a) Na^+ (b) Li^+ (c) H^+ (d) Ca^{2+}

31. Which of the following is the most stable radical?

(a) $CH_3^\bullet$ (b) $RCH_2^\bullet$ (c) $R_2CH^\bullet$ (d) $R_3C^\bullet$

32. Which of the following statements is correct?

(a) + *I* Group stabilises a carbocation (b) + *I* Group stabilises a carbanion

(c) – *I* Group stabilises a carbocation (d) – *I* Group destabilises a carbanion

33. The relative order of stability of carbocations $R\overset{+}{C}{=}CH_2, R\overset{+}{C}H_2$ and $RCH{=}\overset{+}{C}H$ is

(a) $R\overset{+}{C}{=}CH_2 > R\overset{+}{C}H_2 > RCH{=}\overset{+}{C}H$ (b) $R\overset{+}{C}{=}CH_2 < R\overset{+}{C}H_2 < RCH{=}\overset{+}{C}H$

(c) $R\overset{+}{C}{=}CH_2 > R\overset{+}{C}H_2 < RCH{=}\overset{+}{C}H$ (d) $R\overset{+}{C}{=}CH_2 < R\overset{+}{C}H_2 > RCH{=}\overset{+}{C}H$

34. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is

(A) C—C (B) C—H (C) C—O (D) O—H (1988)

35. For the following reactions

$CH_3Cl \rightarrow CH_3^+ + Cl^-$ ΔH_1° $(CH_3)_2CHCl \rightarrow (CH_3)_2CH^+ + Cl^-$ ΔH_3°

$CH_3CH_2Cl \rightarrow CH_3CH_2^+ + Cl^-$ ΔH_2° $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ ΔH_4°

the correct order of enthalpies of ionization is

(a) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ > \Delta H_4^\circ$ (b) $\Delta H_1^\circ < \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$

(c) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ < \Delta H_4^\circ$ (d) $\Delta H_1^\circ > \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$

36. The order of stability of allyl, 3° and vinyl radicals is

(a) allyl > 3° > vinyl (b) 3° > allyl > vinyl (c) 3° > vinyl > allyl (d) vinyl > 3° > allyl

37. Which of the following has the highest nucleophilicity?

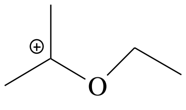
(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^- (2000)

38. The correct order of reactivity of the following types of H atom towards radical substitution is

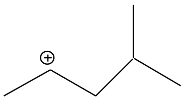
(a) allylic > vinylic > 1° H (b) allylic > 1° H > vinylic

(c) 1° H > allylic > vinylic (d) vinylic > allylic > 1° H

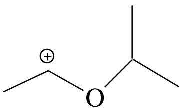
39. The correct stability order for the following species is



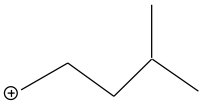
(I)



(II)



(III)

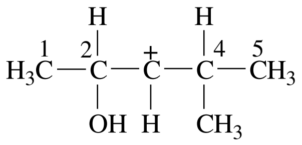


(IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)

(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV) (2008)

40. In the carbocation



$$\mathrm{H_3\overset{1}{C}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{\overset{2}{C}}}-\underset{\underset{H}{|}}{\overset{+}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{\overset{4}{C}}}-\overset{5}{C}H_3}$$

(2009)

the species H/CH_3 that is most likely to migrate the positively charged carbon is

(a) CH_3 at C—4 (b) H at C—4 (c) CH_3 at C—2 (d) H at C—2

41. The order of stability of the given carbocations is

(a) $(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C} > CH_3\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H$

(c) $(CH_3)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > CH_3\overset{+}{C}H_2$ (d) $(CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > (CH_3)_3\overset{+}{C}$

42. The order of stability of the given carbanions is

(a) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > CH_3\bar{C}H_2$ (b) $(CH_3)_3\bar{C} > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H$

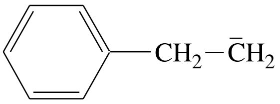
(c) $CH_3\bar{C}H_2 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$ (d) $CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

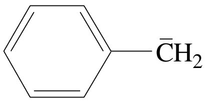
43. The order of stability of the given radical is

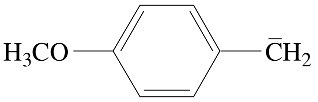
(a) $(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2$ (b) $(CH_3)_3\dot{C} > CH_3\dot{C}H_2 > (CH_3)_2\dot{C}H$

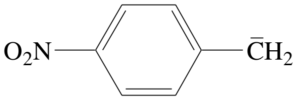
(c) $CH_3\dot{C}H_2 > (CH_3)_2\dot{C}H > (CH_3)_3\dot{C}$ (d) $CH_3\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H$

44. Amongst the given carbanions, which one is the most stable carbanion is

(a) 

(b) 

(c) 

(d) 

Characteristics of Reactions

45. The reaction $C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$ is

(a) an electrophilic addition reaction (b) a nucleophilic substitution reaction

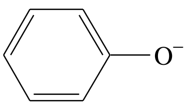
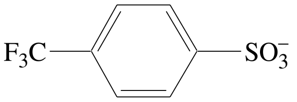
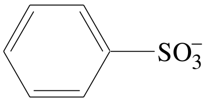
(c) an electrophilic substitution reaction (d) a free redical substitution reaction

46. An S_N2 reaction at an asymmetric carbon of a compound always gives

(a) an enantiomer of the substrate (b) a product with opposite optical rotation

(c) a mixture of diastereomers (d) a single stereoisomer (2001)

47. Amongst the given species, the best leaving group in a nucleophilic substitution reaction is

(a) OH^- (b)  (c)  (d) 

48. Amongst F^-, OH^-, I^- and $CF_3SO_3^-$, the order of tendency of leaving of a nucleophile in nucleophic reactions is

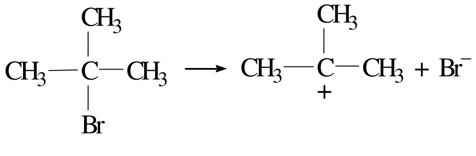
(a) $F^- < OH^- < I^- \quad CF_3SO_3^-$ (b) $CF_3SO_3^- < OH^- < F^- < I^-$

(c) $OH^- < F^- < I^- < CF_3SO_3^-$ (d) $CF_3SO_3^- < I^- < F^- < OH^-$

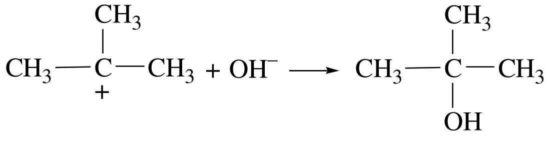
49. Amongst the halides, the order of tendency of leaving of a nucelophite in nucelophilic reactions is

(a) $I^- > Br^- > Cl^-$ (b) $I^- > Cl^- > Br^-$ (c) $Cl^- > Br^- > I^-$ (d) $Cl^- > I^- > Br^-$

50. The mechanism of the reaction between *tert*-butyl alcohol and hydroxide ion involves the following two steps.

Step 1 

$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3 + Br^-$$

Step 2 

$$CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3 + OH^- \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

Which of the following statements hold good for this mechanism?

(a) step 1 is fast and step 2 is slow (b) step 1 is slow and step 2 is fast

(c) both steps 1 and 2 are slow (d) both steps 1 and 2 are fast

Multiple Correct Choice Type

1. Which of the following statements is/are correct?
(a) I^- is a weaker base than F^-. (b) HO^- is a stronger base than H_2N^-.
(c) $HONH_2$ is a weaker base than NH_3. (d) F_3C^- is a stronger base than Cl_3C^-.

2. Which of the following orders regarding the stability of alkyl radicals is/are correct?
(a) benzyl > 3° > 2° > 1° (b) allyl < 3° > 2° > 1°
(c) 3° > 2° > 1° > vinyl (d) vinyl > benzyl > 3° > 2°

3. Which of the following statements is/are correct?
(a) In S_N1 mechanism, the rate determining step involves only one molecule.
(b) In S_N1 mechanism, intramolecular arrangement is possible.
(c) In chiral molecule, the S_N1 mechanism produces racemic mixture.
(d) The intermediate formed in S_N1 mechanisms involves five atoms attached to carbon centre of substitution reaction.

4. Which of the following statements is/are correct?
(a) In S_N2 mechanism, the rate determining step involves two species.
(b) The S_N2 mechanism involves the formation of intermediate carbocation.
(c) The S_N2 mechanism is accompanied with Walden inversion.
(d) The S_N2 mechanisms may involve intramolecular rearrangement.

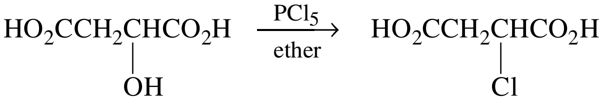
5. Which of the following statements are **not** correct?
(a) Methyl group belongs to $-I$ group.
(b) The $—OCH_3$ group belongs to $+I$ group.
(c) Resonance and tautomerism refer to one and the same phenomenon.
(d) The —OH and $—NH_2$ groups attached to aromatic ring have only resonance effects.

6. Which of the following statements are correct?
(a) BF_3 acts as a Lewis base.
(b) Stronger acids have lesser values of pK_a as compared to weaker acids.
(c) In an equilibrium reaction $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, CH_3COOH and CH_3COO^- constitute conjugate pair of acid and base.
(d) In a carboxylic acid RCOOH, the factor stabilizing the carboxylate anion, $RCOO^-$, relative to RCOOH increases the acidity of the acid.

7. Which of the following statements are correct?
(a) Electron-withdrawing group attached to the carboxyl group decreases the stability of the carboxylic acid.
(b) $+I$ group attached to carboxylic group weakens the acidity of carboxylic acid.
(c) Inductive effect is independent of the distance between the two centres.
(d) The resonate stabilization of formate anion makes formic acid stronger acid than acetic acid.

8. Which of the following statements are **not** correct?
(a) The stability of carbocations follows the order: $CH_3^+ > CH_3CH_2^+ > (CH_3)_2CH^+ > (CH_3)_3C^+$
(b) Nucleophilic substitution reaction involving S_N1 mechanism is always associated with the inversion of configuration of carbon atom.
(c) Nucleophilic substituion reaction involving S_N2 mechanism is always associated with the inversion of configuration of carbon atom.
(d) The $(CH_3)_3\dot{C}$ is more stable than $(CH_3)_2\dot{C}H$.

9. Which of the following statements are **not** correct?
(a) The reaction $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$ proceeds via S_N1 mechanism.
(b) The reaction $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ proceeds via S_N1 mechanism.
(c) The reaction

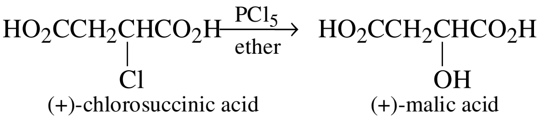


$$HO_2CCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCO_2H \xrightarrow[\text{ether}]{PCl_5} HO_2CCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCO_2H$$

(–)-malic acid (+)-chlorosuccinic acid

proceeds via S_N1 mechanism.

(d) The reaction



$$\underset{\text{(+)-chlorosuccinic acid}}{HO_2CCH_2\underset{\underset{Cl}{|}}{C}HCO_2H} \xrightarrow[\text{ether}]{PCl_5} \underset{\text{(+)-malic acid}}{HO_2CCH_2\underset{\underset{OH}{|}}{C}HCO_2H}$$

proceeds via S_N2 mechanism.

10. Which of the following statements are correct?

(a) The addition across C═O group is an electrophilic addition reaction.

(b) Aryl halides are less reactive than alkyl halides towards nucleophilic reagents.

(c) In acylium ion, the structure $R—C\equiv\overset{+}{O}$ is more stable than $R—\overset{+}{C}═O$.

(d) S_N2 reactions follow second-order kinetics.

Linked Comprehension Type

1. The mechanism of nucleophilic substitution reactions depends upon many factors. The S_N2 mechanism is mainly decided by the factors such as steric effect, nature of attacking nucleophile, the nature of leaving group and the nature of solvent. Identify the molecules/reagents with which the reaction mainly proceeds via S_N2 mechanism.

(i) Molecule proceeding with the maximum rate is

(a) CH_3X (b) $(CH_3)_2CHX$ (c) $(CH_3)_3CCH_2X$ (d) $(CH_3)_3CX$

(ii) Nucleophile leading to maximum reactivity is

(a) Cl^- (b) I^- (c) CN^- (d) HO^-

(iii) Halide leading to the maximum reactivity is

(a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I

2. The mechanism of nucleophilic reactions depends upon many factors. The S_N1 mechanism is mainly decided by the factors such as the nature of substrate, the nature of leaving group and the nature of solvent. Identify the molecule/reagent with which the reaction proceeds with S_N1 mechanism.

(i) Molecule expected to proceed with maximum tendency is

(a) CH_3X (b) $(CH_3)_2CHX$ (c) $(CH_3)_3CCH_2X$ (d) $(CH_3)_3CX$

(ii) Leaving group showing maximum reactivity is

(a) Tosylate anion (b) I^- ion (c) Br^- ion (d) Cl^- ion

(iii) Which of the following statements is correct?

(a) The nature of attacking nucleophile plays a dominant role

(b) The nature of attacking nucleophile plays no kinetic role

(c) Polar solvent decreases the reactivity

(d) Solvent with low dielectric constant increases the reactivity

3. The three steps in the free radical halogenation of methane are as follows.

Step 1 $X_2 \rightarrow 2X^\bullet$

Step 2 $X^\bullet + CH_4 \rightarrow HX + CH_3^\bullet$

Step 3 $CH_3^\bullet + X_2 \rightarrow CH_3X + X^\bullet$

For these three steps, answer the following three questions.

(i) The halogen having the largest bond dissociation enthalpy in Step 1 is

(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

(ii) The halogen radical for which the Step 2 is exothermic in nature is

(a) $F^\bullet$ (b) $Cl^\bullet$ (c) $Br^\bullet$ (d) $I^\bullet$

(iii) The halogen for which the Step 3 is highly exothermic is

(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

4. The three steps in the free radical halogenation of methane are as follows.

Step 1 $X_2 \rightarrow 2X^\bullet$

Step 2 $X^\bullet + CH_4 \rightarrow HX + CH_3^\bullet$

Step 3 $CH_3^\bullet + X_2 \rightarrow CH_3X + X^\bullet$

For these three steps, answer the following three questions.

(i) The halogen having the least bond dissociation enthalpy is
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

(ii) The halogen radical for which the Step 2 is highly endothermic in nature is
(a) $F^{\bullet}$ (b) $Cl^{\bullet}$ (c) $Br^{\bullet}$ (d) $I^{\bullet}$

(iii) The halogen for which the Step 3 is least exothermic is
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

Assertion and Reason Type

Given below are the two statements for each question. Answer these questions based on the following key.

(a) Both Statement-1 and Statement-2 are correct and the Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are correct and the Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	BF_3 exists where as BH_3 does not exist.	BF_3 is stable due to delocalization of electrons from F to B.
2.	Benzylic radical is more stable than 3° radical.	π-electron delocalization form extended conjugation in benzyl radical.
3.	$+I$ Group species stabilises a carbocation.	$+I$ Group species pushes electrons towards $\overset{+}{C}$ atom thereby have the effect of diminishing positive charge and hence enhances its stability.
4.	Resonance effect in a species generally makes it more stable.	Resonance is caused by the movement of delocalized electrons.
5.	In S_N1 mechanism, the nucleophile has no role in determining the rate of reaction.	In S_N1 reaction, the reaction follows first-order kinetics.
6.	The order of reactivity of halogens with methane follows the order $F_2 > Cl_2 > Br_2 > I_2$	The bond dissociation energy of halogens decides the reactivity of halogens with methane.
7.	The reactivity of halogen radical with methane follows the order $F^{\bullet} > Cl^{\bullet} > Br^{\bullet} > I^{\bullet}$	The activation energy for the reaction $X^{\bullet} + CH_4 \rightarrow {}^{\bullet}CH_3 + HX$ increases in the order $F^{\bullet} < Cl^{\bullet} < Br^{\bullet} < I^{\bullet}$
8.	The rate of overall reaction between methane and halogen is controlled by the formation of methyl radical in the reaction $X_2 + CH_4 \rightarrow {}^{\bullet}CH_3 + HX$	The reaction between ${}^{\bullet}CH_3$ radical and X_2 is exothermic in nature.
9.	The reaction of *tert*-butyl bromide and hydroxide ion to yield *tert*-butyl alcohol follows S_N1 mechanism.	In S_N1 mechanism, the rate of reaction depends only on the concentration of a single species.
10.	Carbocation is an exceedingly reactive particles.	The reactivity of carbocation is due to its tendency to complete the octet of carbon.
11.	The reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$ follows S_N1 mechanism.	An S_N2 reaction proceeds with complete stereochemical inversion.
12.	The reaction toward S_N2 substitution decreases as the number of substituents attached to carbon bearing the halogen is increased.	Differences in rate between two S_N2 reactions are mainly due to steric factor around the carbon bearing halogen.
13.	The amount of energy needed to form the various classes of carbocations decreases in the order $CH_3^+ > 1° > 2° > 3°$	The stability of the formed carbocation is reflected from this order which gives the stability as $3° > 2° > 1° > CH_3^+$

14.	The S_N1 reaction may accompany with the rearrangement of carbon skeleton of the molecule.	The order of stability of carbocation is $3° > 2° > 1° > CH_3^+$.
15.	The nature of leaving group in nucleophilic substitution reaction has no role to play in deciding the mechanism (S_N1 or S_N2) of the reaction.	The rate of reaction whether it proceeds via S_N1 or S_N2 is controlled by the nature of leaving group.

Matrix Match Type

1. Column I includes halogens and Column II lists their bond dissociation enthalpies. Match each entry of Column I with those given Column II.

Column I	**Column II**
(a) $F_2(g)$	(p) 243 kJ mol^{-1}
(b) $Cl_2(g)$	(q) 192 kJ mol^{-1}
(c) $Br_2(g)$	(r) 159 kJ mol^{-1}
(d) $I_2(g)$	(s) 151 kJ mol^{-1}

2. For the reaction $X^\bullet + CH_4 \rightarrow HX + {}^\bullet CH_3$, where ${}^\bullet X$ is halogen radical, Column I lists the halogen radicals and Column II lists the enthalpy of reactions. Match each entry of Column I with those of given in Column II

Column I	**Column II**
(a) $F^\bullet$	(p) 138 kJ mol^{-1}
(b) $Cl^\bullet$	(q) 67 kJ mol^{-1}
(c) $Br^\bullet$	(r) 4.2 kJ mol^{-1}
(d) $I^\bullet$	(s) –134 kJ mol^{-1}

3. For the reaction $X_2 + {}^\bullet CH_3 \rightarrow CH_3X + X^\bullet$, where X_2 is halogen, Column I lists the halogens and Column II lists the enthalpy of reactions. Match each entry of Column I with those given in Column II

Column I	**Column II**
(a) $F_2(g)$	(p) – 83.7 kJ mol^{-1}
(b) $Cl_2(g)$	(q) – 100 kJ mol^{-1}
(c) $Br_2(g)$	(r) – 109 kJ mol^{-1}
(d) $I_2(g)$	(s) – 293 kJ mol^{-1}

4. Column I lists some of the alkyl bromides and Column II lists the enthalpy of reaction $RBr \rightarrow R^+ + Br^-$. Match each entry of Column I with those of given in Column II.

Column I	**Column II**
(a) CH_3Br	(p) 623 kJ mol^{-1}
(b) CH_3CH_2Br	(q) 686 kJ mol^{-1}
(c) $CH_3CH(Br)CH_3$	(r) 770 kJ mol^{-1}
(d) $(CH_3)_3CBr$	(s) 916 kJ mol^{-1}

ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (a)	**4.** (c)	**5.** (b)	**6.** (b)	**7.** (a)
8. (b)	**9.** (a)	**10.** (a)	**11.** (b)	**12.** (b)	**13.** (c)	**14.** (a)
15. (b)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (a)	**20.** (d)	**21.** (b)
22. (c)	**23.** (d)	**24.** (d)	**25.** (b)	**26.** (a)	**27.** (a)	**28.** (d)
29. (a)	**30.** (c)	**31.** (d)	**32.** (a)	**33.** (a)	**34.** (d)	**35.** (a)
36. (a)	**37.** (c)	**38.** (d)	**39.** (d)	**40.** (d)	**41.** (a)	**42.** (d)
43. (a)	**44.** (d)	**45.** (c)	**46.** (d)	**47.** (c)	**48.** (c)	**49.** (a)
50. (b)						

Multiple Correct Choice Type

1. (a), (c), (d) **2.** (a), (c) **3.** (a), (b), (c) **4.** (a), (c)
5. (a), (b), (c), (d) **6.** (b), (c), (d) **7.** (b), (d) **8.** (a), (b)
9. (b), (c), (d) **10.** (b), (c), (d)

Linked Comprehension Type

1. **(i)** (a) **(ii)** (c) **(iii)** (d)
2. **(i)** (d) **(ii)** (a) **(iii)** (b)
3. **(i)** (b) **(ii)** (a) **(iii)** (a)
4. **(i)** (d) **(ii)** (d) **(iii)** (d)

Assertion Reason Type

1. (b) **2.** (b) **3.** (a) **4.** (b) **5.** (b) **6.** (d) **7.** (a)
8. (b) **9.** (b) **10.** (a) **11.** (d) **12.** (a) **13.** (a) **14.** (b)
15. (b)

Matrix Match Type

1. (a)-(r); (b)-(p); (c)-(q); (d)-(s) **2.** (a)-(s); (b)-(r); (c)-(q); (d)-(p)
3. (a)-(s); (b)-(r); (c)-(q); (d)-(p) **4.** (a)-(s); (b)-(r); (c)-(q); (d)-(p)

Hints and Solutions

Straight Objective Type

1. The inductive effect implies the atom's ability to cause bond polarization.

2. $+I$ group pushes electrons towards carbon atom. $—CH_3$ belongs to $+I$ group.

3. $–I$ group pushes electrons away from carbon atom. $—C_6H_5$ belongs to $–I$ group.

4. The oxygen atom in phenol has more dominating resonance effect than inductive effect.

5. Resonance effect is not present in $C_6H_5\overset{+}{N}H_3$.

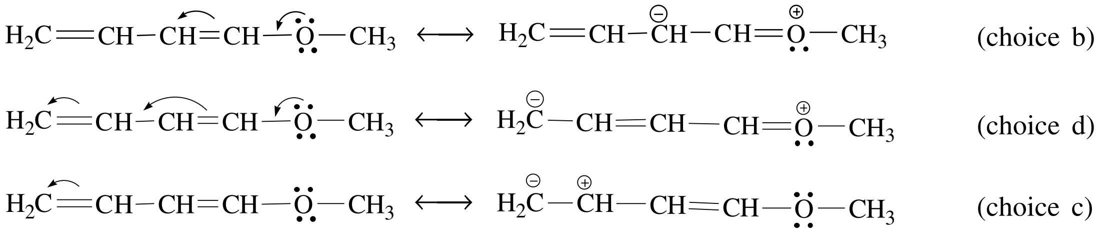
6. Larger the electronegativity of atom attached to carbon, larger its $–I$ effect. Hence, the correct order of $–I$ effect is $—NR_2 < —OR < —F$.

7. The correct order of $–I$ effect is $—I < —Br < —Cl < —F$

8. $\dot{C}H_2CH{=}CH_2 \longleftrightarrow CH_2{=}CH\dot{C}H_2$; there are two resonating structures.

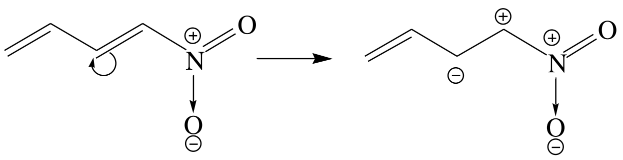
9. 1 methoxy-1, 3-butadiene is $H_2C{=}CH{—}H{=}CH{—}\ddot{\underset{\cdot\cdot}{O}}{—}CH_3$

Its resonanting structures may be visualized as follows.



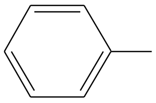
The structure $H_2C{=}CH{—}\overset{\oplus}{C}H{—}\overset{\ominus}{C}H{—}\ddot{\underset{\cdot\cdot}{O}}{—}CH_3$ (choice a) is expected to be least stable as the movement of electrons is in the opposite direction to that of electrons from oxygen of methoxy group.

10. In the structure (a), the movement of π-electrons of $—C{=}C—$ bond moves away from nitro group generating positively charged C near to the neighbouring positively charged N as shown in the following.



This leads to the least stability in the resonance structure.

11. The structure (I) will be the most stable as it maintains conjugation.
The structure (IV) will be the least stable as it loses conjugation and lesser electronegative carbon acquires negative charge
The structure (III) will be more stable than (II) as it maintains a triple bond between two nitrogens. Hence, the correct order of stability is (I) > (III) > (II) > (IV)

12. Hyperconjugation occurs in a molecular of the type CH$_3$ where p orbitals of benzene overlap with σ orbitals of CH$_3$ group. Hence, hyperconjugation involves σ – p orbitals overlap.

14. The order of relative strength of acids is $CH_3COOH > HCN > H_2O > C_2H_5OH$

15. Weaker the acid, stronger the conjugate base. So, the correct order is

$$CH_3COO^- < CN^- < OH^- < C_2H_5O^-$$

16. The acidic order is $HCOOH > CH_3COOH > CH_3CH_2COOH$.

17. The more electron-releasing group attached to NH$_2$, the stronger the base.

18. More near Cl atom to —COOH group, the stronger the acid.

19. Larger the number of Cl atoms, larger the acidity.

20. Larger the number of CH$_3$ groups, weaker the acidity.

21. $H_2O > ROH$ and $ROH > NH_3$.

22. We have RONa > NaOH and NaNH$_2$ > RONa. Hence, the correct order is $OH^- < RO^- < NH_2^-$

23. Bond angle H—P—H in PH$_3$ is near to 90°. The bonding of P with H atoms involves its p orbitals. The lone pair on P is in s atomic orbital. Bond angle H—N—H is near to 109°. The bonding of N with H atoms involves sp^3 orbitals. The fourth sp^3 orbital contains lone pair, which has directional characteristics and more available for bonding. Thus, NH$_3$ is a stronger base than PH$_3$.
H$_2$S is stronger acid than H$_2$O and thus HS$^-$ is weaker than OH$^-$.
CH$_3$COOH is stronger acid than CH$_3$OH and thus CH$_3$COO$^-$ is a weaker base than CH$_3$O$^-$.
The S and Se involve p-d π bonds with the three oxygen atoms, which bear some of the dispersed negative charge. Because of larger size of Se and involvement of 4d orbital in the overlap with 2p orbital of oxygen, there is less overlap and lesser dispersal of negative charge and hence negative charge is more available in $CH_3SeO_3^-$ and thus acts a stronger base than $CH_3SO_3^-$.

24. Weaker acid has smallest value of K_a and thus larger value of pK_a°.

25. CH$_3$ group is electron releasing while F is electron attracting .

26. BF$_3$ is not a nucleophile.

27. BF$_3$ is an electrophile.

28. Tertiary carbocation ($R_3\overset{+}{C}$) is the most stable.

29. An electrophilic reagent must have a vacant orbital.

30. H$^+$ is an electrophile. Na$^+$, Li$^+$ and Ca^{2+} do not have a vacant orbital.

31. Tertiary radical ($R_3\overset{\bullet}{C}$) is the most stable.

32. $+I$ Group stabilizes a carbocation.

33. The order of stability of carbocations is $R_3\overset{+}{C} > R_2\overset{+}{C}H > \underset{\text{secondary vinylic}}{R\overset{+}{C}=CH_2} > RCH_2 > \underset{\text{primary vinylic}}{RCH=\overset{+}{C}H}$

34. O—H will show heterolytic cleavage.

35. The more stable carbocation, the lesser the value of ΔH. Hence, the order is

$$\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ > \Delta H_4^\circ$$

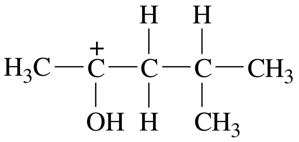
At high temperature, substitution at the allylic carbon occurs.

36. The order of stability of radicals is allyl > 3° > vinyl.

37. Stronger the base, higher the nucleophilicity. The order of acidity is $HF > H_2O > NH_3 > CH_4$ and the order of basicity is $F^- < OH^- < NH_2^- < CH_3^-$.

38. The correct order is allylic > 1° alkyl > vinylic. The less positive ΔH for the dissociation of C—H bond, the more reactive is H atom. The order of ΔH's is allylic < 1° alkyl < vinylic.

39. Electron-donating species stabilizes carbocation. Hence, (I) is more stable than (III).
2° carbocation is more stable than 1° carbocation. Hence, (II) is more stable than (IV).
Of the species (II) and (III), the species (III) will be more stable due to the lone-pair of electrons on oxygen atom. Hence, the order of stability is (I) > (III) > (II) > (IV).

40. It is H at C—2 that migrates to give 

$$H_3C-\overset{+}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_3$$

The positive charge on C—2 is resonance stabilized due to the neighbouring oxygen.

41. Larger the electron releasing group attached to $\overset{+}{C}$, larger the diminution of positive charge and larger the stability.

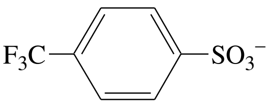
42. Lesser the electron releasing group attached to $\overset{-}{C}$, lesser is the enhancement of negative charge and larger the stability.

43. The carbon of radical is electron-deficient, electron-releasing group stabilizes the radical. Larger the groups attached, larger the stability.

44. Nitro is electron attracting group, it has a diminution effect on the negative charge on $\overset{-}{C}$ and thus causes the stabilization of carbanion.

45. Aromatic substitution is an electrophilic substitution reaction.

46. S_N2 reaction involves two species simultaneously and thus causes the inversion of stereochemistry of carbon.

47. The weaker the leaving base, the more reactivity of neucleophilic substitution reaction. Amongst the gives bases,  is the weakest base.

48. The order of acid strength is $CF_3SO_3H > HI > HF > H_2O$. The basicity of conjugate base follows the reverse order: $CF_3SO_3^- < I^- < F^- < OH^-$. The weaker the base, better the leaving nucelophile in the nucleophilic substitution reactions. Hence, the order of leaving nucleophile is $OH^- < F^- < H^- < CF_3SO_3^-$.

49. The order of acid strength is HI > HBr > HCl. The basicity of conjugate base follows the reverse order: I^- < Br < Cl^-. The weaker the base, better the leaving nucleophile in the nucleophilic substitution reactions. Hence, the order of leaving nucleophile is $I^- > Br^- > Cl^-$.

50. The reaction follows S_N1 mechanism with the formation of carbocation as the rate determining step. Thus, Step 1 is slow while Step 2 is fast.

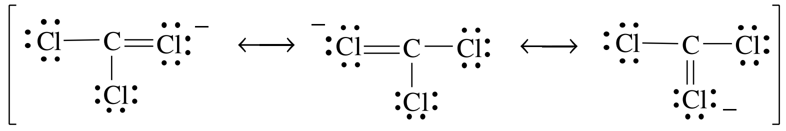
Multiple Correct Choice Type

1. (a) For elements in the same periodic group, the larger the basic site atom the more spread out (delocalized) is the charge and the weaker is the base. Thus, I^- is a weaker base than F^-. Alternatively, HI is stronger acid than HF, the conjugate base follows the reverse order.

(b) H_2O is a stronger acid than NH_3, thus, the conjugate base OH^- is weaker base than NH_2^-.

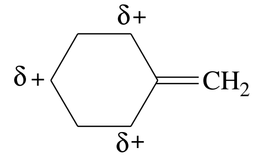
(c) Electron-attracting inductive effect of —OH decreases the electron density on N and thus decreases the basicity of $—NH_2$.

(d) In $Cl_3C{:}^-$, the unshared electron pair of the carbon in the p orbital undergoes extended p-d π bonding into an empty d orbital of each of the three Cl atoms:



Resonance stabilization makes a more dominating role than the inductive effect, making Cl_3C^- a weaker base than F_3C^-. In F, there is no d orbitals, hence, no stabilization occurs in F_3C^-.

2. Benzylic radical is most stable due to extensive π-electron delocalization



Allylic radical is also more stable due to resonance $H_2C{=}CH{-}\dot{C}H_2 \longleftrightarrow H_2\dot{C}{-}CH{=}CH_2$

In general, the stability follows the order 3° > 2° > 1°.

5. (a) A group pushing electrons away from the carbon atom to which it is attached is said to have *–I* effect. An alkyl group pushes electrons towards carbon to which it is attached and thus belongs to *+I* group.
(c) Resonance involves rearrangement of electrons only whereas tautomerism is the shift of active hydrogen from one atom to another in the molecule.
(d) Both inductive and resonance effect operate, but the latter is more predominating over the former.

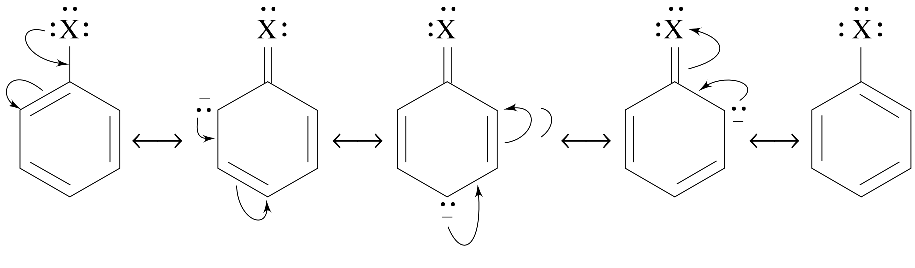
6. (a) BF_3 can accept a pair of electrons and is thus behave as a Lewis acid.

7. (a) Electron-withdrawing group stabilizes the carboxylate anion, hence increases the acidity of carboxylic acid.
(b) *+I* group is electron-releasing group and it destabilizes the carboxylate anion, hence decreases the acidity of carboxylic acid.
(c) Inductive effect is distance dependent.

8. (a) The correct order is $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$.
(b) In S_N1 mechanism, a planar carbocation is formed. Attack of a nuclephile may occur from either sides of planar geometry. Thus, it may or may not lead to inversion. In fact, S_N1 produces both types of configuration, inverted and noninverted.

9. (a) Since 3° carbocation is most stable, the reaction proceeds via the formation of 3° carbocation, i.e. S_N1.
(b) Since 1° carbocation is least stable, the reaction does not proceed via the formation of carbocation, i.e. S_N2.
(c) Since there is inversion in optical rotation, the reaction must have proceeded via S_N2 mechanism.
(d) Since there is no inversion in optical rotation, the reaction must have proceeded by S_N1 mechanism as in S_N2 there occurs inversion of configuration of carbon atom.

10. (a) The addition across $C{=}O$ group is a nucleophilic addition reaction.
(b) This is due to the following two factors.
(i) *Delocalization of electrons*



The delocalization imparts a partial double bond character to C—X bond making it stronger than C—X bond in alkyl halide.
(ii) *Difference in hybridization of carbon*
In alkyl halides, the carbon to which the halogen is attached is sp^3 hybridized while in aryl halide it is sp^2 hybridized. Therefore, the C—X bond in latter is shorter than in former.

(c) The acylium ion $R{-}C{\equiv}\overset{+}{O}{:}$ is more stable than $R{-}\overset{+}{C}{=}O$, the ordinary carbonium ion. In the former the octet of every atom is complete while in the latter it is not so, as in the case of C atom which has only 6 electrons.

CHAPTER 21

ALKANES

METHODS OF PREPARATION

1. **Decarboxylation of sodium salt of fatty acids** Sodium salt of a carboxylic acid produces alkane when it is dry distilled with sodalime (NaOH + CaO):

$$RCO_2Na + NaOH \xrightarrow[CaO]{} RH + Na_2CO_3$$

2. **Wurtz reaction** An alkyl halide produces alkane when it is made to react with Na in dry ether:

$$RBr + 2Na + BrR \xrightarrow[ether]{} R—R + 2NaBr$$

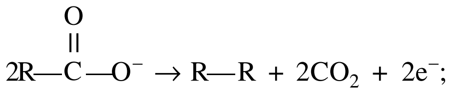
If R and R′ are different alkyl groups, the product obtained is a mixture of R—R, R—R′ and R′—R′.
Wurtz reaction constitutes one of the methods to ascent the alkane series.

3. **Corey-House alkane synthesis** To prepare alkane of the type R—R′, this method can be used. This involves the following three steps:

$$RBr + 2Li \xrightarrow[ether]{} RLi \quad + \quad LiBr; \qquad 2RLi + CuI \rightarrow \underset{\text{Lithium dialkyl cuperate}}{LiR_2Cu} \quad + \quad LiI$$

$$LiR_2Cu + R'Br \rightarrow R—R' + RCu + LiBr$$

4. **Kolbe electrolytic method** Electrolysis of concentrated solution of sodium salt of a carboxylic acid produces alkane.



Anodic reaction $2R—\overset{\overset{\displaystyle O}{||}}{C}—O^- \rightarrow R—R + 2CO_2 + 2e^-$; *Cathodic reaction* $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

5. **Hydrogenation of alkenes and alkynes** Reduction of alkenes and alkynes with H_2 in the presence of Ni catalyst at 200-300 °C produces alkanes:

$$CH_2{=}CH_2 + H_2 \xrightarrow[200\text{-}300°C]{Ni} CH_3—CH_3; \qquad CH{\equiv}CH + 2H_2 \xrightarrow[200 - 300\,°C]{Ni} CH_3—CH_3$$

6. **Reduction of alkyl halide** This may be done by using any of the following reducing agents:

Zn + HCl ; Zn + CH_3COOH ; Zn–Cu couple in ethanol ; $LiAlH_4$

The reaction may be formulated as $R—X + 2H \rightarrow RH + HX$

7. **Hydrolysis of Grignard reagent** $RMgX + H_2O \rightarrow RH + XMgOH$

PHYSICAL PROPERTIES

1. CH_4 to C_4H_{10} are gases, C_5H_{12} to $C_{17}H_{36}$ are liquids and higher ones are solids.
2. Being nonpolar, these are insoluble in water and soluble in nonpolar solvents like benzene and carbon tetrachloride.
3. Boiling point increases with molecular mass; branched chain isomer has a lower boiling point than normal alkane.
4. Liquid alkanes are lighter than water.

CHEMICAL PROPERTIES

Because of stronger C—H and C—C bonds, alkanes at room temperature are stable towards acids, bases, oxidizing and reducing agents and active metals.

A few important reactions of alkanes are as follows.

Halogenation This involves the substitution of hydrogen atom by halogen atom. The order of reactivity is $F_2 > Cl_2 > Br_2 (> I_2)$. Fluorine reacts explosively, chlorination is vigorous, bromination is slow and iodination is reversible.

The mechanism of chlorination and bromination involves free radicals. The reaction is initiated by the absorption of ultraviolet radiations or heating to about 250-400 °C. The following steps are involved in the mechanism of chlorination.

(a) *Chain-Initiation Step*

$$Cl_2 \xrightarrow[h\nu]{} 2\ {}^{\bullet}Cl$$

(b) *Chain-Propagation Step*

$$CH_4 + {}^{\bullet}Cl \rightarrow {}^{\bullet}CH_3 + HCl$$

$$Cl_2 + {}^{\bullet}CH_3 \rightarrow CH_3Cl + {}^{\bullet}Cl$$

$$\text{--------------}\qquad\text{----------------}$$

$$\text{--------------}\qquad\text{----------------}$$

(c) *Chain-Termination Step*

$$Cl^{\bullet} + {}^{\bullet}Cl \rightarrow Cl_2$$

$$CH_3^{\bullet} + {}^{\bullet}Cl \rightarrow CH_3Cl$$

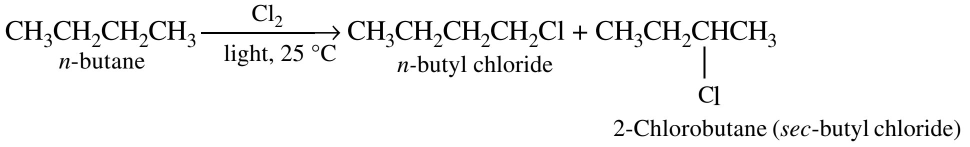
$$CH_3^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_3{-}CH_3$$

The chlorination is continued to produce CH_2Cl_2, $CHCl_3$ and CCl_4 depending upon the initial ratio of Cl_2 and CH_4. Only monochlorinaton takes place if methane is taken in a large excess in comparison to chlorine.

In more complex alkanes, the abstraction of each different kind of H atoms gives a different molecule. The factors determining the relative yields of the isomeric product are as follows.

1. *Probability factor* This factor is based on the number of H atoms of different types. for example, $CH_2CH_2CH_3$ contains six equivalent 1° H's and two equivalent 2° H's. Hence, the chance of removing 1°H relative to 2°H is 6 : 2, i.e., 3 : 1.
2. *Reactivity of* H The order of reactivity of H is 3° > 2° > 1°. At room temperature, the relative rates of abstraction of hydrogen atoms are 5.0 : 3.8 : 1.0.
3. *Reactivity of* X The more reactive $Cl^{\bullet}$ is less selective and more influenced by the probability factor and reactivity of H atoms. The less reactive $Br^{\bullet}$ is more selective and less influenced by the probability factors.

For example, the chlorination of $CH_3CH_2CH_2CH_3$ produces two isomers:



$$\underset{n\text{-butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, 25 °C}]{Cl_2} \underset{n\text{-butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-Chlorobutane (}sec\text{-butyl chloride)}}{CH_3CH_2\underset{|\atop Cl}{C}HCH_3}$$

The relative ratio of the two isomers is as follows.

$$\frac{n\text{-butyl chloride}}{sec\text{-butyl chloride}} = \frac{\text{number of 1° H}}{\text{number of 2° H}} \times \frac{\text{reactivity of 1° H}}{\text{reactivity of 2° H}} = \frac{6}{4} \times \frac{1.0}{3.8} = \frac{6}{15.2}$$

$$\text{Percentage of } n\text{-butyl chloride} = \frac{6}{21.2} \times 100 = 28.3$$

$$\text{Percentage of } sec\text{-butyl chloride} = 71.7$$

Bromination of methane proceeds at a slower rate because of difference in the energy of activation of the first reaction in chain propagation steps, namely,

$$Cl^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HX \qquad \Delta H^{\neq} = 17\ \text{kJ mol}^{-1}$$

$$Br^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HBr \qquad \Delta H^{\neq} = 75\ \text{kJ mol}^{-1}$$

Bromination of higher alkanes is decided by the reactivity H's atoms and not by probability factor. For example, the major product (90%) in the bromination of *n*-butane is 2-bromobutane.

Nitration $\mathrm{RH + HNO_3 \xrightarrow[400\text{-}500^{\circ}C]{} RNO_2 + H_2O}$

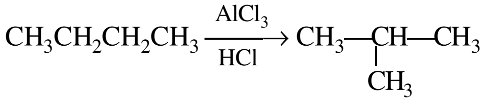
Higher alkanes produce mainly nitrated products because of breaking of C—C bonds.

Sulphonation $\mathrm{RH + \underset{fuming}{HO{-}SO_3H} \longrightarrow R{-}SO_3H + H_2O}$, where R is the larger alkyl group ($\geq C_6H_{13}$).

Oxidation $\mathrm{C}_n\mathrm{H}_{2n+2} + \left(\frac{3n+1}{2}\right)\mathrm{O_2} \rightarrow n\mathrm{CO_2} + (n+1)\ \mathrm{H_2O}$

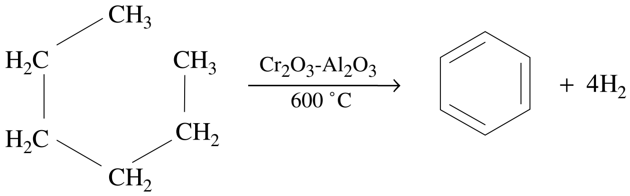
Large quantity of heat is generated in the combustion of alkanes.

Isomerization Normal alkanes are converted into branched-chain isomer in the presence of $AlCl_3$ and HCl.



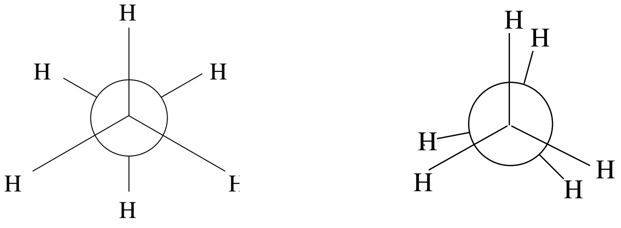
$$\mathrm{CH_3CH_2CH_2CH_3 \xrightarrow[HCl]{AlCl_3} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3}$$

Aromatization For example,



A few facts about alkanes are as follows.

1. CH_4 is known as Marsh gas. Natural gas coming out of petroleum wells contains 80–90 per cent methane. Coal gas contains up to the extent of 35 per cent. Methane can be conveniently prepared by treating aluminium carbide with water or dilute acid. $\mathrm{Al_4C_3 + 12HCl \rightarrow 3CH_4 + 4AlCl_3}$
2. Ethane can exist in different conformations due to the rotation of methyl groups about C—C bond axis. The Newman projection formulae for the conformations of ethane are shown in Fig. 1.



Staggered Eclipsed

Fig. 21.1 Newman projections of ethane

Staggered conformation has the lowest potential energy whereas eclipsed conformation has the highest potential energy. The difference between these two conformers is 11.3 kJ mol^{-1}.

CONFORMATION OF ETHANE AND BUTANE

An open-chain compound can assume different arrangements in space due to rotation of groups attached via C—C sigma bond. These arrangements are called conformations. For example, the rotation of two methyl groups about C—C bond in ethane results in different conformations.

An end-on-view of two carbon atoms attached by a sigma bond is shown by Newman projection in which the front carbon is shown by a projection point (also represents the hidden C—C bond) and the three groups attached to this carbon is shown by lines at 120° with respect to each other. The rear carbon atom is shown by a small circle. (whose centre lies at the projection point) and the three groups attached to it are shown by three partial lines at 120° with respect to each other. Figure 21.2 displays one of the Newman projection of ethane.

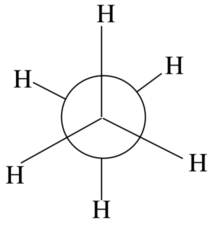


Fig. 21.2 A Newman projection of ethane

Because of rotation about its sigma bond, a molecule can assume a large number of conformations. However, certain conformations are more stable than others. The preferred conformations are called conformers.

The staggered Newman projection of ethane involves hydrogen atoms as far apart as possible from one another (Fig. 21.3a).

The eclipsed Newman projection of ethane involves hydrogen atoms as close as possible (infact, one behind the other). However, these atoms are not shown fully eclipsed so that these are visible (Fig. 21.3b).

The eclipsed conformation of ethane is about 11.3 kJ mol^{-1} less stable (of higher energy) than the staggered conformation. Figure 21.4 displays the variation of potential energy of ethane molecule as one methyl group completes one rotation relative to the other methyl group.

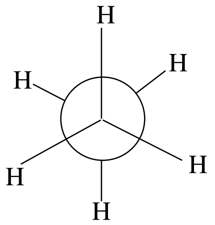


Fig. 21.3a Staggered conformation

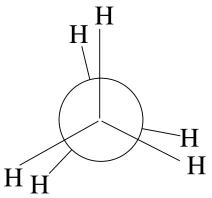


Fig. 21.3b Eclipsed conformation

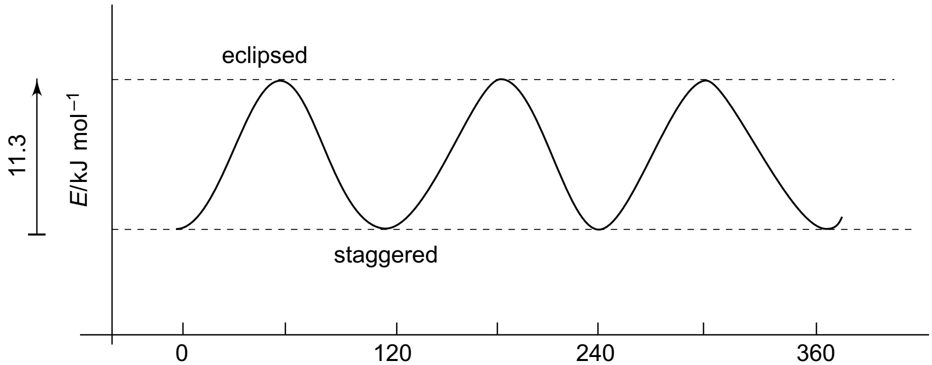


Fig. 21.4 Potential energy variation of ethane

CONFORMATION OF BUTANE

Butane ($CH_3CH_2CH_2CH_3$), like ethane, can exist in eclipsed and staggered conformations. Viewing butane from the centre of two carbons, two types of staggered conformations differing in the positions of the two methyl groups with respect to each other are possible (Fig. 21.5).

The conformer in which methyl groups are far apart is known as ‘anti’ (Greek anti, “against”) and that involving closer separation is known as gauche (French gauche, “left” or “crooked”). There exists larger torsional strain (repulsive forces between bonds on adjacent atoms) in gauche conformer as compared to anti conformer.

Similarly, two types of eclipsed conformations, namely, methyl near to methyl and methyl near to hydrogen, are possible (Fig. 21.5). The former has larger potential energy than the latter due to the larger repulsions between two bulky methyl groups.

Figure 21.6 displays the variation of potential energy of butane when the molecule rotates about C_2—C_3 carbon bond.

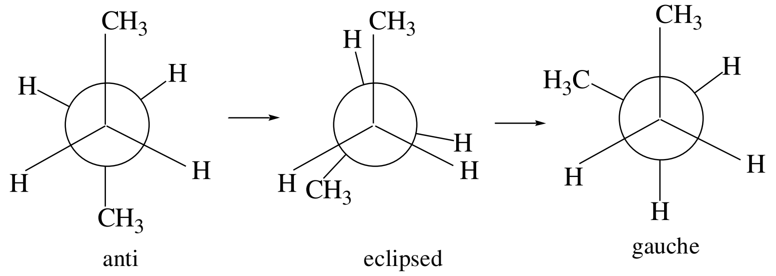


Fig. 21.5 Conformations in butane

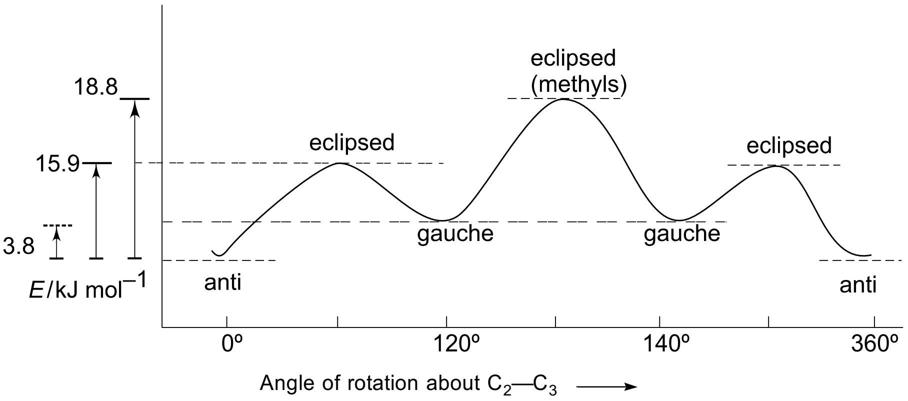


Fig. 21.6 Variation in potential energy caused by rotation about C_2—C_3

CONFORMATION OF CYCLOHEXANE

Cyclohexane exists as puckered ring involving no ring strain. Four conformations of cyclohexane are chair, half-chair, boat and twist-boat. Of these, chair form is most stable and half-chair is least stable. Twist-boat is more stable in boat conformers.

Straight Objective Type

Preparation of Alkanes

1. Electrolysis of concentrated solution of sodium propanate produces the hydrocarbon
   (a) methane (b) ethane (c) propane (d) butane
2. The treatment of C_2H_5MgI with water produces
   (a) methane (b) ethane (c) ethanal (d) ethanol
3. The product obtained on heating *n*-heptane with Cr_2O_3-Al_2O_3 at 600°C is
   (a) cyclohexane (b) cyclohexene (c) benzene (d) toluene
4. Marsh gas is
   (a) methane (b) ethane (c) ethene (d) ethyne
5. The per cent of methane in coal gas is about
   (a) 25 (b) 35 (c) 45 (d) 55
6. The treatment of aluminium carbide with water or dilute acid produces
   (a) acetylene (b) ethene (c) methane (d) ethane
7. Natural gas coming out of petroleum wells contains
   (a) 80-90% methane (b) 80-90% ethane (c) 80-90% propane (d) 80-90% butane
8. Wurtz reaction converts alkyl halide into alkane when it is made to react with
   (a) Na in alcohol (b) Na in dry ether (c) Zn in alcohol (d) Zn in dry ether

Physical Properties of Alkanes

9. The compound with the highest boiling point is
(a) *n*–hexane (b) *n*–pentane (c) 2,2–dimethylpropane (b) 2–methylbutane (1982)

10. The highest boiling point is expected for
(a) isooctane (b) *n*-octane
(c) 2,2,3,3-tetramethylbutane (d) *n*-butane (1986)

11. Which one of the following is expected to have minimum boiling point?
(a) *n*-Butane (b) *n*-Pentane (c) 2-Methylbutane (d) 2,2-Dimethylpropane

12. When cyclohexane is poured on water, it floats, because:
(a) cyclohexane is in 'boat' form (b) cyclohexane is in 'chair' form.
(c) cyclohexane is in 'crown' form (f) cyclohexane is less dense than water.

13. The relative stablility of the three isomers of pentane, namely, *n*-pentane, isopentane and neopentane follows the order
(a) *n*-pentane > isopentane > neopentane (b) *n*-pentane > neopentane > isopentane
(c) neopentane > isopentane > *n*-pentane (d) neopentane > *n*-pentane > isopentane

14. For the equilibrium *n*-butane $\rightleftharpoons$ isobutane, $\Delta G^\circ = -3.8$ kJ mol^{-1}. The K°_{eq} for this equilibrium at 298 K is about
(a) $10^{0.4}$ (b) $10^{0.5}$ (c) $10^{0.67}$ (d) $10^{0.75}$

Chemical Reactions of Alkanes

15. Alkanes can be iodinated in the presence of
(a) HI (b) I_2 and P (c) HIO_3 (d) PI_3

16. A single substitution of H atom in an alkane of molar mass 72 g mol^{-1} by chlorine produces only one product. The alkane is
(a) *n*-pentane (b) 2-methylbutane (c) 2,2-dimethylpropane (d) *n*-butane

17. The reaction conditions leading to the best yield of C_2H_5Cl are
(a) $C_2H_6(\text{excess}) + Cl_2 \xrightarrow{\text{uv ligiht}}$ (b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$
(c) $C_2H_6 + Cl_2(\text{excess}) \xrightarrow{\text{uv light}}$ (d) $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$ (1986)

18. The order of reactivity of halogens towards halogenation of alkanes is
(a) $F_2 > Br_2 > Cl_2$ (b) $F_2 > Cl_2 > Br_2$ (c) $Cl_2 > F_2 > Br_2$ (d) $Cl_2 > Br_2 > F_2$

19. The chlorination of an alkane involves
(a) Cl free radicals (b) Cl^+ species (c) Cl^- species (d) $CH_4^{\bullet}$ free radicals

20. The reactivity of hydrogen atom in an alkane towards substitution by bromine atom is
(a) 1° H > 2° H > 3° H (b) 1° H < 2° H < 3° H
(c) 1° H > 2° H < 3° H (d) 1° H < 2° H > 3° H

21. Bromination of an alkane as compared to chlorination proceeds
(a) at a slower rate
(b) at a faster rate
(c) with equal rates
(d) with equal or different rate depending upon the temperature

22. Bromination of *n*-butane produces
(a) 1-bromobutane as the major product
(b) 2-bromobutane as the major product
(c) both 1-bromo and 2-bromo products with equal percentages
(d) both 1-bromo and 2-bromo products whose percentages depend upon temperature

23. Chlorination of *n*-butane produces
(a) 1-chlorobutane as the chief product
(b) 2-chlorobutane as the chief product
(c) 1-chlorobutane more than 2-chlorobutane
(d) 2-chlorobutane more than 1-cholorobutane

24. Isomerization in alkane may be brought about by using
(a) Al_2O_3 (b) Fe_2O_3 (c) $AlCl_3$ and HCl (d) concentrated H_2SO_4

25. The major product obtained in the photobromination of 2-methylbutane is
(a) 1-bromo-2-methylbutane (b) 1-bromo-3- methylbutane
(c) 2-bromo-3-methylbutane (d) 2-bromo-2-methylbutane

26. The treatment of CH_3OH with CH_3MgI releases 1.04 mL of a gas at STP. The mass of CH_3OH added is
(a) 1.49 mg (b) 2.98 mg (c) 3.71 mg (d) 4.47 mg

27. The addition of 4.12 mg of an unknown alcohol, ROH, to CH_3MgI releases 1.56 mL of a gas at STP. The molar mass of alcohol is
(a) 32 g mol^{-1} (b) 46 g mol^{-1} (c) 61 g mol^{-1} (d) 74 g mol^{-1}

28. A sample of 1.79 mg of a compound of molar mass 90 g mol^{-1} when treated with CH_3MgI releases 1.34 mL of a gas at STP. The number of active hydrogen in the molecule is
(a) 1 (b) 2 (c) 3 (d) 4

29. Which of the following sequences regarding relative stability of free radicals is correct?
(a) $3° < 2° < 1°$ (b) $3° > 2° > 1°$ (c) $3° > 2° < 1°$ (d) $3° < 2° > 1°$

30. Which of the following sequences regarding ease of abstraction of hydrogen atom is correct?
(a) $3° < 2° < 1°$ (b) $3° > 2° > 1°$ (c) $3° < 2° > 1°$ (d) $3° > 2° < 1°$

31. Which of the following radicals has maximum stability?
(a) 3° (b) 2° (c) vinyl (d) benzyl

32. Which of the following radicals has least stability?
(a) 3° (b) 2° (c) vinyl (d) benzyl

33. Which of the following statements is not correct?
(a) At 300 °C, with reaction in the vapour phase, the relative rates of substitution of primary, secondary and tertiary hydrogen atom by chlorine are 1.00 : 3.25 : 4.43
(b) As the temperature increases, the relative rates of substitution of primary, secondary and tertiary hydrogen atom by chlorine become equal, i.e. 1 : 1 : 1
(c) Increasing pressure causes a decrease in the relative rates of primary hydrogen substitution by chlorine
(d) Bromination of alkene is more selective than chlorination.

34. Which of the following statements is not correct?
(a) Bromination takes place with greater difficulty than chlorination.
(b) Chlorine has a much greater tendency than bromine to replace tertiary hydrogen in preference to secondary or primary
(c) More reactive reagent shows less selectivity in reaction
(d) Chlorination of methane is retarded in the presence of oxygen.

35. For which halogen, X_2, the reaction $X_2 \longrightarrow 2\,X^{\cdot}$ has a maximum value of $\Delta H°$?
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

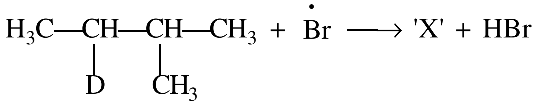
36. For which halogen radical, $X^{\cdot}$, the reaction $X^{\cdot} + CH_4 \longrightarrow HX + CH_3^{\cdot}$ has maximum positive value of $\Delta H°$?
(a) $F^{\cdot}$ (b) $Cl^{\cdot}$ (c) $Br^{\cdot}$ (d) $I^{\cdot}$

37. For which halogen, X_2, the reaction $CH_3^{\cdot} + X_2 \longrightarrow CH_3X + X^{\cdot}$ has the maximum negative value of $\Delta H°$?
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

38. Which of the following molecules has the maximum bond energy of the indicated C—H bond?
(a) $H_3C—H$ (b) $CH_3CH_2—H$ (c) $(CH_3)_2CH—H$ (d) $(CH_3)_3C—H$

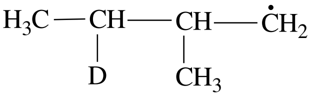
39. Which of the following molecules has the minimum bond energy of the indicated C—H bond?
(a) $CH_3—H$ (b) $CH_3CH_2—H$ (c) $(CH_3)_2CH—H$ (d) $(CH_3)_3C—H$

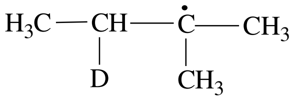
40. Consider the following reaction:

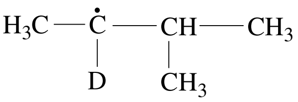


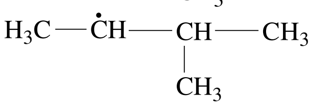
$$H_3C—\underset{D}{CH}—\underset{CH_3}{CH}—CH_3 + \overset{\bullet}{Br} \longrightarrow \text{'X'} + HBr$$

Identify the structure of the major product 'X'

(a) 
$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-\dot{C}H_2$

(b) 
$H_3C-\underset{D}{CH}-\underset{CH_3}{\dot{C}}-CH_3$

(c) 
$H_3C-\underset{D}{\dot{C}}-\underset{CH_3}{CH}-CH_3$

(d) 
$H_3C-\dot{C}H-\underset{CH_3}{CH}-CH_3$

(2002)

41. In the reaction

$(CH_3)_2CHCH_2CH_3 \xrightarrow[hv]{Cl_2}$ N isomers of $C_5H_{11}Cl \xrightarrow[\text{distillation}]{\text{Fractional}}$ n distilled products. The values of N and n respectively are

(a) 6,6 (b) 6,4 (c) 4,6 (d) 4,4 (2006)

Conformations of Alkanes

42. Which of the following will have least hindered rotation about carbon-carbon bond?

(a) Ethane (b) Ethylene (c) Acetylene (d) hexachloroethane (1987)

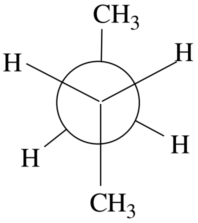
43. Which of the following conformations of cyclohexane has the minimum strain energy?

(a) Chair (b) Half-chair (c) Twist-boat (d) Boat

44. Which of the following conformations of cyclohexane has the maximum strain energy?

(a) Chair (b) Half-chair (c) Twist-boat (d) Boat

45. In the given conformation



C_2 is rotated about C_2—C_3 bond clockwise by an angle of 120°. The obtained conformation is

(a) *anti* conformation (b) *gauche* conformation

(c) partially eclipsed conformation (d) fully eclipsed conformation (2004)

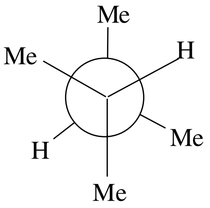
46. The energy difference between *staggered* and *eclipsed* conformations of ethane is 11.5 kJ mol^{-1}. Assuming entropy contribution negligible, the ratio *staggered* : *eclipsed* conformers at 300 K is about

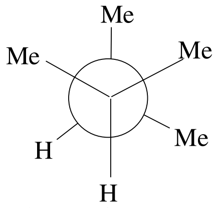
(a) 50 (b) 100 (c) 150 (d) 200

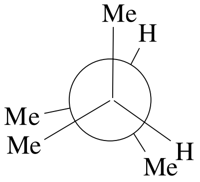
47. The energy difference between *anti* and *gauche* conformers of butane is about 3.8 kJ mol^{-1}. Assuming entropy contribution negligible, the ratio of *anti* : *gauche* conformers at 300 K is about

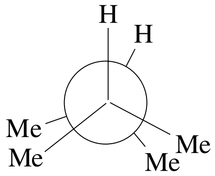
(a) $10^{0.40}$ (b) $10^{0.52}$ (c) $10^{0.66}$ (d) 10

48. Which of the following conformations has maximum potential energy?

(a) 

(b) 

(c) 

(d) 

49. Which of the following conformations of cyclohexane is most stable?

(a) Chair (b) Boat (c) Twist-boat (d) Half-chair

50. Which of the following conformation of cyclohexane is least stable?

(a) Chair (b) Boat (c) Twist-boat (d) Half-chair

Multiple-Correct Choice Type

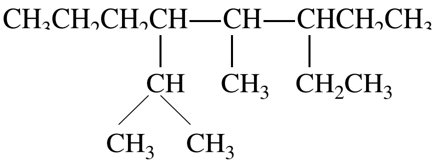
1. Which of the following statements are correct?

(a) Methane does not react with chlorine in the dark.

(b) Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio 9:1.

(c) The chlorination of methane may be limited almost entirely to monochlorination if methane is taken in large excess amount as compared to chlorine.
(d) Fluorination of methane required the use of light or heating to a high temperature.

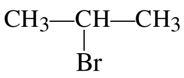
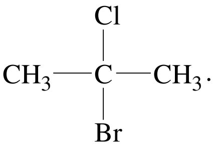
2. Which of the following statements are correct?
(a) The order of reactivity of halogen towards alkanes is $F_2 > Cl_2 > Br_2$.
(b) The reaction of Cl_2 and CH_4 proceeds via ionic mechanism.
(c) Oxygen acts as an inhibitor in the reaction between CH_4 and Cl_2.
(d) Iodine does not react with CH_4 at all.

3. Which of the following statements are **not** correct?
(a) The bond angle HCH in methyl radical is 109°28′.
(b) The eclipsed conformation of ethane has lower potential energy as compared to staggered conformation.
(c) The IUPAC name of  $CH_3CH_2CH_2\underset{\underset{CH_3\quad CH_3}{CH}}{CH}—\underset{CH_3}{CH}—\underset{CH_2CH_3}{CH}CH_2CH_3$ is 3-ethyl-4-methyl-5-isopropyloctane.
(d) Lower alkanes are soluble in water while higher ones are insoluble.

4. Which of the following statements are correct?
(a) Methane is the major constituent of natural gas.
(b) In the reaction $RMgX + NH_3 \rightarrow RH + Mg(NH_2)X$, ammonia acts as a base.
(c) The reactivity of hydrogen atom in alkane towards replacement by a halogen follows the order 3° > 2° > 1°.
(d) The relative enthalpy of formation of a free radical from the corresponding alkane follows the order 1° > 2° > 3°.

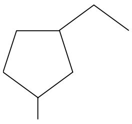
5. Which of the following statements are correct?
(a) The relative stability of free radical is 3° > 2° > 1° > $\dot{C}H_3$.
(b) The more stable the free radical, the more easily it is formed.
(c) When ethanol is treated with HI, ethyl iodide is formed.
(d) Alkanes burn in air with a luminous flame.

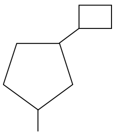
6. Which of the following statements are not correct?
(a) The percentage of *n*-propyl chloride obtained in the chlorination of propane is about 56%.
(b) The percentage of 1-chloro-2-methylpropane obtained in the chlorination of isobutane is about 64%.
(c) The percentage of *n*-propyl bromide obtained in the bromination of propane is 44%. The relative reactivities of 3°, 2° and 1° H atoms are 1600:82:1.
(d) The vinyl radical is more stable than 2° radical.

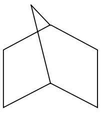
7. Which of the following statements are **not** correct?
(a) The chlorination of  $CH_3—\underset{Br}{CH}—CH_3$ yields  $CH_3—\overset{Cl}{\underset{Br}{C}}—CH_3$.
(b) The number of isomers of dimethylcyclopropane is three.
(c) The number of geometric isomers of 1,2,4-trimethylcyclohexane is three.
(d) Substituted cycloalkanes do not show geometrical isomers.

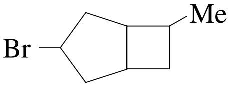
8. Which of the following statements are correct?
(a) Cycloheptane and cyclooctane are more stable than cyclohexane.
(b) The ring strain in cyclopropane is more than that in the cyclobutane.
(c) The C—H bond in cyclopropane is shorter than in propane.
(d) The H atoms in cyclopropane is more acidic than in propane.

9. Which of the following statements are correct?

(a) The IUPAC name of the compound  is 1-methyl-3-ethylcyclopentane.

(b) In IUPAC name of the compound  is 1-cyclobutyl-3-methylcylopentane.

(c) The IUPAC name of the compound  is bicyclo[2.2.1]heptane.

(d) The IUPAC name of the compound 

is 2-methyl-6-bromobicyclo[2.3.0]heptane.

10. Which of the following statements are correct?

(a) The octane value of *n*-heptane is zero.

(b) The octane value of isooctane is 100.

(c) The octane number of a mixture containing 85% isooctane and 15% heptane is 15.

(d) The 3° radicals react more slowly and smoothly with oxygen than the 1° and 2° radicals.

11. Which of the following statements are correct?

(a) The potential energy difference between eclipsed and staggered conformations of ethane is 12.552 kJ mol^{-1}. Ignoring the entropy effect, the ratio of staggered to eclipsed conformation at 25 °C is about 155.

(b) The potential energy difference between *anti* and *gauche* conformations of butane is about 3.8 kJ mol^{-1}. Ignoring the entropy effect, the ratio of *anti* to *gauche* conformations at 25 °C is about 2.6.

(c) The activation energy for the reaction $2\ Cl^{\cdot} \rightarrow Cl_2$ is zero.

(d) The free radical chlorination of CH_4 occurs faster than that of CD_4.

12. Which of the following statements are **not** correct?

(a) The shape of CH_3^+ is planar.

(b) The energy of activation of $Cl^{\bullet} + CH_4 \rightarrow HCl + CH_3^{\bullet}$ is larger than that of $Br^{\bullet} + CH_4 \rightarrow HBr + CH_3^{\bullet}$.

(c) The carbon atom in methyl radical is sp^3 hybridized.

(d) A branched-chain isomer of an alkane has a lower boiling point than a straight-chain isomer.

13. Which of the following statements are **not** correct?

(a) Alkanes are less dense than water.

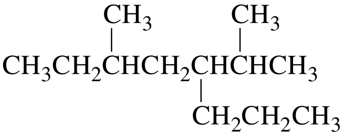
(b) In the reaction $RMgX + CH_3OH \rightarrow RH + Mg(OCH_3)X$, the methanol is a stronger acid than RH.

(c) A hydrocarbon contains all the three types of hydrogen atoms. i.e. 1°, 2° and 3°. The relative ratios of abstraction of 1° : 2° : 3° hydrogen atoms are 5.0 **:** 3.8 **:**1.0.

(d) The addition of 4.12 mg of an unknown alcohol to methylmagnesium iodide generates 1.56 mL of gas at STP. The molar mass of alcohol is 73 g mol^{-1}.

14. Which of the following statements are **not** correct?

(a) A sample of 1.79 mg of a compound (molar mass 90 g mol^{-1}) generates 1.34 mL of gas when treated with CH_3MgBr. The number of active hydrogen in the compound is two.

(b) The IUPAC name of the compound 

$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_3$

is 5-isopropyl-3-methyloctane.

(c) The number of trichloro derivatives of cyclopentane is three.

(d) The number of monochloro derivatives of isohexane is five.

15. Which of the following statements are correct?

(a) Of the vinyl, allyl, 3°, 2°, 1° and benzyl radicals, the least stable one is vinyl.

(b) Of the $C_6H_5CH_3$, $(CH_3)_3CH$, $(CH_3)_2CHCH_3$ and $CH_2{=}CHCH_3$, the maximum ease of abstraction of hydrogen atom is shown by $C_6H_5CH_3$.

(c) Free radical monochlorination of *tert*-butyl bromide gives 1-bromo-2-chloro-2 methyl propane.

(d) Of Cl_2, Br_2, and I_2, the most reactive halogen towards photohalogenation of alkanes is I_2.

16. Which of the following statements are **not** correct?

(a) The electrolysis of concentrated solution of sodium ethonate produces ethene.

(b) If the relative rates of abstraction of 2° and 1° hydrogen atoms are 3.8 and 1.0, respectively, then the percentage ratios of the products 1-chloro-, 2–chloro–, and 3-chloro–, obtained in the photochlorination of *n*-hexane would be 16.48 : 41.76 : 41.76.

(c) The relative rate of abstraction of 3°, 2° and 1° hydrogen atoms is maximum for 1° hydrogen atoms.

(d) The relative rate of abstraction of 3°, 2°and 1° hydrogen atoms is minimum for 3° hydrogen atoms.

17. Which of the following alkanes give only a single product on insertion of : CH_2 species in between the C—H bond?

(a) $CH_3CH_2CH_3$ (b) $(CH_3)_4C$ (c) CH_3CH_3 (d) $(CH_3)_2CHCH_3$

Linked -Comprehension Type

1. For the reaction *n*-Butane → Isobutane; $\Delta H^\circ = -8.37\ \text{kJ mol}^{-1}$ and $\Delta S^\circ = -15.44\ \text{J K}^{-1}\ \text{mol}^{-1}$. Assume that ΔH° do not change with temperature.

(i) The fraction of isobutane present at room temperature (298 K) will be about

(a) 0.18 (b) 0.62 (c) 0.82 (d) 0.92

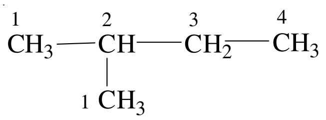
(ii) The temperature at which both are present in equal fraction is about

(a) 542 °C (b) 269 °C (c) 169 °C (d) 100 °C

(iii) The fraction of isobutane present at 800 K will be about

(a) 0.75 (b) 0.55 (c) 0.35 (d) 0.15

2. The relative reactivity of 1° : 2° : 3° hydrogens to chlorination is 1 : 3.8 : 5. The compound 2-methylbutane is monochlorinated. The carbon aroms in this molecule are labelled as follows.



$$\overset{1}{CH_3}-\overset{2}{\underset{\underset{1\,CH_3}{|}}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

(i) The maximum percentage of monochlorination will occur at

(a) carbon-1 (b) carbon-2 (c) carbon-3 (d) carbon-4

(ii) The minimum percentage of monochloriation will occur at

(a) carbon-1 (b) carbon-2 (c) carbon-3 (d) carbon-4

(iii) The percentage of monochloriation occuring at carbon-2 is about

(a) 15 (b) 23 (c) 28 (d) 35

3. Relative reactivity towards chlorination of R_3CH, R_2CH_2 and RCH_3 follows the ratio 5.0 : 3.5 : 1.0. The compound 2-methylbutane can form four different monochloro products.

(i) The relative percentage of $ClCH_2CH(CH_3)CH_2CH_3$ formed will be about

(a) 28% (b) 23% (c) 35% (d) 14%

(ii) The relative percentage of $(CH_3)_2C(Cl)CH_2CH_3$ will be about

(a) 35% (b) 23% (c) 28% (d) 14%

(iii) The relative percentage of $(CH_3)_2CHCH(Cl)CH_3$ will be about

(a) 23% (b) 28% (c) 35% (d) 14%

4. Singlet methylene $(:CH_2)$ may be generated by the decomposition of diazomethane, H_2CN_2. The methylene can be inserted between the C—H bond in alkane giving C—CH_3. This species is one of the most reactive and least selective species in organic chemistry. In an alkane, the insertion of CH_2 is practically random with equal probability. Based on this fact, answer the following three questions.

(i) Per cent yield of $CH_3(CH_2)_4CH_3$ obtained by the insertion of CH_2 in $CH_3(CH_2)_3CH_3$ is about

(a) 16.7 (b) 25 (c) 33.3 (d) 50

(ii) Per cent yield of $CH_3(CH_2)_2CH(CH_3)CH_3$ obtained by the insertion of CH_2 in $CH_3(CH_2)_3CH_3$ is about
(a) 16.7 (b) 25 (c) 33.3 (d) 50

(iii) Per cent yield of $(CH_3CH_2)_2CHCH_3$ obtained by the insertion of CH_2 in $CH_3(CH_2)_3CH_3$ is about
(a) 16.7 (b) 25 (c) 33.7 (d) 50

5. The successive members of cycloalkanes differ by one CH_2 unit. The relative stability of these alkanes may be determined by comparing the enthalpy of combustion per CH_2 unit. These values are obtained by dividing $\Delta_c H$(cycloalkane) by the number of CH_2 unit in the cycloalkane. The less negative the value of $\Delta_c H(CH_2)$, the more stable the cycloalkane. Based on the following $\Delta_c H$ values answer the three questions listed below.

Cyclopropane –2090 kJ mol^{-1} cyclobutane –2718 kJ mol^{-1}
Cyclopentane –3288 kJ mol^{-1} cyclohexane –3918 kJ mol^{-1}
Cycloheptane –4632 kJ mol^{-1}

(i) Which of the following cycloalkanes has the less negative value of $\Delta_c H(CH_2)$?
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane

(ii) Which of the following cycloalkanes has the more negative value of $\Delta_c H(CH_2)$?
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane

(iii) If $\Delta_c H(CH_2)$ reperesents the enthalpy of combustion per CH_2 unit of the most stable cycloalkane, then the value of $[|\Delta_c H(\text{cycloalkane}) - (\text{number of } CH_2 \text{ in cycloalkane}) \times |\Delta_c H(CH_2)||]$ is a measure ring strain in the cycloalkane. Which of the following cycloalkane has a ring-strain value of 106 kJ mol^{-1}?
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cycloheptane

6. Based on hexane (C_6H_{14}), answer the following three questions.

(i) The number of isomers of C_6H_{14} is
(a) 3 (b) 4 (c) 5 (d) 6

(ii) The isomer of hexane giving two different monochlorinated compounds is
(a) *n*-hexane (b) 2-methylpentane (c) 3-methylpentane (d) 2,3-dimethylbutane

(iii) If the relative reactivity 1° : 2° : 3° hydrogens to chlorination is 1 : 3.8 : 5, then the relative ratio of two monochlorinated products obtained in part (ii) is
(a) 61.2 : 38.8 (b) 54.5 : 45.5 (c) 82.0 : 18.0 (d) 25 : 75

Assertion and Reason Type

Given below are the questions, each containing two statements. Answer these with the following key.

(a) Both statements are correct and Statement–2 is correct explanation of Statement–1.
(b) Both statements are correct and Statement–2 is not correct explanation of Statement–1.
(c) Statement–1 is correct and Statement–2 is incorrect.
(d) Statement–1 is incorrect and Statement–2 is correct.

	Statement–1	**Statement–2**
1.	The relative rate of abstraction of H by $Cl^\bullet$ is 3° : 2° : 1° :: 5.0 : 3.8 : 1.0. The relative rate of abstraction of H by Br is $3^\bullet$: 2° : 1° :: 1600 : 82 : 1.	In halogenation of alkanes, the more reactive $Cl^\bullet$ is less selective and the less reactive $Br^\bullet$ is more selective.
2.	The boiling points of alkanes decreases with increase in branching of carbon chain.	The branched alkane is more compact with less surface area and thus involves weaker van der Waals attractions.
3.	Methane does not react with chlorine in dark.	The reaction between methane and chlorine proceeds via ionic mechanism.
4.	The melting points of alkanes decrease with increase in branching of carbon chain.	The branched alkane is more compact and can be packed more closely in a solid lattice.
5.	Free radical chlorination of methane occurs approximately twelve times faster than tetradeuteromethane.	C—D bond is slightly stronger than C—H bond.
6.	Cycloalkanes have higher melting points than *n*-alkanes.	Cyclohexanes are more compact as compared to *n*-alkanes.
7.	Cycloalkanes have higher densities as compared to *n*-alkanes.	Cyclohexanes are more closely packed in the solid state as compared to *n*-alkanes.

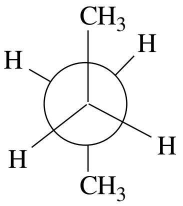
Matrix Match Type

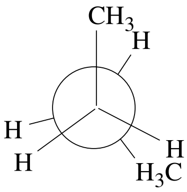
1. Column I lists the four conformations of cyclohexane and their potential energies relative to the most stable conformation are given in Column II. Match the correct entries from these two Columns.

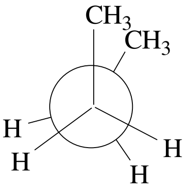
Column I	Column II
(a) Boat conformer	(p) zero
(b) Twist-boat conformer	(q) 23.0 kJ mol^{-1}
(c) Half-chair conformer	(r) 29.7 kJ mol^{-1}
(d) Chair conformer	(s) 46.0 kJ mol^{-1}

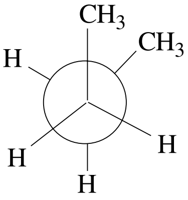
2. Column I lists the four conformations of butane and their potential energies relative to the most stable conformation are given in Column II. Match the correct entries from these two Columns.

Column I

(a)


(b)


(c)


(d)


Column II

(p) 18.4 – 25.5 kJ mol^{-1}

(q) 14.2 kJ mol^{-1}

(r) 3.3 kJ mol^{-1}

(s) zero

Straight Objective Type

1. (d) **2.** (b) **3.** (d) **4.** (a) **5.** (b) **6.** (c) **7.** (a)
8. (b) **9.** (a) **10.** (b) **11.** (d) **12.** (d) **13.** (c) **14.** (c)
15. (c) **16.** (c) **17.** (a) **18.** (b) **19.** (a) **20.** (b) **21.** (a)
22. (b) **23.** (d) **24.** (c) **25.** (d) **26.** (a) **27.** (c) **28.** (c)
29. (b) **30.** (b) **31**. (d) **32.** (c) **33.** (c) **34.** (b) **35.** (b)
36. (d) **37.** (a) **38.** (a) **39.** (d) **40.** (b) **41.** (b) **42.** (a)
43. (a) **44.** (b) **45.** (b) **46.** (b) **47.** (c) **48.** (d) **49.** (a)
50. (d)

Multiple – Correct Choice Type

1. (a), (c) **2.** (a), (c) **3.** (a), (b), (c), (d) **4.** (a), (c), (d)
5. (a), (b) **6.** (a), (c), (d) **7.** (a), (c), (d) **8.** (b), (c), (d)
9. (b), (c) **10.** (a), (b), (d) **11.** (a), (c), (d) **12.** (b), (c)
13. (c), (d) **14.** (a), (c) **15.** (a), (b), (c) **16.** (a), (c), (d)
17. (b), (c)

Linked – Comprehension Type

1. **(i)** (c) **(ii)** (b) **(iii)** (c)
2. **(i)** (c) **(ii)** (d) **(iii)** (b)
3. **(i)** (a) **(ii)** (b) **(iii)** (c)

4. **(i)** (d) **(ii)** (c) **(iii)** (a)
5. **(i)** (d) **(ii)** (a) **(iii)** (b)
6. **(i)** (c) **(ii)** (d) **(iii)** (b)

Assertion and Reason Type

1. (a) **2.** (a) **3.** (c) **4.** (d) **5.** (b) **6.** (a) **7.** (a)

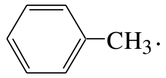
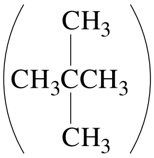
Matrix Match Type

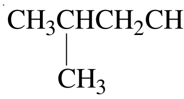
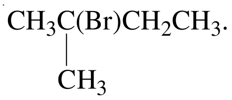
1. (a)–(r), (b)–(q), (c)–(s), (d)–(p)

2. (a)–(s), (b)–(q), (c)–(p), (d)–(r)

Hints and Solutions

Straight Objective Type

1. Electrolysis of CH_3CH_2COONa will produce $CH_3CH_2CH_2CH_3$ (butane).
2. $C_2H_5MgI + H_2O \longrightarrow C_2H_6 + Mg(OH)I$.
3. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow{Cr_2O_3-Al_2O_3}$ 
4. Methane is known as Marsh gas.
5. About 35% of methane is present in coal gas.
6. $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$.
7. Methane is the main product (80–90%) in natural gas.
8. Alkanes can be iodinated in the presence of HIO_3.
9. 2,2-Dimethylpropane  $\left(CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3\right)$ will produce single monochlorinated product as all the four methyl groups are equivalent.
10. The reagent used in Wurtz reaction is Na in dry ether.
11. The boiling point decreases with increasing branching of carbon chain. It increases with increase in the number of carbon atoms. Hence, *n*-hexane is expected to have the highest boiling point.
12. Same as Q.11. *n*-Octane is expected to have the highest boiling point.
13. Same as Q.11. 2,2-Dimethylpropane is expected to have minimum boiling point.
14. Cyclohexane is less dense than water.
15. The stability of structural isomers generally increases with increased branching.
16. $\text{Log } K^\circ_{eq} = -\dfrac{\Delta G^\circ}{2.303\,RT} = \dfrac{(3800\text{ J mol}^{-1})}{(2.303)(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})} = 0.67$
17. Excess quantity of C_2H_6 will yield mono chlorinated product (i.e. C_2H_5Cl).
18. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2$.
19. The chlorination of alkane proceeds via free-radical mechanism.
20. The reactivity of hydrogen atom is $1° < 2° < 3°$.
21. Bromination proceeds with much slower rate as compared to chlorination.
22. 2° H is more reactive. Thus, the product involves 2-bromobutane as the major product. The relative rates of bromination of 1° : 2° : 3° H's 1 : 82 : 1600.
23. 2-chlorobutane is produced more than 1-chlorobutane. The relative rates of chlorination of 1° : 2° : 3° H's are 1 : 3.8 : 5.
24. Isomerization in alkane may be brought about by using $AlCl_3$ and HCl.

25. 2-Methylbutane is  $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$. The major product in the photobromination is  $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}(Br)CH_2CH_3$.

26. $(1.04\ \text{mL}/22400\ \text{mL mol}^{-1})\ (32\ \text{g mol}^{-1}) = 1.49 \times 10^{-3}\ \text{g} = 1.49\ \text{mg}.$

27. $(22400\ \text{mL mol}^{-1}/1.5\ \text{mL})\ (4.12 \times 10^{-3}\ \text{g}) = 61.5\ \text{g mol}^{-1}.$

28. Let the reaction be $R(OH)_n + nCH_3MgI \rightarrow nCH_4 + R(OMgI)_n$.

$$\text{Amount of gas produced} = \frac{1.34\ \text{mL}}{22400\ \text{mL mol}^{-1}} \simeq 6 \times 10^{-5}\ \text{mol}.$$

$$\text{Amount of compound used} = \frac{1}{n}\ (6 \times 10^{-5}\ \text{mol})$$

This is equivalent to $(1.79 \times 10^{-3}\ \text{g}/90\ \text{g mol}^{-1}) \simeq 2 \times 10^{-5}$ mol. Hence $n = \dfrac{6\times10^{-5}\ \text{mol}}{2\times10^{-5}\ \text{mol}} = 3.$

29. The relative stability of free radicals is 3° > 2° > 1°.

30. The ease of abstraction of hydrogen atom is 3° > 2° > 1°.

31. Benzyl radical is the most stable radical. **32.** Vinyl radical is the least stable.

33. Increasing pressure causes an increase in the relative rates of primary hydrogen substitution by chlorine.

34. The relative reactivity of 1° : 2° : 3° H's to chlorination is 1 : 3.8 : 5. The relative reactivity of 1° : 2° : 3° H's to bromination is 1 : 82 : 1600.

35. Bond energy of Cl—Cl has a maximum value. **36.** Iodination involves maximum value of $\Delta H°$.

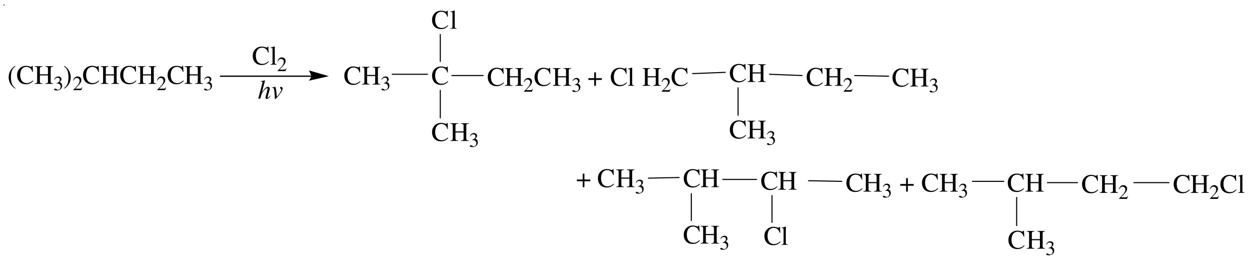
37. Fluorination involves maximum negative value of $\Delta H°$.

38. H_3C—H has the maximum bond enthalpy amongst the given compounds.

39. $(CH_3)_3C$—H has a minimum bond energy because the resultant 3° radical is the most stable.

40. The choice (b) involves 3° radical.

41. Monochlorination of the given compound gives four products.



Of the four products, two are optically active each will produce two isomers. Hence, the number of isomers is 6 and the number of product is 4.

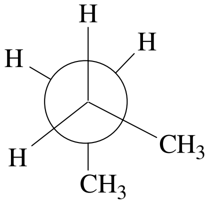
42. Ethane will have least hindered rotation about C—C bond.

43. Chair form has the minimum strain energy.

44. Half-chair form has the maximum strain energy. The order of strain energy is

Half-Chair > Boat > Twist-boat I > Chair.

45. The resultant conformation is gauche.



46. We have Eclipsed ethane $\rightleftharpoons$ Straggered ethane; $\Delta H° = -11.3\ \text{kJ mol}^{-1}$

Since ΔS is negligible, $\Delta G° \simeq \Delta H°$. Hence, from $\Delta G° = -RT \ln K°_{eq}$, we get

$$\log K°_{eq} = \frac{-\Delta G°}{2.303\,RT} = \frac{11.5\times10^{3}\ \text{J mol}^{-1}}{(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})} = 2$$

$$K^{\circ}_{\text{eq}} = \frac{[\text{staggerd ethane}]}{[\text{eclipsed ethane}]} = 10^2 = 100$$

47. We have *gauche* butane $\rightleftharpoons$ *anti* butane; $\Delta H^{\circ} = -3.8 \text{ kJ mol}^{-1}$

$$\log K^{\circ}_{\text{eq}} = \frac{-\Delta G^{\circ}}{2.303\,RT} = \frac{3.8 \times 10^3 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 0.66$$

Multiple Correct Choice Type

1. (a) In the presence of light, Cl_2 dissociates to give $2Cl^{\bullet}$ radicals which react with CH_4 via free radical mechanism.

(b) $Br^{\bullet}$ radical being less reactive is less influenced by the probability factor. The bromination primarily depends on the reactivity of H atom which is 3° > 2° > 1°.

(c) If methane is not in excess, CH_2Cl_2, starts forming if the concentration of CH_3Cl becomes more than that of CH_4. This is continued and thus $CHCl_3$ and CCl_4 may also be formed.

(d) The reaction between CH_4 and F_2 is very vigorous. It can take place even in the dark or at room temperature.

2. (b) The reaction proceeds via free radical mechanism.

(c) This is due to the formation $CH_3—O—O^{\bullet}$ radical which is less reactive than $CH_3^{\bullet}$ radical.

(d) It is due to the fact, that the reaction $I^{\bullet} + CH_4 \rightarrow HI + CH_3^{\bullet}$ is highly endothermic ($\Delta H^{\circ} = 138 \text{ kJ mol}^{-1}$).

3. (a) The bond angle is 120° because carbon is sp^2 hybridized.

(b) In eclipsed conformation, hydrogen atoms of the two carbon atoms are closer to each other, hence more repulsive interactions resulting in the higher potential energy.

(c) The correct name is 3-ethyl-5-isopropyl-4-methyloctane. Isopropyl comes before methyl.

(d) Alkanes are souble in non-polar solvents such as benzene, ether and chloroform.

4. (a) Natural gas contains about 97% of methane.

(b) Here NH_3 acts a stronger acid and RH as a weak acid.

(d) The more stable the free radical, the lesser the enthalpy of formation of the free radical from the corresponding alkane.

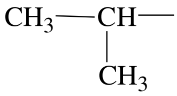
5. (c) Ethane is produced.

6. (a) The chlorination of propane gives two isomeric products: 1-chloropropane and 2-chloropropane. Their relative ratio would be given as

$$\frac{\text{1-Chloropropane}}{\text{2-Chloropropane}} = \frac{\text{no. of 1° H}}{\text{no. of 2° H}} \times \frac{\text{reactivity of 1° H}}{\text{reactivity of 2° H}} = \frac{6}{2} \times \frac{1.0}{3.8} = \frac{6.0}{7.6}$$

$$\text{Percentage of 1° isomer} = \frac{6.0}{6.0 + 7.6} \times 100 = 44\%$$

(b) Isobutane is



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$$

. Its chlorination would give two isomers.

$$\frac{\text{1° isomer}}{\text{3° isomer}} = \frac{\text{no. of 1° H}}{\text{no. of 3° H}} \times \frac{\text{reactivity of 1°H}}{\text{reactivity of 3°H}} = \frac{9}{1} \times \frac{1}{50} = \frac{9}{5}$$

$$\text{Percentage of 1° isomer} = \frac{9}{9+5} \times 100 = 64.3\%$$

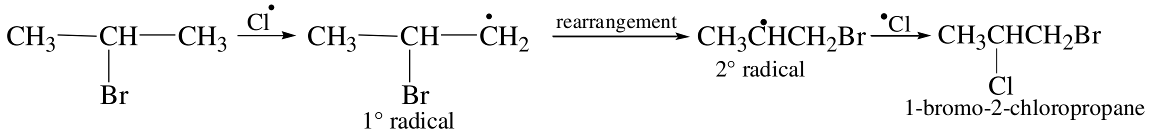
(c) The propane is $CH_3CH_2CH_3$. The relative ratio of the two isomers is

$$\frac{\text{1° isomer}}{\text{2° isomer}} = \frac{\text{no. of 1° H}}{\text{no. of 2° H}} \times \frac{\text{reactivity of 1° H}}{\text{reactivity of 2° H}} = \frac{6}{2} \times \frac{1}{82} = \frac{6}{164}$$

$$\text{Percentage of 1° isomer} = \frac{3}{3+164} \times 100 \simeq 4$$

(d) The homolytic bond dissociation energy of vinylic H is greater than that of 2° H. Hence, vinylic radical is less stable than 2° radical.

7. (a)



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\dot{C}l} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2 \xrightarrow{\text{rearrangement}} CH_3\dot{C}HCH_2Br \xrightarrow{\dot{C}l} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2Br$$

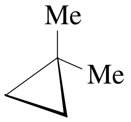
1° radical

2° radical

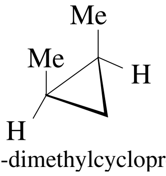
1-bromo-2-chloropropane

Although alkyl free radicals seldom if ever rearrange by migration of hydrogen or alkyl, but they can rearrange by migration of halogen.

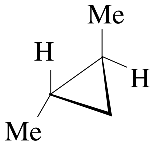
(b) The number of isomers is three



1,1-dimethylcyclopropane



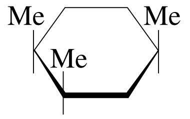
cis-1,2-dimethylcyclopropane



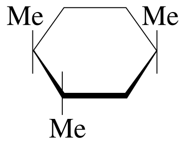
trans-1,2-dimethylcyclopropane

*C*is-and *trans*-isometers are due to the rigidity of the ring. The rotation about the ring C—C bonds is prohibitive.

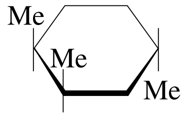
(c) There are four geometric isomers.



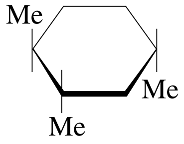
cis, *cis*-1,2,4-Trimethylcyclohexane



trans-2-*cis*-4-Trimethylcyclohexane



cis-2-*trans*-4-Trimethylcyclohexane



trans-2-*trans*-4-Trimethylcyclohexane

8. (a) Both are slightly less stable than cyclohexane.

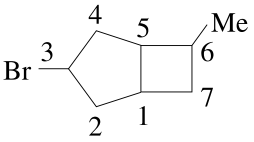
(c) The observed bond angle H—C—H in cyclopropane is 114°. To account for this angle, it is postulated that the hybrid orbital of C involves more s-character as compared to the sp^3 hybrid orbital.

(d) The C—H bonds in cyclopropane involves more s-character than those of an alkane.

9. (a) The name is 1-ethyl-3-methylcyclopentane.

(c) The prefix bicyclo- is combined with a pair of brackets enclosing numbers separated by periods, which is followed by the name of the alkane whose number of Cs is equal to the number of Cs in the rings. The bracketed numbers show how many Cs are in each bridge and are cited in decreasing order.

(d) To number bicycles, start at one bridgehead C and move along the longest chain to the next bridgehead C. Continue along the next longest chain to return to the first bridgehead C so that the shortest bridge is numbered last.



Following these guidelines, the correct name of the compound is 3-Bromo-6-methylbicyclo[3.2.0]heptane.

10. (c) The octane value is 85.

11. (a) Here $\Delta G^\circ \simeq \Delta H^\circ$. Using $\Delta G^\circ = -RT \ln K^\circ$, we get

$$\ln K^\circ = -\frac{\Delta G^\circ}{RT} = \frac{(12.552\times 10^3\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\ (298\ \text{K})} = 5.066 \quad \Rightarrow \quad K^\circ = 158.57$$

(b) Here $\Delta G^\circ \simeq \Delta H^\circ$. Using $\Delta G^\circ = -RT \ln K^\circ$, we get

$$\ln K^\circ = -\frac{\Delta G^\circ}{RT} = \frac{3.8 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1}\text{mol}^{-1})\,(298 \text{ K})} = 1.534 \quad \Rightarrow \quad K^\circ = 4.64$$

(c) In this case, no bonds are broken, they are only formed.

(d) The C—D bonds in CD_4 are slightly stronger than C—H bonds in CH_4. Thus, ΔH for abstraction of D is slightly greater than for H. The abstraction being the slow step, the removal of H will be faster.

12. (b) The energy of activation is smaller for $Cl^\bullet + CH_4 \rightarrow HCl + CH_3^\bullet$

(c) It is sp^2 hybridized.

13. (c) The relative ratio of abstraction is 3° : 2° : 1°

$$\text{Amount of } CH_4 \text{ gas evolved} = \frac{1.56 \text{ mL}}{22400 \text{ mL mol}^{-1}} = 6.96 \times 10^{-5} \text{ mol}$$

Amount of alcohol = 6.96×10^{-5} mol

$$\text{Molar mass of alcohol} = \frac{4.12 \times 10^{-3} \text{ g}}{6.96 \times 10^{-5} \text{ mol}} = 59.28 \text{ g mol}^{-1}$$

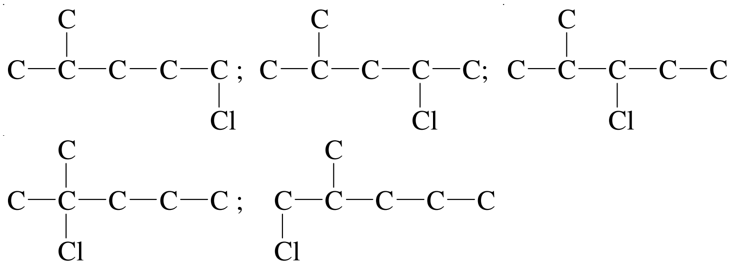
14. (a) $$\text{Amount of } CH_4 \text{ gas evolved} = \frac{1.34 \text{ mL}}{22400 \text{ mL mol}^{-1}} = 5.98 \times 10^{-5} \text{ mol}$$

$$\text{Amount of compound} = \frac{1.79 \times 10^{-3} \text{ g}}{90 \text{ g mol}^{-1}} = 1.99 \times 10^{-5} \text{ mol}$$

$$\text{Number of active hydrogens} = \frac{5.98 \times 10^{-5}}{1.99 \times 10^{-5}} = 3$$

(c) 1, 1, 2-; 1, 1, 3-; 1, 2, 3-; 1, 2, 4-trichloropentane

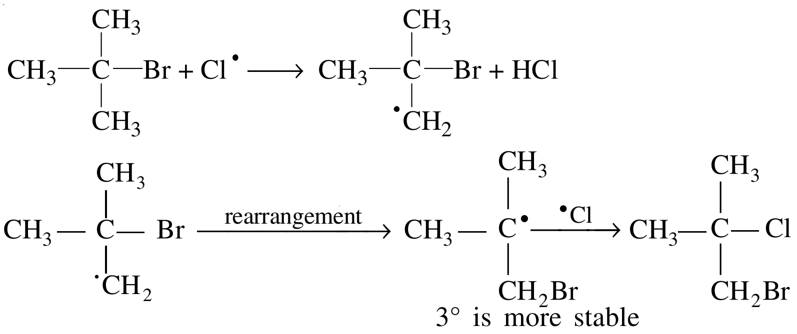
(d) The carbon skeleton of the five compounds are:



(a) The stability of free radicals follows the sequence Allyl, benzyl > 3° > 2° > 1° > methyl, vinyl

(b) The sequence of ease of abstraction of hydrogen atoms is Allylic, benzylic > 3° > 2° > 1° > CH_4, vinylic

(c) 1-bromo-2-chloro-2-methylpropane



(d) The most reactive halogen is Cl_2

16. (a) ethane is the product of eleclrolysis

(b) 6 × 1 : 4 × 3.8 : 4 × 3.8 :: 16.48% : 41.76% : 41.76%

(c) 3°

(d) 1°

17. (b) and (c) give one product as there is one type of H atoms

CHAPTER 22

ALKENES

METHODS OF PREPARATION

1. **Dehydrohalogenation of alkyl halides** Heating of alkyl halides with alcoholic KOH produces alkenes:

$$RCH_2CH_2X + KOH \xrightarrow[\Delta]{\text{ethanol}} R—CH{=}CH_2 + KX + H_2O$$

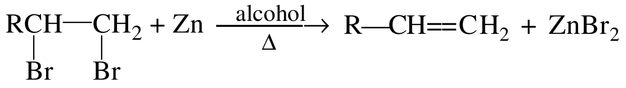
The ease of dehydrohalogenation is 3° alkyl halide > 2° alkyl halide > 1° alkyl halide.

2. **Dehydration of alcohols** Sulphuric acid is a dehydrating agent.

$$R—CH_2—CH_2OH \xrightarrow[\Delta]{H_2SO_4} R—CH{=}CH_2 + H_2O$$

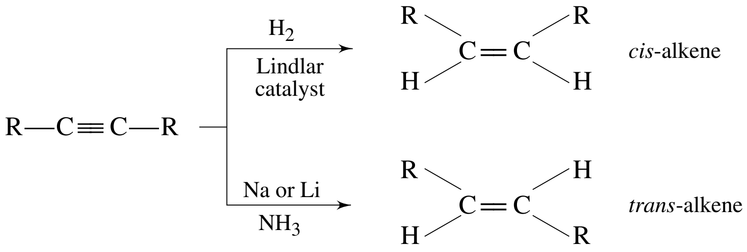
The ease of dehydration is 3° alcohol > 2° alcohol > 1° alcohol.

3. **Dehalogenation of vicinal dihalides** This is carried out by heating with zinc dust in ethyl alcohol.



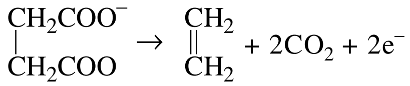
$$\underset{\substack{|\\Br}}{RCH}—\underset{\substack{|\\Br}}{CH_2} + Zn \xrightarrow[\Delta]{\text{alcohol}} R—CH{=}CH_2 + ZnBr_2$$

4. **Partial reduction of alkynes**



5. **Kolbe's electrolytic method** The electrolysis of an aqueous solution of potassium salt of a saturated dicarboxylic acid produces alkene.

Anodic reaction



$$\begin{array}{l}CH_2COO^-\\ |\\ CH_2COO\end{array} \rightarrow \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + 2CO_2 + 2e^-$$

Cathodic reaction $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

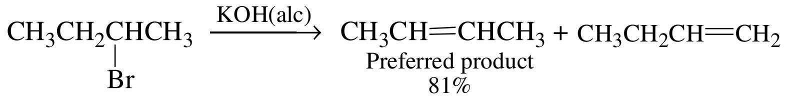
Saytzeff Rule In dehydrohalogenation or dehydration, the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

The alkene with the greater number of alkyl groups is the preferred product because it is formed faster than alternative alkenes. The sequence showing the relative rates of formation of alkenes is

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2, RCH{=}CHR > RCH{=}CH_2$$

The sequence of stability of alkenes also follows the above order. Hence, the more stable the alkene, the faster it is formed.

For example,

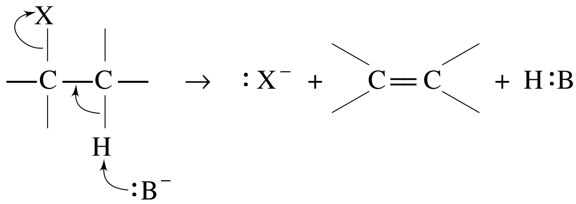


$$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{KOH(alc)} \underset{\substack{\text{Preferred product}\\ 81\%}}{CH_3CH{=}CHCH_3} + CH_3CH_2CH{=}CH_2$$

The more substituted product is known as *Saytzeff product* and the least substituted product is known as *Hofmann product*.

Mechanism of Dehydrohalogenation

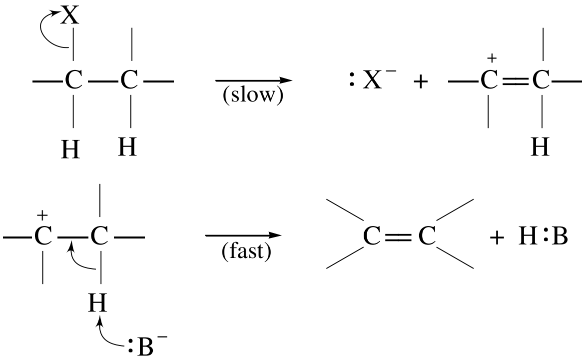
E2 *mechanism* The base : B^- (such as $\bar{:}OC_2H_5$) pulls a proton away from carbon, simultaneously a halide ion departs and the double bond is formed.



$$-\overset{\overset{X}{|}}{\underset{|}{C}}-\overset{|}{\underset{\underset{\underset{:B^-}{\uparrow}}{H}}{\underset{|}{C}}}- \rightarrow :X^- + \;>C{=}C<\; + H:B$$

This mechanism of elimination is not accompanied by rearrangement.

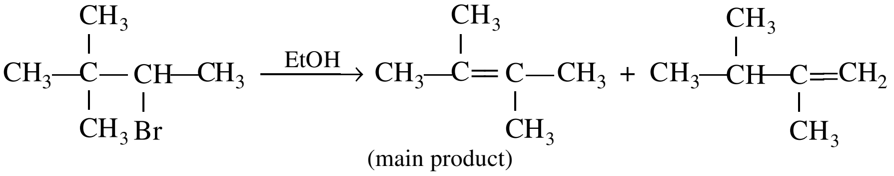
E1 *mechanism* Two steps involved in this mechanism are:



$$-\overset{\overset{X}{|}}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}- \xrightarrow[\text{(slow)}]{} :X^- + -\overset{+}{\underset{|}{C}}=\overset{|}{\underset{\underset{H}{|}}{C}}-$$

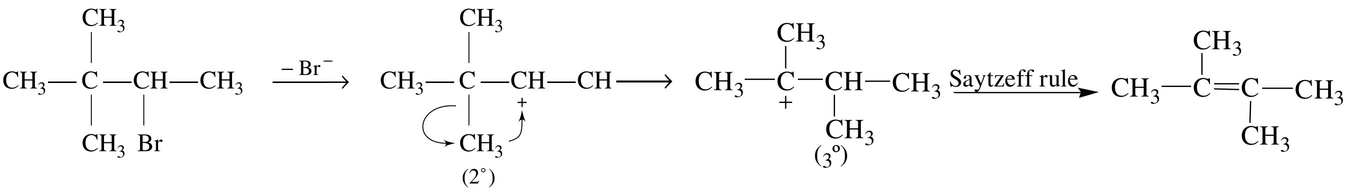
$$-\overset{+}{\underset{|}{C}}-\overset{|}{\underset{\underset{\underset{:B^-}{\uparrow}}{H}}{\underset{|}{C}}}- \xrightarrow[\text{(fast)}]{} \;>C{=}C<\; + H:B$$

A carbocation formed as an intermediate is particularly prone to rearrangement. For example, the following reaction involves rearrangement.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{EtOH} \underset{\text{(main product)}}{CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3} + CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{C}=CH_2$$

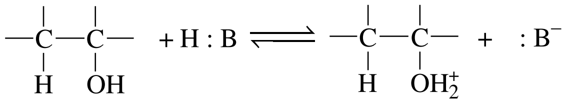
This arrangement is due to the formation of more stable 3° carbocation from the lesser stable 2° carbocation**:**



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{-Br^-} \underset{(2^\circ)}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{CH}-CH} \longrightarrow \underset{(3^\circ)}{CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3} \xrightarrow{\text{Saytzeff rule}} CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

Mechanism of dehydration The steps involved are as follows.

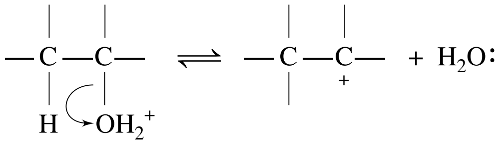
1. Acid-base reaction between the alcohol and catalyzing acid.



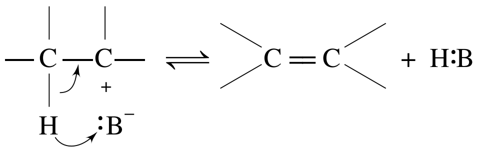
$$-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{OH}{|}}{C}}- + H:B \rightleftharpoons -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{OH_2^+}{|}}{C}}- + :B^-$$

The role of acid is to convert —OH to $—OH_2^+$ so that very good leaving group H_2O (a very weak base) is eliminated

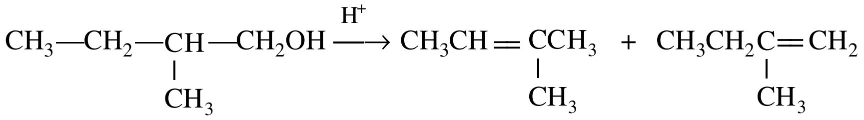
2. Heterolysis of the protonated alcohol to form the carbocation



3. Formation of alkene from carbocation

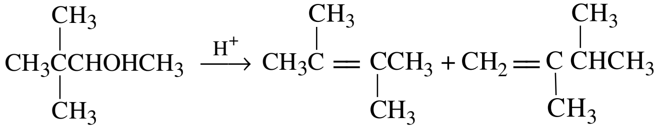


The ease of dehydration of alcohols (3° > 2° > 1°) is in agreement with the formation of carbocation as the intermediate. Wherever possible, rearrangement takes place. For example



$$CH_3-CH_2-\underset{CH_3}{CH}-CH_2OH \xrightarrow{H^+} CH_3CH=\underset{CH_3}{C}CH_3 + CH_3CH_2\underset{CH_3}{C}=CH_2$$

(main product)



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CHOHCH_3 \xrightarrow{H^+} CH_3\overset{CH_3}{C}=\underset{CH_3}{C}CH_3 + CH_2=\overset{CH_3}{\underset{CH_3}{C}}CHCH_3$$

(main product)

CHEMICAL PROPERTIES

Electrophilic Addition Reactions

Because of loosely held π electrons, the carbon-carbon double bond serves as a source of electrons and thus addition reactions across the double bond are initiated by an electrophilic attack. The addition reactions exhibited by alkenes are as follows.

1. *Addition of hydrogen* A solution of the alkene is shaken under a slight pressure of hydrogen gas in the presence of a small amount of the catalyst (Pt, Pd, or Ni)

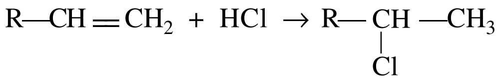
$$RCH=CH_2 \xrightarrow{H_2,\ Ni} RCH_2CH_3$$

The addition of H_2 to the double bond takes place from the same side. This addition is called *syn addition*.

The reaction is quantitative, the volume of hydrogen gas consumed provides the number of double bond in the compound.

Heats of hydrogenation provide the information regarding the relative stabilities of unsaturated compounds. Of simple dialkylethylenes, the *trans* isomer is the more stable. It is also found that the greater the number of alkyl groups attached to the doubly bonded carbon atoms, lesser the heat of hydrogenation and thus more stable the alkene—a conclusion which is in agreement with the Saytzeff rule.

2. *Addition of hydrogen halide* When dry gaseous hydrogen halide is directly passed into an alkene, the corresponding alkyl halide is formed. The addition of HX follows Markovnikov's rule which states that the hydrogen of acid attaches itself to the carbon that already holds the greater number of hydrogens. For example,

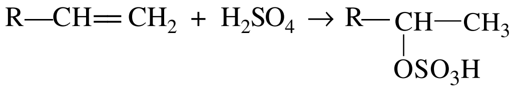


$$R-CH=CH_2 + HCl \rightarrow R-\underset{Cl}{CH}-CH_3$$

In the presence of peroxide, the addition of HBr does not follow Markovnikov's rule. The addition is just a reverse of Markovnikov's rule and this fact is known as anti-Markovnikov's rule. For example,

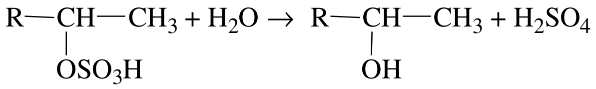
$$R-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} R-CH_2-CH_2Br$$

3. *Addition of sulphuric acid* When a gaseous alkene is passed through concentrated sulphuric acid in cold or a liquid alkene is stirred with the acid, the addition of a molecule of H_2SO_4 takes place:



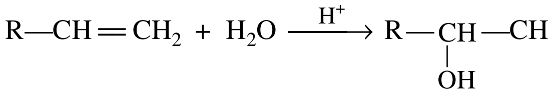
$$R\text{—}CH{=}CH_2 + H_2SO_4 \rightarrow R\text{—}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\text{—}CH_3$$

The addition of sulphuric acid follows Markovnikov's rule. The resultant hydrogen sulphate when heated with water produces the corresponding alcohol:



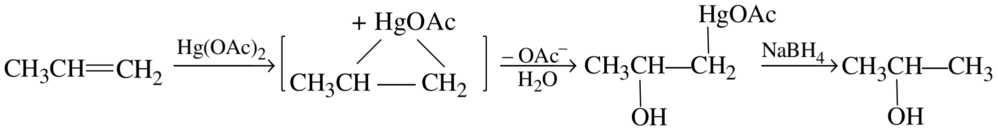
$$R\text{—}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\text{—}CH_3 + H_2O \rightarrow R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_3 + H_2SO_4$$

4. *Addition of water* In the presence of acids, water adds to the more reactive alkenes. The addition is in accordance with the Markovnikov's rule.



$$R\text{—}CH{=}CH_2 + H_2O \xrightarrow{H^+} R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH$$

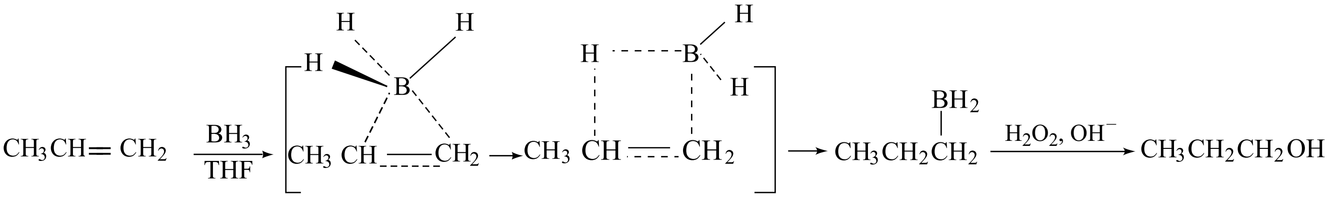
Oxymercuration-Demercuration Process Alkenes in tetrahtydrofuran react with mercury acetate in the presence of water to give hydroxymercurial compounds which on reduction with sodium borohybride ($NaBH_4$) yield alcohol. The net result is the addition of H_2O to the double bond and the product obtained is in agreement with Markovnikov's rule. For example,



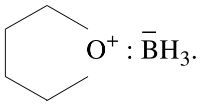
$$CH_3CH{=}CH_2 \xrightarrow{Hg(OAc)_2} \left[\overset{+\,HgOAc}{CH_3CH\text{——}CH_2}\right] \xrightarrow[H_2O]{-\,OAc^-} CH_3\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}\overset{\displaystyle HgOAc}{\overset{|}{CH_2}} \xrightarrow{NaBH_4} CH_3\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_3$$

The electrophile of $Hg(OAc)_2$ is $+HgOAc$. No rearrangement occurs in this reaction.

Hydroboration–Oxidation Process Alkenes undergo hydroboration with diborane in THF to yield alkylboranes which on oxidation with alkaline H_2O_2 give alcohols. The net result is the addition of H_2O to the double bond and the product obtained is in accordance with the anti-Markovnikov's rule. For example,

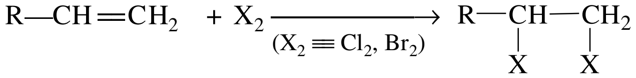


B_2H_6 in THF exists as BH_3, which is stabilized by forming a coordinate covalent bond with the O of THF



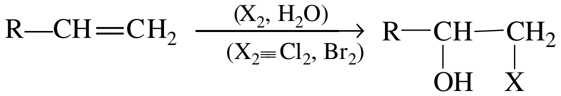
$O^+ : \bar{B}H_3$.

5. *Addition of halogens* Chlorine or bromine readily adds to double bond. Iodine does not react.



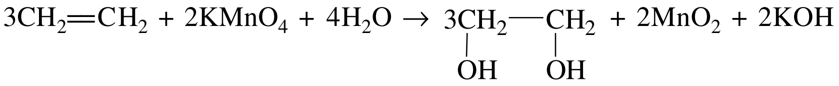
$$R\text{—}CH{=}CH_2 + X_2 \xrightarrow[(X_2\,\equiv\,Cl_2,\,Br_2)]{} R\text{—}\underset{\displaystyle X}{\underset{|}{CH}}\text{—}\underset{\displaystyle X}{\underset{|}{CH_2}}$$

6. *Addition of hypohalous acids* (Chlorine or bromine in the presence of water)



$$R\text{—}CH{=}CH_2 \xrightarrow[(X_2\equiv Cl_2,\,Br_2)]{(X_2,\,H_2O)} R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}\underset{\displaystyle X}{\underset{|}{CH_2}}$$

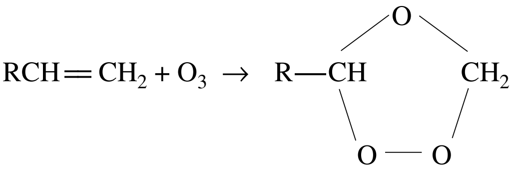
7. *Hydroxylation of olefins* The reaction in which two hydroxyl groups are added to the double bond is known as hydroxylation. This can be achieved by treating the compound containing double bond with cold alkaline potassium permanganate (Baeyer's reagent). Mild conditions of oxidation are the essential requirement as otherwise the resultant compound may be oxidized further. The reaction is



$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \rightarrow 3\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} + 2MnO_2 + 2KOH$$

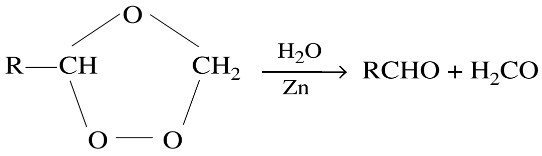
8. *Ozonolysis of olefins* Ozone can be used to break the double bond to give two smaller molecules. The reaction takes place in two steps.

Step 1 Formation of ozonide



ozonide

Step 2 Hydrolysis of ozonide in the presence of a reducing agent (frequently $(CH_3)_2S$ or zinc dust and acetic acid)



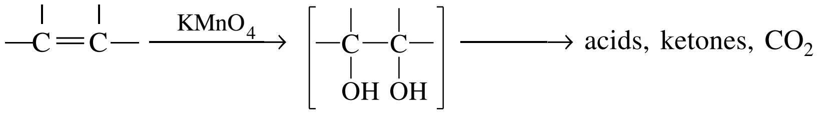
The cleavage products are aldehydes or ketones depending upon the atom or group attached to carbons of the double bond.

The function of reducing agent is to prevent the formation of H_2O_2 which would otherwise react with aldehydes and ketones.

9. *Polymerization of alkenes* Ethylene produces polyethylene when it is heated under pressure with oxygen.

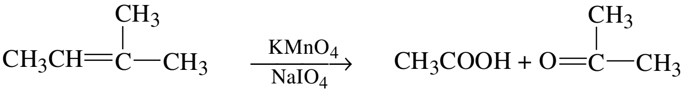
$$nCH_2{=}CH_2 \xrightarrow[\text{pressure}]{O_2,\ \text{heat}} (-CH_2-CH_2-)_n$$

10. *Degradation by sodium periodate* ($NaIO_4$) *in the presence of potassium permanganate* ($KMnO_4$).



$$-\overset{|}{C}{=}\overset{|}{C}- \xrightarrow{KMnO_4} \left[-\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}-\right] \longrightarrow \text{acids, ketones, } CO_2$$

Carboxylic acid is obtained instead of aldehydes. The terminal $=CH_2$ group is oxidized to CO_2.

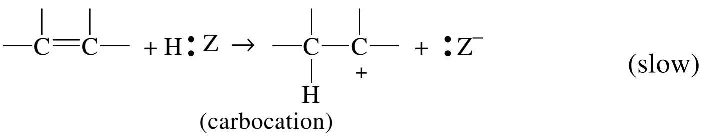


$$CH_3CH{=}\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[NaIO_4]{KMnO_4} CH_3COOH + O{=}\overset{CH_3}{\overset{|}{C}}-CH_3$$

$$CH_3CH_2CH{=}CH_2 \xrightarrow[NaIO_4]{KMnO_4} CH_3CH_2COOH + CO_2$$

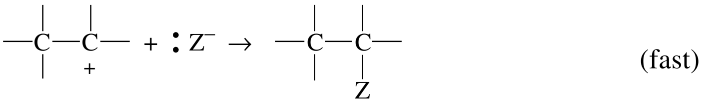
Mechanism of Electrophilic Addition The addition of the acidic reagent, HZ, follows the mechanism given below:

Step 1 Transfer of proton



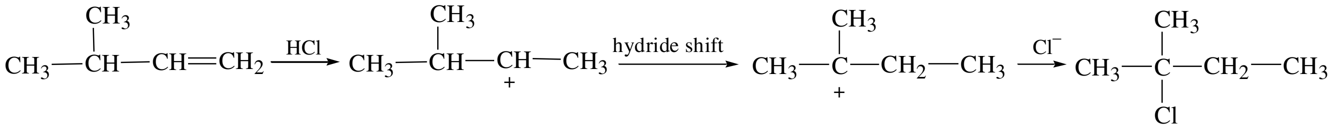
$$-\overset{|}{C}{=}\overset{|}{C}- + H{:}Z \rightarrow -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{+}{\overset{|}{C}}- + {:}Z^- \qquad \text{(slow)}$$

Step 2 Combination of the carbocation with the base $:Z^-$.



$$-\underset{|}{\overset{|}{C}}-\underset{+}{\overset{|}{C}}- + {:}Z^- \rightarrow -\underset{|}{\overset{|}{C}}-\underset{Z}{\underset{|}{\overset{|}{C}}}- \qquad \text{(fast)}$$

Step 1 is slow and is thus rate determining step. Because of the formation of carbocation, the reaction may involve rearrangement which is due to the formation of more stable carbocation from the lesser stable one. For example,

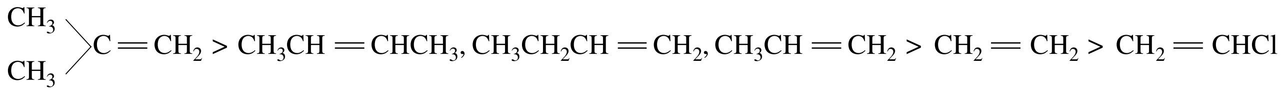


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH=CH_2 \xrightarrow{HCl} CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{+}{CH}-CH_3 \xrightarrow{\text{hydride shift}} CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3 \xrightarrow{Cl^-} CH_3-\underset{\underset{Cl}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3$$

In the light of the above mechanism, the Markovnikov's rule may be stated as follows.

The electrophilic addition to a carbon-carbon double bond involves the intermediate formation of the more stable carbocation.

The rate of addition of an acid to a double bond depends upon the stability of the carbocation being formed. For a given acid, the order of reactivity of alkenes is as follows.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH_2 > CH_3CH=CHCH_3, CH_3CH_2CH=CH_2, CH_3CH=CH_2 > CH_2=CH_2 > CH_2=CHCl$$

Mechanism of Addition of HBr in the Presence of Peroxide

Anti-Markovnikov addition of HBr in the presence of peroxide occurs via free-radical mechanism:

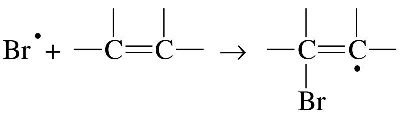
Chain-Initiating Steps

$$\text{Peroxide} \rightarrow \text{Radical}^\bullet$$

$$\text{Radical} + H:Br \rightarrow \text{Radical}:H + Br^\bullet$$

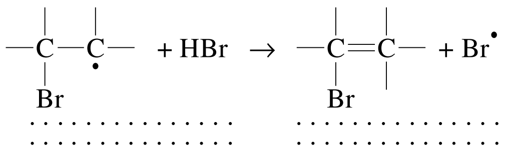
Chain-Propagating Steps

Step 1



$$Br^\bullet + -\overset{|}{C}=\overset{|}{C}- \rightarrow -\underset{\underset{Br}{|}}{\overset{|}{C}}=\underset{\bullet}{\overset{|}{C}}-$$

Step 2



$$-\underset{\underset{Br}{|}}{\overset{|}{C}}-\underset{\bullet}{\overset{|}{C}}- + HBr \rightarrow -\underset{\underset{Br}{|}}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}- + Br^\bullet$$

Factors that stabilize the free radical also stabilize the incipient free radical in the transition state. For example, secondary free radical, being more stable than primary radical, is formed faster in the reaction between $R-CH=CH_2$ and HBr and thus the product obtained is RCH_2CH_2Br.

Step 1 and Step 2 of chain-propagation steps involve the following energies of reactions.

	HCl	HBr	HI
Step 1	-75.3 kJ mol^{-1}	-25.1 kJ mol^{-1}	$+29.3$ kJ mol^{-1}
Step 2	$+21$ kJ mol^{-1}	-41.8 kJ mol^{-1}	-113 kJ mol^{-1}

Based on these values, it can be explained that HCl and HI do not show peroxide effect. These are as follows.

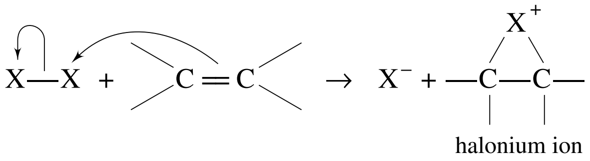
- With HCl, step 2 is endothermic owing to strong H—Cl bond. An endothermic step is reversible and do not allow the chain to propagate.
- With HI, step 1 is endothermic owing to weak H—I bond. In fact, HI is oxidized to I_2 by peroxide.

With HBr, both the steps are exothermic which help propagating the chain reaction.

Mechanism of addition of halogens

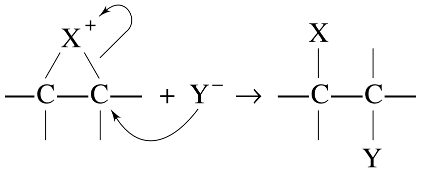
Two steps involved are as follows.

Step 1 Formation of halonium ion



$$X-X + \;>C=C< \;\rightarrow X^- + -\overset{\overset{X^+}{/\;\backslash}}{\underset{|\;\;\;|}{C-C}}-$$

Step 2 Addition of halide ion (or any other species similar to it) to halonium ion

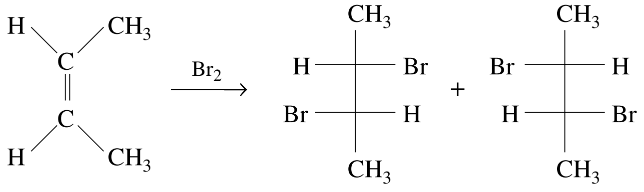


For example, the additon of Br_2 to ethylene in the presence of NaCl in aqueous medium, Y^- may be Br^-, Cl^- or OH^- and thus all the three compounds given below are formed.

$BrCH_2CH_2Br$, $BrCH_2CH_2Cl$, $BrCH_2CH_2OH$

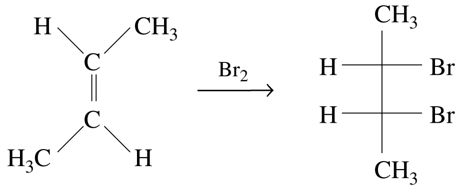
The additon of Cl_2 or Br_2 to double bond involves *anti-addition*, i.e. halogen atoms are attached at the opposite faces of the double bond.

If the compound containing double bond exists in two stereoisomers, namely, *cis* and *trans,* then the addition of halogen may generate chiral carbon atoms and thus the product will exhibit optical isomers. The addition of halogen across the double bond is stereoselective and stereospecific. The *cis* alkene yields only *racemic mixture* whereas *trans* alkene produces *meso* compound. For example,



cis-2-butene

rac-2, 3-dibromobutane

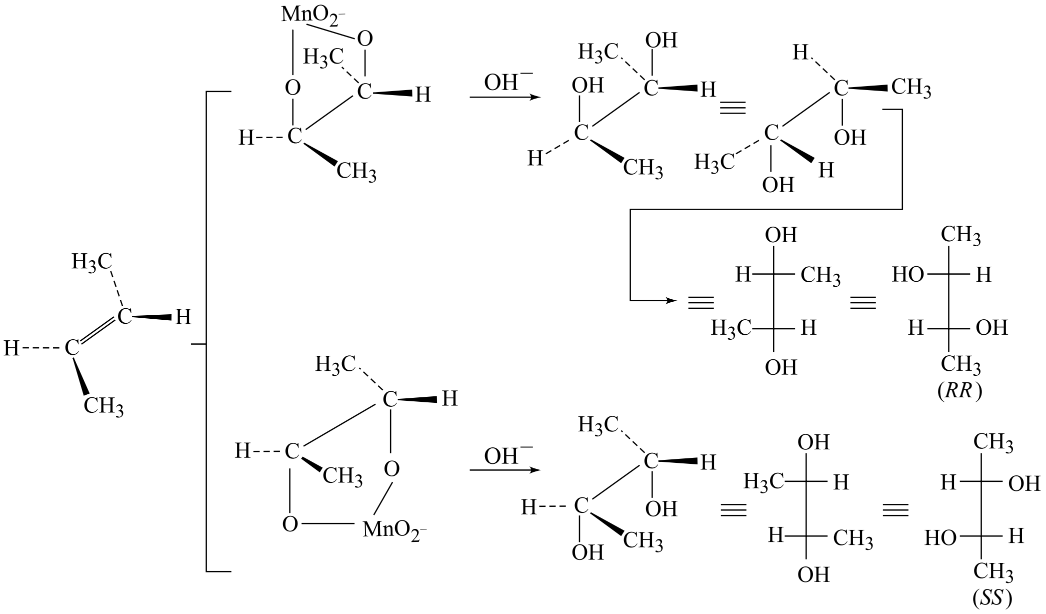


trans-2-butene

meso-2, 3-dibromobutane

Mechanism of Hydroxylation

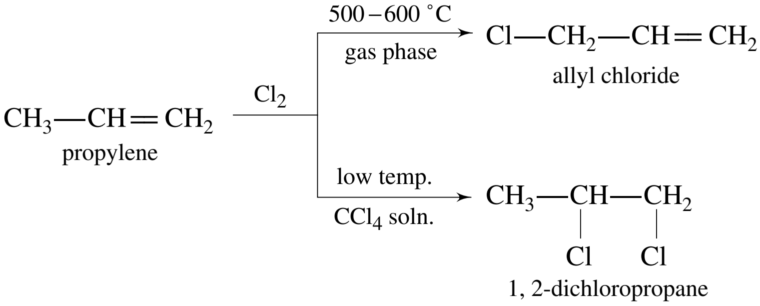
Hydroxylation of alkene is carried out by using cold alkaline $KMnO_4^-$ or with OsO_4 in H_2O_2. The addition occurs via *syn* mode.



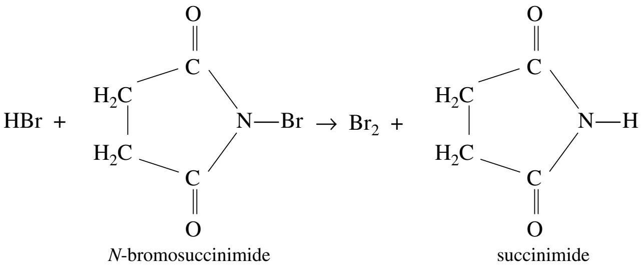
Cis-isomer produces *meso* product.

Substitution Reactions

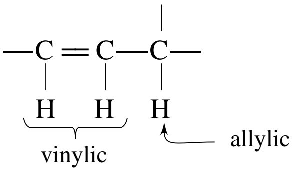
An alkyl group attached to a double bond can undergo substitution reaction involving halogen—a typical reaction shown by alkanes. The working conditions are the high temperature (500–600 °C) in the gaseous phase. These may be compared with those of addition reaction which are low temperature in the absence of light and the medium of the reaction is generally the liquid phase. For example,



Substitution reaction at alkyl group occurs via free-radical mechanism. It is also found that the low concentration of halogen can be used instead of high temperature to cause substitution at the allylic position. The compound *N*-bromosuccinimide has been used to brominate alkenes at the allylic position. As each molecule of HBr is formed by the bromination, *N*- bromosuccinimide generates Br_2 according to the reaction



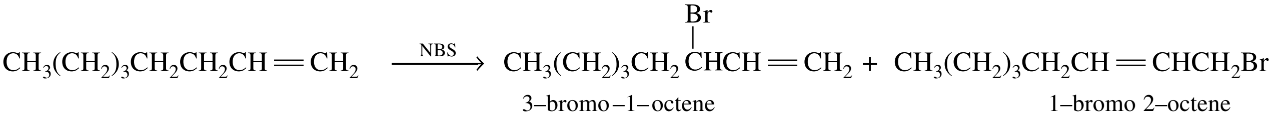
Since substitution of H by X occurs only at allylic position and not at vinylic position, the following conclusions may be drawn.



Ease of abstraction of hydrogen atoms allylic > 3° > 2° > 1° > CH_4 > vinylic

Ease of formation of free radical
or
Stability of free radical
allyl > 3° > 2° > 1° > $\dot{C}H_3$ > vinyl

Since the allyl radical involves resonance ($CH_2{=}CH{-}\dot{C}H_2 \leftrightarrow \dot{C}H_2{-}CH{=}CH_2$), the allylic substitution may give two different products. For example, 1-octene on treating with *N*-bromosuccinimide gives the following two products:



$$CH_3(CH_2)_3CH_2CH_2CH{=}CH_2 \xrightarrow{NBS} CH_3(CH_2)_3CH_2\overset{Br}{C}HCH{=}CH_2 + CH_3(CH_2)_3CH_2CH{=}CHCH_2Br$$

3–bromo – 1– octene

1–bromo 2–octene
(larger amount)

The resonance in allylic radical makes it more stable than other alkene.

Conjugated Polyenes A compound containing alternate double and single bonds is known as conjugated polyene. The simplest example is butadiene ($CH_2{=}CH{-}CH{=}CH_2$). Due to the extended conjugation, polyenes are more stable than the compound containing the same number of isolated double bonds. For examples, heats of hydrogenation of 1,4-pentadiene and 1,3-pentadiene are 254.4 and 226.4 kJ mol^{-1}, respectively, indicating that 1,3-pentadiene is more stable than 1, 4-pentadiene.

The electrophilic addition of 1,3-butadiene produces not only 1,2-addition product but also 1,4-addition product. These two products are present in equilibrium with each other. Their relative amounts depend on temperature; 1,2-addition product predominates at low temperature and its amount decreases with increase in temperature.

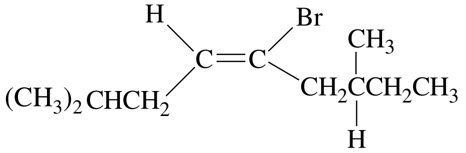
Straight Objective Type

General Characteristics

1. Baeyer's reagent is
(a) alkaline potassium permanganate solution (b) acidified potassium permangnate solution
(c) neutral potassium permangnate solution (d) aqueous bromine solution (1984)

2. Of the following compounds, which will have a zero dipole moment?
(a) 1,1-dichloroethylene (b) *cis*-1,2-dichloroethylene
(c) *trans*-1,2-dichloroethylene (d) none of these compounds (1987)

3. The order of stability of three alkenes $R_2C{=}CR_2$, $R_2C{=}CHR$ and $RCH{=}CHR$ is
(a) $RCH{=}CHR > R_2C{=}CHR > R_2C{=}CR_2$ (b) $RCH{=}CHR < R_2C{=}CHR > R_2C{=}CR_2$
(c) $RCH{=}CHR > R_2C{=}CHR < R_2C{=}CR_2$ (d) $RCH{=}CHR < R_2C{=}CHR < R_2C{=}CR_2$

4. The IUPAC name (including its configuration) of  is
(a) (*E*) (*R*)-5-Bromo-2,7-dimethyl-4-nonene (b) (*E*) (*S*)-5-Bromo-2,7-dimethyl-4-nonene
(c) (*Z*) (*R*)-5-Bromo-2,7-dimethyl-4-nonene (d) (*Z*) (*S*)-5-Bromo-2,7-dimethyl-4-nonene

5. The correct order of increasing stability if the given alkenes is
(a) 1-pentene > *cis*-pentene > *trans*-pentene > 2-methyl-2-butene
(b) 1-pentene > *trans*-pentene > *cis*-pentene > 2-methyl-2-butene
(c) 1-pentene < *cis*-pentene < *trans*-pentene < 2-methyl-2-butene
(d) 1-pentene < *cis*-pentene < *cis*-pentene < 2-methyl-2-butene

6. Which of the following facts regarding dipole moments of *trans*-1,2-dichloroethene (A) and *cis*-1,2-dichloroethene (B) is correct?
(a) $p_A > p_B$ (b) $p_A < p_B$ (c) $p_A = p_B$ (d) $p_B = 1.4\ p_A$

Preparation of Alkenes

7. *n*-Propyl bromide on treating with ethanolic potassium hydroxide produces
(a) propane (b) propene (c) propyne (d) propanol (1987)

8. 1–Chlorobutane on reaction with alcoholic potash gives
(a) 1-butene (b) 1-butanol (c) 2-butene (d) 2-butanol (1991)

9. The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is
(a) 3° > 2° > 1° (b) 3° < 2° < 1° (c) 3° > 2° < 1° (d) 3° < 2° > 1°

10. The ease of dehydration of an alcohol with concentrated H_2SO_4 is
(a) 3° > 2° > 1° (b) 3° < 2° < 1° (c) 3° > 2° < 1° (d) 3° < 2° > 1°

11. The dehydrohalogenation of 2-bromobutane with alcoholic KOH gives
(a) only 2-butene (b) only 1-butene
(c) 2-butene as the major product (d) 1-butene as the major product

12. The main product produced in the dehydrohalogenation of 2-bromo-3,3-dimethylbutane is
(a) 3,3-dimethylbutene (b) 2,3-dimethylbutene (c) 2,3-dimethylbut-2-ene (d) 4-methylpent-2-ene

13. The dehydration of 2-methylbutanol with concentrated H_2SO_4 produces
(a) 2-methylbutene as the major product (b) 2-methylbut-2-ene as the major product
(c) 1-pentene (d) pent-2-ene

14. During debromination of *meso*-dibromobutane, the major compound formed is
(a) *n*-butane (b) 1-butene (c) *cis*-2-butene (d) *trans*-2-butene (1997)

Addition Reactions

15. Anti-Markovnikov addition of HBr is not observed in
(a) propene (b) butene (c) 2-butene (d) 2-pentene (1985)

16. 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

17. The addition of HI in the presence of peroxide does not follow anti-Markovnikov's rule because
(a) HI bond is too strong to be broken homolytically
(b) I atom is not reactive enough to add on to a double bond
(c) I combines with H to give back HI
(d) HI is a reducing agent

18. The addition of HCl in the presence of peroxide does not follow anti-Markovnikov's rule because
(a) HCl bond is too strong to be broken homolytically
(b) Cl atom is not reactive enough to add on to a double bond
(c) Cl combines with H to give back HCl
(d) HCl is a reducing agent

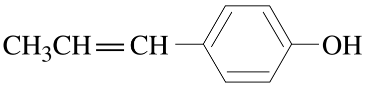
19. The peroxide effect involves
(a) ionic mechanism (b) free-radical mechanism
(c) heterolytic fission of double bond (d) homolytic fission of double bond

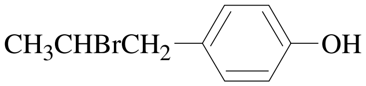
20. The addition of HCl to 3,3,3-trichloropropene gives
(a) $Cl_3CCH_2CH_2Cl$ (b) $Cl_3CCH(Cl)CH_3$ (c) $Cl_2CHCH(Cl)CH_2Cl$ (d) $Cl_2CHCH_2CHCl_2$

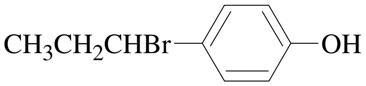
21. The intermediate during the addition of HCl to propene in the presence of peroxide is

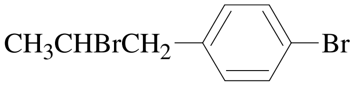
(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$ (c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

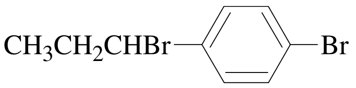
(1997)

22. The reaction of  with HBr gives

(a) 

(b) 

(c) 

(d)  (1998)

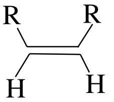
23. The addition of halogen to an alkene involves the formation of
(a) carbocation as the intermediate (b) carbanion as the intermediate
(c) free radical as the intermediate (d) halonium ion as the intermediate

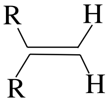
24. The addition of Br_2 to *cis*-2-butene produces
(a) (+)-2,3-dibromobutane only (b) (–)-2,3-dibromobutane only
(c) *rac*-2,3-dibromobutane (d) *meso*-2,3-dibromobutane

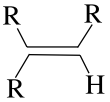
25. The addition of Br_2 to *trans*-2-butene produces
(a) (+)-2,3-dibromobutane (b) (–)-2,3-dibromobutane
(c) *rac*-2,3-dibromobutane (d) *meso*-2,3-dibromobutane

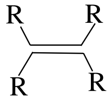
26. When ethene reacts with bromine in aqueous sodium chloride solution, the product(s) obtained is (are)
(a) ethylene dibromide only (b) ethylene dibromide and 1-bromo-2-chloroethane
(c) 1–bromo–2–chloroethane only (d) ethylene dichloride only

27. Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition

(a) 

(b) 

(c) 

(d) 

(2000)

28. The electrophilic addition of 1,4-butadiene produces
- (a) 1,2–addition product only
- (b) 1,4–addition product
- (c) both 1,2– and 1,4– addition products which are not at equilibrium with each other
- (d) both 1,2– and 1,4-addition products which are at equilibrium with each other

29. The addition reactions shown by alkenes are the example of
- (a) electrophilic addition reactions
- (b) nucleophilic addition reactions
- (c) free radical addition reactions
- (d) the formation of carbanion as the intermediate

30. The addition of Br_2 to cyclohexene in the presence of NaCl gives
- (a) only *trans*-1,2-dibromocyclohexane
- (b) only *cis*-1,2-dibromocyclohexane
- (c) *trans*-1,2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane
- (d) *cis*-1,2-dibromocyclohexane and *cis*-1-bromo-2-chlorocyclohexane

31. The addition of Br_2 dissolved in CH_3OH to cyclohexene gives
- (a) a mixture of *trans*-and *cis*-dibromocyclohexane
- (b) a mixture of *trans*-1-bromo-2-methoxycyclohexane and *trans*-dibromocyclohexane
- (c) a mixture of *cis*-1-bromo-2-methoxycyclohexane and *trans*-1-bromo-2-methyoxycyclohexane
- (d) only dibromocyclohexane.

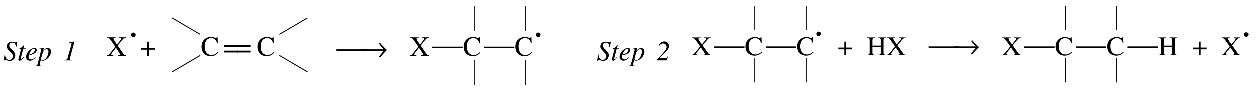
32. The addition of Br_2 to *cis*-2-butene gives
- (a) (*R*,*R*)-2,3-dibromobutane only.
- (b) (*S*,*S*)-2,3-dibromobutane only.
- (c) (*R*,*S*)-dibromobutane.
- (d) a mixture of (*R*,*R*) and (*S*,*S*)-dibromobutane.

33. The addition of Br_2 to *trans*-2-butene gives
- (a) (*R*,*R*)-2,3-dibromobutane
- (b) (*S*,*S*)-2,3-dibromobutane
- (c) (*R*,*S*)-dibromobutane
- (d) a mixture of (*R*,*R*) and (*S*,*S*)-dibromobutane.

34. Which one of the following has the smallest heat of hydrogenation per mole?
- (a) 1-Butene
- (b) *trans*-2-Butene
- (c) *cis*-2-Butene
- (d) 1,3-Butadiene

(1993)

35. The propagation steps involved in the free radical addition of HX across a double bond are



HCl does not follow free-radical addition because
- (a) Step 1 is exothermic and step 2 is endothermic
- (b) Step 1 is endothermic and step 2 is exothermic
- (c) Steps 1 and 2 are exothermic
- (d) Steps 1 and 2 are endothermic

36. The propagation steps involved in the free radical addition of HX across a double bond are

HI does not follow free-radical addition because
- (a) Step 1 is exothermic and Step 2 is endothermic
- (b) Step 1 is endothermic and Step 2 is exothermic
- (c) Both steps are exothermic
- (d) Both steps are endothermic

37. The treatment of ethene with cold alkaline potassium permanganate produces
- (a) ethylene glycol
- (b) formaldehyde
- (c) formic acid
- (d) carbon dioxide and water

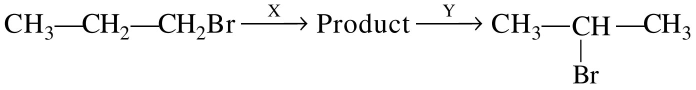
38. The treatment of *cis*-2-butene with Baeyer's reagent produces
(a) (2*S*,3*S*)-2,3-dihydroxybutane
(b) (2*R*,3*R*)-2,3-dihydroxybutane
(c) (2*R*,3*S*)-2,3-dihydroxybutane
(d) a mixture of (2*S*,3*S*) and (2*R*,3*R*)-2,3-dihydroxybutane.

39. The treatment of *trans*-2-butene with Baeyer's reagent produces
(a) (2*S*,3*S*)-2,3-dihydroxybutane only
(b) (2*R*,3*R*)-2,3-dihydroxybutane only
(c) (2*R*,3*S*)-2,3-dihydroxybutane
(d) a mixture of (2*S*,3*S*) and (2*R*,3*R*)-2,3-dihydroxybutane.

40. The reaction of propene with HOCl proceeds via the addition of
(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step (2001)

41. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Mardovnikov addition to alkenes because
(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases (2001)

42. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations:



$$CH_3{-}CH_2{-}CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_3$$

(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

43. The product of acid catalysed hydration of 2-phenylpropene is
(a) 1-phenyl-2-propanol
(b) 2-phenyl-2-propanol
(c) 1-phenyl-1-propanol
(d) 2-phenyl-1-propanol (2004)

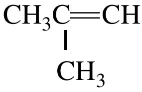
44. In the reaction $CH_3{-}CH = CH_2 \xrightarrow{NOCl} A$, the compound A is
(a) $CH_3CH(NO)CH_2Cl$
(b) $CH_3CHClCH_2NO$
(c) $CH_2(NO)CH_2CH_2Cl$
(d) $CH_3CH(Cl)CH_2CH(Cl)CH_3$ (2006)

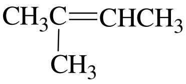
45. The addition of HBr to the alkenes $CF_3CH{=}CH_2$ and $BrCH{=}CH_2$, respectively, produces
(a) $CF_3CH_2CH_2Br$ and Br_2CHCH_3
(b) $CF_3CH(Br)CH_3$ and $BrCH_2CH_2Br$
(c) $CF_3CH_2CH_2Br$ and $BrCH_2CH_2Br$
(d) $CF_3CH(Br)CH_3$ and Br_2CHCH_3.

46. The addition of HBr to $CH_3OCH{=}CHCH_3$ produces
(a) $CH_3OCH_2CH(Br)CH_3$
(b) $CH_3OCH(Br)CH_2CH_3$
(c) $CH_3OCH_2CH_2CH_2Br$
(d) $BrCH_2OCH_2CH_2CH_3$

47. Cyclopentene is treated with Br_2 in H_2O. The product is
(a) *cis*-2-bromocyclopentanol only
(b) *trans*-2-bromocyclopentanol only
(c) *rac-cis*-2-bromocyclopentanol
(d) *rac-trans*-2-bromocyclopentanol

Oxidation/Degration Reactions

48. The treatment of  $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$ with $NaIO_4$ or boiling $KMnO_4$ produces
(a) $CH_3COCH_3 + CH_2O$
(b) $CH_3CHO + CH_3CHO$
(c) $CH_3COCH_3 + CO_2$
(d) $CH_3COCH_3 + HCOOH$

49. 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

50. The treatment of $CH_3CH{=}CHCH_3$ with $NaIO_4$ or boiling $KMnO_4$ produces

(a) CH_3CHO only (b) CH_3COOH only
(c) CH_3CHO and CH_3COOH (d) $CH_3COCH_3 + HCOOH$

51. The ozonolysis of an olefin gives only propanone. The olefin is

(a) propene (b) but–1–ene (c) but–2–ene (d) 2,3–dimethylbut–2–ene

52. An alkene on treating with hot acidified $KMnO_4$ gives propanoic acid and carbon dioxide. The alkene is

(a) $CH_3CH{=}CH_2$ (b) $CH_3CH_2CH{=}CH_2$ (c) $CH_3CH{=}CHCH_3$ (d) $(CH_3)_2C{=}CH_2$

53. An alkene on treating with hot acidified $KMnO_4$ gives two molecules of ethanoic acid. The alkene is

(a) 1-butene (b) 2-butene (c) 2-methylpropene (d) cyclobutene

54. An alkene on treating with hot acidified $KMnO_4$ gives acetone and carbon dioxide. The alkene is

(a) 1-butene (b) 2-butene (c) 2-methylpropene (d) cyclobutene

55. An alkene on treating with hot acidified $KMnO_4$ gives succinic acid. The alkene is

(a) 1-butene (b) 2-butene (c) 2-methylbutene (d) cyclobutene

56. An alkene on treating with hot acidified $KMnO_4$ gives 4-oxopentanoic acid. The alkene is

(a) 1-pentene (b) 2-pentene
(c) 1-methylcyclobutene (d) 1,2-dimethylcyclopropene

57. An alkene on treating with hot acidified $KMnO_4$ gives hexane-2, 5-dione. The alkene is

(a) hexene (b) 2-hexene
(c) 1-methylcyclopentene (d) 1,2-dimethylcyclobutene

58. An alkene on reductive ozonolysis gives 2 molecules of $CH_2(CHO)_2$. The compound is

(a) 2,4-hexadiene (b) 1,3-cyclohexadiene
(c) 1,4-cyclohexadiene (d) 1-methyl-1,3-cyclopentadiene

59. An alkene on oxidative ozonolysis gives adipic acid? The alkene is

(a) cyclohexene (b) 1-methylcyclopentene
(c) 1,2-dimethylcyclobutene (d) 3-hexene

60. The treatment of propene with Cl_2 at 500–600 °C produces

(a) 1,2–dichloropropane (b) allyl chloride (c) 2,3–dichloropropene (d) 1,3–dichloropropene

Multiple Correct Choice Type

1. Dipole moment is shown by

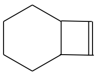
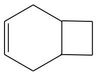
(a) 1,4-dichlorobenzene (b) *cis*-1,2-dichloroethene
(c) *trans*-1,2-dichloroethene (d) 1,2-dichloro-2-pentene (1986)

2. The molecules that will have dipole moment are

(a) 2,2-dimethylpropane (b) *trans*-2-pentene
(c) *cis*-3-hexene (d) 2,2,3,3-tetramethylbutane (1992)

3. Which of the following statements is/are Correct?

(a) *cis*-Alkene can be converted into *trans*-alkene on heating with I_2.

(b) The compound  Shows a faster rate of catalytic hydrogenation than the compound .

(c) The larger the enthalpy of formation of an alkene, the more stable the alkene.

(d) The compound $C_2H_5CH(Cl)CH_2{=}CH_2$ on hydrogenation produces an optically inactive compound.

4. Which of the following compounds will show geometrical isomerism?

(a) 2–butene (b) propene
(c) 1–phenylpropene (d) 2–methyl–2–butene (1998)

5. Which of the following statements are **not** correct?

(a) Propene reacts with HBr to give *n*-propyl bromide.

(b) Moist ethylene can be dried by passing it through concentrated sulphuric acid.

(c) The reaction of vinyl choloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule.
(d) Isobutylene exhibits geometric isomerism.

6. Which of the following statements are correct?
(a) Stereoisomers refer only to configurational and geometric isomers and not to conformational isomers.
(b) Geometric isomers have different physical properties.
(c) The unsaturated group $CH_2 = CH—$ is known as allyl group.
(d) The lower alkenes are soluble in water whereas the higher ones are insoluble in water.

7. Which of the following statements are correct?
(a) In general, *cis* isomer has higher boiling point and lower melting point as compared to its *trans* isomer.
(b) The treatment of vicinal dihalides with zinc generates carbon-carbon triple bond.
(c) A carbon-carbon double bond can be protected by firstly converting it into vicinal dihalide and then regenerating it by treating with zinc.
(d) The ease of dehydrohalogenation of alkyl halides is 3° > 2° > 1°.

8. Which of the following statements are correct?
(a) The ease of dehydration of alcohols is 1° > 2° > 3°.
(b) The dehydrohalogenation of alkyl halides is an example of 1,2-elimination and is brought about by action of a base.
(c) 1-2 Elimination reaction involving E2 mechanism does not involve any rearrangement of carbon skeleton.
(d) 1-2 Elimination reaction involving E1 mechanism may involve the rearrangement of carbon skeleton.

9. Which of the following statements are correct?
(a) EI mechanism of 1-2 elimination involves two molecules undergoing covalency changes in the rate-determining step.
(b) The strength of carbon-halogen bonds follows the sequence R—F > R—Cl > R—Br > R—I.
(c) The reactivity of RX towards 1,2-dehydrohalogenation following E2 mechanism is

$$R—F > R—Cl > R—Br > R—I.$$

(d) In dehydrohalogenation, the preferred product is the alkene that has the greater number of alkyl group attached to the doubly bonded carbon atoms.

10. Which of the following statements are correct?
(a) In dehydrohalogenation, the more stable the alkene, the faster it is formed.
(b) The order of reactivity of alkyl halides towards E2 dehydrohalogenation is 3° > 2° > 1°.
(c) Hydrogenation of an alkene is an exothermic reaction.
(d) *n*-propyl alcohol can be produced by treating propylene with 80% H_2SO_4 followed by heating with water.

11. Which of the following statements are correct?
(a) The electophilic addition across the double bond may be accompanied with the rearrangement of carbon skeleton.
(b) Markovnikov's rule is in agreement with Saytzeff's rule.
(c) The rate of addition of a hydrogen ion to a double bond depends upon the stability of the carbocation being formed.
(d) The more stable the carbocation formed as an intermediate in the addition reaction of alkene, the slower it is formed.

12. Which of the following statements are **not** correct?
(a) Duting the addtion of halogens to alkenes, a carbocation is formed as an intermediate.
(b) The addition of aqueous Br_2 to ethylene in the presence of NaCl forms only dibromoethylene.
(c) Polyethylene is essentially an alkane with a very long chain.
(d) Treatment of an alkene with cold alkaline potassium permangate breakes the double bond.

13. Which of the following statements are **not** correct?
(a) 1,2-dichloroethene is more reactive towards addition of H_2SO_4 in comparison to vinyl chloride.
(b) The function of the zinc dust in the ozonolysis of an alkene is to destroy H_2O_2 which is formed during the reaction.
(c) Dehydration of 1-butanol mainly gives 2-butene.
(d) Dehydrohalogenation of 2-bromopentane results in the formation of 1-pentene.

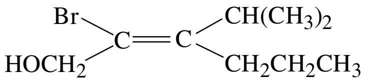
14. Which of the following statements are correct?
(a) The addition of HBr to an alkene proceeds through ionic mechanism.
(b) The addition of HBr to an alkene in the presence of peroxide proceeds through ionic mechanism.
(c) Diphenylamine or catechol can prevent the abnormal addition of HBr to an alkene in the presence of peroxide.
(d) The IUPAC name of the alkne $[(CH_3)_2CH]_2 = C[CH(CH_3)_2]_2$ is tetraisopropylethene.

15. Which of the following statements are **not** correct?
(a) The addition of HBr to 1,3-butadiene at – 80 °C produces 1-bromo-2-butene as the major product.
(b) The addition of HBr to 1,3-butadiene at 40 °C produces 3-bromo-1-butene as the major product.
(c) The addition of HBr to 1,3-butadiene produces both 1-bromo-2-butene and 3-bromo-1-butene which are in equilibrium with each other. The relative amounts of the two are temperature dependent.
(d) The treatment of gaseous propene with chlorine at 500-600 °C yields 1,2-dichloropropane.

16. Which of the following statements are correct?
(a) The treatment of propene with chlorine in CCl_4 solution at low temperature yields allyl chloride.
(b) More energy is evolved in the hydrogenation of the *cis*-2-butene as compared to that of *trans*-2-butene.
(c) Alkenes are less reactive toward catalytic hydrogenation in comparison to other functional groups such as ketones, aldehydes and nitriles.
(d) An ozonide product of an alkene produces carbonyl compound when treated with Zn and acid while alcohols are produced when treated with sodium borohydride.

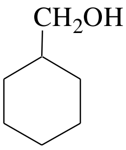
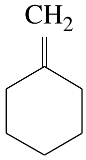
17. Which of the following statements are correct?
(a) The treatment of propene with *N*-bromosuccinimide in aqueous dimethyl sulphoxide produces 1-promo-2-propanol as the major product.
(b) The number of isomers of pentene (C_5H_{10}) is 4.
(c) The dipole moment of *cis*-2,3-dichloro-2-butene is smaller than that of *cis*-1,2-dichloroethene.
(d) The dipole moment of *cis*-1,2-dichloro-1,2-dibromoehene is smaller than that of *cis*-1,2-dichloroethene.

18. Which of the following statements are **not** correct?
(a) The major product in the dehydrohalogenation of 2-chloro-2,3-dimethylbutane is 2,3-dimethyl-1-butene.
(b) The order of reactivity of *n*-propyl bromide, isobutyl bromide and ethyl bromide towards E2 dehydrohalogenation is ethyl > *n*-propyl > isobutyl.
(c) Of the simple dialkyl ethylenes, the *cis* isomer is more stable than the *trans* isomer.
(d) If enthalpy of combustion of *cis*-2-butene is more negative than *trans*-2-butene, then the conversion of *cis* to *trans* isomer is exothermic.

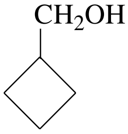
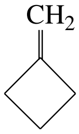
19. Which of the following statements are correct?
(a) The compound  has *E* configuration.

(b) The number of the structural isomers and stereoisomers of C_5H_{10} is six.
(c) The dipole moment of 1,1-dichloroethene is smaller than that of *cis*-1,2-dichloroethene.
(d) The enthalpy of combustion of *trans*-2-butene has a lesser negative value as compared to that of cis-2-butene.

20. Which of the following statements are **not** correct?
(a) The *trans*-2-butene is more stable than *cis*-2-butene.
(b) The acid-catalysed dehydration of an alcohol follows E2 mechanism.
(c) The dehydration of an alcohol can be carried out in the presence of a base.

(d) The acid-catalysed dehydration of  produces  as the major product.

21. Which of the following statements are correct?

(a) The acid-catalysed dehydration of  produces  as the major product.

(b) The addition of HBr to $CH_3OCH = CHCH_3$ produces $CH_3OCH_2CHBrCH_3$.

(c) The addition of HBr to $CF_3CH = CH_2$ gives $CF_3CH_2CH_2Br$.

(d) The addition of HBr to $BrCH = CH_2$ gives Br_2CHCH_3.

22. Which of the following statements are **not** correct?

(a) The addition of Br_2 to cyclohexene produces *cis* 1,2-dibromocyclohexane.

(b) The addition of Br_2 to cyclohexene in the presence of NaCl produces a mixture of *trans*-dibromohexane, *trans*-1-bromo-2-chlorohexane and *trans*-dichloro-hexane.

(c) The addition of Br_2 to *cis*-2-butene produces *meso*-2,3-dibromobutane.

(d) The addition of Br_2 to *trans*-2-butene produces *racemic*-2,3-dibromobutane.

23. Which of the following statements are correct?

(a) The addition of H_2 to *cis*-2,3-dibromobutene produces *meso*-2,3-dibromobutane.

(b) The addition of H_2 to *trans*-2,3-dibromobutene produces *racemic*-2,3-dibromobutane.

(c) The hydroxylation of *cis*-2,3-dimethylbutene with Baeyers's reagent produces *racemic*-2,3-dihydroxybutane.

(d) The hydroxylation of *trans*-2,3-dimethylbutene with Baeyer's reagent produces *meso*-2,3-dihydroxybutane.

24. Which of the following statements are correct?

(a) The dehalogenation of *meso*-2,3-dibromobutane produces *cis*-2-butene.

(b) The dehalogenation of (*S*,*S*)-2,3-dibromobutane produces *trans*-2-butene.

(c) Dehydrobromination of (*R*,*R*)-2,3-dibromobutane produces *trans*-or (Z)-2-bromo-2-butene.

(d) Dehydrobromination of *meso*-2,3-dibromobutane produces *cis*-or (*E*)-2-bromo-2-butene.

25. Which of the following statements are **not** correct?

(a) The main product obtained when ethene mixed with air is passed under pressure over catalyst at 250°C is ethylene oxide.

(b) The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with acetylene.

(c) 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide provided peroxide is present.

(d) Kolbe electrolysis of potassium succinate gives CO_2 and $CH_3CH = CH_2$.

26. Which of the following statements are **not** correct?

(a) The allyl group is represented as $CH_2{=}CH{-}CH_2{-}$.

(b) Alkanes are less dense than water.

(c) The reduction of $RC{\equiv}CR$ to $RCH{=}CHR$ with H_2 and Lindlar catalyst produces *trans* isomer.

(d) The reduction of $RC{\equiv}CR$ to $RCH{=}CHR$ with Na or Li and NH_3 produces *cis* isomer.

27. Which of the following statements are correct?

(a) E1 mechanism of 1-2 elimination follows first order rate law.

(b) E2 mechanism of 1-2 elimination follows second order rate law.

(c) The dehydration of alcohols producing alkenes is catalyzed by acid.

(d) The enthalpies of hydrogenation of *cis*- and *trans*-2-butene are 119.7 kJ mol^{-1} and 115.5 kJ mol^{-1} respectively. This implies that the *cis*- form is more stable than the *trans*-form.

28. Which of the following statements are correct?

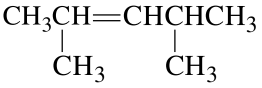
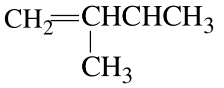
(a) The additon of HBr to an alkene in the presence of diphenylamine follows markovnikov rule.

(b) Isobutyl alcohol cannot be produced by treating isobutylene with H_2SO_4 followed by heating with water.

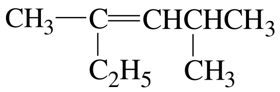
(c) Water adds to the more reactive alkenes in the presence of acid to yield alcohol.
(d) The addition of reagents across the double bond is an example of nucleophilic addition.

29. Which of the following statements are **not** correct?
(a) Isobutylene, which forms a tertiary cation, reacts faster with acids than the isomer 2-butene, which forms a secondary cation.
(b) Propylene, which forms a secondary cation, reacts faster with acids than ethylene, which forms a primary cation.
(c) Vinyl chloride is more reactive towards addition reactions as compared to ethylene.
(d) An alkyl group attached to a carbocation destabilised the latter.

30. Which of the following statements are **not** correct?
(a) A chlorine attached to a carbocation stabilizes the latter.
(b) An alkyl group attached to a carbanion stabilizes the latter.
(c) A chlorine attached to a carbanion stabilizes the latter.
(d) Polymerizatione of alkene involves free radical mechanism.

31. Which of the following statements are **not** correct?
(a) The structure of compound producing CH_3CHO, HCHO and $OHC—CH_2CHO$ on ozonolysis is 1,4-hexadiene.
(b) The structure of compound producing $OCHCH_2CH_2CH_2CHO$ on ozonolysis is *n*-hexene
(c) The product of ozonolysis of  $\mathrm{CH_3\underset{CH_3}{\underset{|}{C}}H{=}CH\underset{CH_3}{\underset{|}{C}}HCH_3}$ are CH_3COCH_3 and $CH_3CH(CH_3)CHO$.
(d) The product of ozonlysis of  $\mathrm{CH_2{=}\underset{CH_3}{\underset{|}{C}}HCHCH_3}$ are HCOOH and $CH_3CH(CH_3)CHO$.

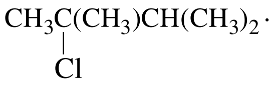
32. Which of the following statements are **not** correct?
(a) The alkene which on ozonolysis gives 2 molecules of propanal is $CH_3CH{=}CHCH_3$.
(b) The treatment of 1-pentene with $NaIO_4$ gives CO_2 and $CH_3CH_2CH_2COOH$.
(c) The treatment of 4-methyl-2-pentene with $NaIO_4$ gives CH_3CH_2COOH and CH_3COOH.
(d) The treatment of 2,3-dimethyl-2-butene with $NaIO_4$ or hot $KMnO_4$ produces CH_3CHO and CH_3COCH_3.

33. Which of the following statements are correct?
(a) The IUPAC name of  $\mathrm{CH_3{—}\underset{C_2H_5}{\underset{|}{C}}{=}CH\underset{CH_3}{\underset{|}{C}}HCH_3}$ is 2,4-dimethyl-3-hexene.
(b) Of the two dienes $CH_2{=}CH—CH{=}CH—CH_3$ and $CH_2{=}C{=}CH—CH_2CH_3$, the more stable diene would be $CH_2{=}CH—CH{=}CH—CH_3$.
(c) The structure of the compound giving $O{=}CHCH_2CH_2CH{=}O$ on ozonolysis is 1,3-cyclohexadiene.
(d) The allyl radical is represented as $CH_3—CH{=}CH—CH_2$.

34. Which of the following statements are correct?
(a) Low concentration of halogen instead of high temperature favours substitution reaction in propylene instead of addition across the double bond.
(b) The compound N-bromosuccinimide is used for the specific purpose of brominating alkenes at the allylic position.
(c) The resonance in allyl radical is represented as $CH_2{=}CH\dot{C}H_2 \leftrightarrow \dot{C}H_2—CH{=}CH_2$.
(d) In general, *cis* alkenes are more stable than their *trans* isomers.

35. Which of the following statements are correct?
(a) Between 2-bromo-2-methylbutane and 3-bromopentane, the more reactive towards dehydrohalogenation is 2-bromo-2-methylbutane.
(b) Between 2-bromo-2-methylbutane and 3-bromo-2-methylbutane, the more reactive towards dehydrohalogenation is 2-bromo-2-methylbutane.
(c) Heating of $(CH_3)_3CCH_2OH$ with acid gives 2-methyl-2-butene as a major product and 2-methyl-1-butene as a minor product.

(d) The treatment of 3,3-dimethyl-1-butene with hydrogen chloride gives products $CH_3C(CH_3)_2CH(Cl)\ CH_3$ and

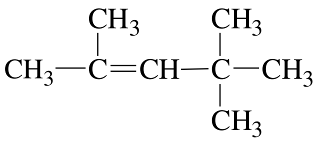


$CH_3\underset{\underset{Cl}{|}}{C}(CH_3)CH(CH_3)_2$.

36. Which of the following statements are **not** correct?

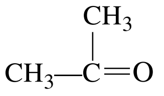
(a) Of the compounds 1-butene, *cis*-2-butene and *trans*-2-butene, the compound having the lowest enthalpy of combustion is *cis*-2-butene and that having the highest value is 1-butene.

(b) The treatment of



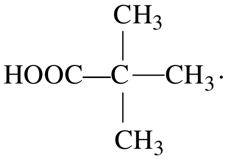
$CH_3—\overset{\overset{CH_3}{|}}{C}=CH—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$

with $KMnO_4$ and $NaIO_4$ gives



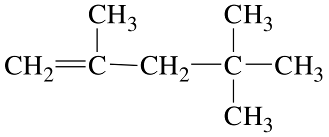
$CH_3—\overset{\overset{CH_3}{|}}{C}=O$

and



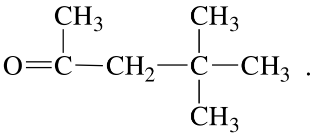
$HOOC—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$.

(c) The treatment of



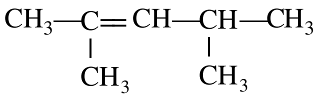
$CH_2=\overset{\overset{CH_3}{|}}{C}—CH_2—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$

with $KMnO_4$ and $NaIO_4$ gives HCHO and



$O=\overset{\overset{CH_3}{|}}{C}—CH_2—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$.

(d) The treatment of



$CH_3—\underset{\underset{CH_3}{|}}{C}=CH—\underset{\underset{CH_3}{|}}{CH}—CH_3$

with $KMnO_4$ and $NaIO_4$ gives CH_3COCH_3 and $(CH_3)_2CHCOOH$.

37. Which of the following statements are correct?

(a) An alkene on treating with $KMnO_4$ and $NaIO_4$ gave CH_3COOH and CH_3CH_2COOH. The alkene is $CH_3CH = CHCH_2CH_3$.

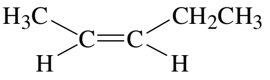
(b) A diene on treating with $KMnO_4$ and $NaIO_4$ gave CO_2, $(COOH)_2$ and CH_3COOH. The diene is $CH_2 = CH—CH = CH–CH_3$.

(c) The relative reactivities in radical substitution of the H in C—H bond in the given type of H is allyl > 3° > 2° > 1° Me > vinyl.

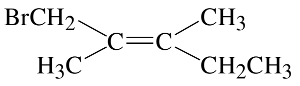
(d) 3,3-Dimethyl-1-butene gives only one addition product.

38. Which of the following alkenes have Z configuration?

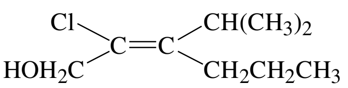
(a)



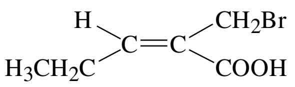
(b)



(c)



(d)



39. The addition of HBr to 3,3-dimethyl-1-butene results in the formation of

(a) 3-bromo-2,2-dimethylbutane

(b) 2-bromo-2,3-dimethylbutane

(c) 1-bromo-2-methyl-3,3-dimethylbutane

(d) 4-bromo-3-methyl-2,2-dimethylbutane

Linked Comprehension Type

1. Water can be added across a double bond through the following two methods.

Method- I	Oxymercuration and demercuration
Method-II	Hydroboration–oxidation

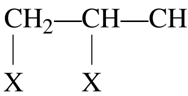
(i) The addition of water is in accordance with
(a) Markovnikov's rule in both the methods
(b) anti-Markovmikov's rule in both the methods
(c) Markovnikov's rule in method-I and anti-Markovnikov's rule in method-II
(d) anti-Markovnikov's rule in method-I and Markovnikov's rule in method-II

(ii) The final steps in the two methods involve
(a) oxidation in both the methods by H_2O_2/OH^-
(b) reduction in both the methods by $NaBH_4/OH^-$
(c) oxidation in method-I by H_2O_2/OH^- and reduction in method-II by $NaBH_4/OH^-$
(d) reduction in method by $NaBH_4/OH^-$ and oxidation in method-II by H_2O_2/OH^-

(iii) The addition of water involves
(a) rearrangement of carbon skeleton in both the methods
(b) no rearrangement of carbon skeleton in both the methods
(c) rearrangement in method-I and no-rearrangement in method-II of carbon skeleton
(d) no rearrangement in method-I and rearrangement in method-II of carbon skeleton

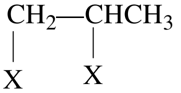
2. In the compound $CH_2{=\!=}CH{-\!-}CH_3$, the methyl hydrogens are known as allylic hydrogen atoms and CH_2 hydrogen atoms are known as vinylic hydrogen atoms. The reaction of $CH_2{=\!=}CH{-\!-}CH_3$ with halogens depends upon experimental conditions.

(i) In the reaction $CH_2{=\!=}CH{-\!-}CH_3 + X_2 \xrightarrow[CCl_4]{\text{low temperature}} P$ or/and Q

where P is  $\underset{X}{\underset{|}{CH_2}}{-\!-}\underset{X}{\underset{|}{CH}}{-\!-}CH_3$ and Q is $CH_2{=\!=}CH{-\!-}CH_2X$. The product(s) obtained is/are

(a) P only (b) Q only
(c) Equal mixture of P and Q (d) Unequal mixture of P and Q

(ii) In the reaction $CH_2{=\!=}CH{-\!-}CH_3 + X_2 \xrightarrow[\text{low cone of } X_2]{\text{high temperature}} P$ or/and Q

where P is  $\underset{X}{\underset{|}{CH_2}}{-\!-}\underset{X}{\underset{|}{C}}HCH_3$ and Q is $CH_2{=\!=}CH{-\!-}CH_2X$. The product(s) obtained is/are

(a) P only (b) Q only
(c) Equal mixture of P and Q (d) Unequal mixture of P and Q

(iii) Which of the following radicals is most stable?
(a) allylic (b) 3° (c) 2° (d) vinylic

3. Simple alkenes can be hydrated by reaction with hot sulphuric acid followed by the treatment of the intermediate sulphate with water. This method is of little value for most laboratory applications due to high temperature and strongly acidic conditions. In practice, most alkenes are best hydrated by the oxymercuration procedure.

(i) In the oxymercuration method, an alkene is treated with
(a) mercuric sulphate in dilute acidic medium followed by the treatment with excess of water
(b) mercuric acetate in aqueous tetrahydrofuran followed by the treatment with sodium borohydride
(c) mercuric acetate in aqueous tetrahydrofuran followed by the treatment with H_2O_2
(d) mercuric acetate in methanol followed by the treatement with excess of water.

(ii) The reaction proceeds via the formation of
(a) electrophilic addition of Hg^{2+} ion (b) cyclic acetoxymercurinium ion
(c) cyclic mercurium bisulphate ion (d) carbocation resulted from the addition of H^+

(iii) The overall addition of water follows
(a) Markovnikov rule (b) *anti*-Markovnikov rule
(c) no particular rule (d) complicated route with side products

4. The addition of water across a double bond can be carried out by hydroboration method.

(i) The reagent used in this method is
(a) BH_3 in aqueous medium
(b) BH_3—THF (tetrahydrofuran) complex followed by treatment with aqueous H_2O_2 in basic medium
(c) BH_3 in acidic medium
(d) BH_3—THF complex followed by treatment with sodium borohydride

(ii) The reaction proceeds via the formation of
(a) cyclic four-membered transition state
(b) cyclic three-membered transition state
(c) no cyclic transition state
(d) positively charged boron complex with boron attached to more substituted carbon.

(iii) The addition of water follows
(a) Markovnikov rule
(b) *anti*-Markovnikov rule
(c) no particular pattern
(d) complicated mechanism with side effects.

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.
(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explantation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement – 1	**Statement – 2**
1.	Addition of Br_2 to 1-butene gives two optical isomers.	The product contains one asymmetric carbon. (1998)
2.	1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.	It involves the formation of a primary radical. (2000)
3.	Addition of bromine to *trans*-2-butene yields *meso*-2,3-dibromobutane.	Bromine addition to an alkene is an electroph--ilic addition. (2001)
4.	Dimethylsuphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.	It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. (2001)
5.	In the dehydrobromination of 2-bromobutane with alc.KOH, 81% product is Sayteff product ($CH_3CH{=}CHCH_3$) and 19% product is Hofmann product ($CH_3CH_2CH{=}CH_2$).	The alkene with greater number of alkyl group is formed faster than alternative alkene.
6.	The addition of Br_2 to *cis*-2-butene produces *meso*-2,3-dibromobutane.	The addition of Br_2 acros a double bond invo--lves the formation of a bromonium ion followed by the *anti*-addition of Br^-.
7.	The addition of Br_2 to *trans*-2-butane produces *meso*-2,3-dibromobutane.	The addition of Br_2 across a doublr bond involves the formation of brominium ion followed by the *anti*-addition of Br^-.
8.	The addition of H_2 to *cis*-2,3-dibromobutene produces *meso*-2,3-dibromobutene.	The addition of H_2 occurs with *anti* stereochemistry.
9.	The addition of H_2 to *trans*-2,3-dibromobutene produces *racemic*-2,3-dibromobutene.	The addition of H_2 occurs with *syn* stereochemistry.
10.	Alkynes are generally less reactive than alkenes towards electrophilic reagents such as H^+.	The reaction of alkyne or alkene with the electrophilic reagents proceeds through the formation of a carbocation.
11.	In general, *trans* isomers of alkenes are more stable than *cis* isomers.	*Trans* isomer involves less steric strain than the *cis* isomer.
12.	Addition of Br_2 in the presence of NaCl produces *trans*-1,2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane and no 1,2-dichlorocyclohexane is obtained.	The addition of Br_2 to alkene is electrophilic and *anti* addition. The formation of 1,2- di-chlorocyclohexane requires the presence of Cl^+ which is not available.
13.	$Cl_2C{=}CCl_2$ does not add Cl_2 under usual reaction conditions.	Four electron-attracting Cl's decreases the nucleophilicity of the π e^-s of the alkene.
14.	The addition of Cl_2 to $Cl_2C{=}CCl_2$ is catalyzed by a small amount of $AlCl_3$.	$AlCl_3$ generates $AlCl^-_4$ and Cl^+ on reacting with Cl_2.

15.	*Cis* alkene may be made to exist in equilibrium with its *trans*-form on heating with I_2.	The addition of one $I^{\bullet}$ converts double bond to single bond around which rotation converts *cis*- to *trans*-form and vice versa.
16.	The addition reactions shown by alkenes are stereospecific in nature.	The addition occurs only via *syn* mode.

Matrix Match Type

1. Column I gives some additional reactions. The nature of products and their mode of additions are given in Column II. Match each entry of Column I with the correct answers given in Column II.

Column I	**Column II**
(a) Bromination of *cis*-2-butene	(p) Enantiomers
(b) Bromination of *trans*-2-butene	(q) *meso*-product
(c) Hydrogenation of *cis*-2,3-dibromo-2-butene	(r) *Syn* addition
(d) Hydrogenation of *trans*-2,3-dibromo-2-butene	(s) *Anti* addition

2. Column I gives some of the reactions. Their characteristics are given in Column II. Match each entry of Column I with the correct choice(s) from Column II.

Column I	**Column II**
(a) Oxymercuration-demercuration process	(p) Markovnikov addition
(b) Hydroboration-oxidation process	(q) Anti-Markovnikov addition
(c) Hydroxylation of *cis*-2-butene by alkaline $KMnO_4$	(r) Rearrangement of carbon skeleton
(d) alcoholic KOH + 3-bromo-2,3-dimethyl pentane	(s) *Racemic* mixture
	(t) *meso* product

ANSWERS

Straight Objective Type

1. (a)	**2.** (c)	**3.** (d)	**4.** (b)	**5.** (c)	**6.** (b)
7. (b)	**8.** (a)	**9.** (a)	**10.** (a)	**11.** (c)	**12.** (c)
13. (b)	**14.** (d)	**15.** (c)	**16.** (c)	**17.** (b)	**18.** (a)
19. (b)	**20.** (a)	**21.** (b)	**22.** (d)	**23.** (d)	**24.** (c)
25. (d)	**26.** (b)	**27.** (a)	**28.** (d)	**29.** (a)	**30.** (c)
31. (b)	**32.** (d)	**33.** (c)	**34.** (d)	**35.** (a)	**36.** (b)
37. (a)	**38.** (c)	**39.** (d)	**40.** (b)	**41.** (c)	**42.** (b)
43. (b)	**44.** (b)	**45.** (a)	**46.** (b)	**47.** (d)	**48.** (c)
49. (a)	**50.** (b)	**51.** (d)	**52.** (b)	**53.** (b)	**54.** (c)
55. (d)	**56.** (c)	**57.** (d)	**58.** (c)	**59.** (a)	**60.** (b)

Multiple Correct Choice Type

1. (b), (d)	**2.** (b), (c)	**3.** (a), (b), (d)	**4.** (a), (b)
5. (a), (b), (c), (d)	**6.** (a), (b)	**7.** (a), (c), (d)	**8.** (b), (c), (d)
9. (b), (d)	**10.** (a), (b), (c)	**11.** (a), (b), (c)	**12.** (a), (b), (d)
13. (a), (c), (d)	**14.** (a), (c)	**15.** (a), (b), (d)	**16.** (b), (d)
17. (a), (d)	**18.** (a), (b), (c)	**19.** (b), (d)	**20.** (b), (c), (d)
21. (c), (d)	**22.** (a), (b), (c), (d)	**23.** (a), (b)	**24.** (c), (d)
25. (b), (d)	**26.** (c), (d)	**27.** (a), (b), (c)	**28.** (a), (b), (c)
29. (c), (d)	**30.** (a), (b)	**31.** (b), (d)	**32.** (c), (d)
33. (a), (b)	**34.** (a), (b), (c)	**35.** (a), (b), (c), (d)	**36.** (a), (c)
37. (a), (b), (c)	**38.** (a), (c)	**39.** (a), (b)	

Linked Comprehension Type

1. **(i)** (c) **(ii)** (d) **(iii)** (b)
2. **(i)** (a) **(ii)** (b) **(iii)** (a)
3. **(i)** (b) **(ii)** (b) **(iii)** (a)
4. **(i)** (b) **(ii)** (b) **(iii)** (b)

Assertion and Reason Type

1. (a) **2.** (c) **3.** (b) **4.** (a) **5.** (a) **6.** (d) **7.** (a)
8. (c) **9.** (a) **10.** (b) **11.** (a) **12.** (a) **13.** (a) **14.** (b)
15. (a) **16.** (c)

Matrix Match Type

1. (a) – (p), (s); (b) – (q), (s); (c) – (q), (r); (d) – (p), (r)
2. (a) – (p); (b) – (q); (c) – (p), (t); (d) – (r)

Hints and Solutions

Straight Objective Type

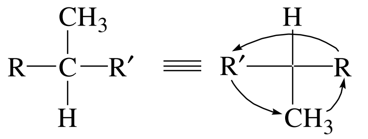
1. Baeyer's reagent is an alkaline potassium permanganate solution.

2. *trans*-1, 2-dichloroethene will have zero dipole moment.

3. According to Saytzeff rule, more substitute alkene is more stable. Hence, the order of stability is

$$RCH{=}CHR < R_2C{=}CHR < R_2C{=}CR_2$$

4. High periority substituents are in opposite side. Thus the compound has E configuration. The asymmetric carbon has S configuration



(S-configuration)

5. Saytzeff's rule dictates 2-methyl-2-butene to be more stable than pentenes. *Trans*-pentene is more stable than *cis*-pentene due to less crowding of bulky groups. 1-pentene will be least stable. Hence, the correct order of stability is 1-pentene < *cis*-pentene < *trans*-pentene < 2-methylbutene.

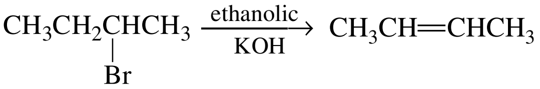
6. *Trans*-isomer have equal and opposite bond moments resulting a zero dipole moment. *Cis*-isomer has a nonzero dipole moment.

7. $CH_3CH_2CH_2Br \xrightarrow[KOH]{ethanolic} CH_3CH{=}CH_2$. **8.** $CH_3CH_2CH_2CH_2Cl \xrightarrow[KOH]{ethanolic} CH_3CH_2CH{=}CH_2$

9. The more stable intermediate 3° carbocation is formed more easily than 2° and 2° is formed faster than 1°. Hence, the ease of dehydrohalogenation follows the order 3° > 2° > 1°.

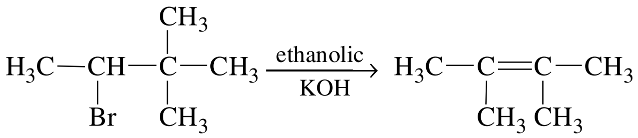
10. Same as Q.9.

11. The more stable alkene is formed faster



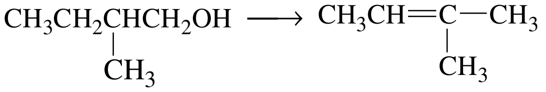
$$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[KOH]{ethanolic} CH_3CH{=}CHCH_3$$

12. Dehydrohalogenation proceeds via rearrangement to give more stable product.



$$H_3C{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3 \xrightarrow[KOH]{ethanolic} H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$$

13. The dehydration involves rearrangement of double bond



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2OH \longrightarrow CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$$

14. Debromination of *meso*-dibromobutane, produces *trans*-2-butene as the major product.

15. 2-Butene is $CH_3CH{=}CHCH_3$. The addition of HBr gives the same product whether it occurs via Markovnikov or anti-Markovnikov rule.

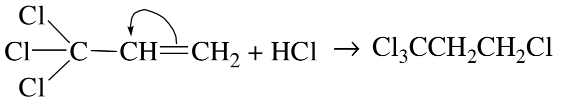
16. The addition of HBr across a double bond in the presence of peroxide involves free radical addition.

17. The addition of HI in the presence of peroxide does not follow anti-Markovnikov's rule because I atom is not reactive enough to add on a double bond.

18. The addition of HCl in the presence of peroxide does not follow anti-Markovnikov's rule because HCl bond is too strong to be broken homolytically.

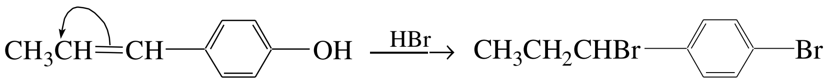
19. The peroxide effect involves free-radical mechanism.

20.



21. The addition of HCl proceeds via the formation of carbocation $CH_3\overset{+}{C}HCH_3$. The peroxide is not able to produce radicals from HCl as the bond H—Cl cannot be broken into radicals.

22.



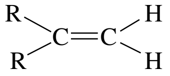
23. The addition of halogen to an alkene involves the formation of halonium ion as the intermediate.

24. The addition of Br_2 to *cis*-2-butene produces *rac*-2, 3-dibromobutane.

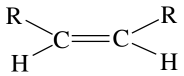
25. The addition of Br_2 to *trans*-2-butene produces *meso*-2, 3-dibromobutane.

26. The products are ethylene dibromide and 1-bromo-2-chloroethane.

27.



is more stable then



28. The electrophilic addition of 1, 3-butadiene gives both 1,2-and 1,4-addition products which are at equilibrium with each other.

29. Addition across a double bond proceeds via electrophilic addition.

30. The addition of halogen to a double bond is stereoselective and stereospecific. The first step is the formation of a bridged cation, called a bromonium ion. In the second step, the nucleophile (Br^- or another anion) adds to the face away from the bridging group to yield the *anti* addition product. So, the products are *trans*-1, 2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane.

31. A mixture of *trans*-1, 2-dibromocyclohexane and *trans*-1-bromo-2-methoxycyclohexane is obtained.

32. The addition of Br_2 to *cis*-2-butene gives a mixture of (R, R) and (S, S)-dibromobutane

33. The addition of Br_2 to *trans*-2-butene gives (R, S)-dibromobutane

34. The more stable the compound, the smallest is the heat of hydrogenation per mole.

35. For Step I. $\Delta H = \varepsilon(C{=}C) - \varepsilon(C{-}C) - \varepsilon(C{-}Cl) = [612 - (348 + 338)]\ kJ\ mol^{-1}$ = negative
Step II. $\Delta H = \varepsilon(H{-}Cl) - \varepsilon(C{-}H) = (431 - 412)\ kJ\ mol^{-1}$ = positive
Thus, step 1 is exothermic and step 2 is endothermic.

36. For Step I. $\Delta H = \varepsilon(C{=}C) - \varepsilon(C{-}C) - \varepsilon(C{-}I) = [612 - (348 + 238)]\ kJ\ mol^{-1}$ = positive
For Step II. $\Delta H = \varepsilon(HI) - \varepsilon(C{-}H) = (299 - 412)\ kJ\ mol^{-1}$ = negative
Thus, step 1 is endothermic and step 2 is exothermic.

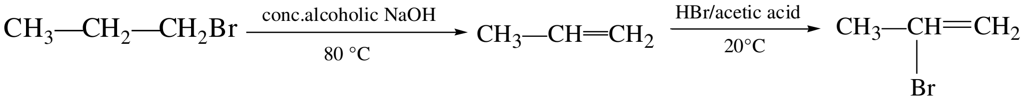
37. The treatment of ethene with cold alkaline potassium permanganate produces ethylene glycol.

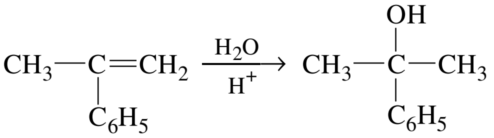
38. There is *syn* addition of the two —OH groups. The product is (2R, 3S)-dihydroxybutane for *cis*-2-butene.

39. The product is a mixture of (2S, 3S) and (2R, 3R)-2, 3-dihydroxybutane for *trans*-2-butenen.

40. The addition involves the electrophilic attack by Cl^+ as the first step.

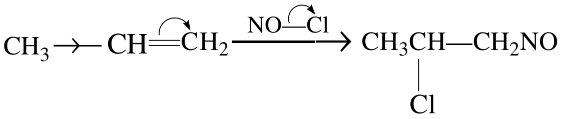
41. In the propagation steps, one of the two steps is endothermic in case of HCl and HI.

42. 
$CH_3—CH_2—CH_2Br \xrightarrow[80\ °C]{\text{conc.alcoholic NaOH}} CH_3—CH{=}CH_2 \xrightarrow[20°C]{\text{HBr/acetic acid}} CH_3—\underset{\underset{Br}{|}}{C}H{=}CH_2$

43. The reaction is 
$CH_3—\underset{\underset{C_6H_5}{|}}{C}{=}CH_2 \xrightarrow[H^+]{H_2O} CH_3—\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}—CH_3$

2-phenyl-2-propanol

44. Due to the electron-releasing methyl group, the reaction proceeds as follows.

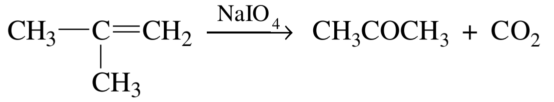

$CH_3 \rightarrow CH{=}CH_2 \xrightarrow{NO—Cl} CH_3\underset{\underset{Cl}{|}}{C}H—CH_2NO$

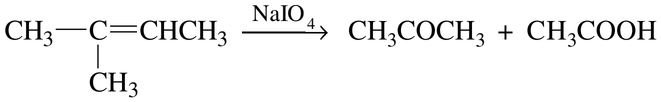
45. An electron-withdrawing groups attached to the C that has lesser H's would tend to destabilized a positive charge on this C and thus cause the addition to be anti-Markovnikov. In othe words, the polarization in $CF_3CH{=}CH_2$ would be $\overset{\delta^-}{CF_3CH}{=}\overset{\delta^+}{CH_2}$.

In $BrCH{=}CH_2$, the inductive effect of Br is superseded by extended π delocalization of an unshared electron pair from Br to C^+ thereby stabilizing the R^+ i.e. the polarization occurs as $:\ddot{Br}—CH{=}\underset{\delta-}{CH_2}$ and thus Markovnikov product is obtained.

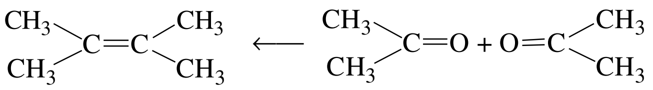
46. Here, the polarization occurs as $CH—\ddot{O}—CH{=}CHCH_3 \xrightarrow{HBr} CH_3OCH(Br)CH_2CH_3$

47. *Anti* addition yields *rac*-*trans*-2-bromocyclopentanol.

48. 
$CH_3—\underset{\underset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{NaIO_4} CH_3COCH_3 + CO_2$

49. 
$CH_3—\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 \xrightarrow{NaIO_4} CH_3COCH_3 + CH_3COOH$

50. $CH_3CH{=}CHCH_3 \xrightarrow{NaIO_4} 2CH_3COOH.$

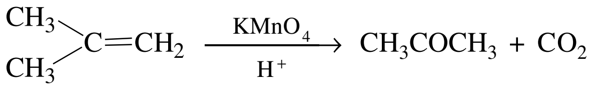
51. 

2,3-dimethylbut-2-ene

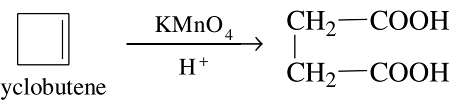
52. $CH_3CH_2CH{=}CH_2 \xrightarrow[H^+]{KMnO_4} CH_3CH_2COOH + CO_2.$

53. $CH_3CH{=}CHCH_3 \xrightarrow[H^+]{KMnO_4} 2CH_3COOH$

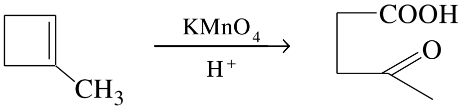
2-butene

54. 

2-methylpropene

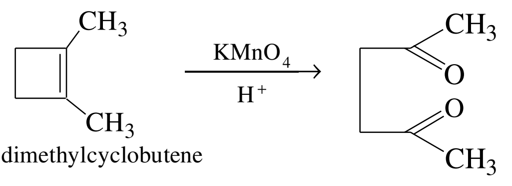
55. 

Cyclobutene

56. 

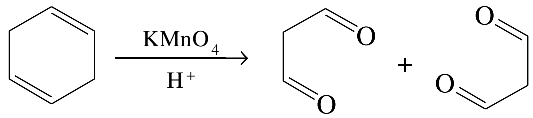
1-methylcyclobute

4-oxopentanoic acid

57. 

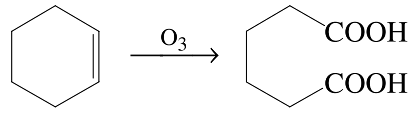
1,2-dimethylcyclobutene

Hexane-2,5-dione

58. 

1,4-cyclohexadiene

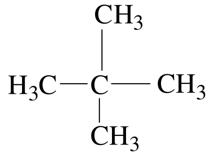
2 molecules of $CH_2(CHO)_2$

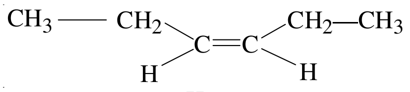
59. 
Cyclohexane Adipic acid

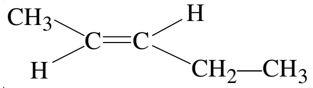
60. $CH_3CH{=}CH_2 + Cl_2 \xrightarrow[500\text{–}600\,°C]{} ClCH_2CH{=}CH_2$

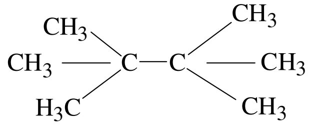
Multiple Correct Choice Type

1. *cis*-1, 2-dichloroethene ($ClHC{=}CHCl$) and 1,2-dichloro-2-pentene ($CH_3CH_2CH{=}C(Cl)\,CH_2Cl$) will have dipole moment.
2. *trans*-2-pentene and *cis*-3-hexene will have nonzero dipole moment.

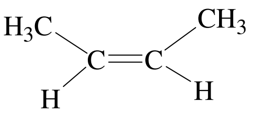

no dipole moment

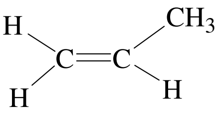

has dipole moment

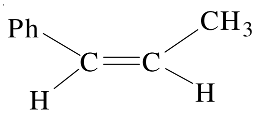

has dipole moment

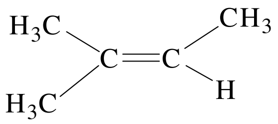

no dipole moment

4. The structures of the given compounds are

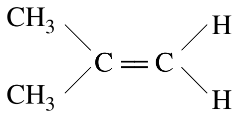

2-butene


propene


1-phenylpropene


2-methyl-2-butene

Only 2-butene and 1-phenylpropene an show geometrical isomerism (*cis*–and *trans*-isomers).

5. (a)In the presence of peroxide, HBr reacts with propene to give *n*-propyl bromide (anti-Markovnikov's rule). In the absence of peroxide, normal addition takes place. It gives isopropyl bromide as secondary carbocation is more stable than primary one.
   (b) With H_2SO_4, ethylene will give additional product.
   (c) Anti-Markovnikov's rule is applicable to the addition of HBr in the presence of peroxide.
   (d) The structure of isobutylene is 
6. (c) The group $CH_2{=}CH—$ is known as vinyl group where $CH_2{=}CH—CH_2—$ is known as allyl group.
   (d) Alkenes are insoluble in water, but quite soluble in non-polar solvents like benzene, ether and chloroform.
7. (a) In general, *cis* isomer has higher polarity and hence has higher boiling point. On the other hand, because of lower symmetry, *cis* isomer fits more poorly into a crystalline lattice, hence has lower melting point.
   (b) With zinc, dehalogenation occurs producing carbon-carbon double bond. The use of alcoholic KOH followed by KNH_2 produces carbon-carbon triple bond.
8. (a) The correct order is 3° > 2° > 1°.
   (c) E2 mechanism involves simultaneous elimination of atoms from the neighbouring carbon atoms, hence no rearrangement is possible.

(d) E1 mechanism involves the formation of carbocation which may rearrange so as to give most stable carbocation.

9. (a) E1 mechanism involves only one molecule whereas E2 mechanism involves two molecules in the rate-determining step.

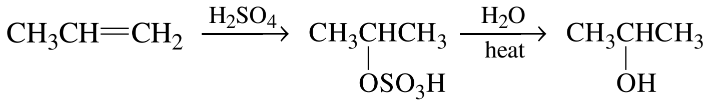
(b) Heterolytic bond dissociation energies follow the order C—F > C—Cl > C—Br > C—I.

(c) The rate of breaking the carbon-halogen bond follows the order. C—I > C—Br > C—Cl > C—F and thus reactivity towards E2 also follows the same order.

(d) This rule is known as Saytzeff rule.

10. (b) This is due to the fact that the intermediate carbocation has the stability in the order 3° > 2° > 1°.

(d) The addition of H_2SO_4 to double bond follows Markovnikov's rule



$$CH_3CH{=}CH_2 \xrightarrow{H_2SO_4} \underset{\displaystyle OSO_3H}{CH_3\underset{|}{C}HCH_3} \xrightarrow[\text{heat}]{H_2O} \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}$$

Hence, *n*-propyl alcohol cannot be produced by this method.

11. (b) Both Markovnikov and Saytzeff rules follows from the fact that there is an intermediate formation of the more stable carbocation.

(c) The more stable the carbocation, the more quickly it is formed.

12. (a) A halonium ion is formed as the intermediate instead of a carbocation.

(b) Besides dibromo compound, the bromochloro and bromoalcohol compounds are also formed.

(c) The structure of polyethylene is $(—CH_2—CH_2—)_n$.

(d) A diol is formed.

13. (a) Two chlorine atoms attached to ethylene destabilizes the intermediate carbocation more than the monochloro substituted ethene.

14. (b) The correct name is 3,4-diisopropyl-2,5-dimethyl-3-hexene.

15. (a) At lower temperature, 1,2-adduct predominates over the 1,4-adduct. Hence, the major component is 3-bromo-1-butene.

(b) At higher temperature, 1,4-adduct predominates over the 1,2-adduct. Hence, the major component is 1-bromo-2-butene.

(d) At the given conditions, substitution at alkyl group takes place. This gives allyl chloride.

16. (a) At the given conditions, addition across the double bond takes place giving 1,2-dichloropropane.

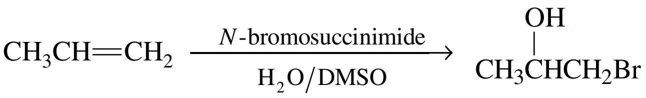
(b) *cis*-2-butene is less stable, therefore, it lies at higher level as compared to *trans* isomer in the potential energy versus reaction coordinate diagram. Thus, the difference $H_{\text{butane}}—H_{\text{cis}}$ is more than $H_{\text{butane}}—H_{\text{trans}}$.

(c) Alkenes are more reactive towards hydrogenation. Functional groups require more drastic conditions. For example,

$$CH_3CH{=}CH_2CH_2CN \xrightarrow[\text{Pd/C}]{H_2} CH_3CH_2CH_2CH_2CN$$

(d) This technique helps in converting alkene into a carbonyl compounds or alcoholic compounds.

17. (a)

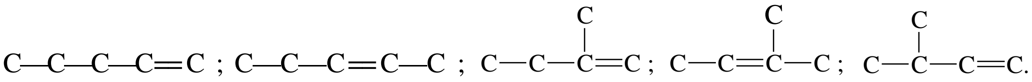


$$CH_3CH{=}CH_2 \xrightarrow[H_2O/DMSO]{N\text{-bromosuccinimide}} CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2Br$$

The reaction proceeds as follows.

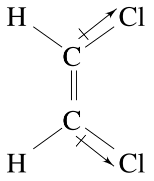
$$CH_3CH{=}CH_2 \xrightarrow{Br^+} [CH_3\overset{+}{C}HCH_2Br] \xrightarrow{H_2O} CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2Br + H^+$$

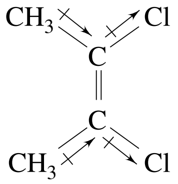
(b) There are five isomers whose carbon skeletons are



$$C—C—C—C{=}C\ ;\ C—C—C{=}C—C\ ;\ C—C—\overset{\displaystyle C}{\overset{|}{C}}{=}C\ ;\ C—C{=}\overset{\displaystyle C}{\overset{|}{C}}—C\ ;\ C—\overset{\displaystyle C}{\overset{|}{C}}—C{=}C.$$

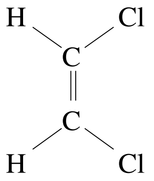
(c)

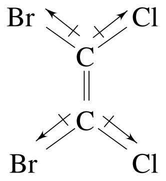




The dipole moment of *cis*-2,3-dichloro-2-butene is greater than that of *cis*–1, 2–dichloroethene because the two methyl groups in the $C_4C_6Cl_2$ compound releases electron in the same direrction of C—Cl dipoles.

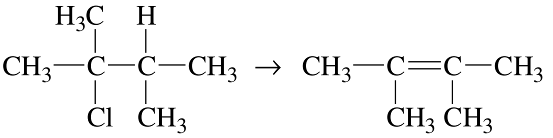
(d)





The bromine atoms pull electron in the opposite direction of C—Cl dipoles. Hence, the dipole moment of bromo derivative will be smaller than the other compound.

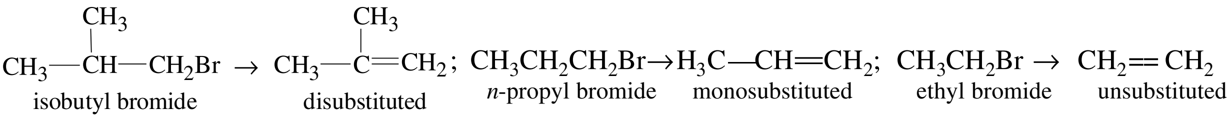
18.(a) According to Saytzeff's rule, the more substituted alkene is more stable and is thus a preferred product. Thus, the major product is



$$CH_3-\underset{Cl}{\overset{H_3C}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

2,3-dimethyl-2-butene

(b) Reactivity in E2 dehydrohalogenation depends mainly upon the stability of the alkenes being formed.



$$CH_3-\overset{CH_3}{CH}-CH_2Br \rightarrow CH_3-\overset{CH_3}{C}=CH_2;\ CH_3CH_2CH_2Br \rightarrow H_3C-CH=CH_2;\ CH_3CH_2Br \rightarrow CH_2=CH_2$$

isobutyl bromide disubstituted *n*-propyl bromide monosubstituted ethyl bromide unsubstituted

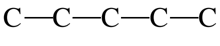
According to Saytzeff's rule, the stability of alkenes increases with increase in the number of substituents on the doubly bonded carbons. Hence, the order of reactivity towards dehydrohalogenation is isobutyl > *n*-propyl > ethyl

(c) A *trans* isomer is usually more stable than a *cis* isomer.

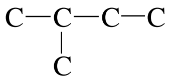
19.(a) The alkene has *E* configuration if the two high-priority substituents (in Cahn-Ingold-prelog sequence rules) are on the opposite side of the double bond. The configuration is *Z* if they are on the same side.

In the given compound, the priority sequence is Br > $CH(CH_3)_2$ > CH_2OH > $CH_2CH_2CH_3$. The two high priority substituents are on the same side of the double bond. Hence, its configuration is *Z*.

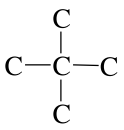
(b) The carbon skeletons of C_5 are



(I)



(II)

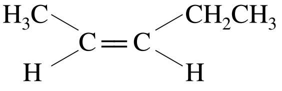


(III)

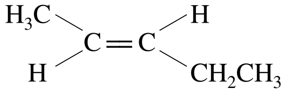
The skeleton (I) gives three isomers

$H_2C=CHCH_2CH_2CH_3$

1-pentene

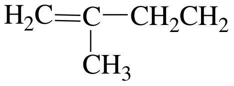


(Z)-2-pentene



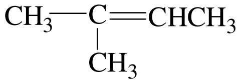
(*E*)-2-pentene

The skeleton (II) also given three isomers



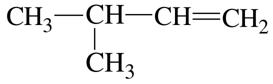
$H_2C{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2CH_2$

2-methyl-1-butene



$CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CHCH_3$

2-methyl-2-butene

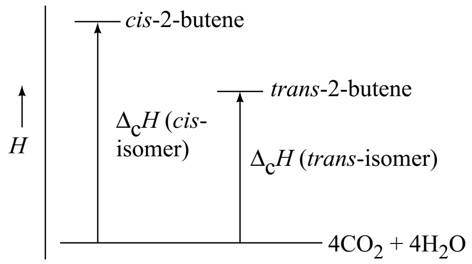


$CH_3{-}\underset{CH_3}{\underset{|}{CH}}{-}CH{=}CH_2$

3-methyl-1-butene

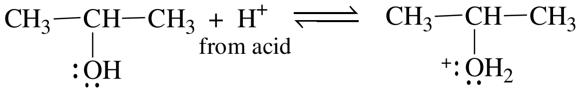
(c) 1,1-Dichloroethene has a smaller angle of separation of the two Cls than has the *cis* isomer resulting in a greater dipole moment.

(d) The enthalpy of the given compounds are as follows.



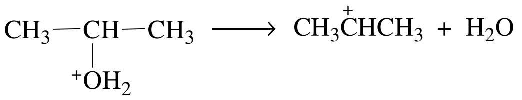
20. (b)The mechanism for the acid-catalysed dehydration of an alcohol (say, isopropyl alcohol) is as follows.

Step 1



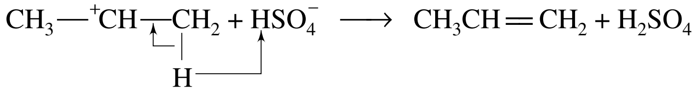
$$CH_3{-}\underset{:\underset{\cdot\cdot}{O}H}{\underset{|}{CH}}{-}CH_3 + \underset{\text{from acid}}{H^+} \rightleftharpoons CH_3{-}\underset{^+:\underset{\cdot\cdot}{O}H_2}{\underset{|}{CH}}{-}CH_3$$

Step 2



$$CH_3{-}\underset{^+OH_2}{\underset{|}{CH}}{-}CH_3 \longrightarrow CH_3\overset{+}{C}HCH_3 + H_2O$$

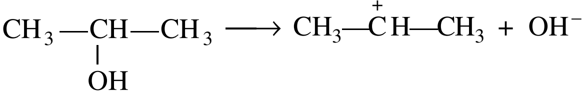
Step 3



$$CH_3{-}\overset{+}{C}H{-}\underset{H}{\underset{|}{CH_2}} + HSO_4^- \longrightarrow CH_3CH{=}CH_2 + H_2SO_4$$

Step 1 is fast equilibrium reaction. Step 2 is the slowest step as bond breaking involves high energy intermediate. It is also a rate determining step. Since it involves only one species, the elimination reaction follows E1 mechanism.

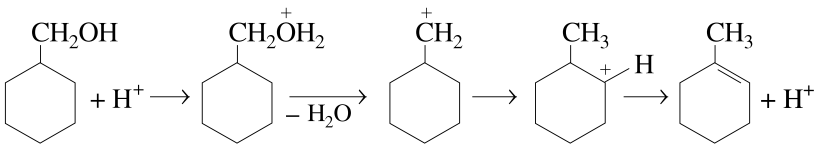
(c) The base catalysed reaction will involve the reaction



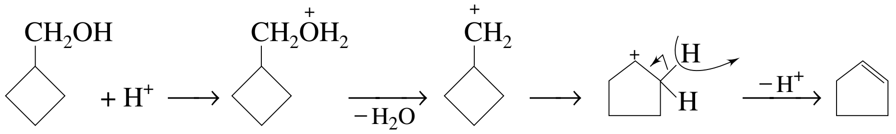
$$CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 \longrightarrow CH_3{-}\overset{+}{C}H{-}CH_3 + OH^-$$

which is not possible, as the leaving group OH^- is a strong base and is a poor leaving group. In the presence of acid, the poor leaving group OH^- is converted into a good leaving group H_2O (a very weak base).

(d) The product is 1-methylcyclohexene. An :H shift converts the less stable 1° to a more stable 3° carbocation.



21.(a) The product is cyclopentene. The side of the ring CH_2 shifts to give a 2° carbocation whose new five-membered ring is more stable than the old four-membered ring.



(b) The electron-withdrawing inductive effect of oxygen is superseded by extended π-delocalisation of an unshared electron pair from O to adjacent C^+, thereby stabilising the $CH_3O\overset{+}{C}HCH_2CH_3$. The attack of Br^- then gives $CH_3OCHBrCH_2CH_3$. In general, when the inductively electron-withdrawing group attached to the double-bonded C has an unshared pair of electrons. Markovnikov addition is observed.

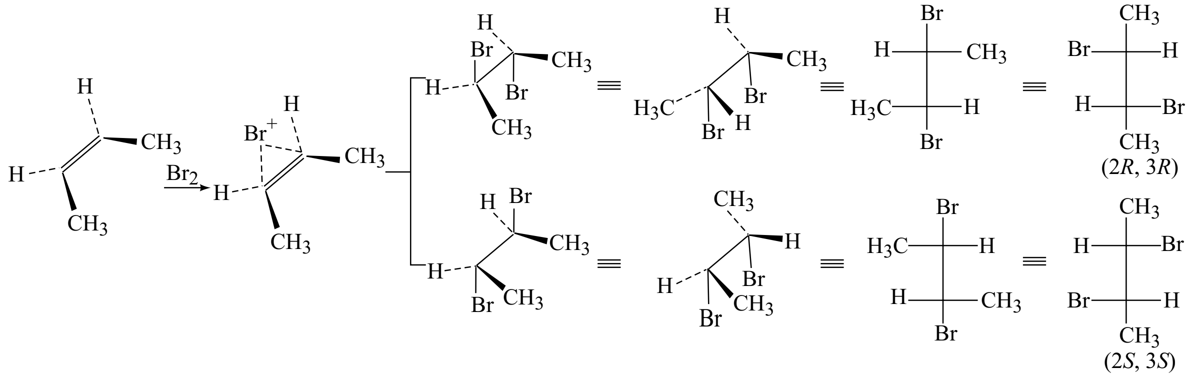
(c) The electron-withdrawing group attached to the C makes the carbocation $CF_3CH_2\overset{+}{C}H_2$ more stable than $CF_3\overset{+}{C}HCH_3$. Hence, the addition follows anti-Markovnikov rule.

22.(a) The addition of halogen to an alkene involves *anti*-addition. Thus, *trans*-1,2-dibromocyclohexane is obtained.

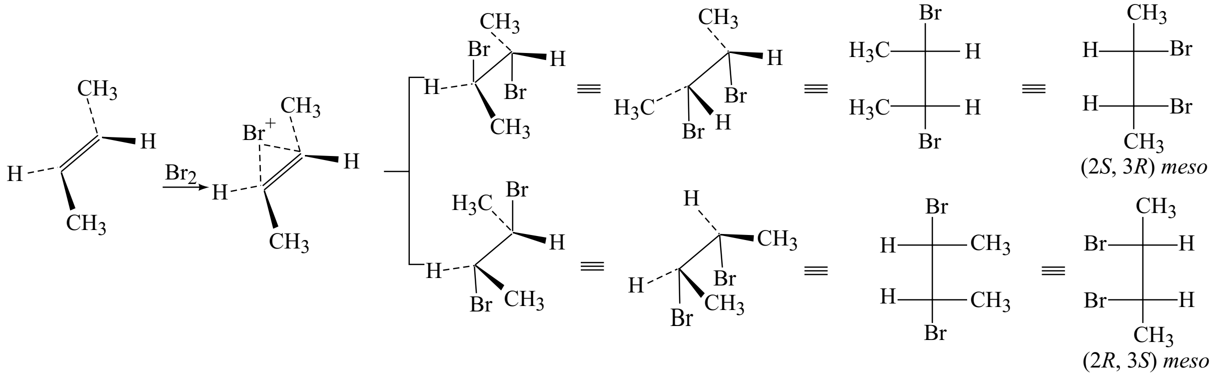
(b) Only a mixture of *trans*-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane is obtained. *Trans*-dichlorocyclohexane is not obtained as it will require the presence of Cl^+ which is not available.

(c) The addition of Br_2 across a double bond involves the formation of a bromonium ion intermediate, followed by the *anti* addition of Br^-. For *cis*-2-butene, the reaction proceeds so as to form *racemic*-2,3-dibromobutane.

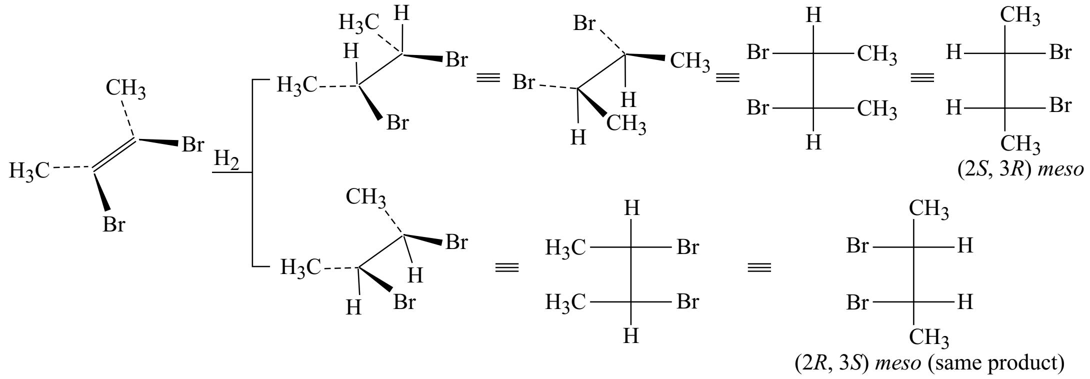
(c)



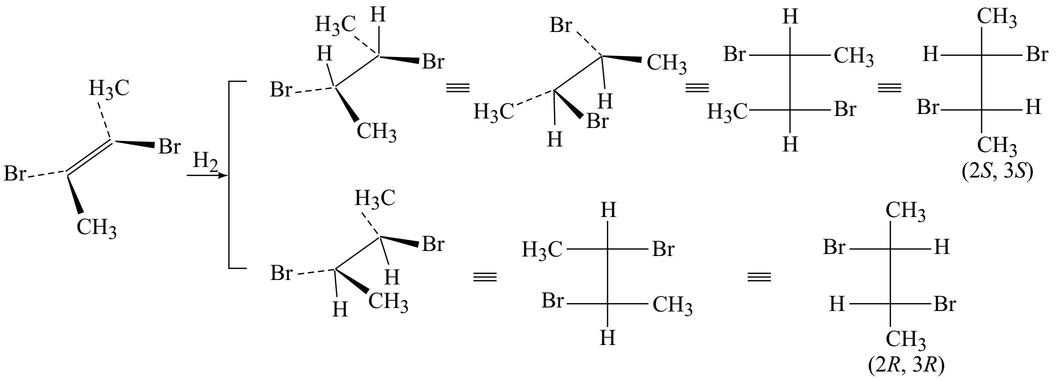
(d)



23. (a) Hydrogenation of an alkene is a heterogeneous process which occurs on the surface of a solid catalyst (PtO_2 or Pd/C). The addition occurs with *syn* stereochemistry (both hydrogens add from the same side). For *cis* isomer, the product is a *meso* compound.



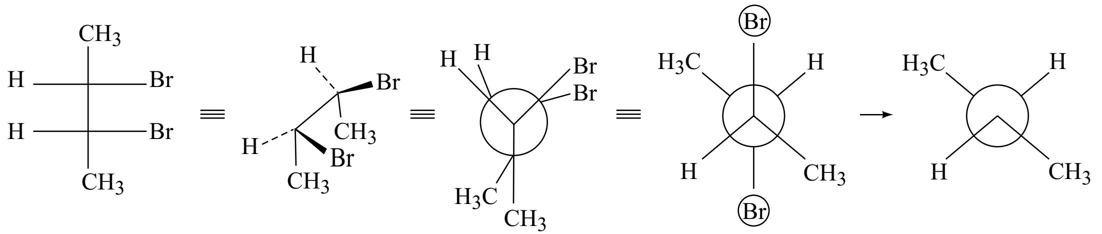
(b) The product is a racemic mixture.



(c) The addition of two hydroxyl groups involves *syn* addition (on the same side of a double bond). The result is same as that of hydrogenation. The *cis* isomer produce *meso* compound.

(d) The addition of two hydroxyl groups involves *syn* addition (on the same side of a double bond). The result is same as that of hydrogenation. The *trans* isomer produces *racemic* mixture.

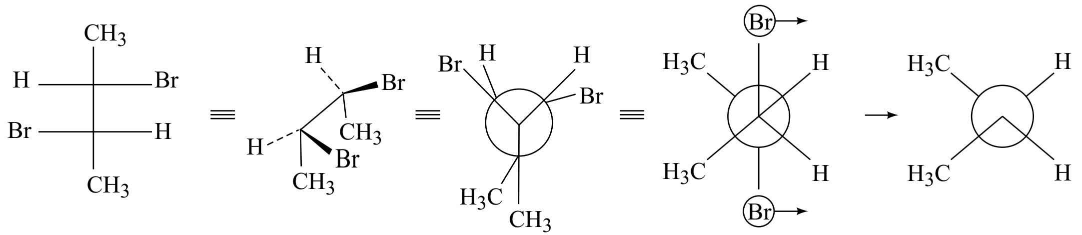
24.(a) The product is *trans*-2-butene.



meso-2,3-dibromo-
butane

trans-2-butene

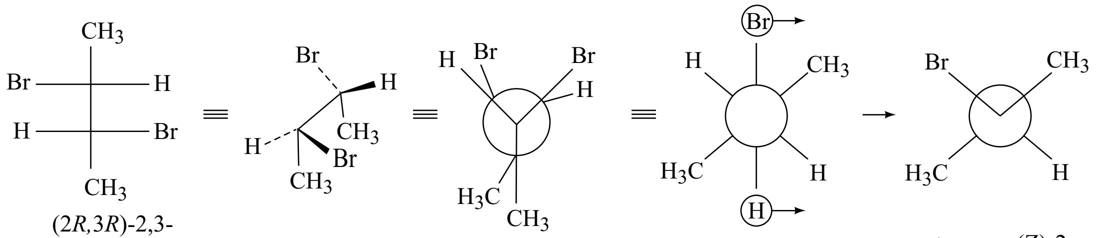
(b) The product is *cis*-2-butene.



(*S, S*)-2,3-
dibromobutane

cis-2-butene

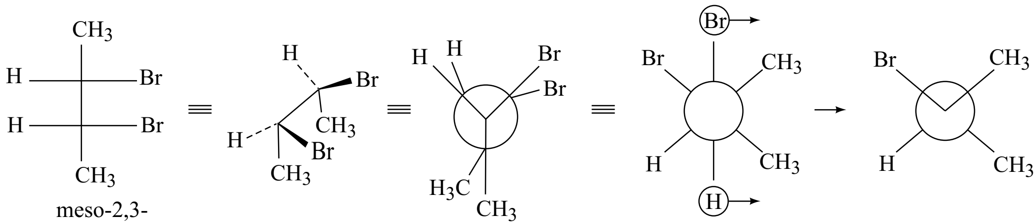
(c)



(2*R*,3*R*)-2,3-
dibromobutane

trans-or (Z)-2-
bromo-2-butene

(d)



meso-2,3-
dibromobutane

cis (*E*)-2-
bromo-2-butene

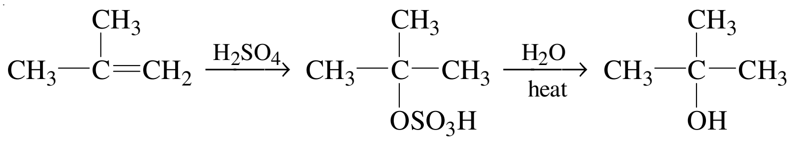
25. (b) The starting material is ethylene. (d) The product is $CH_2{=}CH_2$.

26. (c) The product is *cis* isomer. (d) The product is *trans* isomer

27. (d) The *cis*-form is less stable than the *trans*-form.

28. (a) Diphenylamine acts as an inhibitor.

(b) The product is tertiary butyl alcohol. The reaction is



$$CH_3-\overset{\overset{\Large CH_3}{|}}{C}{=}CH_2 \xrightarrow{H_2SO_4} CH_3-\underset{\underset{\Large OSO_3H}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{heat}]{H_2O} CH_3-\underset{\underset{\Large OH}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-CH_3$$

tert-butyl alcohol

(d) The addition is electrophilic.

29. (c) Chlorine destabilizes the carbocation which is formed as the intermediate in the addition reaction. So it is formed at the slower rate. (d) The carbocation is stabilized.

30. (a) The carbocation is destabilised (b) The carbanion is destablized

31. (b) The compound is cyclohexene (d) The products are HCHO and $CH_3CH(CH_3)CHO$

32. (c) $CH_3CH(CH_3)COOH$ and CH_3COOH (d) CH_3COCH_3 and CH_3COCH_3

33. (c) The compound is 1,5-cyclooctadiene (d) The allyl radical is $CH_2 = CH{-}\dot{C}H_2$

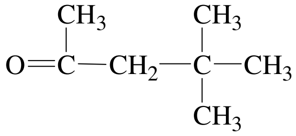
34. (d) The *cis*-alkenes are less stable than *trans*-isomer. In *cis* isomer, steric strain between the two bulky substituents on the same side is more than in the *trans* isomer, where they are in opposite side.

36. (a) The products are *trans*-2-butene and 1-butene

The most highly branched alkene is usually the most stable (lowest energy content); a *trans* isomer is usually more stable (lower energy content) than a *cis* isomer.

The lowest energy content means more heat would be required to fragment the compound and thus its enthalpy of combustion would be minimum.

(c) The products are CO_2,

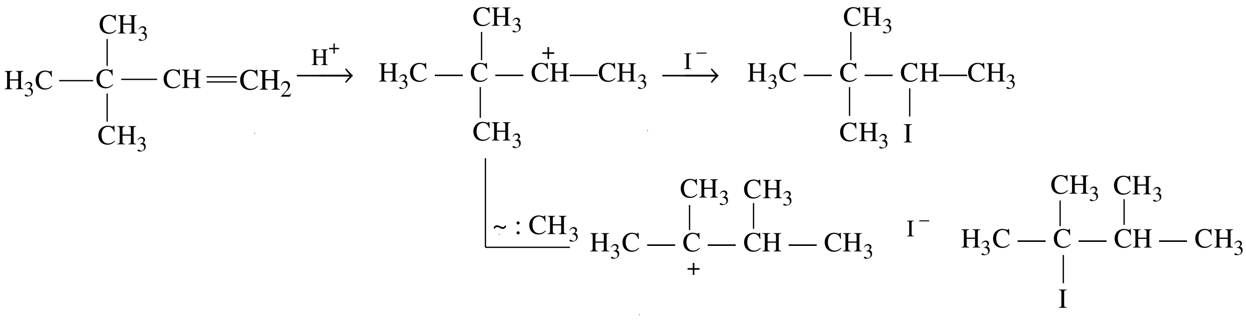


$$O{=}\overset{\overset{\Large CH_3}{|}}{C}-CH_2-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-CH_3$$

37. (c) The less positive the bond dissociation energy of C—H, more is the reactivity towards radical substitution of H. The bond dissociation energies in kJ mol^{-1} are as follows

H_3C—**H**	435 ;	$H_2C{=}CH$ —**H**(vinylic)	452
$H_2C{=}CHCH_2$ — **H** (allylic)	368 ;	$CH_3CH_2CH_2$—**H**(1°)	410
$(CH_3)_2CH$—**H**(2°)	395 ;	$(CH_3)_3C$—**H**(3°)	381

(d) Two products are as follows:

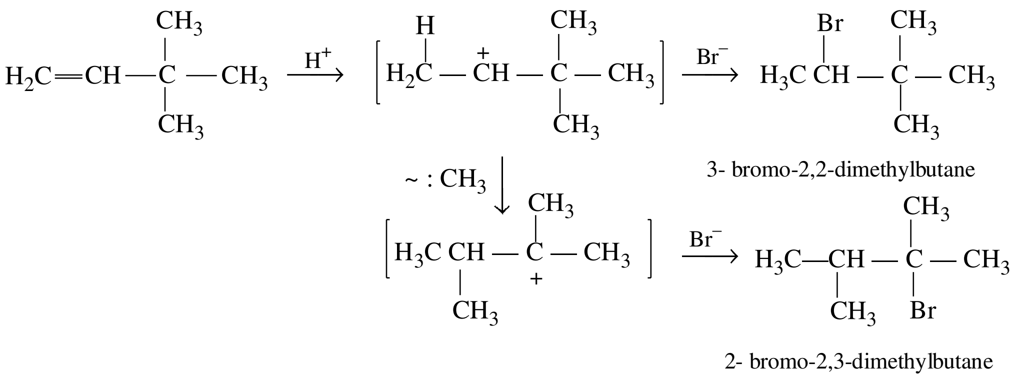


$$H_3C-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-CH{=}CH_2 \xrightarrow{H^+} H_3C-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-\overset{+}{C}H-CH_3 \xrightarrow{I^-} H_3C-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-\underset{\underset{\Large I}{|}}{CH}-CH_3$$

$$\xrightarrow{\sim :CH_3} H_3C-\underset{+}{\overset{\overset{\Large CH_3}{|}}{C}}-\overset{\overset{\Large CH_3}{|}}{CH}-CH_3 \quad I^- \quad H_3C-\underset{\underset{\Large I}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-\overset{\overset{\Large CH_3}{|}}{CH}-CH_3$$

38. The configuration **Z** implies the two high-priority substituents on the same side of the double bond and the configuration is E if they are on opposite sides.

39. The addition of HBr (without peroxide) proceeds via ionic mechanism similar to that of HI. The carbocation formed also undergoes rearrangement to form two products as shown in the following.

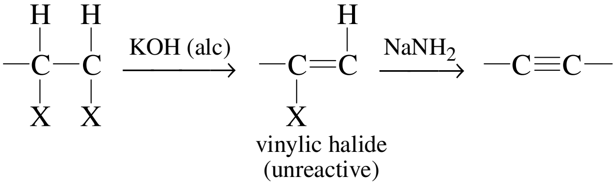


CHAPTER 23

ALKYNES

METHODS OF PREPARATION

1. **Dehydrohalogenation of vicinal dihalides** Dehydrohalogenation takes place in two stages



$$-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}} \xrightarrow{\text{KOH (alc)}} -\underset{X}{C}=\overset{H}{C} \xrightarrow{\text{NaNH}_2} -C\equiv C-$$

vinylic halide (unreactive)

First stage requires mild conditions whereas second stage requires more vigorous conditions as vinylic halide is unreactive.

2. **Reaction of metal acetylides with primary alkyl halides**

$$-C\equiv C-H \xrightarrow{\text{LiNH}_2} -C\equiv\bar{C}\text{:}\ Li^+ + RX \rightarrow -C\equiv C-R + LiX$$

(R must be 1°)

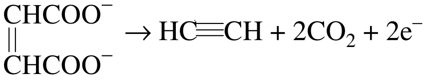
With secondary and tertiary halides, elimination is the predominant reaction which results in the formation of alkenes. This method can be used to generate larger alkyne from the smaller one.

3. **Hydrolysis of** CaC_2 **and** Mg_2C_3 Calcium carbide gives acetylene whereas Mg_2C_3 gives propyne.

$$CaC_2 + 2H_2O \rightarrow HC\equiv CH + Ca(OH)_2; \qquad Mg_2C_3 + 4H_2O \rightarrow CH_3C\equiv CH + 2Mg(OH)_2$$

4. **Kolbe's electrolytic method** The electrolysis of an aqueous solution of potassium salt of an unsaturated dicarboxylic acid forms alkyne.

Anodic reaction



$$\begin{array}{l} CHCOO^- \\ \| \\ CHCOO^- \end{array} \rightarrow HC\equiv CH + 2CO_2 + 2e^-$$

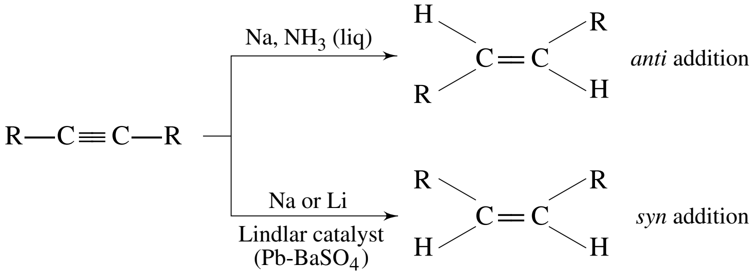
Cathodic reaction $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

5. **Dehalogenation of vic-tetrahalogen compounds**

$$CH_3-CBr_2-CBr_2-CH_3 + 2Zn \xrightarrow[\text{heat}]{C_2H_5OH} CH_3-C\equiv C-CH_3 + 2ZnBr_2$$

CHEMICAL PROPERTIES

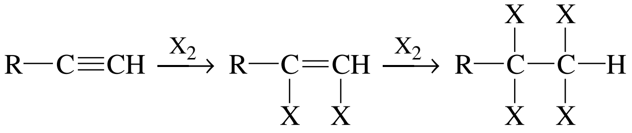
Addition of hydrogen If the triple bond is not present at the end of the chain of the molecule, its reduction produces either a *cis* alkene or a *trans* alkene depending upon the choice of reducing agent.



Further reduction produces an alkane. Catalytic hydrogenation occurs at the surface of catalyst resulting into *cis* addition.

In general, alkyne undergoes catalytic hydrogenation at faster rate than alkene. This is due to the fact that the alkyne forms less constrained transition state with the surface of a catalyst as compared to that formed by an alkene.

Addition of halogens Chlorine and bromine add on alkyne:

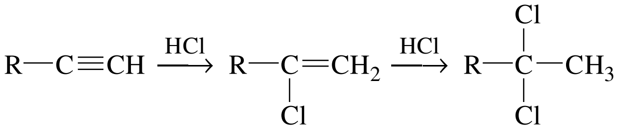


$$\mathrm{R{-}C{\equiv}CH \xrightarrow{X_2} R{-}C(X){=}CH(X) \xrightarrow{X_2} R{-}CX_2{-}CX_2{-}H}$$

Alkynes are less reactive than alkenes. The mechanism of the reaction involves the initial formation of a cyclic halonium ion which is formed with greater difficulty in case of alkynes resulting in the lower activity of alkynes.

In fact, the cyclic halonium ion formed from alkyne is more strained due to the presence of double bond (shorter bond length). Moreover, its carbon atoms have more s-character. These factors make the halonium ion less stable than that formed from alkene.

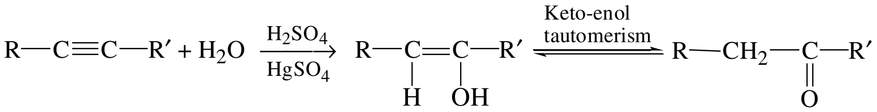
Addition of hydrogen halides (HCl, HBr, HI)



$$\mathrm{R{-}C{\equiv}CH \xrightarrow{HCl} R{-}C(Cl){=}CH_2 \xrightarrow{HCl} R{-}CCl_2{-}CH_3}$$

The addition takes place in accordance with Markovnikov's rule. Peroxides have the same effect on addition of HBr to acetylenes as they have on alkenes.

Addition of water In the presence of acid and $HgSO_4$, a molecule of water adds to the triple bond. Initially enol is formed which is rapidly converted into an equilibrium mixture containing keto form in excess.



$$\mathrm{R{-}C{\equiv}C{-}R' + H_2O \xrightarrow[HgSO_4]{H_2SO_4} R{-}C(H){=}C(OH){-}R' \xrightleftharpoons{\text{Keto-enol tautomerism}} R{-}CH_2{-}C({=}O){-}R'}$$

The final product is a mixture of both possible ketone (RCH_2COR' and $RCOCH_2R'$).

Formation of metal acetylides A triply bonded carbon which is sp hybridized has a high electronegativity and hydrogen atom attached to it shows appreciable acidity. For example, acetylene reacts with Na and Li liberating H_2 gas:

$$\mathrm{HC{\equiv}C{-}H + Na \rightarrow \underset{\text{sodium acetylide}}{HC{\equiv}\overset{-}{C}{:}Na^+} + \tfrac{1}{2}H_2}$$

Compared to H_2O, NH_3 and alkane, the order of acidity of acetylene is as follows.

$$\mathrm{H_2O > HC{\equiv}CH > NH_3 > RH}$$

The order of conjugate base will be $\mathrm{OH^- < HC{\equiv}C^- < NH_2^- < R^-}$

Acetylene like any other acid undergoes Bronsted acid-base reaction. For example

$$\mathrm{\underset{\text{stronger acid}}{HC{\equiv}CH} + \underset{\text{stronger base}}{Li^+\,NH_2^-} \rightleftharpoons \underset{\text{weaker acid}}{NH_3} + \underset{\text{weaker base}}{HC{\equiv}C^-\,Li^+}}$$

$$\underset{\substack{\text{stronger}\\ \text{acid}}}{H_2O} + \underset{\substack{\text{stronger}\\ \text{base}}}{HC{\equiv}C^-Li^+} \rightleftharpoons \underset{\substack{\text{weaker}\\ \text{acid}}}{HC{\equiv}CH} + \underset{\substack{\text{weaker}\\ \text{base}}}{Li^+\ OH^-}$$

Lithium acetylide has been used to convert lower alkynes into the bigger one using the reaction

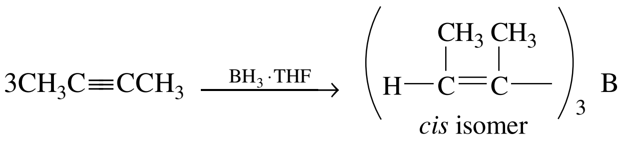
$$R{-}C{\equiv}C{-}Li + \underset{(1^\circ \text{ alkyl halide})}{R'X} \rightarrow R{-}C{\equiv}C{-}R' + LiX$$

Heavy metal ions, mainly, Ag^+ and Cu^+, react with acetylinic hydrogen to form insoluble acetylides. This reaction can be used to differentiate between terminal and nonterminal alkynes:

$$R{-}C{\equiv}C{-}H \xrightarrow[\substack{\text{(Tollens}\\ \text{reagent)}}]{\substack{\text{ammoniacal}\\ Ag^+}} \underset{\text{precipitate}}{R{-}C{\equiv}C{-}Ag}; \qquad H{-}C{\equiv}C{-}H \xrightarrow{2Ag^+} Ag{-}C{\equiv}C{-}Ag$$

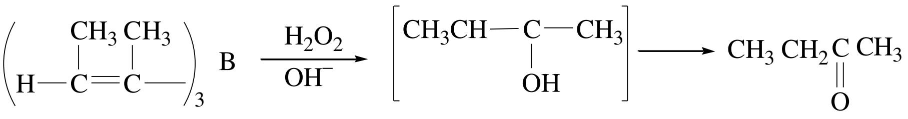
$$R{-}C{\equiv}C{-}H \xrightarrow[\substack{\text{ammoniacal}\\ \text{medium}}]{Cu^+} R{-}C{\equiv}C{-}Cu$$

Hydroboration-Oxidation The reaction of an alkyne with BH_3 complexed with tetrahydrofuran ($BF_3 \cdot THF$) is known as hydroboration of alkyne. For example,



$$3CH_3C{\equiv}CCH_3 \xrightarrow{BH_3\cdot THF} \underset{cis \text{ isomer}}{\left(H{-}\overset{\overset{\large CH_3}{|}}{C}{=}\overset{\overset{\large CH_3}{|}}{C}{-}\right)_3} B$$

The oxidation of the product by H_2O_2 in alkaline medium gives the keto compound.



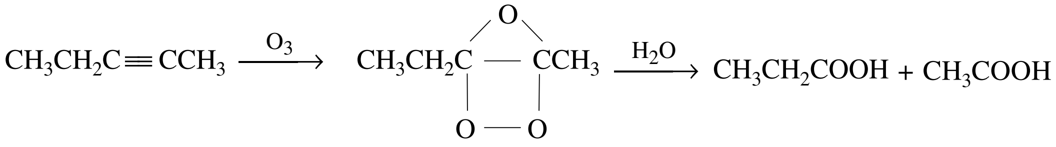
$$\left(H{-}\overset{\overset{\large CH_3}{|}}{C}{=}\overset{\overset{\large CH_3}{|}}{C}{-}\right)_3 B \xrightarrow[OH^-]{H_2O_2} \left[CH_3CH{-}\underset{\underset{\large OH}{|}}{C}{-}CH_3\right] \longrightarrow CH_3\,CH_2\underset{\underset{\large O}{\|}}{C}\,CH_3$$

An aldehyde is formed with terminal alkynes.

Reaction with Grignard reagent or alkyllithium The acetylinic hydrogen on reacting with R′MgBr or R′Li produces the alkane R′H:

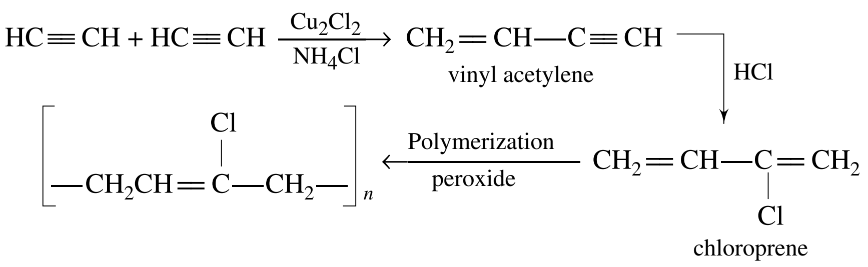
$$RC{\equiv}CH + R'MgBr \rightarrow R'H + RC{\equiv}CMgBr; \qquad RC{\equiv}CH + R'Li \rightarrow R'H + RC{\equiv}CLi$$

Ozonolysis Alkynes produces carboxylic acids.



$$CH_3CH_2C{\equiv}CCH_3 \xrightarrow{O_3} CH_3CH_2C\overset{O}{—}CCH_3 \ (\text{with } O{-}O \text{ bridge}) \xrightarrow{H_2O} CH_3CH_2COOH + CH_3COOH$$

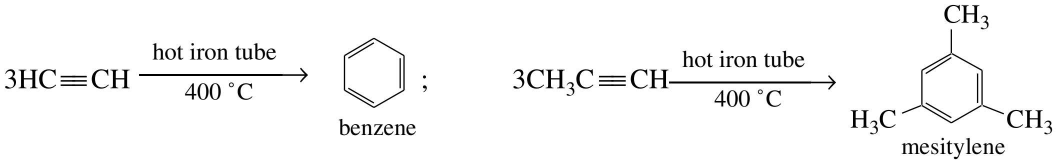
Polymerization Acetylene dimerizes in the presence of cuprous chloride and ammonium chloride to give vinyl acetylene which on reacting with HCl gives chloroprene. The latter polymerizes to give neoprene—a synthetic rubber. The reactions are:



$$HC{\equiv}CH + HC{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{vinyl acetylene}}{CH_2{=}CH{-}C{\equiv}CH} \xrightarrow{HCl} \underset{\text{chloroprene}}{CH_2{=}CH{-}\underset{\underset{\large Cl}{|}}{C}{=}CH_2}$$

$$\left[{-}CH_2CH{=}\overset{\overset{\large Cl}{|}}{C}{-}CH_2{-}\right]_n \xleftarrow[\text{peroxide}]{\text{Polymerization}} CH_2{=}CH{-}\underset{\underset{\large Cl}{|}}{C}{=}CH_2$$

Cylic polymerization The cyclic polymerization takes place when alkyne is passed through red hot iron tube at 400 °C.



Isomerization The following reactions can be used to convert 1-alkyne to 2-alkyne and vice versa.

$$\begin{tikzcd} CH_3CH_2C\equiv CH \arrow[r, "\text{KOH (alc)}"] & \underset{\text{allene}}{CH_3CH{=}C{=}CH_2} \arrow[d] \\ CH_3CH_2C\equiv CNa \arrow[u, "H_2O"'] & CH_3C\equiv CCH_3 \arrow[l, "\text{NaNH}_2\text{ in}"', "\text{inert solvent}"] \end{tikzcd}$$

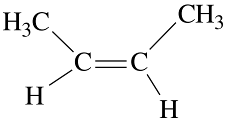
Straight Objective Type

Preparation and General Characteristics

1. Propyne is produced during the hydrolysis of
(a) CaC_2 (b) Al_4C_3 (c) Mg_2C_3 (d) SiC

2. Acetylene is produced during the electrolysis of
(a) potassium acetate (b) potassium succinate (c) potassium fumarate (d) potassium carbonate

3. Which of the following hydrocarbons has the lowest dipole moment?

(a)


(b) $CH_3C\equiv CCH_3$ (c) $CH_3CH_2C\equiv CH$ (d) $CH_2{=}CH{-}C\equiv CH$

(2002)

4. Which of the following compounds does not have the general formula as alkynes?
(a) dienes (b) cycloalkenes (c) bycyclics (d) cycloalkanes

5. Which of the following compounds has positive value of $\Delta_f H°$?
(a) Methane (b) Acetylene (c) Methanal (d) Methanol

6. The correct IUPAC name of $HC\equiv CCH_2CH{=}CH_2$ is
(a) 1-penten-4-yne (b) 1-pentyn-4-ene (c) proplenylacetylene (d) acetylproplene

Acidic Nature of Acetylinic Hydrogen

7. Acidic hydrogen is present in
(a) ethyne (b) ethene (c) benzene (d) ethane (1985)

8. Ethene can be separated from ethyne by passing the mixture through
(a) concentrated H_2SO_4 (b) ammoniacal Cu_2Cl_2 (c) pyrogallol (d) charcoal powder

9. Which of the following compounds react with an aqueous solution of $Ag(NH_3)_2OH$?
(a) Ethane (b) Ethene (c) 1-Butyne (d) 2-Butyne

10. The compounds 1-butyne and 2-butyne can be distinguished by using
(a) bromine water (b) $KMnO_4$ solution (c) Tollens reagent (d) chlorine gas

11. Propyne and propene can be distinguished by
(a) Conc. H_2SO_4 (b) Br_2 in CCl_4 (c) dil $KMnO_4$ (d) $AgNO_3$ in ammonia

12. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne:
(a) bromine, CCl_4 (b) H_2, Lindlar catalyst
(c) dilute H_2SO_4, $HgSO_4$ (d) ammoniacal Cu_2Cl_2 solution (2002)

13. The reaction of $CH_3CHBrCH_2Br$ with one equivalent of alcoholic KOH gives
(a) $CH_3CH{=}CHBr$ as the major product and $CH_3CBr{=}CH_2$ as the minor product
(b) $CH_3CH{=}CHBr$ as the minor product and $CH_3CBr{=}CH_2$ as the major product
(c) $CH_2{=}CHCH_2Br$ as the major product
(d) 50% each of $CH_3CH{=}CHBr$ and $CH_3CBr{=}CH_2$

Comparison of Acid Strength

14. What is the decreasing order of strength of the bases OH^-, NH_2^-, $HC{\equiv}\overset{-}{C}$ and $CH_3CH_2^-$?
(a) $CH_3{-}CH_2^- > NH_2^- > H{-}C{\equiv}C^- > OH^-$ (b) $H{-}C{\equiv}C^- > CH_3{-}CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC{\equiv}C^- > CH_3{-}CH_2^-$ (d) $NH_2^- > H{-}C{\equiv}C^- > OH^- > CH_3{-}CH_2^-$ (1993)

15. Which of the following orders regarding acid strength is correct?
(a) $CH_3COOH > CH_3CH_2OH > HC{\equiv}CH$ (b) $CH_3COOH > HC{\equiv}CH > CH_3CH_2OH$
(c) $HC{\equiv}CH > CH_3COOH > CH_3CH_2OH$ (d) $HC{\equiv}CH > CH_3CH_2OH > CH_3COOH$

16. Which of the following orders regarding base strength is correct?
(a) $CH_3COO^- > CH_3CH_2O^- > HC{\equiv}C^-$ (b) $CH_3COO^- < CH_3CH_2O^- < HC{\equiv}C^-$
(c) $HC{\equiv}C^- > CH_3COO^- > CH_3CH_2O^-$ (d) $HC{\equiv}C^- > CH_3CH_2O^- > CH_3COO^-$

17. For the following reactions

$$HC{\equiv}CH \xrightarrow[\text{catalyst}]{H_2} H_2C{=}CH_2 \quad \Delta H_1^\circ; \qquad H_2C{=}CH_2 \xrightarrow[\text{catalyst}]{H_2} CH_3{-}CH_3 \quad \Delta H_2^\circ$$

which of the following facts is expected to be correct?
(a) $|\Delta H_1^\circ| = |\Delta H_2^\circ|$ (b) $|\Delta H_1^\circ| > |\Delta H_2^\circ|$ (c) $|\Delta H_1^\circ| < |\Delta H_2^\circ|$ (d) $|3\Delta H_1^\circ| = |2\Delta H_2^\circ|$

18. From the following reactions

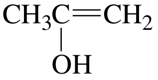
$$HC{\equiv}CH + LiNH_2 \rightleftharpoons NH_3 + HC{\equiv}CLi$$
$$NH_3 + R^- \rightleftharpoons NH_2^- + RH$$

predict which of the following orders regarding base strength is correct?
(a) $R^- < NH_2^- < HC{\equiv}C^-$ (b) $R^- > NH_2^- > HC{\equiv}C^-$
(c) $R^- > NH_2^- < HC{\equiv}C^-$ (d) $R^- < NH_2^- > HC{\equiv}C^-$

Chemical Properties

19. When propyne is treated with aqueous H_2SO_4 in the presence of $HgSO_4$, the major product is
(a) propanol (b) propyl hydrogen sulphate
(c) acetone (d) propanol (1983)

20. Water can be added across a triple bond in the presence of
(a) acidic medium (b) alkaline medium (c) neutral medium (d) acid and $HgSO_4$

21. The addition of water to propyne in the presence of $HgSO_4$–H_2SO_4 produces
(a) $CH_3CH{=}CHOH$ (b) 
$CH_3C(OH){=}CH_2$
(c) $CH_3CH_2CH_2OH$ (d) CH_3CHO

22. Which of the following statements is correct?
(a) Alkynes are reduced less readily than alkenes
(b) Alkynes are reduced more readily than alkenes
(c) Both alkynes and alkenes are reduced with equal speeds
(d) Alkynes cannot be reduced to the alkene stage

23. The reduction of an alkyne to alkene using Lindlar catalyst results into
(a) *cis* addition of hydrogen atoms
(b) *trans* addition of hydrogen atoms
(c) a mixture obtained by *cis* and *trans* additions of hydrogen which are in equilibrium with each other.
(d) a mixture obtained by *cis* and *trans* additions of hydrogen atoms which are not in equilibrium with each other.

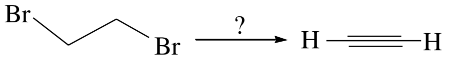
24. The reduction of an alkyne to alkene using lithium metal in liquid ammonia as solvent results into
(a) *cis* addition of hydrogen atoms

(b) *trans* addition of hydrogen atoms
(c) both *cis* and *trans* additions of hydrogen atoms. The relative amounts of the two depends on temperature.
(d) both *cis* and *trans* additions of hydrogen atoms. The relative amounts depend on the nature of alkyne.

25. Which of the following statements is correct?
(a) Alkynes are more reactive than alkenes towards halogen additions
(b) Alkynes are less reactive than alkenes towards halogen additions
(c) Both alkynes and alkenes are equally reactive towards halogen additions
(d) Primiary vinylic cation ($RCH{=}\overset{+}{C}H$) is more reactive than secondary vinylic cation ($R\overset{+}{C}{=}CH_2$)

26. The product(s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be
(a) $CH_3CH_2COCH_3$ (b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHO + HCHO$ (d) $CH_3CH_2COOH + HCOOH$ (1999)

27. Lindlar's catalyst is
(a) Na in liquid NH_3 (b) Pt in ethanol (c) Ni in ether (d) Pd with $BaSO_4$

28. 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 (2007)

29. The treatment of $R'MgBr$ with $RC{\equiv}CH$ produces an alkane
(a) RH (b) R′H (c) R—R (d) R′—R

30. In the reaction

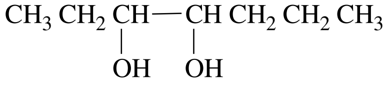
$$Ph{-}C{\equiv}C{-}CH_3 \xrightarrow{Hg^{2+}/H^+} A$$

the product A is
(a) $PhCOCH_2CH_3$ (b) $PhCH_2COCH_3$ (c) $PhC(OH){=}CH{-}CH_3$ (d) $PhC{=}(OH)CH_3$ (2003)

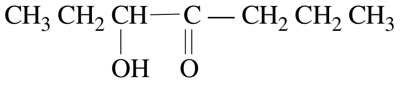
31. Which of the following reagents is used for the conversion of 2-hexyne into *cis*-2-hexene?
(a) $H_2/Pd\text{-}BaSO_4$ (b) H_2, EtOH (c) Zn/HCl (d) $Li\text{-}NH_3/C_2H_5OH$ (2004)

32. The reaction of one equivalent of HBr with 1-pentene-yne gives
(a) $BrCH_2CH_2CH_2C{\equiv}CH$ (b) $CH_3CHBrCH_2C{\equiv}CH$
(c) $CH_2{=}CHCH_2C(Br){=}CH_2$ (d) $CH_2{=}CHCH_2CH{=}C(Br)H$

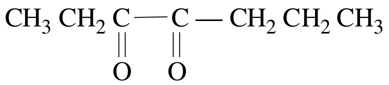
33. The treatment of $CH_3CH_2C{\equiv}CCH_2CH_2CH_3$ with $KMnO_4$ under neutral conditions at room temperature gives

(a) 

$CH_3CH_2\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}CH_2CH_2CH_3$

(b) 

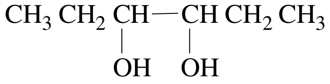
$CH_3CH_2\underset{OH}{\underset{|}{CH}}{-}\underset{O}{\underset{\|}{C}}{-}CH_2CH_2CH_3$

(c) 

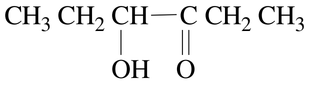
$CH_3CH_2\underset{O}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}CH_2CH_2CH_3$

(d) $CH_3CH_2COOH + CH_3CH_2CH_2COOH$

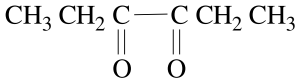
34. The treatment of $CH_3CH_2C{\equiv}CCH_2CH_3$ with $KMnO_4$ in alkaline or acidic conditions at higher temperatures gives

(a) 

$CH_3CH_2\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}CH_2CH_3$

(b) 

$CH_3CH_2\underset{OH}{\underset{|}{CH}}{-}\underset{O}{\underset{\|}{C}}CH_2CH_3$

(c) 

$CH_3CH_2\underset{O}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}CH_2CH_3$

(d) CH_3CH_2COOH

35. The ozonolysis of a triple bond produces
(a) a mixture of aldehyde/ketone and carboxylic acid
(b) a mixture of aldehydes/ketones
(c) a mixture of carboxylic acids
(d) CO_2 and H_2O

36. The ozonolysis of $HC{\equiv}C\ CH_2CH_2CH_3$ gives
(a) $HCOOH + CH_3CH_2CH_2COOH$ (b) $HCHO + CH_3CH_2CH_2CHO$
(c) $CO_2 + CH_3CH_2CH_2COOH$ (d) $CH_3COOH + CH_3CH_2COOH$.

37. Ethyne when passed through hot iron tube at 400°C produces
(a) benzene (b) toluene (c) xylene (d) mesitylene

38. The treatment of one mole of 1-butyne with two moles of a very strong base such as butyllithium produces

(a) $\overset{-}{\ddot{C}}H_2CH_2C\equiv\overset{-}{C}:$ (b) $CH_3\overset{-}{\ddot{C}}HC\equiv\overset{-}{C}:$ (c) $\overset{-}{\dot{C}}H_2\overset{-}{\dot{C}}HC\equiv CH$ (d) $CH_3\,\underset{\cdot\cdot}{\overset{2-}{\ddot{C}}}\,C\equiv CH$

Multiple Correct Choice Type

1. Methylacetylene contains

(a) six sigma bonds and two pi bonds. (b) three sigma and two pi bonds.
(c) one methyl group and one triple bond. (d) one sigma and two pi bonds.

2. Which of the following statements is/are **not** correct?

(a) Acetylene is more reactive than ethylene to an electrophilic attack.
(b) Acetylene is less reactive than ethylene to an electrophilic attack.
(c) Acetylene and ethylene show identical reactivities towards an electrophilic attack.
(d) The reactivities of acetylene and ethylene towards electrophilic attack depend on the electrophilic reagent.

3. Which of the following statements are **not** correct?

(a) Ethyne and its derivatives give white precipitate with ammoniacal silver nitrate solution.
(b) The carbon-carbon triple bond in acetylene has a bond length of 121 pm.
(c) Alkynes are more dense than water.
(d) The hydrohalogenation of vinylic halide requires mild conditions.

4. Which of the following statements are **not** correct?

(a) The electrophilic addition of hydrogen halides to alkyne proceeds via the formation of an intermediate carbocation.
(b) The addition of protic acids to alkynes takes place at very much the same rate as to alkenes.
(c) The addition of halogens to alkynes takes place at very much the same rate as to alkenes.
(d) The equilibrium $-\overset{|}{C}=\overset{|}{C}-OH \rightleftharpoons -\underset{H}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}=O$ lies much in favour of enol form.

5. Which of the following statements are correct?

(a) Tautomers differ in the arrangement of atoms and are also in rapid equilibrium with each other.
(b) Keto-enol tautomerism is an equilibrium between two acids favouring the formation of the stronger acid.
(c) A pair of electron in an sp hybrid orbital of carbon is more near to the nucleus as compared to that in an sp^3 hybrid orbital.
(d) 2-Butyne reacts with ammoniacal silver nitrate solution.

6. Which of the following statements are correct?

(a) The addition of hydrogen acids to acetylene follows Markovnikov's rule.
(b) Anti-Markovnikov's rule is not applicable for the addition of HBr to an alkyne in the presence of peroxide.
(c) The ozonolysis of acetylene produces methanol.
(d) The treatment of iodoform with silver powder produces acetylene.

7. Which of the following statements are correct?

(a) Vinyl alcohol on isomerization produces ethanal.
(b) Acetylene is produced by the action of water on aluminium carbide.
(c) Acetylene on reacting with HOCl produces 1,2-dichlor-1,2-ethandiol.
(d) 1-Pentyne can be distinguished from 2-pentyne with the help of ammoniacal $AgNO_3$ solution.

8. Which of the following statements are **not** correct?

(a) Alkynes are isomeric with alkadienes.
(b) The molecule $CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-C\equiv CH$ is more stable than $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=CH-C\equiv CH$..
(c) it is easy to add bromine in 2,3-dibromo-2-butene as compared to 2-butene.
(d) The addition of bromine to 2-butyne can be carried out upto first stage by dripping bromine solution in 2-butyne.

9. Which of the following statements are **not** correct?

(a) The addition of H_2 to 2-butyne using Na in liquid NH_3 gives *cis*-1,2-dimethylethene.

(b) The addition of H_2 to 2-butyne using H_2 and Lindlar catalyst gives *cis*-1,2-dimethylethene.

(c) The *cis*-1,2-dimethylethene is more stable than its *trans* isomer.

(d) *cis-trans* mixture of 2-pentene cannot be converted to either *cis* or *trans* form.

10. Which of the following statements are **not** correct?

(a) The addition of HCl to 3,3-dimethyl-1-butyne exclusively gives 2,2-dichloro-3,3-dimethylbutane.

(b) The number of isomers (including structural and stereoisomers) of alkynes C_6H_{10} is six.

(c) The treatment of 1,1-dibromopentane with KOH(s) at 200 °C produces 1-pentyne.

(d) The treatment of 1,1-dibromopentane with $NaNH_2$ followed by acid gives 2-pentyne.

11. Which of the following statements are correct?

(a) The treatment of 2-butyne with one mole of H_2/Pt produces (*E*)-2-butene.

(b) The treatment of 2-butyne with Na in EtOH produces (*E*)-2-butene.

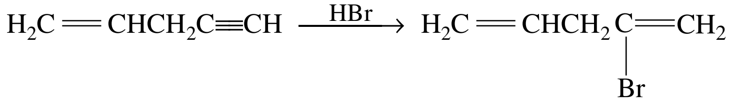
(c) The reduction 2-butyne $\longrightarrow$ 2-butene $\longrightarrow$ butane can be carried out in a stepwise manner.

(d) Acetylene, like ethylene, is soluble in concentrated H_2SO_4.

12. Which of the following statements are correct?

(a) 2-Butyne is not soluble in concentrated H_2SO_4.

(b) The reaction of one mole of HBr with 1-pentene-4-yne is



$$H_2C{=}CHCH_2C{\equiv}CH \xrightarrow{HBr} H_2C{=}CHCH_2\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2$$

(c) Alkynes are less reactive than alkenes toward addition of Br_2.

(d) Alkynes are more reactive than alkenes toward catalytic hydrogenation.

13. Which of the following statements are correct?

(a) The treatment of 3-heptyne with $KMnO_4$ under neutral conditions at room temperature gives CH_3CH_2COOH and $CH_3CH_2CH_2COOH$.

(b) The treatment of 3-heptyne with $KMnO_4$ under alkaline or acidic conditions at higher temperatures gives $CH_3CH_2COCOCH_2CH_2CH_3$.

(c) The addition of HBr to 1,3-pentadiene proceeds at a faster rate than that to 1,4-pentadiene.

(d) The addition of HBr to butadiene at –80 °C to give 1,2-adduct is kinetically controlled while that at 40 °C to give 1,4-adduct is thermodynamically controlled.

14. Which of the following statements are **not** correct?

(a) The treatment of the compound obtained by the hydration of ethyne with dilute alkali gives $CH_3CH(OH)CH_2CH_3$.

(b) Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess of methyl iodide. The final product is $CH_3C{\equiv}CH$.

(c) Addition of water to acetylenic compounds is catalyzed by H_2SO_4 and $HgSO_4$.

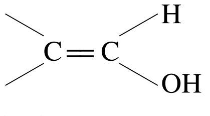
(d) The hydrogen in acetylene has basic character.

15. Which of the following statements are **not** correct?

(a) The partial reduction of an alkyne R—C≡C—R with sodium or lithium in liquid ammonia produces *cis* alkene.

(b) The partial reduction of an alkyne R—C≡C—R with H_2 and Lindlar catalyst produces *trans*-alkene.

(c) A structure



is known as enol structure.

(d) If NH_2^- holds the proton more tightly than $HC{\equiv}C^-$, then NH_3 must be a weaker acid than $HC{\equiv}CH$.

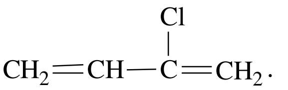
16. Which of the following statements are **not** correct?

(a) The addition of acteylene to lithium amide dissolved in ether produces NH_3 and $HC{\equiv}\bar{C}Li^+$.

(b) If water can generate $HC{\equiv}CH$ from $HC{\equiv}CLi$ then water must be a stronger acid than acetylene.

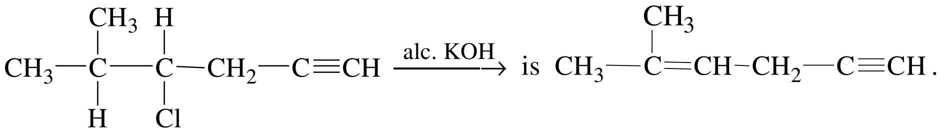
(c) Acetylide ion (which has a pair of electrons in sp orbital of carbon) is more stronger base than ethide ion, $C_2H_5^-$ (which has a pair of electrons in sp^3 orbital of carbon).

(d) Lindlar catalyst is ammoniacal $AgNO_3$.

17. Which of the following statements are correct?
- (a) The raw material used for the preparation of Buna N synthetic rubber is vinyl cyanide.
- (b) The cyclic polymerization of acetylene can be obtained by passing it through hot iron tube at 400°C. The product obtained is benzene.
- (c) Baeyer's reagent is alkaline potassium permanganate
- (d) Chloroprene is  $CH_2{=}CH{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH_2$.

18. Which of the following statements are **not** correct?
- (a) The polymerization of chloroprene gives synthetic rubber known as neoprene.
- (b) The ozonlysis of propyne produces acetic acid.
- (c) The IUPAC name of $HC{\equiv}C{-}CH_2{=}CH_2$ is 4-pentyne-1-ene.
- (d) The number of isomer of alkyne C_6H_{10} is six.

19. Which of the following statements are **not** correct
- (a) The product obtained in the reaction



$$CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}CH_2{-}C{\equiv}CH \xrightarrow{\text{alc. KOH}} \text{ is } CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2{-}C{\equiv}CH.$$

- (b) Dimerization of acetylene in the presence of $Cu(NH_3)_2^+\ Cl^-$ and H_2O produces vinylacetylene, $CH_2{=}CH{-}C{\equiv}CH$.
- (c) The ozonolysis of 1,3-pentadiene gives products HCHO, CH_3CHO and OHC—CHO
- (d) The ozonolysis of 1,4-pentadiene gives products HCHO, CH_3COCH_3 and OHC—CHO.

20. Which of the following statements regarding hydrogenation of alkyne are correct?
- (a) The addition is *syn* addition
- (b) The addition is *anti* addition
- (c) $\Delta H°$ for the addition of 1 mol of H_2 to $CH_3C{\equiv}CCH_3$ is more negative than to $CH_3CH{=}CHCH_3$.
- (d) $\Delta H°$ for the addition of 1 mol of H_2 to $CH_3C{\equiv}CCH_3$ is less negative than to $CH_3CH{=}CHCH_3$.

21. Which of the following alkynes give a single carbonyl compound on hydroboration-oxidation?
(a) 1-Pentyne (b) 3-Hexyne (c) 2-Pentyne (d) 4-Methyl-2-pentyne

Linked Comprehension Type

1. Based on the reaction

$$HC{\equiv}CH + LiNH_2 \rightleftharpoons NH_3 + HC{\equiv}CLi$$

$$H_2O + CH{\equiv}CLi \rightleftharpoons HC{\equiv}CH + LiOH$$

answer the following three questions.

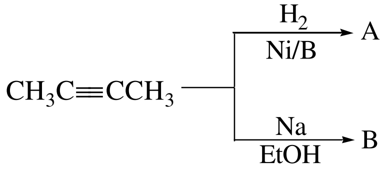
(i) The correct order of acid strength is
- (a) $HC{\equiv}CH > H_2O > NH_3$
- (b) $HC{\equiv}CH > NH_3 > H_2O$
- (c) $H_2O > HC{\equiv}CH > NH_3$
- (d) $H_2O > NH_3 > HC{\equiv}CH$

(ii) The correct order of base strength is
- (a) $LiNH_2 > HC{\equiv}CLi > LiOH$
- (b) $LiNH_2 > LiOH > HC{\equiv}CLi$
- (c) $HC{\equiv}CLi > LiNH_2 > LiOH$
- (d) $HC{\equiv}CLi > LiOH > LiNH_2$

(iii) The correct order of base strength is
- (a) $HC{\equiv}C^- < OH^- < NH_2^-$
- (b) $HC{\equiv}C^- < NH_2^- < OH^-$
- (c) $OH^- < NH_2^- < HC{\equiv}C^-$
- (d) $OH^- < HC{\equiv}C^- < NH_2^-$

2. The addition reactions shown by alkenes and alkynes follow either *syn* addition or *anti*-addition mechanism. For example, catalytic addition of H_2 proceeds via *syn* mechanism whereas halogens adds via *anti* mechanism. Based on these facts, answer the following three questions.

(i) In the reaction



$$CH_3C\equiv CCH_3 \begin{cases} \xrightarrow[\text{Ni/B}]{H_2} \text{A} \\ \xrightarrow[\text{EtOH}]{\text{Na}} \text{B} \end{cases}$$

which one of the following products is correct?

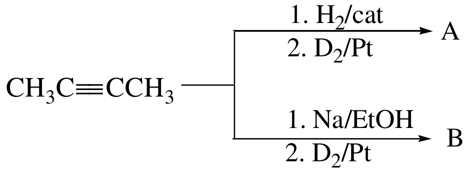
(a) A is (Z)-$CH_3CH{=}CHCH_3$ and B is (E)-$CH_3CH{=}CHCH_3$

(b) A is (E)-$CH_3CH{=}CHCH_3$ and B is (Z)-$CH_3CH{=}CHCH_3$

(c) Both A and B are (Z)-$CH_3CH{=}CHCH_3$

(d) Both A and B are (E)-$CH_3CH{=}CHCH_3$

(ii) In the reaction



$$CH_3C\equiv CCH_3 \begin{cases} \xrightarrow[\text{2. } D_2/\text{Pt}]{\text{1. } H_2/\text{cat}} \text{A} \\ \xrightarrow[\text{2. } D_2/\text{Pt}]{\text{1. Na/EtOH}} \text{B} \end{cases}$$

which one of the following products is correct?

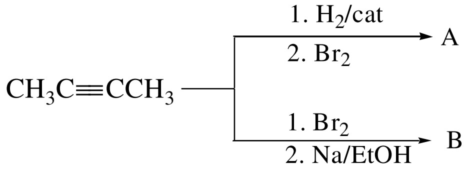
(a) Both A and B are *meso*-2, 3-dideuterobutane

(b) Both A and B are *rac*-2, 3-dideuterobutane

(c) A is *meso*-2, 3-dideuterobutane and B is *rac*-2, 3-dideuterobutane

(d) A is *rac*-2, 3-dideuterobutane and B is *meso*-2, 3-dideuterobutane.

(iii) In the reaction



$$CH_3C\equiv CCH_3 \begin{cases} \xrightarrow[\text{2. } Br_2]{\text{1. } H_2/\text{cat}} \text{A} \\ \xrightarrow[\text{2. Na/EtOH}]{\text{1. } Br_2} \text{B} \end{cases}$$

which one of the following products is correct?

(a) Both A and B are *meso*-2, 3-dibromobutane

(b) Both A and B are *rac*-2, 3-dibromobutane

(c) A is *meso*-2, 3-dibromobutane and B is *rac*-2, 3-dibromobutane

(d) A is *rac*-2, 3-dibromobutane and B is *meso*-2, 3-dibromobutane.

Assertion and Reason Type

Given below are the two statements for each questions. Based on the following key, answer correctly each question.

(a) Both statements are correct and Statement-2 is a correct explanation of Statement-1.

(b) Both statements are correct but Statement-2 is not a correct explanation of Statement-1.

(c) Statement-1 is correct and Statement-2 is incorrect.

(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	Alkynes are less reactive than alkene towards bromination.	The bromination of alkyne follows free radical mechanism while than of alkene follows *syn*-addition of Br_2.
2.	The terminal C—H in alkyne is more acidic as compared to that of alkene.	The more s character in the orbital used by the C bonded to the H, the more acidic is the H.
3.	$CH_3CHBrCH_2Br$ on treatment with with alcoholic KOH gives $CH_3CBr{=}CH_2$ as the major product.	In E2 elimination the more acidic H is removed preferentially.

4.	In $CH_3\overset{-}{\ddot{C}}H—C\equiv\overset{-}{C}:$ the propargylic carbanion is more basic than the terminal acetylinic carbanion.	The acetylinic H is more acidic than propargylic C—H.
5.	The correct order of bond enthalpies is $\equiv C—H > = C—H > — C— H$	The more s character in the hybrid orbital used by C in bonding H, the stronger the σ C—H bond.
6.	Catalytic hydrogenation in the case of of an alkyne is faster than in the case of an alkene	An alkyne forms less contrained transition state with the surface of the catalyst as compared to that formed by an alkene.
7.	2-Butyne with 1 mol of H_2 produces *cis*-2-butene when H_2/Pt is used whereas *trans*-2-butene is produced with Na in EtOH.	The product of hydrogenation depends on the mode of addition, whether it is *syn*- or *anti*-addition.
8.	The addition of one mole of HBr occurs across the triple bond instead of the double bond in $H_2C=CHCH_2C\equiv CH$.	Carbocation formed from alkene group is more stable than the vinyl carbocation formed from the alkyne group.

ANSWERS

Straight Objective Type

1. (c) **2.** (b) **3.** (b) **4.** (d) **5.** (b) **6.** (a) **7.** (a)
8. (b) **9.** (c) **10.** (c) **11.** (d) **12.** (d) **13.** (a) **14.** (a)
15. (a) **16.** (b) **17.** (b) **18.** (b) **19.** (c) **20.** (d) **21.** (b)
22. (b) **23.** (a) **24.** (b) **25.** (b) **26.** (a) **27.** (d) **28.** (b)
29. (b) **30.** (a) **31.** (a) **32.** (b) **33.** (c) **34.** (d) **35.** (c)
36. (c) **37.** (d) **38.** (b)

Multiple Correct Choice Type

1. (a), (c) **2.** (a), (c), (d) **3.** (a), (c), (d) **4.** (b), (c), (d)
5. (a), (c) **6.** (a), (d) **7.** (a), (d) **8.** (b), (c)
9. (a), (c), (d) **10.** (a), (b), (c), (d) **11.** (b), (c) **12.** (c), (d)
13. (c), (d) **14.** (b), (d) **15.** (a), (b) **16.** (c), (d)
17. (a), (b), (c), (d) **18.** (b), (c), (d) **19.** (a), (d) **20.** (a), (c)
21. (a), (b)

Linked Comprehension Type

1. **(i)** (c) **(ii)** (a) **(iii)** (d)
2. **(i)** (c) **(ii)** (d) **(iii)** (d)

Assertion Reason Type

1. (c) **2.** (a) **3.** (c) **4.** (a) **5.** (a) **6.** (b) **7.** (b)
8. (d)

Hints and Solutions

Straight Objective Type

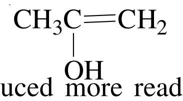
1. $Mg_2C_3 + 4H_2O \longrightarrow CH_3C\equiv CH + 2Mg(OH)_2$

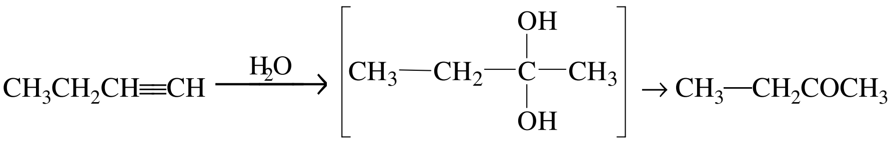
2. $KOOCCH_2COOK \xrightarrow{\text{Electrolysis}} HC\equiv CH$

3. The dipole moment of $CH_3C\equiv CCH_3$ is zero. it is a linear molecule and has symmetrical arrangements of methyl substituents.

4. For example, butyne (C_4H_6) has the same molecular formula as those of 1,3-butadiene, cyclobutene and bicyclobutane.
5. The formation of acetylene is accompanied with the positive value of $\Delta_f H^\circ$.
6. C=C has priority over C≡C and gets the smaller number.
7. Ethyne (HC≡CH) contains acidic hydrogen.
8. Ammonium chloride precipitates ethyne whereas ethane remains unreacted.
9. 1-Butyne ($CH_3CH_2C{\equiv}CH$) contains active hydrogen. It will react with an aqueous solution of $Ag(NH_3)_2OH$.
10. 1-Butyne contains active hydrogen while 2-butyne does not. These two can be distinguished by using Tollens reagent.
11. Propyne contains active hydrogen. It is precipitated by $AgNO_3$ in ammonia.
12. Same as Q. 11. 1-Butyne contains acetylinic hydrogen atom. It will form insoluble acetylides.
13. In E2 elimination the more acidic H is removed preferentially. The inductive effect of the Br's increases the acidity of the H's on the C's to which the Br's are bonded. The increasing order of acidity is $CH_3 < CHBr < CH_2Br$. Methyl group attached to CHBr decreases the acidity of H attached to CHBr. Therefore, $CH_3CH{=}CHBr$ is the major product and $CH_3CBr{=}CH_2$ as the minor product. The compound $CH_2{=}CHCH_2Br$ is not formed.
14. The strength of conjugate acids follows the order $CH_3CH_3 < NH_3 < HC{\equiv}CH < H_2O$
The strength of given bases follows the order $CH_3CH_2^- > NH_2^- > HC{\equiv}C^- > OH^-$
15. Carboxylic acid is stronger than alcohol which, in turn, is stronger than acetylene.
16. Base strength follows the reverse order of their conjugate acid. hence, the order is

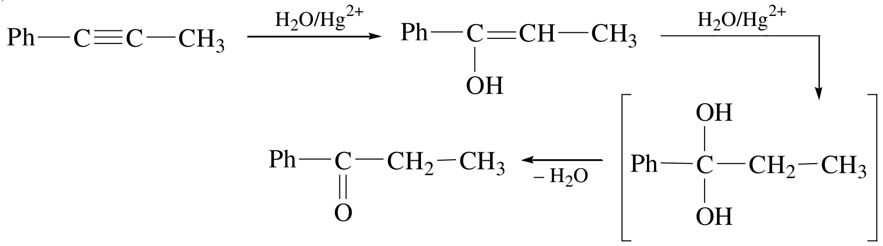
$$CH_3COO^- < CH_3CH_2O^- < HC{\equiv}C^-$$

17. The values of ΔH's of hydrogenation are – 175.7 kJ mol^{-1} and – 138.1 kJ mol^{-1} for triple to double and double to single bonds, respectively. Most of alkyne is hydrogenated before alkene starts hydrogenated.
18. We have $LiNH_2 > HC{\equiv}CLi$ and $R^- > NH_2^-$. Hence, the correct order is $R^- > NH_2^- > HC{\equiv}C^-$.
19. $CH_3C{\equiv}CH \xrightarrow{H_2SO_4/HgSO_4} CH_3COCH_3$.
20. Water can be added across a triple bond in the presence of acid and $HgSO_4$.
21. The product is  $CH_3\underset{\displaystyle OH}{\underset{|}{C}}{=}CH_2$ which rearranges to CH_3COCH_3.
22. Alkyne are reduced more readily than alkenes.
23. Lindlar catalyst causes *syn* addition. Hence, *cis* addition of hydrogen atoms occur.
24. Lithium metal in liquid ammonia causes *anti* addition. Hence, *trans* addition of hydrogen atoms occurs.
25. Alkynes are less reactive than alkenes towards halogen addition.
26. In oxymercuration, addition of water follows. Markovnikov's rule.



$$CH_3CH_2CH{\equiv}CH \xrightarrow{H_2O} \left[CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}{-}CH_3\right] \rightarrow CH_3{-}CH_2COCH_3$$

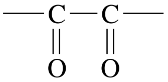
27. Pb with $BaSO_4$ is known as Lindlar's catalyst.
28. It is more difficult to dehydrohalogenate vinyl bromide (obtained by the elimination of the first HBr) than an alkyl bromide. Thus, a stronger base is required after the removal of the first HBr.
29. $R'MgBr + RC{\equiv}CH \rightarrow R'H + Mg(C{\equiv}CR)Br$.
30. The carbocation $Ph{-}\overset{+}{C}{=}CH{-}CH_3$ is more stable than $PH{-}CH{=}\overset{+}{C}{-}CH_3$. Hence OH group is added to the former molecule.



$$Ph{-}C{\equiv}C{-}CH_3 \xrightarrow{H_2O/Hg^{2+}} Ph{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}CH{-}CH_3 \xrightarrow{H_2O/Hg^{2+}} \left[Ph{-}\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}{-}CH_2{-}CH_3\right] \xrightarrow[-H_2O]{} Ph{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_2{-}CH_3$$

31. The use of Lindlar catalyst (Pb-$BaSO_4$) produces *cis* product. Hydrogenation occurs on the plane of the catalyst. Thus, *syn* addition occurs.

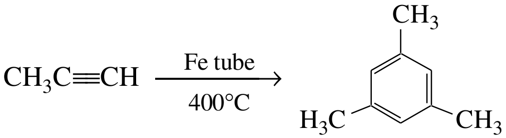
32. The reaction proceeds through a carbocation. The alkyl carbocation from the alkene group is more stable than the vinyl carbocation formed from the alkyne group. Thus, alkene reacts at a faster rate than alkyne toward electrophilic addition.

33. At neutral conditions and at room temperature, —C≡C—is oxidized to  $—\underset{\displaystyle O}{\underset{\|}{C}}—\underset{\displaystyle O}{\underset{\|}{C}}—$.

34. At alkaline or acidic conditions at higher temperatures causes oxidation upto carboxylic acid with the cleavage of —C≡C— bond.

35. The ozonolysis of a triple bond produces a mixture of carboxylic acids.

36. Terminal triple bond gives CO_2 from the terminal atom and the remaining fragment gives carboxylic acid.

37. 

Mesitylene

38. Two moles of butyllithium converts 1-butyne into a dianion by removing the terminal H and a propargylic H.

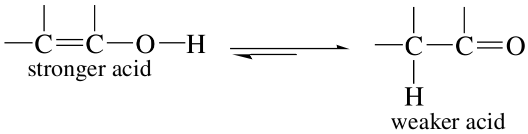
Multiple Correct Choice Type

3. (a) White precipitate is obtained only when —C≡C— functional group is present at the terminal(s) of the molecule, since only then it will have acidic hydrogen atom. (d) A vinylic halide is very unreactive. The use of vigorous conditions (such as the use of a strong base, $NaNH_2$) are required to remove HX.

4. (c) Alkynes are considerably less reactive than alkenes as for as the addition of halogen is concerned. This is due to the difficulty of alkynes to form cyclic halonium ion as the intermediates.

(d) It lies much in favour of keto form.

5. (b) Equilibrium reaction always favours the formation of weaker substances. In keto-enol tautomerism, we have



$$\underset{\text{stronger acid}}{—\overset{|}{C}=\overset{|}{C}—O—H} \rightleftharpoons \underset{\text{weaker acid}}{—\underset{H}{\underset{|}{\overset{|}{C}}}—\overset{|}{C}=O}$$

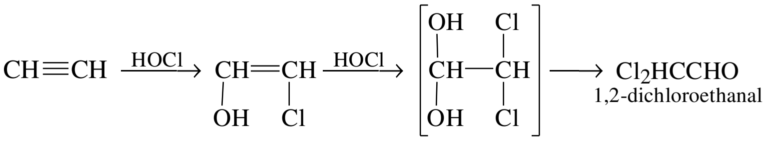
(c) An sp hybrid orbital has more s-character as compared to an sp^3 hybrid orbital.

(d) 2-butyne does not contain acetylinic hydrogen atom.

6. (c) Methanoic acid is produced.

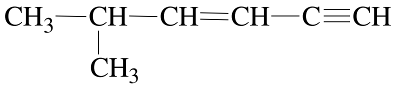
7. (b) Calcium carbide on treating with water gives acetylene.

(c) $CaC_2 + 2H_2O \rightarrow CH{\equiv}CH + Ca(OH)_2$



$$CH{\equiv}CH \xrightarrow{HOCl} \underset{OH\quad Cl}{\underset{|\qquad |}{CH{=}CH}} \xrightarrow{HOCl} \left[\begin{matrix} OH & Cl \\ | & | \\ CH & —CH \\ | & | \\ OH & Cl \end{matrix}\right] \longrightarrow \underset{\text{1,2-dichloroethanal}}{Cl_2HCCHO}$$

(d) 1-Pentyne forms acetylide whereas 2-pentyne does not.

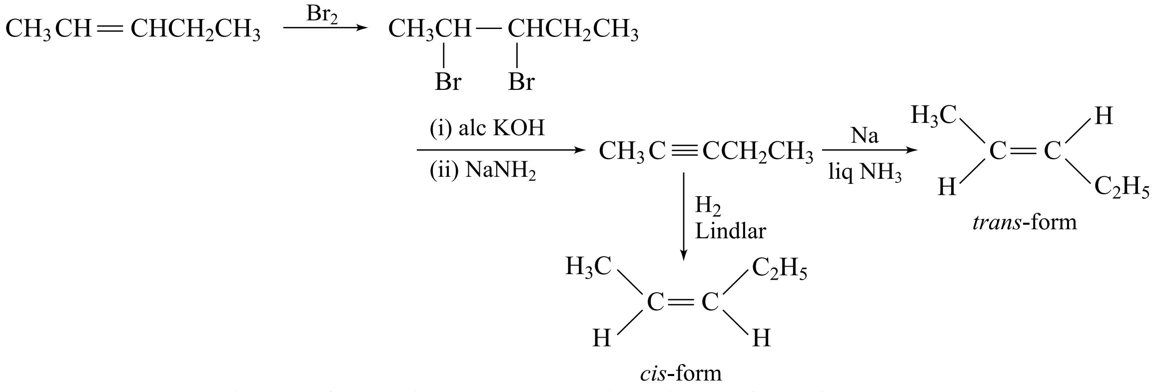
8. (b) The molecule  $CH_3—\underset{CH_3}{\underset{|}{CH}}—CH{=}CH—C{\equiv}CH$ contains conjugated double bond, hence it is more stable.

(c) Bromine atom in 2,3-dibromo-2-butene deactivates the double bond because of electron withdrawal.

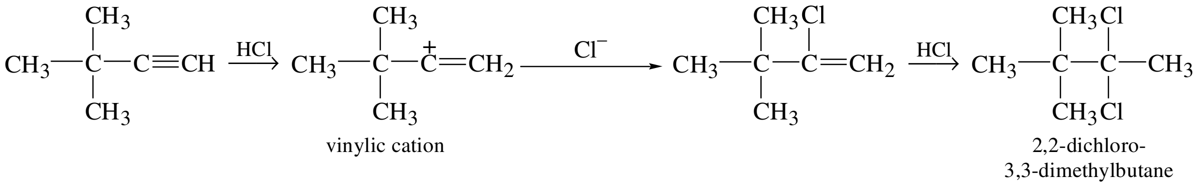
(d) Dripping bromine avoids the temporary excess of Br_2.

9. (a) The *trans* isomer is obtained. (c) The *trans* isomer is more stable than its *cis* isomer.

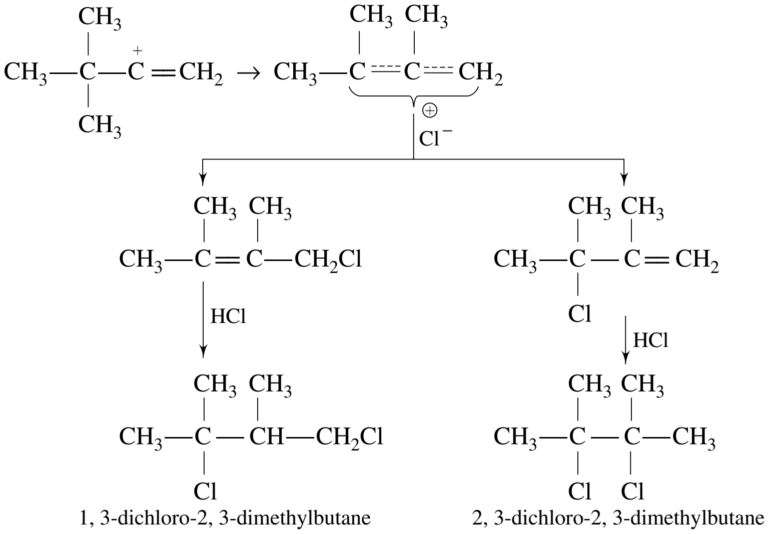
(d) The conversion may be achieved as follows.



10. (a) The product is a mixture of three isomers as explained in the following.



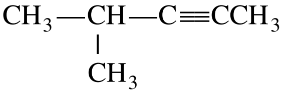
Besides this, the other products are obtained due to the methyl shift in vinylic cation.



(b) There are eight isomers including stereoisomers.

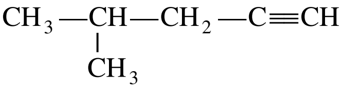
$HC\equiv CCH_2CH_2CH_2CH_3$; $CH_3C\equiv CCH_2CH_2CH_3$; $CH_3CH_2C\equiv CCH_2CH_3$;

1-hexyne 2-hexyne 3-hexyne



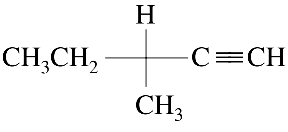
$CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv CCH_3$

4-methyl-2-pentyne



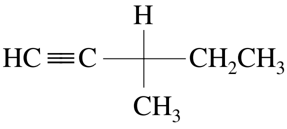
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-C\equiv CH$

4-methyl-1-pentyne

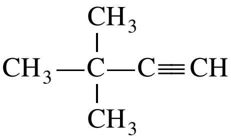


;

(*S*)-3-methyl-1-pentyne



(*R*)-3-methyl-1-pentyne



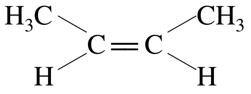
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH$

3,3-dimethyl-1-butyne

(c) The initially formed 1-pentyne is converted into 2-pentyne because the more highly *R*-substituted alkyne is more stable. (d) The very strong base $NaNH_2$ removes the terminal proton from the dehydrohalogenation product and thus it cannot rearrange.

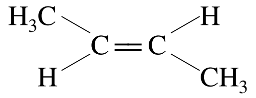
$$CH_3CH_2CH_2CH_2CHBr_2 \xrightarrow{NaNH_2} CH_3CH_2CH_2C{\equiv}C^- \xrightarrow{H_3O^+} CH_3CH_2CH_2C{\equiv}CH$$

11. (a) The product is (Z)-2-butene $H_3C{-}C{\equiv}C{-}CH_3 \xrightarrow{[H]}$



;

(b) $H_3C{-}C{\equiv}C{-}CH_3 \xrightarrow{[H]}$



(c) The Δ*H*s of hydrogenation are

$$CH_3C{\equiv}CCH_3 \xrightarrow{H_2} CH_3CH{=}CHCH_3 \qquad \Delta H^\circ = -\ 175.7\ \text{kJ mol}^{-1}$$

$$CH_3CH{=}CHCH_3 \xrightarrow{H_2} CH_3CH_2CH_2CH_3 \qquad \Delta H^\circ = -\ 138.1\ \text{kJ mol}^{-1}$$

Since the first step involves more liberation of heat, the reaction takes place in a stepwise manner. The Lindlar's catalyst can be used for this purpose.

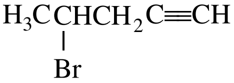
(d) Ethylene is soluble in concentrated H_2SO_4 because of the formation of alkyl carbocation salt.

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow (CH_3CH_2^+)(HSO_4^-)$$

Acetylene is not soluble since the vinyl carbocation ($CH_2{=}\overset{+}{C}{-}H$) is not stable. The more s-character in the positively-charged C, the less stable the carbocation and the less likely it is formed.

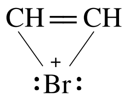
12. (a) The vinyl carbocation from 2-butyne is more stable because of the presence of electron-repelling CH_3 group attached to C^+ (i.e. $CH_3{-}\overset{+}{C}{=}CH{-}CH_3$). Thus, 2-butyne is soluble in concentrated H_2SO_4 due to the formation of the salt $(CH_3{-}\overset{+}{C}{=}CH{-}CH_3)(HSO_4^-)$.

(b) The addition of HBr proceeds through the formation of a carbocation. The alkyl carbocation formed from the alkene group ($H_3C{-}\overset{+}{C}HCH_2C{\equiv}CH$) is more stable than the vinyl carbocation ($CH_2{=}CHCH_2\overset{+}{C}{=}CH_2$) from the alkyne group. The $\Delta H^\ddagger$ for the former is lesser than that of the latter resulting in the addition to HBr across the double bond, i.e. the alkene reacts at a faster rate than the alkyne towards electrophilic addition. Thus, the reaction taking place is

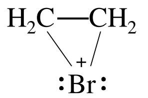


$$H_2C{=}CHCH_2C{\equiv}CH + HBr \longrightarrow H_3C\underset{\substack{|\\ Br}}{C}HCH_2C{\equiv}CH$$

(c) The addition of Br_2 across a double or triple bond occurs via the formation of the three membered ring of bromonium ion.



(from alkyne)

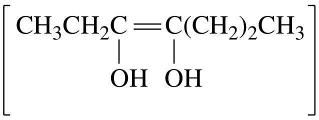


(from alkene)

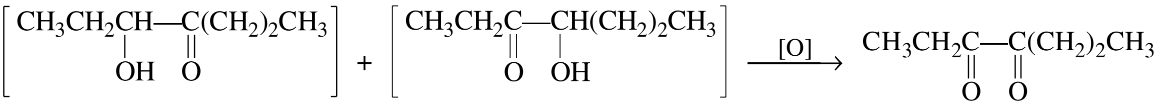
The brominium ion from alkyne is more strained due to the presence of double bond (shorter bond length). Moreover, its carbon atoms have more s-character. These factors make this brominium ion less stable than that from the alkene makiang alkynes less reactive than alkenes.

(d) The hydrogenation proceeds via the adsorption on the surface of the catalyst. The adsorption of alkene occurs when the plane of the π-bond approaches perpendicular to the catalyst. The alkyne, any direction (parallel to C—C bond) can lead to the adsorption due to the cylindrical nature of the π-bonds. Thus, the transition state in case of alkynes is less constrained leading to the more positive value of $\Delta S^\ddagger$. This makes alkynes to react at a faster rate than alkenes.

13. (a) With neutral conditions at room temperature, a diketone is formed via the hydroxylation reaction.



$$CH_3CH_2C{\equiv}C(CH_2)_2CH_3 \longrightarrow \left[\begin{array}{c} CH_3CH_2\underset{\substack{|\\ OH}}{C}{=}\underset{\substack{|\\ OH}}{C}(CH_2)_2CH_3 \end{array}\right] \longrightarrow$$



$$\left[\begin{array}{c}\mathrm{CH_3CH_2\underset{|}{\underset{OH}{C}}H{-}\underset{\|}{\underset{O}{C}}(CH_2)_2CH_3}\end{array}\right] + \left[\begin{array}{c}\mathrm{CH_3CH_2\underset{\|}{\underset{O}{C}}{-}\underset{|}{\underset{OH}{C}}H(CH_2)_2CH_3}\end{array}\right] \xrightarrow{[O]} \mathrm{CH_3CH_2\underset{\|}{\underset{O}{C}}{-}\underset{\|}{\underset{O}{C}}(CH_2)_2CH_3}$$

(b) Under neutral or alkaline conditions at higher temperatures, the triple bond is cleaved to give carboxylic acids.

$$\mathrm{CH_3CH_2C{\equiv}C(CH_2)_2CH_3 \xrightarrow{[O]} CH_3CH_2COOH + HOOC(CH_2)_2CH_3}$$

(c) The addition of HBr proceeds via the formation of carbocation.

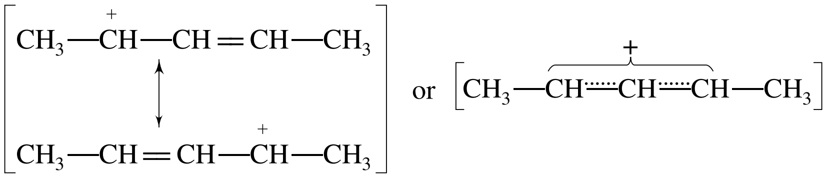
$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_3 \xrightarrow{H^+} CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3}$$

allylic carbocation

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{H^+} CH_3{-}\overset{+}{C}H{-}CH_2{-}CH{=}CH_2}$$

2° carbocation

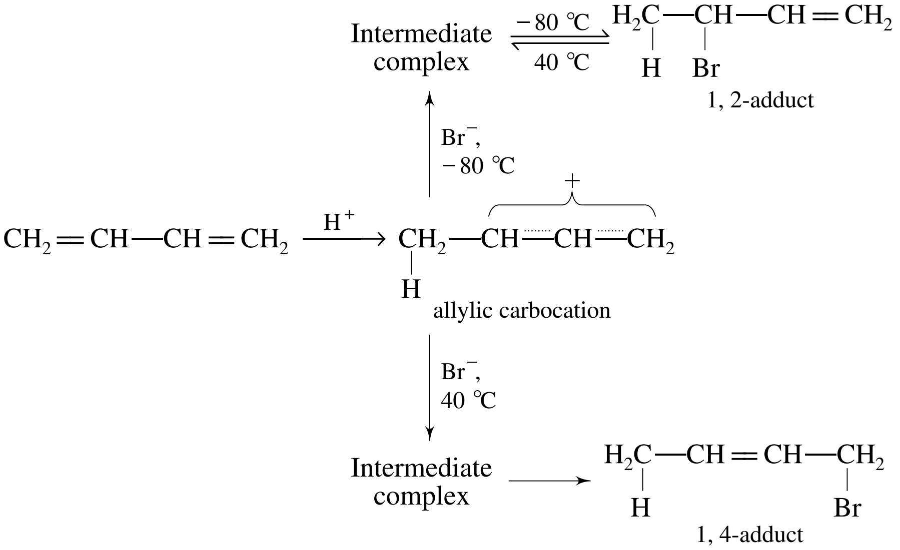
Allylic carbocation is more stable due to resonance



$$\left[\begin{array}{c}\mathrm{CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3}\\ \updownarrow \\ \mathrm{CH_3{-}CH{=}CH{-}\overset{+}{C}H{-}CH_3}\end{array}\right] \text{ or } \left[\mathrm{CH_3{-}\overset{+}{\overbrace{CH{\cdots}CH{\cdots}CH}}{-}CH_3}\right]$$

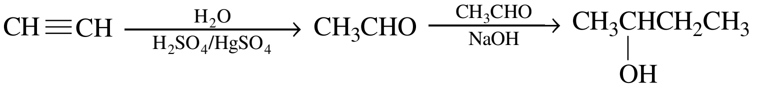
Its formation requires lesser $\Delta H^{\ddagger}$ as compared to 2° carbocation and hence is formed at a faster rate.

(d) The additions may be depicted as follows.



The conversion allylic carbocation → 1,2-adduct involves a lower $\Delta H^{\ddagger}$ as compared to carbocation → 1,4-adduct. At low temperature, 1,2-adduct is formed due to the lower $\Delta H^{\ddagger}$. Thus, it formation is kinetically-controlled. As temperature is raised, 1,2-adduct passes over to the allylic carbocation and then to thermodynamically more stable 1,4-adduct. The 1,4-adduct is more stable as it is a more substituted alkene. Once, 1,4-adduct is formed, it cannot be converted to 1,2-adduct on lowering temperature as the conversion of 1,4-adduct to intermediate complex involves a larger $\Delta H^{\ddagger}$ value.

14. (a) The reaction is



$$\mathrm{CH{\equiv}CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3CHO \xrightarrow[NaOH]{CH_3CHO} CH_3\underset{|}{\underset{OH}{C}}HCH_2CH_3}$$

(b) The product is $\mathrm{CH_3{\equiv}CCH_3}$. $\mathrm{CH{\equiv}CH \xrightarrow[NH_3]{Na} NaC{\equiv}CNa \xrightarrow{CH_3I} CH_3C{\equiv}CCH_3}$

(d) The hydrogens are acidic in nature.

15. (a) The product is *trans*-alkene. (b) The product is *cis*-alkene

(d) We have $\underset{\text{stronger acid}}{HC{\equiv}CH} + NH_2^- \rightleftharpoons HC{\equiv}C^- + \underset{\text{weaker acid}}{NH_3}$

16. (c) Acetylide is a weaker base than ethide ion. A pair of electrons is more tightly bound in acetylene than in ethide ion. (d) The Lindlar catalyst is $Pd/BaSO_4$

18. (b) $CH_3C{\equiv}CH \xrightarrow{O_3} CH_3COOH + HCOOH$

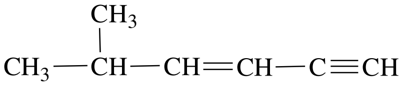
(c) The correct name is 1-penten-4-yne

C=C has priority over C≡C and gets the smaller number

(d) There are seven isomers.

1-hexyne 2-hexyne, 3-hexyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 3-methyl-1-pentyne, 3, 3-dimethyl-1-butyne

19. (a) The product is



$$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH{=}CH{-}C{\equiv}CH$$

The product obtained involves conjugation and hence is more stable.

(d) $H_2C{=}CH{-}CH_2{-}HC{=}CH_2 \xrightarrow{O_3} HCHO + OCHCH_2CHO + HCHO$

Linked Comprehension Type

1. **(i)** The reaction proceeds more towards weaker substances. From the given reactions, the order of acid strengths is $HC{\equiv}CH > NH_3$ and $H_2O > HC{\equiv}CH$.

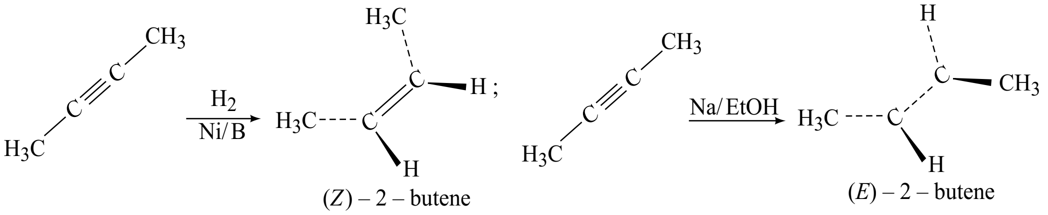
Hence, the correct order of acid strength is $H_2O > HC{\equiv}CH > NH_3$.

(ii) From the given reactions, the order of base strengths is: $LiNH_2 > HC{\equiv}CLi$ and $HC{\equiv}CLi > LiOH$. Hence, the correct order of base strength is $LiNH_2 > HC{\equiv}CLi > LiOH$

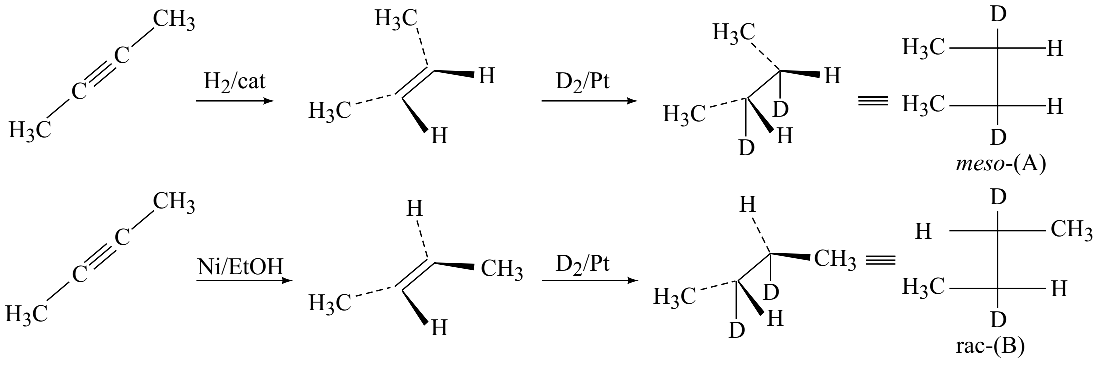
(iii) $LiNH_2 > HC{\equiv}CLi$ and $HC{\equiv}CLi > LiOH$

Thus, the correct order is $OH^- < HC{\equiv}C^- < NH_2^-$.

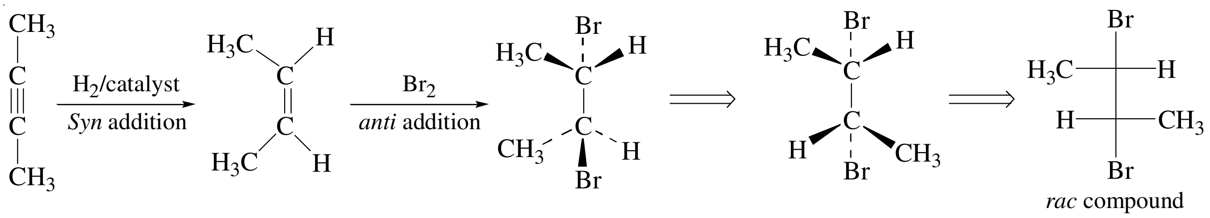
2. **(i)** The catalytic hydrogenation causes *syn*-addition while the use of Na/EtOH causes *anti*-addition.

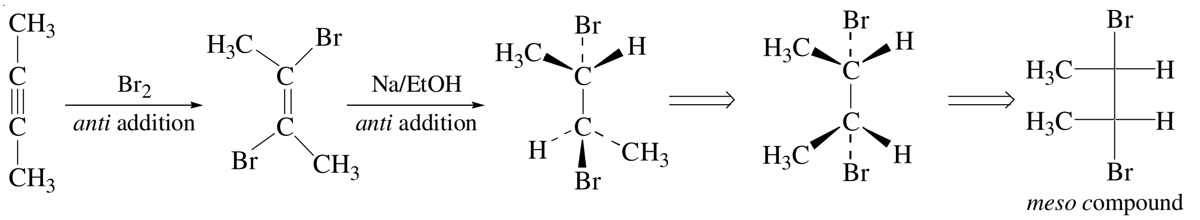


(ii) The use of H_2/cat. causes *syn*-addition while the use of Na/EtOH causes *anti*-addition. Hence



(iii)





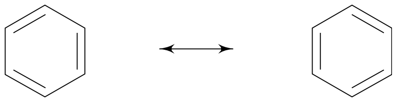
(**Note**: In general, *syn* + *syn* additions or *anti* – *anti* additions give *meso* compound and *syn* – *anti* additions or *anti* – *syn* additions give *rac* compound. Also note that *anti* addition to an alkene does not occur readily, so this addition may be carried out at the alkyne stage.)

CHAPTER 24

BENZENE

STRUCTURE OF BENZENE

According to Kekule, benzene is a resonance hybrid of the following resonating structures.



The resonance energy of benzene is about 150.6 kJ mol^{-1}, i.e. benzene is more stable than cyclohexatriene by 150.6 kJ mol^{-1}. The above structure of benzene accounts for the following characteristics of benzene.

1. Molecular formula of benzene is C_6H_6.
2. Benzene yields only one monosubstitution product.
3. Benzene yields three isomeric disubstitution products.
4. All carbon-carbon bond distance in benzene are equal (139 pm) and are intermediate in length between single (154 pm) and double bonds (134 pm).
5. Benzene undergoes substitution rather than addition reactions.

For example, the addition reaction of alkenes with cold dilute/alkaline $KMnO_4$, Br_2/CCl_4 and HCl are not shown by benzene. However, under drastic conditions benzene is reduced to cyclohexane. Benzene undergoes substitution reactions in which H is replaced by another atom or group of atoms. For examples

(i) $C_6H_6 + HONO_2 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5\text{—}NO_2} + H_2O$

(ii) $C_6H_6 + Cl_2 \xrightarrow{Fe} \underset{\text{chlorobenzene}}{C_6H_5\text{—}Cl} + HCl$

(iii) $C_6H_6 + HOSO_3H \xrightarrow{SO_3} \underset{\text{Benzenesulphonic acid}}{C_6H_5\text{—}SO_3H} + H_2O$

(iv) $C_6H_6 + RCl \longrightarrow \underset{\text{alkylbenzene}}{C_6H_5\text{—}R} + HCl$

(v) $C_6H_6 + ROCl \xrightarrow{AlCl_3} C_6H_5\text{—}COCH_3 + HCl$

Reaction (iv) is known as Friedel-Crafts alkylation and reaction (v) is known as Friedel-Crafts acylation.

6. The enthalpies of hydrogenation and combustion of benzene are lower than those expected for cyclohexatriene.

Orbital Representation of Benzene Benzene is a planar molecule where each carbon is sp^2 hybridized. Of the three hybrid orbitals, two are used in σ–bonding with two other carbon atoms and the third is used in σ–bonding with hydrogen atom. In addition to these orbitals, each carbon has one p orbital occupied by one electron. Since this orbital lies perpendicular to the plane of benzene ring, the electron in this orbital is of π–type. The p orbital of each carbon atom can overlap with the adjacent p orbitals of carbon atoms making additional bond of π-type. But this bond is not localized between two carbon atoms but form two continuous doughtnut-shaped electrons cloud one lying above and the other below the plane of cyclic carbon skelton. It is the overlap of the p orbitals in both directions that corresponds to the resonance hybrid of two Kekule structures. The delocalization of π-electrons gives rise to resonance energy and makes the molecule more stable.

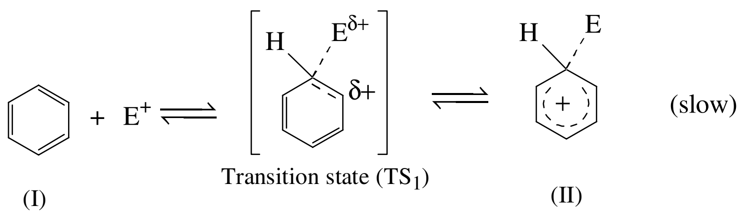
Substitution Reactions in Benzene The typical reactions of the benzene ring are those in which the π-electrons serve as a source of electrons for electrophilic (acidic) reagents. Because of delocalization of π-electrons, benzene does not show additional reactions as in the case of alkenes but undergoes substitution reactions in which hydrogen atom attached to carbon atom is replaced by another atom or group of atoms.

The Hückel 4*n* + 2 Rule A molecule acquires aromatic characteristics provided it has cyclic clouds of delocalized π electrons above and below the plane of the molecule and this π clouds has a total of $(4n + 2)$ π electrons. The requirement of $4n + 2$ electrons is known as $4n + 2$ rule or Hückel rule. Examples are benzene ($n = 1$), naphthalene ($n = 2$) and anthracene ($n = 3$). Besides these, cyclopentadienyl anion and cycloheptatrienyl cation (tropylium ion) also have aromatic characteristics. The flat ring formed by five and seven carbon atoms do not involve much strain as compared to the ideal six carbon-atom ring and also there is a reasonably good overlap for π-bond formation in these two rings. In smaller or bigger rings, it is difficult to accommodate trigonally hybridized atoms very well, so that any stabilization caused by aromaticity may be largely offset by angle strain or poor overlap of p orbitals or both.

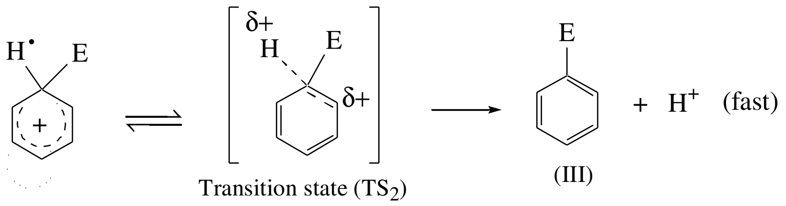
MECHANISM OF ELECTROPHILIC SUBSTITUTION REACTIONS

In general, electrophilic substitution reactions involve the following steps.

Step 1. Formation of arenium cation



Step 2. Formation of substituted product



The potential energy diagram for the substitution reaction is as shown in Fig. 24.1.

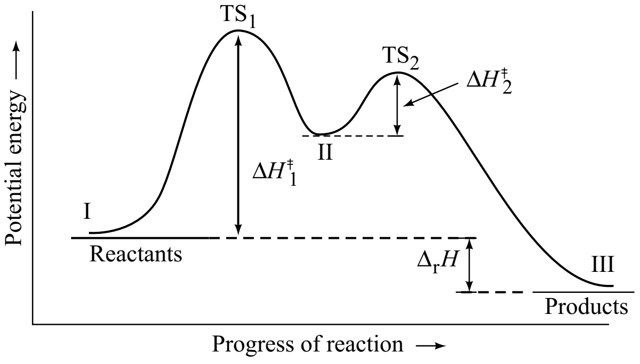


Fig. 24.1

Formation of the intermediate arenium cation in step 1 is usually slow and rate-determining. Formation of product in Step 2 is fast as it restores aromaticity. It has no effect on the overall reaction rate.

Since C—H bond is broken in step 2, the replacement of H by D in the benzene has no affect on the rate of reaction, that is, the rates of reactions.

$$C_6H_6 + E^+ \rightarrow C_6H_5E + H^+ \quad \text{and} \quad C_6D_6 + E^+ \rightarrow C_6D_5E + D^+$$

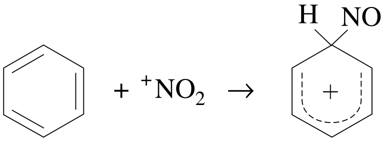
will have the same value.

A few specific examples of substitution reactions are described in the following.

1. Nitration A mixture of nitric acid and sulphuric acid is the nitrating reagent. The steps involved in the mechanism are as follows.

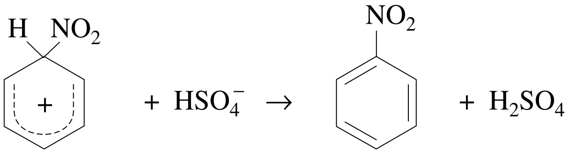
(a) Formation of nitronium ion $HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + {}^+NO_2$

(b) Electrophilic attack by nitronium ion



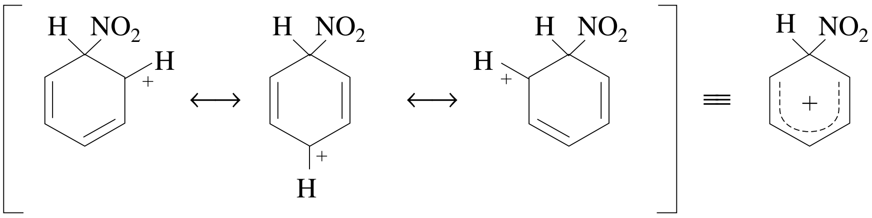
benzenonium ion

(c) Removal of proton



(fast)

The rate determining step is the formation of carbocation, which is the resonance hybrid of the following three structures.

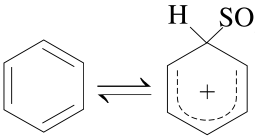


The dispersal of positive charge over the molecule by resonance makes this ion more stable than with a localized positive charge. Probably because of this, a carbocation is formed from the relatively stable benzene.

2. Sulphonation The involved steps are

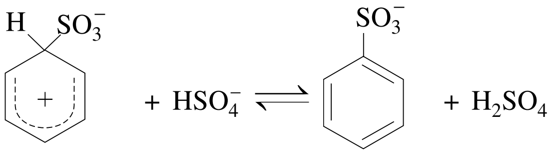
(a) $2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$

(b) SO_3 +



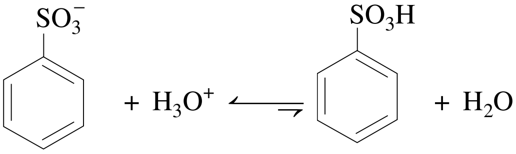
(slow)

(c)



(fast)

(d)



(equilibrium far to the left)

In fact, the entire sulphonation process is an equilibrium process

$$C_6H_6 + H_2SO_4 \overset{H^+}{\rightleftharpoons} C_6H_5SO_3H + H_2O$$

For sulphonation, we require excess of H_2SO_4 along with SO_3 and for desulphonation we use excess of H_2O along with heating (100–175°C).

The reversible nature of sulphonation may be explained as follows.

Electrophilic substitution may be abbreviated as

$$\text{ArH} + \text{E}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\text{H}\diagdown_{\text{Ar}}\diagup^{\text{E}}\right]^+ \xrightarrow{k_2} \text{ArE} + \text{H}^+$$

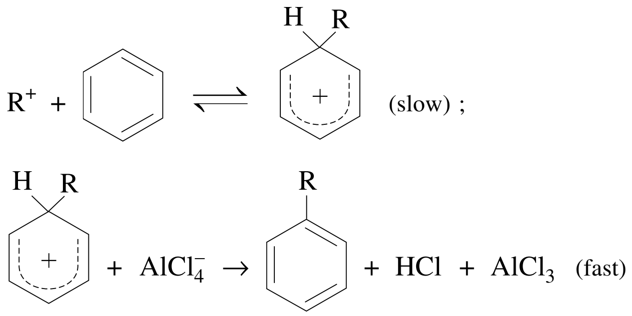
In most electrophilic substitution reactions, the rate constant k_2 is much larger than the value of k_{-1}, resulting the reaction to proceed in the forward direction.

In sulphonation reaction, k_2 is only slightly larger than k_{-1} and it also decides the rate of overall rate of reaction. Desulphonation may be achieved by using hot dilute aqueous solution of H_2SO_4.

Since the bond dissociation energies follow the order $\varepsilon(\text{C} - \text{T}) > \varepsilon(\text{C—D}) > \varepsilon(\text{C—H})$, the rates of sulphonation follow the order $k(C_6T_6) < k(C_6D_6) < k(C_6H_6)$.

3. Friedel-Crafts alkylation The steps are:

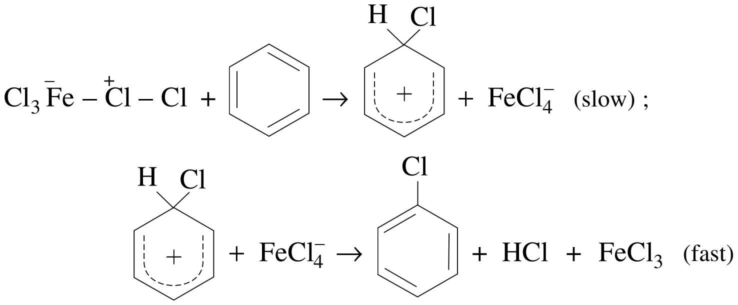
$$RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$$



Here $AlCl_3$ acts as a Lewis acid.

4. Mechanism of halogenation The steps are

$$Cl_2 + FeCl_3 \rightleftharpoons Cl_3\bar{F}e - \overset{+}{Cl} - Cl$$



THEORY OF ORIENTATION

A group attached to benzene has a directing influence on the electrophilic substitution reaction. Two types of groups have been classified based on their orientation effects.

Activating Group A group that releases electrons to benzene ring is an activating group. It directs the incoming electrophile to *ortho* or *para* position. Examples include

Strongly activating :	—NH_2, —NHR, —NR_2, —OH
Moderately activating:	—OCH_3, —$NHCOCH_3$
Weakly activating:	—CH_3, —C_6H_5

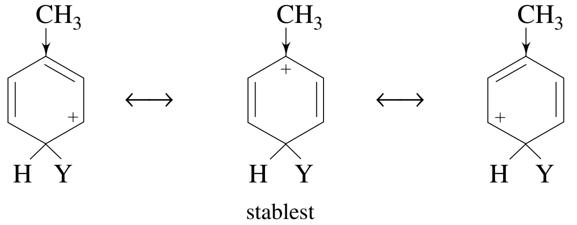
Deactivating group A group that withdraws electrons from benzene is a deactivating group. It directs the incoming electrophile to *meta* positon. Examples include

$$—NO_2, —CN, —COOH, —SO_3H, —CHO, —COR \text{ and } —N(CH_3)_3^+$$

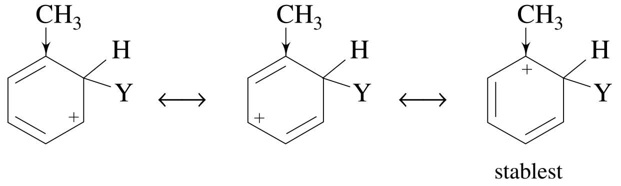
A group attached to benzene also affects the rate of electrophilic substitution reaction. An electron-releasing group disperses the positive charge of carbocation and thus makes it more stable causing the reaction to proceed faster as compared to the substitution reaction involving benzene. On the other hand, electron withdrawing group intensifies the positive charge of carbocation and thus makes it less stable causing the reaction to proceed slower as compared to the substitution reaction involving benzene.

An activating group activates all the positions of a benzene ring; even the positions *meta* to it are more reactive than any single position in the benzene ring itself. It directs *ortho* and *para* simply because it activates the *ortho* and *para* positions much more than it does the *meta*. Alternatively, only in the *ortho* and *para* attack by an electrophile, a carbocation is generated in which positive charge is located on the carbon atom to which electron-releasing group is directly attached making this carbocation to be much more stable than the other resonating structures. Because of contribution from the stable structure, the hybrid carbocations resulting from an attack at *ortho* and *para* positions are more stable than the carbocation formed during the attack at *meta* position and since the stable hybrid carbocation is formed faster, it follows that the electron-releasing or activating group is *ortho* and *para* directing. The above facts are depicted in the following structures.

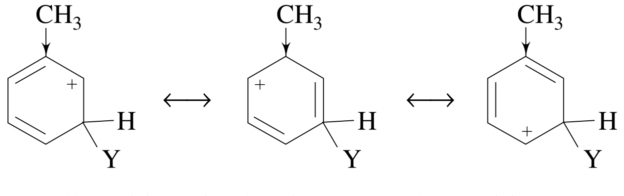
Para attack



Ortho attack



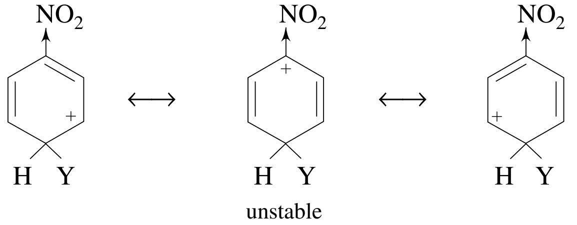
Meta attack

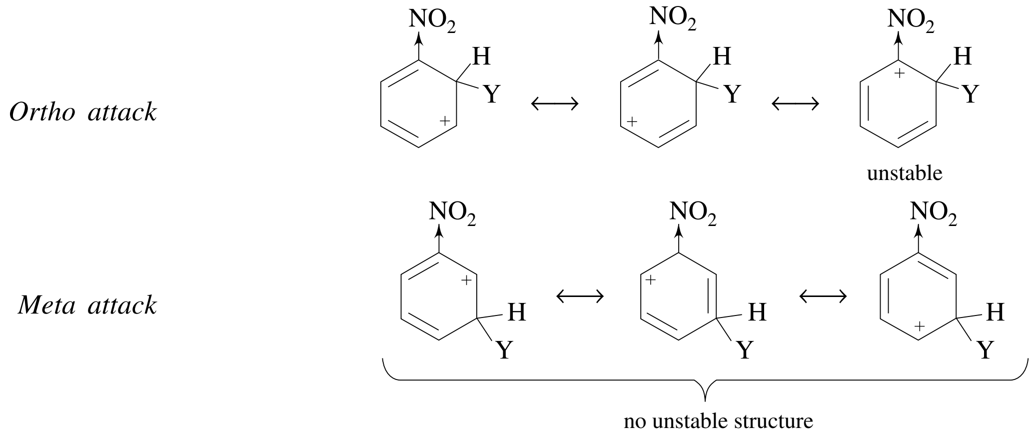


A deactivating group deactivates all positions in the ring, even the positions *meta* to it. It directs *meta* simply because it deactivates the *ortho* and *para* positions even more than it does the *meta*.

Alternatively, only in the *ortho* and *para* attack by an electrophile a carbocation is generated in which positive charge is located on the carbon atom to which electron-attracting group is directly attached making this carbocation to be much more unstable than the other resonating structures. Because of contribution from the unstable structure, the hybrid resulting from attack at *ortho* and *para* positions are more unstable than the carbocation formed during the attack at *meta* position and since the stable carbocation is formed faster, it follows that the electron-attracting or deactivating group is *meta* directing. The above facts are depicted in the following structures.

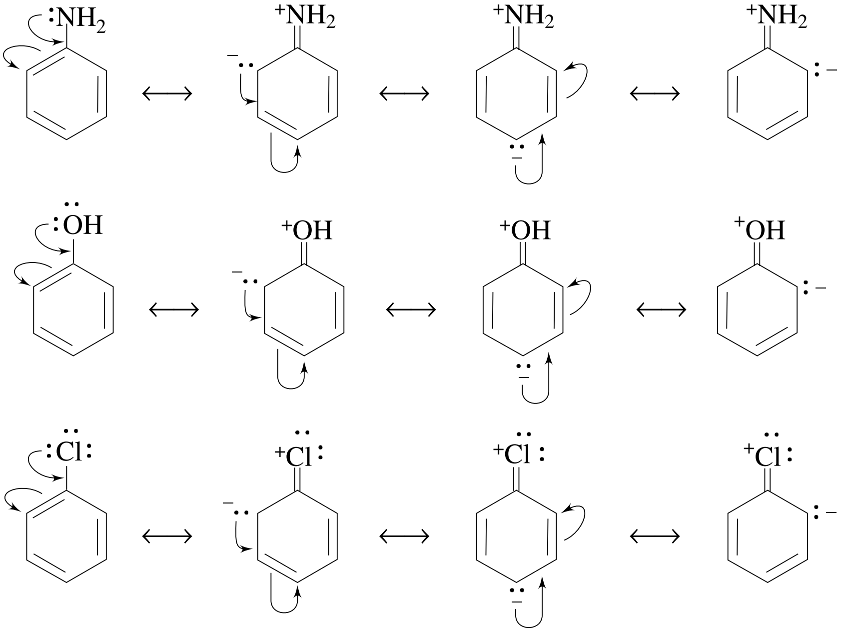
Para attack





Activation of Benzene via Resonance

The groups —NH_2, —OH, and —Cl can activate benzene ring. This is shown in the following structures.



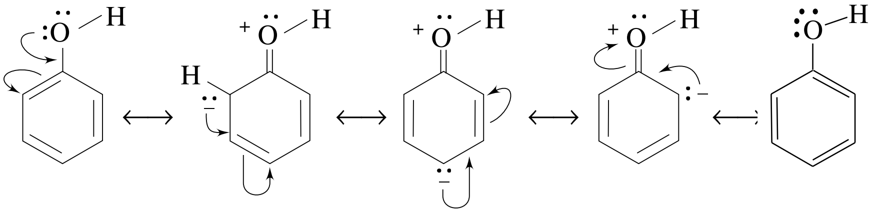
For —NH_2 and —OH, the resonance effect is much more important than the inductive effect. In the former benzene is activated whereas in the latter, it is deactivated. In —Cl, both the resonance and inductive effects are evenly matched. It is because of this that —Cl occupies the unusual position of being deactivating group but *ortho* and *para* director.

Effect of Activating and Deactivating Groups on Weak Organic Acids and Bases

(a) *Benzoic acid* If an electron-releasing group is present at the *para* position (where resonance effect outweighs the inductive effect) of the —COOH group, the tendency to release proton from —COOH group is decreased making such a substituted benzoic acid weaker than benzoic acid itself. For example, *p*-toluic acid, *p*-hydroxybenzoic acid and *p*-anthranilic acid are weaker than benzoic acid. On the other hand, if such a group is present at the *meta* position (where inductive effect outweights the resonance effect), the electron-withdrawing tendency of the group makes the *meta* substituted acid stronger than benzoic acid.

The presence of electron-withdrawing group present at *para* position also makes the substituted benzoic acid more strong than benzoic acid itself. For example, *p*-nitrobenzoic acid is a stronger acid than benzoic acid itself.

(b) *Phenol* Phenol is a weaker acid. This is because of the resonating structures in which oxygen atom acquires positive charge making removal of proton from —OH group more easily.



The electron-withdrawing group present at the *para* or *meta* position makes oxygen atom more positive and thus helps in releasing the proton and thus such a substituted phenol is more acidic than phenol itself. For example, *p*-nitrophenol is more acidic than phenol. On the other hand, electron-releasing group at the *para* position (where resonance effect outweights inductive effect) decreases the positive charge on oxygen making the release of proton more difficult. For example, *p*-cresol is less acidic than phenol.

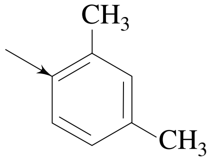
Ortho-substituted acids and phenols do not fit into the pattern set by their *meta* and *para* isomers. Nearly all *ortho* substitutents exert an effect of the same kind—acid strengthening—whether they are electron-withdrawing or electron-releasing, and the effect is a unusually large. The *ortho* effect undoubtedly has to do with the nearness of the groups involved, but is more than just steric hindrance arising from their bulk.

(c) *Aniline* Aniline is a weaker base. It is a Lewis base, i.e. the lone pair present on nitrogen can be given to the Lewis acids. The electron-releasing group present at the *para* position increases the electron density on nitrogen and thus makes it more basic. For example, *para*-toluidine is more basic than aniline. On the other hand, the presence of electron-withdrawing group decreases the electron density on nitrogen and hence makes it less basic. For example, *p*-nitroaniline is less basic than aniline.

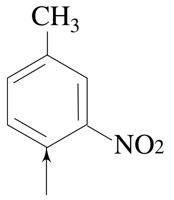
RULES FOR PREDICTING ORIENTATION IN DISUBSTITUTED BENZENES

The following rules are followed.

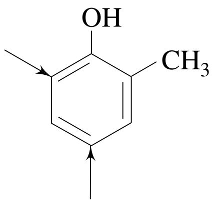
1. If the groups reinforce each other, there is no problem.
   For example,

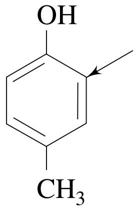


2. If an *ortho-para* director and *meta* director are not reinforcing, the *ortho-para* director *controls* the orientation. The incoming group goes mainly to *ortho* to the *meta* director. For example,

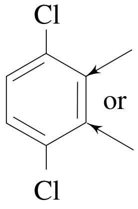


3. A strongly activating group, competing with a weakly activating group, controls the orientation. For example,

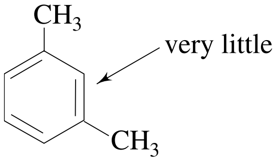




4. When two weakly (or strongly) activating or deactivating groups compete, substantial amounts of both isomers are obtained for example,



5. Very little substitution occurs in the sterically hindered position between *meta* substituents.

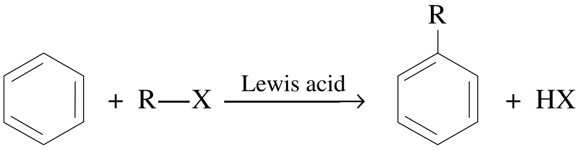


ARENES (AROMATIC-ALIPHATIC HYDROCARBONS)

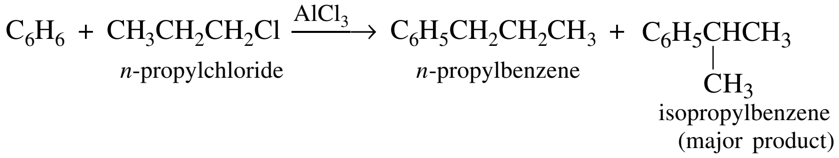
Arenes contain both aliphatic and aromatic units. Examples include ethylbenzene, toluene, xylenes and ethyl toluenes. These compounds show two sets of chemical properties: aromatic ring shows electrophilic substitution and side chain undergoes free radical substitution. Each portion of the molecule affects the reactivity of the other portion and determines the orientation of attack.

Alkyl benzenes can be prepared in one of the following two ways.

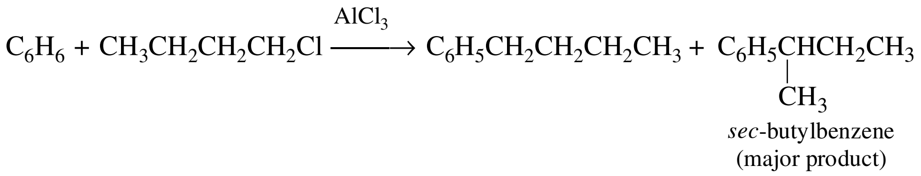
1. *Friedel-Crafts Alkylation*



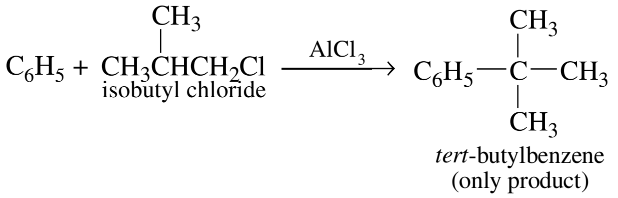
The intermediate electrophilic is carbocation, it may undergo rearrangement so as to give more stable carbocation. For example,



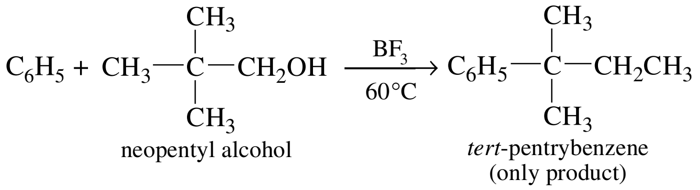
$$C_6H_6 + \underset{n\text{-propylchloride}}{CH_3CH_2CH_2Cl} \xrightarrow{AlCl_3} \underset{n\text{-propylbenzene}}{C_6H_5CH_2CH_2CH_3} + \underset{\substack{\text{isopropylbenzene}\\ \text{(major product)}}}{C_6H_5\underset{\underset{CH_3}{|}}{C}HCH_3}$$



$$C_6H_6 + CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_2CH_3 + \underset{\substack{sec\text{-butylbenzene}\\ \text{(major product)}}}{C_6H_5\underset{\underset{CH_3}{|}}{C}HCH_2CH_3}$$

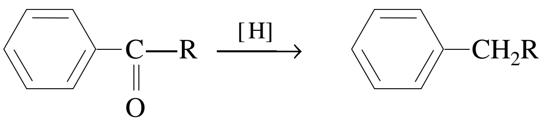


$$C_6H_5 + \underset{\text{isobutyl chloride}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2Cl} \xrightarrow{AlCl_3} \underset{\substack{tert\text{-butylbenzene}\\ \text{(only product)}}}{C_6H_5—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3}$$



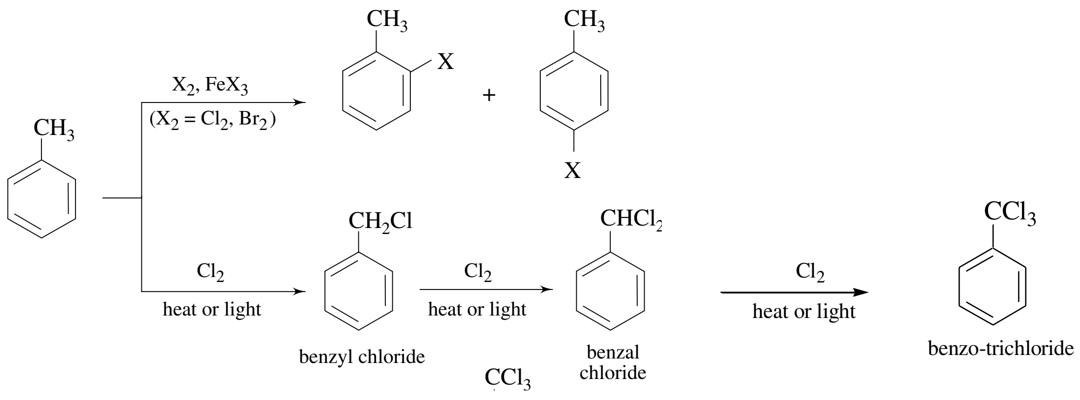
$$C_6H_5 + \underset{\text{neopentyl alcohol}}{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2OH} \xrightarrow[60°C]{BF_3} \underset{\substack{tert\text{-pentrybenzene}\\ \text{(only product)}}}{C_6H_5—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2CH_3}$$

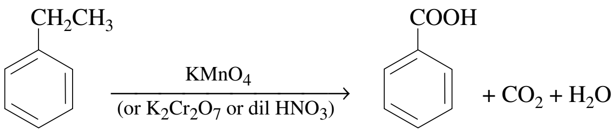
2. *Conservation of Side Chain*



Amalgamated zinc and HCl (Clemmensen reduction) or hydrazine and strong base (Wolff-Kishner reduction) may be used for reduction.

Reactions shown by alkyl benzenes are electrophilic substitution on the ring and free radical substitution at the side alkyl group. For example,

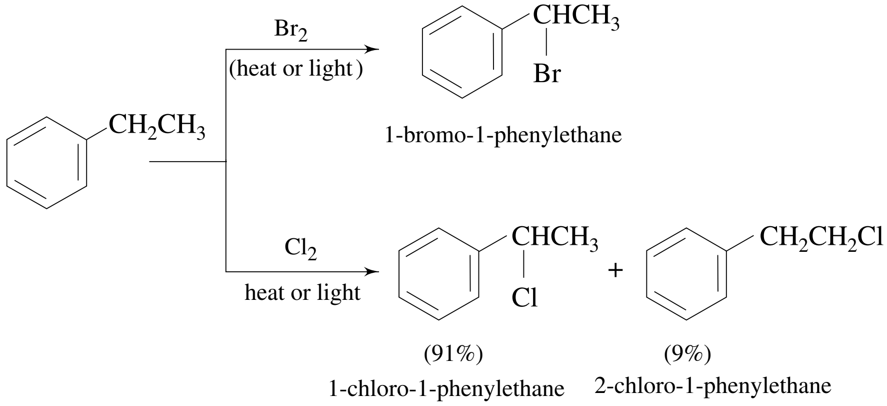




In the side chain halogenation, ease of abstraction of hydrogen atom is as follows.

$$\begin{matrix}\text{allylic}\\ \text{benzylic}\end{matrix} > 3° > 2° > 1° > CH_4 > \text{vinylic}$$

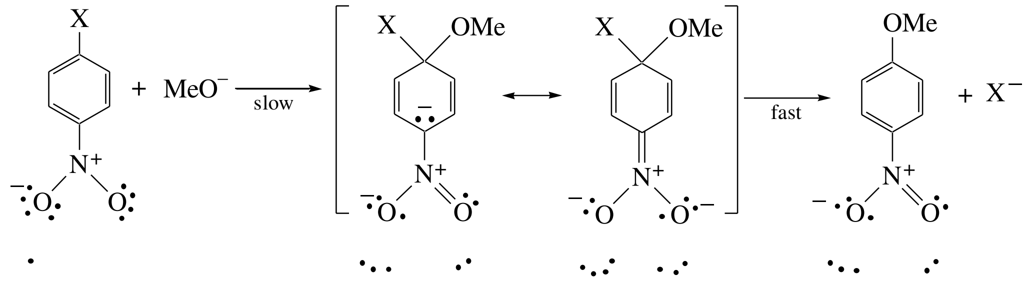
The benzylic hydrogen is the hydrogen atom attached to carbon joined directly to an aromatic ring. The ease of formation of free radicals and stability of free radicals are also the same as shown above. For example, the halogenation of ethylbenzene is as follows.



NUCLEOPHILIC AROMATIC SUBSTITUTION

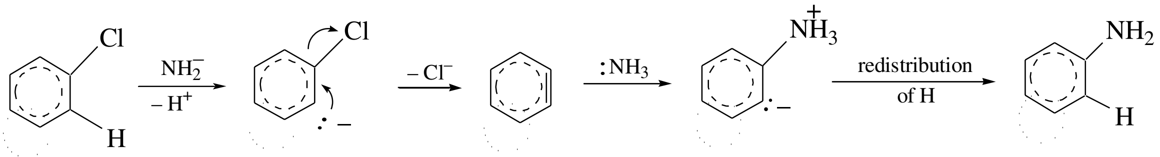
A good leaving group such as halides is displaced from the benzene ring especially when electron-attracting substituents (such as —NO_2 and —C≡N) are present at *ortho* and/or *para* positions to the C bearing halogen. The larger the number of electron-attracting substituents, the more rapid the displacement with less vigorous experimental conditions.

The reaction proceed via *addition-elimination mechanism* in nucleophile is attached to C bearing halogen in a slow rate-determining step followed by the rapid removal of halide ion.



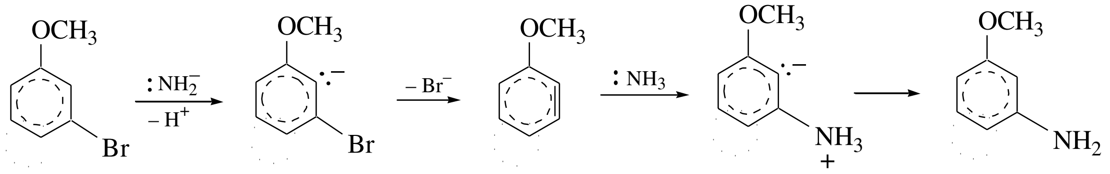
The order of reactivity is ArF >> ArCl, ArBr > ArI.

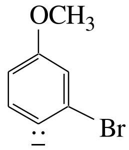
The nucleophilic aromatic substitution also occurs via *elimination-addition mechanism* in which a strong base NH_2^- (from $K^+NH_2^-$ in liquid NH_3) abstracts H^+ from the *ortho* position to the halogen to give a high energy carbanion. The latter ejects X^- to give a triple-bonded benzyne. This is followed by the addition of nucleophilic solvent which on redistribution of H gives the final substituted product.



Note: NH_3 can attack at either end of triple bond.

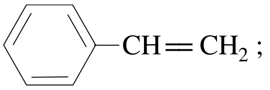
In a species such as *m*-$CH_3OC_6H_4Br$, the negative charge of the carbanion is better stabilized if it occupies *ortho* position to the electron-withdrawing —OCH_3 group.



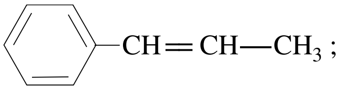
The carbanion  is less stable and is not formed in the reaction.

ALKENYL BENZENES

Alkenyl benzenes contain a double bond in the side chain of benzene ring. For example,

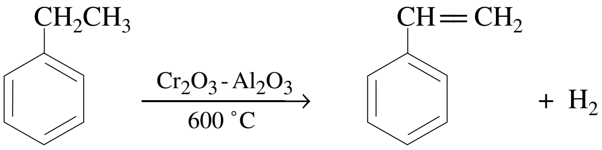


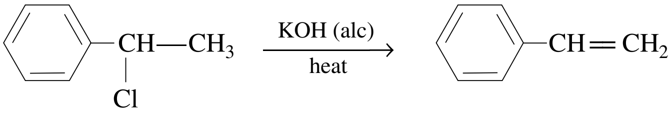
styrene

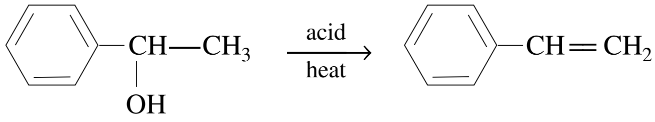


1-phenylpropene

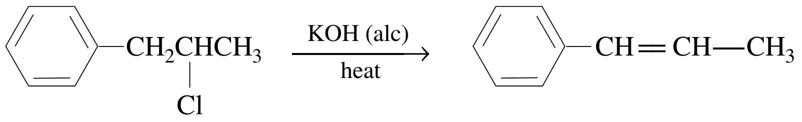
These compounds may be prepared by dehydrogenation, dehydrohalogenation and dehydration of the side chain. For example,



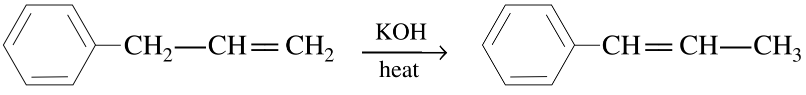




Dehydrohalogenation and dehydration proceeds in accordance with Saytzeff's rule. For example, dehydrohalogenation of 1-phenyl-2-chloro-propane produces 1-phenylpropene and not 3-phenylpropene, i.e.



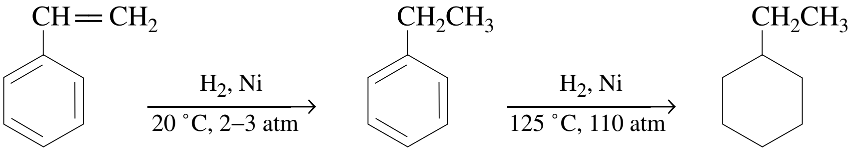
The fact that 1-phenylpropene is more stable than 3-phenylpropene is shown by the following reaction which takes place quite rapidly.



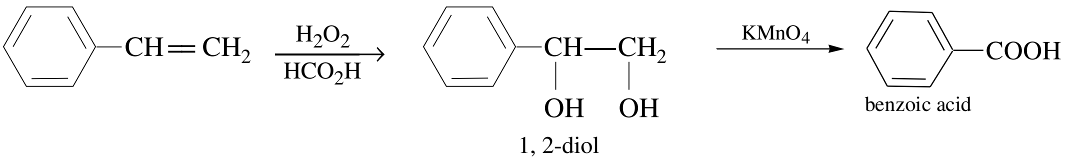
3-phenylpropene 1-phenylpropene

This is primarily due to the fact that double bond in conjugation with benzene ring is more stable than the corresponding unconjugated system.

Alkenylbenzenes show both substitution in the ring and addition to the double bond in the side chain. The reactivity of the double bond is greater than the benzene towards electrophilic reagents. Thus, mild conditions are required for the addition reaction across the double bond as compared to those required for the benzene ring. For example,



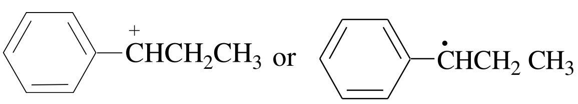
styrene ethylbenzene ethylcyclohexane



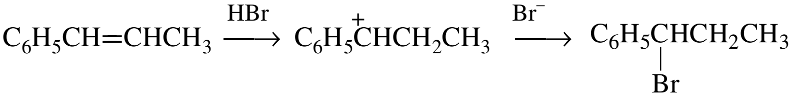
The first step in any addition reaction is the formation of carbocation or free radical.

$$\text{Reactant} \longrightarrow \begin{bmatrix}\text{Carbocation}\\ \text{or}\\ \text{free radical}\end{bmatrix} \longrightarrow \text{Product}$$

The more stability of benzyl cation or radical

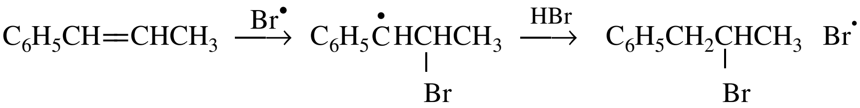


relative to the conjugated alkenylbenzene makes the latter more reactive than simple alkenes. Also more stability of benzyl cation or radical relative to other possibilities, such as $C_6H_5CH_2\overset{+}{C}HCH_3$ and $C_6H_5CH_2CH_2\overset{+}{C}H_2$, determines the nature of final product. For example,



$$C_6H_5CH{=}CHCH_3 \xrightarrow{HBr} C_6H_5\overset{+}{C}HCH_2CH_3 \xrightarrow{Br^-} C_6H_5\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$$

In the presence of peroxides, the reaction taking place is



$$C_6H_5CH{=}CHCH_3 \xrightarrow{Br^\bullet} C_6H_5\overset{\bullet}{C}H\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{HBr} C_6H_5CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3\ \ Br^\bullet$$

Straight Objective Type

General Characteristics

1. The number of disubstituted products of benzene is

(a) 2 (b) 3 (c) 4 (d) 5

2. Which of the following is the benzo group?

(a) $C_6H_5CH_2—$ (b) $C_6H_5\overset{|}{C}H—$ (c) $(C_6H_5)_2CH—$ (d) $C_6H_5—\underset{|}{\overset{|}{C}}—$

3. Which of the following is the benzal group?

(a) $C_6H_5CH_2—$ (b) $(C_6H_5)_2CH—$ (c) $(C_6H_5)_3C—$ (d) $C_6H_5\overset{|}{C}H—$

4. Which of the following is the trityl group?

(a) $C_6H_5CH_2—$ (b) $(C_6H_5)_2CH—$ (c) $(C_6H_5)_3C—$ (d) $C_6H_5\overset{|}{C}H—$

5. Which of the following is the benzhydryl group?

(a) $C_6H_5CH_2—$ (b) $(C_6H_5)_2CH—$ (c) $(C_6H_5)_3C—$ (d) $C_6H_5\,\overset{|}{C}H—$

6. Which of the following is the benzyl group?

(a) $C_6H_5CH_2—$ (b) $(C_6H_5)_2CH—$ (c) $(C_6H_5)_3C—$ (d) $C_6H_5\overset{|}{C}H—$

7. Which of the following is the styryl group?

(a) $C_6H_5\,\underset{|}{C}HCH_3$ (b) $C_6H_5CH_2CH_2—$ (c) $C_6H_5CH{=}CH—$ (d) $C_6H_5CH{=}CHCH_2—$

8. Which of the following is the cinnamyl group?

(a) $C_6H_5\,\underset{|}{C}HCH_3$ (b) $C_6H_5CH_2CH_2—$ (c) $C_6H_5CH{=}CH—$ (d) $C_6H_5CH{=}CHCH_2—$

9. Which of the following species is the smallest aromatic substance?

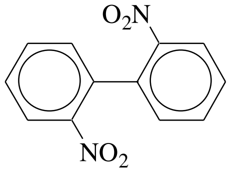
(a) cyclopropenyl cation (b) cyclobutadiene (c) cyclopentadiene (d) benzene

10. Which of the following does not have aromatic characteristics?

(a) cycloheptatriene (b) cyclopentadienyl anion

(c) cyclopropenyl cation (d) Azulene ($C_{10}H_8$)

11. The heating of o-$O_2NC_6H_4I$ with Cu gives

(a) o-$O_2NC_6H_5$ (b) C_6H_4I (c)  (d) C_6H_6

12. The compound that is not a Lewis acid is

(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$ (1985)

13. Arrange the following compounds in order of increasing dipole moment.

Toluene (I); m-dichlorobenzene (II); o-dichlorobenzene (III); p-dichlorobenzene (IV)

(a) I < IV < II < III (b) IV < I < II < III (c) IV < I < III < II (d) IV < II < I < III

(1997)

Electrophilic Substitution

14. Among the following, the compound that can be most readily sulphonated is

(a) benzene (b) nitrobenzene (c) toluene (d) chlorobenzene (1982)

15. The compound that is most reactive towards electrophilic nitration is

(a) toluene (b) benzene (c) benzoic acid (d) nitrobenzene (1985)

16. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly

(a) benzoyl chloride (b) m-chlorotoluene (c) benzyl chloride (d) o- and p-chlorotoluene

(1986)

17. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives
(a) *o*-cresol (b) *p*-cresol (c) 2,4-dihydroxytoluene (d) benzoic acid (1990)

18. The electrophile in aromatic nitration is
(a) nitronium ion (b) nitrinium ion (c) nitrite ion (d) nitrate ion

19. The direct iodination of benzene is not possible because
(a) iodine is an oxidizing agent (b) resulting C_6H_5I is reduced to C_6H_6 by HI
(c) HI is unstable (d) the ring gets deactivated

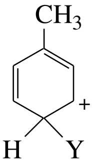
20. Amongst the following, the compound that can be most difficult to sulphonate is
(a) benzene (b) nitrobenzene (c) toluene (d) chlorobenzene

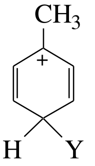
21. Amongst the following, the moderately activating group is
(a) —NHR (b) —$NHCOCH_3$ (c) —NR_2 (d) —CH_3

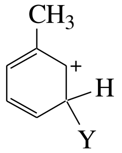
22. Amongst the following, the weakly activating group is
(a) —NH_2 (b) —NR_2 (c) —C_6H_5 (d) —$NHCOCH_3$

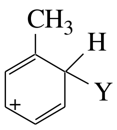
23. An activating group
(a) activates only *ortho* and *para* positions (b) deactivates *meta* position
(c) activates *ortho* and *para* more than *meta* (d) deactivates *meta* more than *ortho* and *para*

24. Which of the following carbocations is expected to be most stable?

(a) 

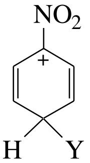
(b) 

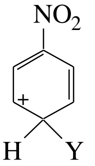
(c) 

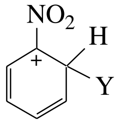
(d) 

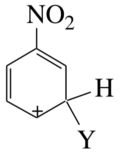
25. A deactivating group
(a) decativates only *ortho* and *para* positions (b) deactivates *meta* position
(c) deactivates *ortho* and *para* more than *meta* (d) deactivates *meta* more than *ortho* and *para*

26. Which of the following carbocations is expected to be most stable?

(a) 

(b) 

(c) 

(d) 

27. In aniline, the —NH_2 group
(a) activates the benzene ring via both inductive and resonance effects
(b) deactivates the benzene ring via both inductive and resonance effects
(c) activates the benzene ring via resonance effect and deactivates it via inductive effect
(d) activates the benzene ring via inductive effect and deactivates it via resonance effect

28. In chlorobenzene, the —Cl group
(a) activates the benzene ring more via resonance effect than deactivating it via inductive effect
(b) deactivates the benzene ring more via inductive effect than activating it via resonance effect
(c) activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effects are evenly matched
(d) is a net deactivating group with *meta* director characteristics

29. The reaction of toluene with chlorine in the presence of light gives
(a) benzoyl chloride (b) benzyl chloride (c) *o*- and *p*-chlorotoluene (d) *m*-chlorotoluene

30. The main reaction -product when toluene is treated with concentrated HNO_3 in the presence of concentrated H_2SO_4 is
(a) 2, 4, 6-trinitrotoluene (b) 2, 4-dinitrotoluene (c) *p*-nitrotoluene (d) *m*-nitrotoluene

31. The treatment of benzene with benzoyl chloride in the presence of $AlCl_3$ gives
(a) benzaldehyde (b) benzophenone (c) diphenyl (d) cyclohexane

32. In the Friedel-Crafts acylation, the electrophile is
(a) $C_6H_5^+$ (b) $AlCl_3^-$ (c) CH_3CO^+ (d) $C_6H_5CH_2^+$

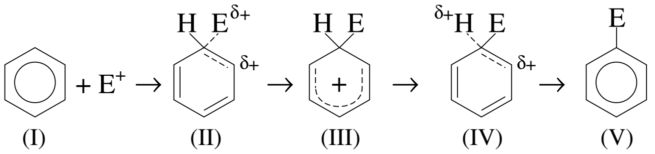
33. The correct sequence of activating power of a group in benzene is
(a) $—NH_2 > —NHCOCH_3 > —CH_3$ (b) $—NH_2 < —NHCOCH_3 < —CH_3$
(c) $—NH_2 > —NHCOCH_3 < —CH_3$ (d) $—NH < —NHCOCH_3 > —CH_3$

34. 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 (1997)

35. 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. (1997)

36. 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 (1998)

37. Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction?



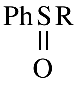
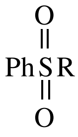
(a) Species (II) (b) Species (III) (c) Species (IV) (d) Species (V)

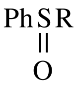
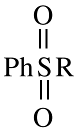
38. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?
(a) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (b) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$ (c) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (d) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

39. For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?
(a) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (b) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$ (c) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (d) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

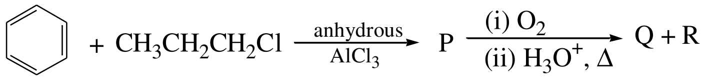
40. Which of the following sequences regarding the rate of halogenation is correct?
(a) Fluorination > chlorination > bromination (b) Fluorination < chlorination < bromination
(c) Fluorination < chlorination > bromination (d) Fluorination > chlorination < bromination

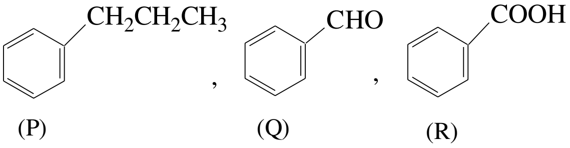
41. Which of the following sequences regarding activating effects of the given *o*, *p*-directors is correct?
(a) $—O^- < —OH < —OCOCH_3$ (b) $—O^- > —OH > —OCOCH_3$
(c) $—O^- > —OH < —OCOCH_3$ (d) $—O^- < —OH > —OCOCH_3$

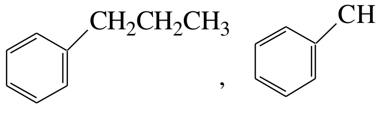
42. Of the species PhSH,  $\mathrm{Ph}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}\mathrm{R}$ and  $\mathrm{Ph}\overset{\underset{\|}{\mathrm{O}}}{\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}}\mathrm{R}$, the *meta*-substituted product is obtained from

(a) PhSR (b)  $\mathrm{Ph}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}\mathrm{R}$ (c)  $\mathrm{Ph}\overset{\underset{\|}{\mathrm{O}}}{\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}}\mathrm{R}$ (d) none of the species

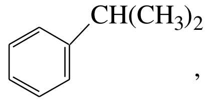
43. Identify the major products P, Q and R in the following reaction.

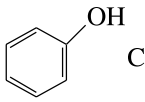


(a) 

(b) 

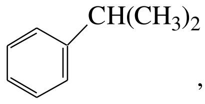
CH_3CH_2OH
(R)

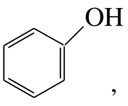
(c) 

, 

CH_3COCH_3

(P) (Q) (R)

(d) 

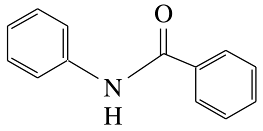
, 

, $CH_3CH(OH)CH_3$

(P) (Q) (R)

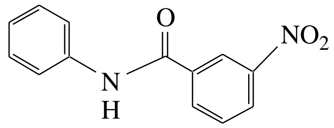
(2006)

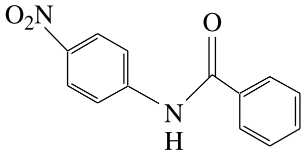
44. In the following reaction,

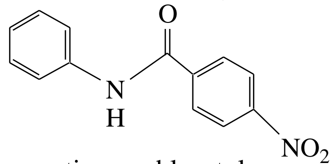


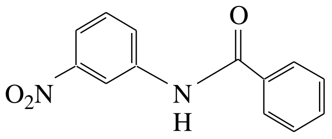
$\xrightarrow[\text{conc.H}_2\text{SO}_4]{\text{conc.HNO}_3}$

the structure of the major product ‘X’ is

(a) 

(b) 

(c) 

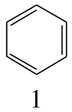
(d) 

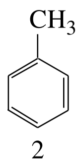
(2007)

45. In the reaction *p*-chlorotoluene with KNH_2 in liq. NH_3, the major product is:

(a) *o*-toluidine (b) *m*-toluidine (c) *p*-toluidine (d) *p*-chloroaniline. (1997)

46. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:


1



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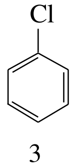
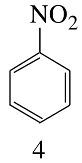
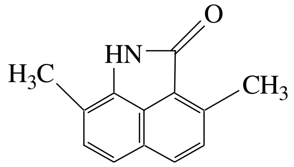


3

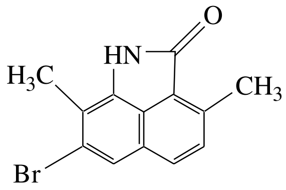


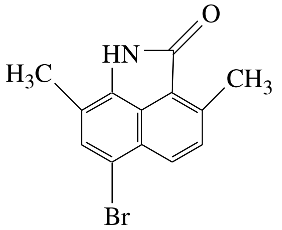
4

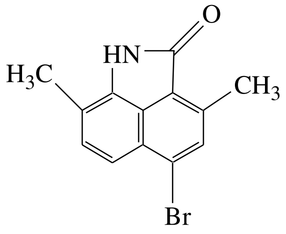
(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1 (c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4 (2002)

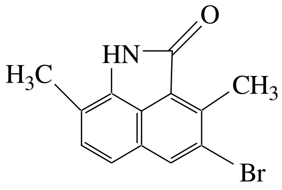
47. The major product obtained when Br_2/Fe is treated with


is

(a) 

(b) 

(c) 

(d) 

(2004)

48. The oxidation of 1-nitronaphthalene and α-naphthylamine results, respectively, into

(a) Phthalic acid and 3-nitrophthalicm acid (b) Phthalic acid and phthalic acid

(c) 3-nitrophthalic acid and phthalic acid (d) 3-nitrophthalic acid and 3-nitrophthalic acid

49. The oxidation of naphthalene with (i) CrO_3/acetic acid and (ii) O_2/V_2O_5, heat results, respectively, into

(a) Phthalic acid and phthalic acid (b) Phthalic acid and 1, 4-naphthaquinone

(c) 1,4-Naphthaquinone and 1,4-naphthaquinone (d) 1,4-naphthaquinone and phthalic acid

50. The sulphonation of toluene at 100 °C produces

(a) more of *ortho*-product than *para*-product

(b) more of *para*-product than *ortho*-product

(c) 50% each of *ortho*- and *para*-products

(d) 66% of *ortho*- and 33% *para*- product since there are two *ortho*-positions and one *para*-position.

51. The mononitration of Ph—Ph produces

(a) *o*-$O_2NC_6H_4$Ph as the major product (b) *p*-$O_2NC_6H_4$Ph as the major product

(c) *m*-$O_2NC_6H_4$Ph as the major product (d) 50% each of *o*-$O_2NC_6H_4$Ph and *p*-$O_2NC_6H_4$Ph

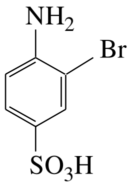
52. The relative reactivity of *p*-nitrochlorobenzene (X), chlorobenzene (Y) and 2,4-dinitrochlorobenzene (Z), with electrophilic reagent E^+ is

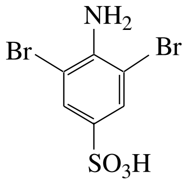
(a) $X > Y > Z$ (b) $X > Z > Y$ (c) $Y > X > Z$ (d) $Y > Z > X$

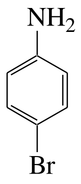
53. The relative reactivity of acetanilide (X), aniline (Y) and acetophenone (Z) with electrophilic reagent E^+ is

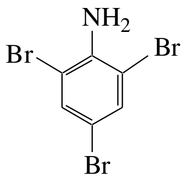
(a) $X > Y > Z$ (b) $X > Z > Y$ (c) $Y > X > Z$ (d) $Y > Z > X$

54. The treatment of *p*-$H_2NC_6H_4SO_3H$ with bromine in water gives

(a) 

(b) 

(c) 

(d) 

55. The order of relative reactivity of the given halides towards S_N1 reaction is

(a) benzylchloride > *p*-methoxybenzylchloride > *p*-nitrobenzylchloride

(b) *p*-methoxylbenzylchloride > benzylchloride > *p*-nitrobenzylchloride

(c) *p*-methoxybenzylchloride > *p*-nitrobenzylchloride > benzylchloride

(d) benzylchloride > *p*-nitrobenzylchloride > *p*-methoxybenzylchloride

56. The order of relative reactivity of the given halides towards S_N1 reaction is

(a) $PhCH_2Cl > PhCHClCH_3 > PhCCl(CH_3)_2$ (b) $PhCH_2Cl < PhCHClCH_3 < PhCCl(CH_3)_2$

(c) $PhCH_2Cl > PhCCl(CH_3)_2 > PhCHClCH_3$ (d) $PhCCl(CH_3)_2 > PhCH_2Cl > PhCHClCH_3$

57. The order of relative reactivity of the given halides toward S_N2 reaction is

(a) $PhCH_2Cl > PhCHCl(CH_3) > PhCCl(CH_3)_2$ (b) $PhCH_2Cl < PhCHCl(CH_3) < PhCCl(CH_3)_2$

(c) $PhCHCl(CH_3) > PhCH_2Cl > PhCCl(CH_3)_2$ (d) $PhCHCl(CH_3) > PhCCl(CH_3)_2 > PhCH_2Cl$

58. The treatment of $PhCH{=}CHCH_2CH_3$ with (i) HBr and (ii) HBr in the presence of peroxide, respectively, give

(a) $PhCH_2CH(Br)CH_2CH_3$ and $PhCH(Br)CH_2CH_2CH_3$

(b) $PhCH(Br)CH_2CH_2CH_3$ and $PhCH_2CH(Br)CH_2CH_3$

(c) $PhCH_2CH(Br)CH_2CH_3$ and $PhCH_2CH(Br)CH_2CH_3$

(d) $PhCH(Br)CH_2CH_2CH_3$ and $PhCH(Br)CH_2CH_2CH_3$

59. The correct order of reactivity of PhMe(A), $PhNMe_2$(B) and $PhN(Me)_3^+$ (c) towards electrophilic substitution is

(a) $B > A > C$ (b) $B > C > A$ (c) $C > A > B$ (d) $C > B > A$

60. Silver nitrate is added to each of 7-bromo-1,3,5-cycloheptatriene (A) and 5-bromo-1, 3-cyclopentadiene(B). It is observed that

(a) both A and B give AgBr precipitation

(b) both A and B do not give AgBr precipitation

(c) A gives AgBr precipitation while B does not give AgBr precipitation

(d) A does not give AgBr precipitation while B forms AgBr precipitation.

Acid-Base Strengthening

61. Which of the following order regarding the acidity of aromatic acids is correct?
(a) benzoic acid < *p*-toluic acid < *p*-hydroxybenzoic acid
(b) benzoic acid > *p*-toluic acid > *p*-hydroxybenzoic acid
(c) benzoic acid > *p*-toluic acid < *p*-hydroxybenzoic acid
(d) benzoic acid < *p*-toluic acid > *p*-hydroxybenzoic acid

62. Which of the followng orders regarding the acidity of aromatic acids is correct?
(a) *p*-nitrobenzoic acid < benzoic acid < *p*-anthranilic acid
(b) *p*-nitrobenzoic acid > benzoic acid > *p*-anthranilic acid
(c) *p*-nitrobenzoic acid > benzoic acid < *p*-anthranilic acid
(d) *p*-nitrobenzoic acid < benzoic acid > *p*-anthranilic acid

63. Which of the following orders regarding the basic strength of aromatic bases is correct?
(a) *p*-nitroaniline > aniline > *p*-toluidine (b) *p*-nitroaniline < aniline < *p*-toluidine
(c) *p*-nitroaniline < aniline > *p*-toluidine (d) *p*-nitroaniline > aniline < *p*-toludine

64. Which of the following orders regarding the acid strength of aromatic acids is correct?
(a) *p*-hydroxybenzoic acid < *p*-methoxybenzoic acid < *p*-toluic acid
(b) *p*-hydroxybenzoic acid > *p*-methoxybenzoic acid > *p*-toluic acid
(c) *p*-hydroxybenzoic acid < *p*-methoxybenzoic acid > *p*-toluic acid
(d) *p*-hydroxybenzoic acid > *p*-methoxybenzoic acid < *p*-toluic acid

65. Which of the following orders regarding the acid strength of aromatic acids is correct?
(a) *p*-nitrobenzoic acid < *p*-cyanobenzoic acid < *p*-chlorobenzoic acid
(b) *p*-nitrobenzoic acid > *p*-cyanobenzoic acid > *p*-chlorobenzoic acid
(c) *p*-nitrobenzoic acid < *p*-cyanobenzoic acid > *p*-chlorobenzoic acid
(d) *p*-nitrobenzoic acid > *p*-cyanobenzoic acid < *p*-chlorobenzoic acid

66. Which of the following orders regarding the basic strength of aromatic bases is correct
(a) *p*-methylaniline > *p*-methoxyaniline > *p*-aminoaniline
(b) *p*-methylaniline < *p*-methoxyaniline < *p*-aminoaniline
(c) *p*-methylaniline > *p*-methoxyaniline < *p*-aminoaniline
(d) *p*-methylaniline < *p*-methoxyaniline > *p*-aminoaniline

67. Which of the following orders regarding the basic strength of aromatic bases is correct?
(a) *p*-nitroaniline > *p*-cyanoaniline > *p*- chloroaniline (b) *p*-nitroaniline < *p*-cyanoaniline < *p*-methylaniline
(c) *p*-nitroaniline > *p*-cyanoaniline < *p*-methylaniline (d) *p*-nitroaniline < *p*-cyanoaniline > *p*-methylaniline

68. Which of the following orders regarding the acid strength of phenol is correct?
(a) *p*-aminophenol < *p*-chlorophenol < *p*-nitrophenol (b) *p*-aminophenol > *p*-chlorophenol > *p*-nitrophenol
(c) *p*-aminophenol < *p*-chlorophenol > *p*-nitrophenol (d) *p*-aminophenol > *p*-chlorophenol < *p*-nitrophenol

Multiple Correct Choice Type

1. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are
(a) The electron density on *meta* carbon is more than that on *ortho* and *para* positions.
(b) The intermediate carbonium ion formed after initial attack of Br^+ at the *meta* position is least destabilised
(c) Loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position
(d) Easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* positions (1992)

2. Which of the following groups in aromatic compounds is/are electron releasing group(s)?
(a) $—CH_3$ (b) $—N^+H_3$ (c) $—NO_2$ (d) $—OCH_3$

3. The substance(s) that can be used as a catalyst for the following reaction

$$CH_2{=}CH_2 + C_6H_6 \longrightarrow C_6H_5CH_2CH_3$$

is/are
(a) BF_3 (b) NH_3 (c) $SnCl_4$ (d) $ZnCl_2$

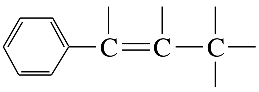
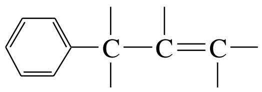
4. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer is:
  - (a) Electron density at *meta* carbon position is more than that at *ortho* and *para* positions.
  - (b) The intermediate carbonium ion formed after an initial attack of Br^+ at the *meta* position is least destabilised.
  - (c) There is loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position.
  - (d) It is easier to remove H^+ from the *meta* position to regain aromaticity than from *ortho* and *para* positions.

5. Which of the following statements are **not** correct?
  - (a) Although benzene contains three double bonds, normally it does not undergo addition reaction.
  - (b) *m*-chlorobromobenzene is an isomer of *m*-bromochlorobenzene.
  - (c) In benzene, carbon uses all the three *p* orbitals for hybridization.
  - (d) An electron donating substitutent in benzene orients the incoming electrophilic group to the *meta* position.

6. Which of the following statements are correct?
  - (a) Heats of hydrogenation and combustion of benzene are lower than the expected values.
  - (b) Benzene undergoes nucleophilic substitution reactions.
  - (c) For a molecule to be aromatic, it must contain $4n+2$ delocalized π electronic cyclic cloud above and below the plane of the molecule.
  - (d) Cycloheptatrienyl cation has unusually low stability.

7. Which of the following statements are correct?
  - (a) No organic molecule other than benzene has a molecular formula of C_6H_6.
  - (b) The electrophile in the sulphonation of aromatic molecule may be either SO_3 or HSO_3^+.
  - (c) In Friedel-Crafts alkylation the electrophile is a carbocation.
  - (d) In Friedel-Crafts alkylation, $AlCl_3$ acts as a Lewis base.

8. Which of the following statements are correct?
  - (a) A substituent which stabilises the intermediate carbocation in the electrophilic substitution in benzene activates the latter.
  - (b) An activating group activates only *ortho* and *para* positions in benzene ring.
  - (c) A deactivating group deactivates *ortho* and *para* positions whereas the *meta* position is activated.
  - (d) Benzene in the presence of $AlCl_3$ reacts with isobutyl bromide to give *tert*-butylbenzene.

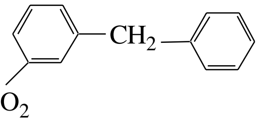
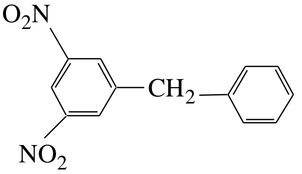
9. Which of the following statements are **not** correct?
  - (a) The monobromination of acetanilide proceeds slower than benzene.
  - (b) The monobromination of acetophenone proceeds faster than benzene.
  - (c) The reduction of —CO— group into —CH_2— group may be carried out via Clemmensen reduction which involves the use of hydrazine and strong base.
  - (d) The structure  is less stable than 

10. Which of the following statements are **not** correct?
  - (a) Benzene readily docolourises dilute $KMnO_4$ solution.
  - (b) The inductive effect is the only factor which decides the orientation effects in the monosubstituted benzene.
  - (c) The number of isomers of aromatic compound tribromobenzene is four.
  - (d) The dipole moment of *p*-nitrotoluene is expected to be larger than *p*-chloronitrobenzene.

11. Which of the following statements are **not** correct?
  - (a) The principal mononitration product of *o*-cresol is 2-methyl-4-nitrophenol.
  - (b) The carbon-hydrogen homolytic bond dissociation energy for benzene is considerable smaller than for cyclohexane.
  - (c) The number of isomers of mononitration of *o*-dichlorobenzene is 4.
  - (d) A tribromobenzene gives two isomers when it is mononitrated. The compound is 1,2,4-tribromobenzene.

12. Which of the following statements are **not** correct?

(a) Monobromination of *p*-toluenesulphonic acid followed by treatment with acid and superheated steam gives *m*-bromotoluene.

(b) The mononitration of  gives the product 

(c) The reactivity towards ring nitration of 2,4-dinitrotoluene is greater than that of *m*-dinitrobenzene.

(d) The reactivity towards ring nitration of 2,4-dinitrophenol is smaller than that of 2,4-dinitrochlorobenzene.

13. Which of the following statements are correct?

(a) The order of reactivity towards ring nitration is *p*-xylene > toluene > *p*-toluic acid > terephthalic acid

(b) The order of reactivity towards ring nitration is $Ph(CH_2)_2NO_2 > PhCH_2NO_2 > PhNO_2$

(c) The order of reactivity towards electrophilic substitution is

$$C_6H_5CH_3 < C_6H_5CH_2COOC_2H_5 < C_6H_5CH(COOC_2H_5)_2$$

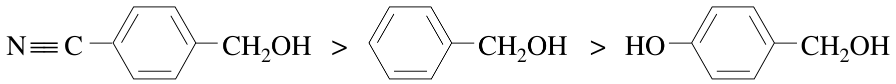
(d) Each ring of biphenyl, $C_6H_5—C_6H_5$, is more reactive than benzene towards electrophilic substitution, and the chief products are *ortho* and *para* isomers.

14. Which of the following statements are correct?

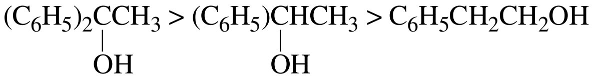
(a) In benzyl radical, the two side chain hydrogens are perpendicular to the benzene ring.

(b) The order of acidity in the following compounds is triphenylmethane > diphenylmethane > toluene

(c) The order of reactivity toward aqueous HBr in the following alcohols is



(d) The order of ease of dehydration in the following compound is



$$\underset{\text{OH}}{(C_6H_5)_2\overset{|}{C}CH_3} > \underset{\text{OH}}{(C_6H_5)\overset{|}{C}HCH_3} > C_6H_5CH_2CH_2OH$$

15. Which of the following statements are correct?

(a) In electrophilic aromatic substitution reaction, the formation of intermediate arenium cation is the rate-determining step.

(b) The C—H bond in benzene is slightly stronger than the C—D bond in deuterated benzene (C_6D_6).

(c) The overall rate of an electrophilic substitution reaction, except sulphonation in benzene and deuterated benzene, are identical.

(d) The sulphonation reaction involving benzene is a reversible reaction.

16. Which of the following statements are correct?

(a) All electrophilic substitution reactions except sulphonation involving benzene are irreversible.

(b) The rates of sulphonation reactions involving benzene and deuterated benzene are slightly different.

(c) Iodine solution in benzene is brown due to the formation of charge-transfer complex between iodine and benzene.

(d) The reaction of benzene with *n*-propyl chloride in the presence of $AlCl_3$ gives 1-phenylpropane as the only product.

17. Which of the following statements are correct?

(a) The iodination of benzene can be carried out by using ICl.

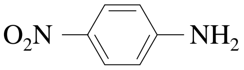
(b) The $—NH_2$ group is a better *o*, *p*-director as compared to $—NH_2COCH_3$.

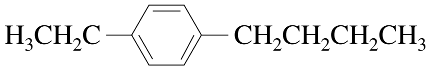
(c) The nitroso-group (—N==O) deactivates the benzene ring inductively but is an *ortho* and *para* director due to the donation of the paired electrons on nitrogen.

(d) Though $—N(CH_3)_2$ is an *ortho*- and *para*-director yet it gives *meta* nitrated product with the more powerful electrophilic regent HNO_3/H_2SO_4.

18. Which of the following statements are correct?
- (a) The sulphonation of toluene at low temperatures is kinetically controlled while at higher temperatures it is thermodynamically controlled.
- (b) Benzene is not a suitable solvent for the Friedel-Crafts alkylation of PhBr while nitrobenzene can be employed for this purpose.
- (c) In spite of electron-attracting inductive effect of the phenyl group, the electrophilic substitution of biphenyl occurs at *o*, *p*-positions.
- (d) An ipso substitution involves the displacement of one ring substituent by another.

19. Which of the following statements are correct?
- (a) Phenyl cation is more stable than cyclohexyl cation.
- (b) Phenyl anion is more stable than cyclohexyl anion.
- (c) 1, 4-Disubstituted benzenes generally have higher melting points than the corresponding 1,2- or 1,3-isomers.
- (d) Benzene-water forms a higher boiling azeotrope.

20. Which of the following statements are **not** correct?
- (a) The compound 

is named 4-aminonitrobenzene.
- (b) The compound 

is named 1-ethyl-4-butylbenzene.
- (c) Cyclopentadiene is much more acidic than 1,3-cyclohexadiene.
- (d) The two phenyl groups in biphenyl lie in the same plane.

21. Which of the following statements are correct?
- (a) Azulene is a aromatic molecule.
- (b) The main contributing structures in azulene involve the negative charge on the five-membered ring and positive-charge on the seven-membered ring.
- (c) The Birch reduction involves the reduction of benzene to 1,4-cyclohexadiene by Li or Na in liquid NH_3 and EtOH.
- (d) Birch reduction of toluene gives 1-methyl-1,4-cyclohexadiene and not its isomer, 3-methyl-1,4 cyclohexadiene.

22. Which of the following statements are correct?
- (a) Birch reduction of benzoic acid gives 2,5-cyclohexadiene-1-carboxylic acid and not its 1,4-isomer.
- (b) All C—C bond lengths in naphthalene are identical.
- (c) Naphthalene is the resonance hybrid of three structures.
- (d) Three resonating structures of naphthalene contribute equally in the hybrid.

23. Which of the following statements are correct?
- (a) The resonance stabilization of naphthalene is twice that of benzene.
- (b) The oxidation of one ring of naphthaline to give phthalic acid is easily performed as compared to the oxidation of benzene.
- (c) The oxidation of 1-nitronaphthalene gives phthalic acid.
- (d) The oxidation of α-naphthylamine yields phthalic acid.

24. Which of the following statements are **not** correct?
- (a) The oxidation of naphthalene with $KMnO_4$ in acid gives phthalic acid.
- (b) The oxidation of naphthalene with O_2/V_2O_5 gives 1, 4-naphthaquinone.
- (c) Treatment of *p*-chlorotoluene with NaOH(aq) at 340 °C exclusively gives *p*-hydroxytoluene.
- (d) Chlorine in *p*-chlorotoluene is replaced by OH when taken in NaOH(aq) at 340 °C. No such replacement occurs for 2,6-dimethylchlorobenzene.

25. Which of the following statements are correct?
- (a) Benzyl radical is more stable than 3° radical.
- (b) The addition of one mole of H_2/Pt to $PhCH{=}CH{-}CH{=}CHCH_3$ gives $PhCH_2CH{=}CHCH_2CH_3$.
- (c) The number of isomeric benzene ring-substituted compounds of C_8H_{10} is four.

(d) The number of isomeric benzene ring–substituted compounds of C_9H_{12} is eight.

26. Which of the following structures are **not** correct.

(a) The structure of the intermediate product, formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde, is $C_6H_5CH_2OCOCH_3$.

(b) The carbon-carbon bond length in benzene is 139 pm.

(c) Cyclopentadienyl anion has unusually low stability.

(d) Cycloheptatrienyl cation is also known as tropylium ion.

27. Which of the following statements are **not** correct?

(a) A group that makes the ring more reactive than benzene is known as activating group.

(b) A group that makes the ring less reactive than benzene is known as deactivating group.

(c) Nitration of toluene occurs slower than benzene.

(d) Chlorobenzene is more reactive that benzene towards nitration.

28. Which of the following statements are correct?

(a) Halogens are deactive benzene ring and are *ortho-para* directors.

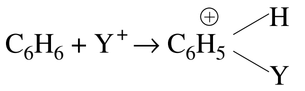
(b) Mononitration of 4-methylphenol yields 2-nitro-4-methylphenol.

(c) The electrophile in the nitration of benzene is NO_2^+.

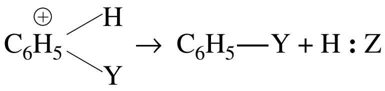
(d) The electrophile is electronic cloud seeking species.

29. Which of the following statements are **not** correct?

(a) Of the reactions

(i) 

$C_6H_6 + Y^+ \rightarrow \overset{\oplus}{C_6H_5}\langle^{H}_{Y}$

(ii) 

$\overset{\oplus}{C_6H_5}\langle^{H}_{Y} \rightarrow C_6H_5—Y + H:Z$

the slow reaction is (i) and the rate determining reaction is (i).

(b) Of the two groups —CH_3 and —CCl_3, the more deactivating group is —CCl_3.

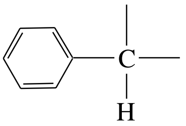
(c) Benzene in the presence of $AlCl_3$ reacts with *n*-propyl bromide to give propylbenzene

(d) The principal organic product obtained in the mononitration of *m*-dibromobenzene is 2-bromo-1,3-dibromobenzene.

30. Which of the following statements are **not** correct?

(a) Wolff-Kishner reduction of —CO— group into —CH_2— group involves the use of hydrazine and strong base.

(b) Halogenation in the side chain of $C_6H_5CH_3$ can be carried out by using halogen and $FeCl_3$.

(c) Hydrogen atom shown in the structure  is known as benzylic hydrogen.

(d) Benzylic hydrogen is difficult to abstract as compared to 3° hydrogen.

31. Which of the following statements are **not** correct?

(a) The addition of HBr to $C_6H_5CH{=}CHCH_3$ yields $C_6H_5CH_2CH(Br)CH_3$

(b) The addition of HBr to $C_6H_5CH{=}CHCH_3$ in the presence of peroxide yields $C_6H_5CH(Br)CH_2CH_3$

(c) The bromination of phenylethane in the presence of heat and light mainly produces $C_6H_5CH(Br)CH_3$

(d) Each carbon atom in benzene is sp^2 hybridized.

32. Which of the following statements are **not** correct?

(a) The electrophile in nitration is produced by using a mixture of concentrated HNO_3 and concentrated H_2SO_4.

(b) Xylene which gives a single monobromo derivative is *p*-xylene.

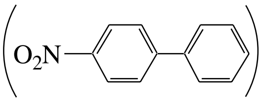
(c) Xylene which gives three monobromo derivatives is *o*-xylene

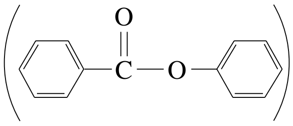
(d) Xylene which gives two monobromo derivatives is *m*-xylene

33. Which of the following statements are correct?

(a) The main product in the electrophilic substitution of *m*-nitrotoluene will occur at *para* position to methyl group and *ortho* position to nitro group.

(b) The IUPAC name of mesitylene is 1,3,5-trimethylbenzene

(c) In the mononitration of *p*-nitrobiphenyl , the nitro group enters in the phenyl

(d) In the mononitration of phenyl benzoate , the nitro group enters in the phenyl group attached to oxygen atom.

34. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the CH_3 group
(a) is *para* directing
(b) is *meta* directing
(c) activates the ring by hyperconjugation
(d) deactives the ring (1999)

35. An aromatic molecule will
(a) have $4n$ π electrons
(b) have $(4n + 2)\pi$ electrons
(c) be planar
(d) be cyclic (1999)

Linked Comprehension Type

1. Benzene and its derivatives undergo substitution reactions.

(i) Which of the following electrophilic substitution reactions does not involve positively charged electrophile?
(a) Nitration (b) Sulphonation (c) Alkylation (d) Halogenation

(ii) Which of the following electrophilic substitution reactions is a reversible reaction?
(a) Nitration (b) Alkylation (c) Acylation (d) Sulphonation

(iii) Which of the following compounds does not undergo electrophilic substitution reactions in the presence of $AlCl_3$?
(a) Chlorobenzene (b) Benzene (c) Nitrobenzene (d) Phenol

2. The electrophilic aromatic substitution of monosubstituted benzene is decided by the substituent in benzene ring. Identify the characteristics of the indicated substituent in the benzene ring.

(i) Methyl group has
(a) weak electron-donating inductive effect with none resonance effect.
(b) weak electron-donating inductive effect with strong electron-donating resonance effect.
(c) strong electron-withdrawing inductive effect with weak electron-donating resonance effect.
(d) Strong electron-withdrawing inductive effect with strong electron-donating resonance effect.

(ii) Chlorine has
(a) weak electron-donating inductive effect with none resonance effect.
(b) weak electron-donating inductive effect with strong electron-donating resonance effect.
(c) strong electron-withdrawing inductive effect with weak electron-donating resonance effect.
(d) strong electron-withdrawing inductive effect with strong electron-donating resonance effect.

(iii) —CHO group has
(a) weak electron-donating inductive effect with none resonance effect.
(b) weak electron-donating inductive effect with strong electron-donating resonance effect.
(c) strong electron-withdrawing inductive effect with weak electron-donating resonance effect.
(d) strong electron-withdrawing inductive effect with strong electron-donating resonance effect.

3. The strain in cycloalkanes may be estimated from the values of their enthalpy of combustion data. The more strain the compound contains, the more heat is released on combustion. Based on this fact, answer the following questions.

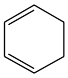
(i) The compound with largest magnitude of enthalpy of combustion is
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane

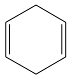
(ii) The compound with the largest magnitude of enthalpy of combustion per mole of CH_2 is
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane

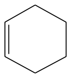
(iii) The compound having minimum strain energy is
(a) cyclopropane (b) cyclobutane (c) cyclopentane (d) cyclohexane

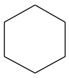
4. The Birch reduction involves the reduction of alkynes to alkenes. The reagent used in this reduction is Li or Na in liquid NH_3 and EtOH. An alkali metal in liquid NH_3 is a source of solvated electrons which is responsible for reduction. Even benzene undergoes reduction by this method. Based on this reduction of benzene, answer the following three questions.

(i) The rate-controlled product in Birch reduction of benzene is

(a) 

(b) 

(c) 

(d) 

(ii) Birch reduction of toluene gives
- (a) 50% yield of 1-methyl-1, 4-cyclohexadiene free from its isomeric 3-methyl-1, 4-cyclohexadiene.
- (b) 50% yield of 3-methyl-1, 4-cyclohexadiene free from its isomeric 1-methyl-1, 4-cyclohexadiene
- (c) 50% yield of both 3-methyl-1, 4-cyclohexadiene and 1-methyl-1, 4-cyclohexadiene
- (d) 1-methylhexaene as the only product.

(iii) Birch reduction of benzoic acid gives
- (a) 1, 4-cyclohexadiene-1-carboxylic acid
- (b) a mixture of 1, 4-cyclohexadiene-1-carboxylic acid and 2, 5-cyclohexadiene-1-carboxylic acid.
- (c) 2, 5-cyclohexadiene-1-carboxylic acid
- (d) 1-cyclohexaene-1-carboxylic acid.

Assertion Reason Type

Given below are the two statements for each question. Based on the following key, answer correctly each question.
(a) Both statements are correct and Statement-2 is a correct explanation of Statement-1.
(b) Both statements are correct but Statement-2 is not a correct explanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement 1	**Statement-2**
1.	The overall rate of an electrophilic reaction, except sulphonation in benzene and deuterated benzene, are identical.	The rate-determining step in electrophilic substitution reaction is the binding of the electrophile to the aromatic ring without cleavage of a C—H or C—D bond.
2.	Iodine solution in benzene is brown in colour.	Brown colour is due to charge-transfer complex between iodine and benzene.
3.	Phenyl cation is more stable than cyclohexyl cation.	Vinyl carbocation is less stable than 2° carbocation.
4.	Azulene is a aromatic molecule.	Azulene satisfies $4n + 2$ rule.
5.	Benzene is a suitable solvent for the Friedel-Crafts alkylation of PhBr.	Benzene is more reactive than bromobenzene in the Friedel-Crafts reaction.
6.	Both cyclopentadienyl anion and cyclohexadienyl anion contain 6 electrons in the ring but only former is aromatic.	There exists continuous cyclic overlap in cyclopentadienyl anion and not in cyclohexadienyl anion.
7.	Cyclopentadiene is much less acidic than 1,3-cyclohexadiene	Removal of H^+ converts cyclopentadiene into aromatic species but not in 1,3-cyclohexadiene
8.	Though [14]-annulene ($C_{14}H_{14}$) contains 14 electrons ($= 4 \times 3 + 2$), yet it is not aromatic	[14]-annulene is not a planar molecule
9.	Unlike in benzene, all bond lengths in naphthalene are not of the same size.	Naphthalene is the resonance hybrid of three structures.
10.	Borazine behaves as an aromatic molecule	Borazine is planar with six delocalized electrons.
11.	Iodine solution in benzne is brown in colour.	Iodine forms brown-coloured π complex with benzene.

12.	PhNMe_2 is mononitrated at the *meta* position with the more powerfully electrophilic reagent $\text{HNO}_3/\text{H}_2\text{SO}_4$.	In acid medium, PhNMe_2 is converted into $\text{Ph}\overset{+}{\text{N}}\text{HMe}_2$ and $—\overset{+}{\text{N}}\text{HMe}_2$ is benzene deactivator group.
13.	Nitrobenzene does not undergo the Friedel-Crafts reaction.	Deactivating effect of nitro group makes benzene ring unfit for Friedel-Crafts reaction.
14.	α-position in naphthalene reacts more preferentially than β-position with the reagent E^+.	Carbocations formed with the attachement at α- or β-position has the same stability.
15.	Naphthalene is less reactive than benzene towards electrophilic substitution reactions.	There is less loss of resonance energy in naphthalene as compare to that of benzene.
16.	*tert*-Butylbenzene is not oxidized to benzoic acid when treated with acidic KMnO_4.	*tert*-Butylbenzene does not have benzylic hydrogen.

ANSWERS

Straight Objective Type

1. (b) **2.** (d) **3.** (d) **4.** (c) **5.** (b) **6.** (a) **7.** (c)
8. (d) **9.** (a) **10.** (a) **11.** (c) **12.** (c) **13.** (b) **14.** (c)
15. (a) **16.** (d) **17.** (d) **18.** (a) **19.** (b) **20.** (b) **21.** (b)
22. (c) **23.** (c) **24.** (b) **25.** (c) **26.** (d) **27.** (c) **28.** (c)
29. (b) **30.** (c) **31.** (b) **32.** (c) **33.** (a) **34.** (a) **35.** (c)
36. (c) **37.** (a) **38.** (c) **39.** (a) **40.** (a) **41.** (b) **42.** (c)
43. (c) **44.** (b) **45.** (b) **46.** (d) **47.** (b) **48.** (c) **49.** (d)
50. (b) **51.** (b) **52.** (c) **53.** (c) **54.** (d) **55.** (b) **56.** (b)
57. (a) **58.** (b) **59.** (a) **60.** (c) **61.** (b) **62.** (b) **63.** (b)
65. (a) **65.** (b) **66.** (b) **67.** (b) **68.** (a)

Multiple Correct Choice Type

1. (a), (b), (c), (d) **2.** (a), (d) **3.** (a), (c), (d) **4.** (a), (d)
5. (b), (c), (d) **6.** (a), (c) **7.** (b), (c) **8.** (a), (d)
9. (a), (b), (c), (d) **10.** (a), (b), (c) **11.** (b), (c), (d) **12.** (a), (b), (d)
13. (a), (c), (d) **14.** (b), (d) **15.** (a), (c), (d) **16.** (a), (b), (c)
17. (a), (b), (c), (d) **18.** (a), (b), (c), (d) **19.** (b), (c) **20.** (a), (b), (d)
21. (a), (b), (c), (d) **22.** (a), (c) **23.** (b), (d) **24.** (a), (b), (c)
25. (a), (c), (d) **26.** (a), (c) **27.** (c), (d) **28.** (a), (b), (c), (d)
29. (c), (d) **30.** (b), (d) **31.** (a), (b) **32.** (c), (d)
33. (a), (b), (c), (d) **34.** (a), (c) **35.** (b), (c), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (d) **(iii)** (c)
2. **(i)** (a) **(ii)** (c) **(iii)** (d)
3. **(i)** (d) **(ii)** (a) **(iii)** (d)
4. **(i)** (b) **(ii)** (a) **(iii)** (c)

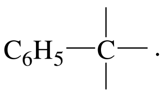
Assertion and Reason Type

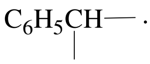
1. (a) **2.** (a) **3.** (d) **4.** (a) **5.** (d) **6.** (a) **7.** (d)
8. (a) **9.** (b) **10.** (a) **11.** (b) **12.** (a) **13.** (a) **14.** (c)
15. (d) **16.** (b)

Hints and Solutions

Straight Objective Type

1. The disubstituted products of benzene are three in number (*ortho*, *meta* and *para*).

2. The benzo group is  $C_6H_5—\overset{|}{\underset{|}{C}}—$.

3. The benzal group is  $C_6H_5\underset{|}{C}H—$.

4. The trityl group is $(C_6H_5)_3C—$.

5. The benzhydryl group is $(C_6H_5)_2CH—$.

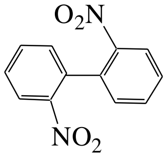
6. The benzyl group is $C_6H_5CH_2—$.

7. The styryl group is $C_6H_5CH{=}CH—$.

8. The cinnamyl group is $C_6H_5CH{=}CHCH_2—$.

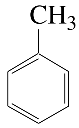
9. Cyclopropenyl cation is the smallest aromatic compound which satisfies $4n + 2$ rule with $n = 0$.

10. In cycloheptatriene, one of the C's is sp^3 hybridized, thereby preventing a completely cyclic overlapping π system.

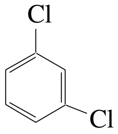
11. The reaction observed is $2(o–O_2NC_6H_4I) \longrightarrow$ 

12. $BeCl_2$ does not act as Lewis acid.

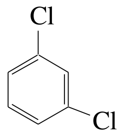
13.

(I) 

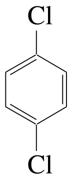
: dipole moment is smaller than chlorobenzene

(II) 

: dipole moment is identical to monochlorobenzene

(III) 

: dipole moment is 1.732 times that of monochlorobenzene

(IV) 

: zero dipole moment

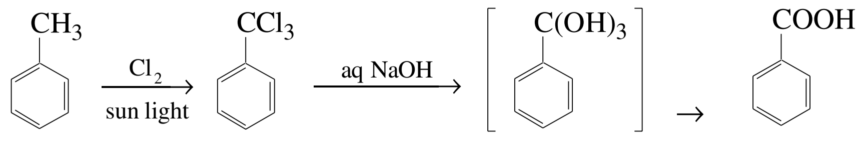
Hence, the increasing order is IV < I < II < III

14. Methyl group is electron-releasing group. It makes benzene ring more active towards electrophilic substitution reaction.

15. Same as Q.14.

16. Methyl group is *ortha* and *para* directing.

17. In the presence of sun light, side chain is chlorinated.



18. Nitronium ion is the electrophile in aromatic nitration.

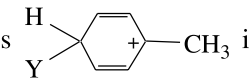
19. Direct iodination of benzene is not possible because the resulting C_6H_5I is reduced to C_6H_6 by HI.

20. Nitro is electron withdrawing group. It deactivates benzene ring towards electrophilic substitution.

21. $—NHCOCH_3$ is moderately activating group.

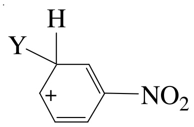
22. $—C_6H_5$ is a weakly activating group.

23. An activating group activates *ortho* and *para* more than *meta*.

24. The species 

is expected to most stable as the electron-releasing group is attached to carbon atom bearing positive charge.

25. A deactivating group deactivates *ortho* and *para* more than *meta*.

26. $—NO_2$ is *meta* directing, therefore  is expected to most stable.

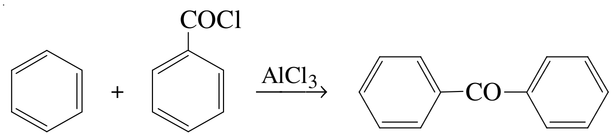
27. $—NH_2$ group activates the benzene ring via resonance effect and deactivates it via inductive effect.

28. —Cl group activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effects are evenly matched.

29. In the presence of sun light, chlorination occurs in the side chain. The product is benzyl chloride.

30. The product is *p*-nitrotoluene.

31.



32. In the Friedel-Crafts acylation, the electrophile is CH_3CO^+.

33. The correct sequence of activating power of a group in benzene is $—NH_2 > —NHCOCH_3 > —CH_3$

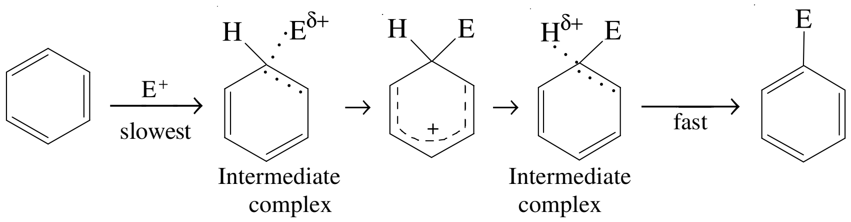
34. HNO_3 acts as a base in the nitrating mixture.

35. The statement that the rate of nitration of benzene is greater than that of hexadeuterobenzene is incorrect because in the rate-determining step does not involve breaking of the C—H or C—D bond.

36. Cl_2 in the presence of sun light is used to carry out the side chain halogenation.

37. The transition state II will have maximum enthalpy.

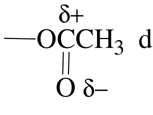
38. The rate-determining step in electrophilic substitution reaction is the binding of the electrophile to the aromatic ring without cleavage of a C—H or C—D bond. This bond is broken in the fast second step that restores the stable aromatic system.



Hence, the rate constant of nitration will follow the relation. $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$

39. For a reversible electrophilic substitution reactions, the rate constant involving the last step (where C—H or C—D or C—T) is broken to regain aromaticity) is comparable with that of the first step (where electrophile attaches with benzene ring). Since $\nu(C—H) > \nu(C—D) > \nu(C—T)$, the rate constant all show the same trend, i.e. $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$. This follows from the fact the second intermediate complex (shown in Q.38) has higher enthalpy involving T atom and hence leads to the lower rate constant.

40. The rate follows the order fluorination > chlorination > bromination.

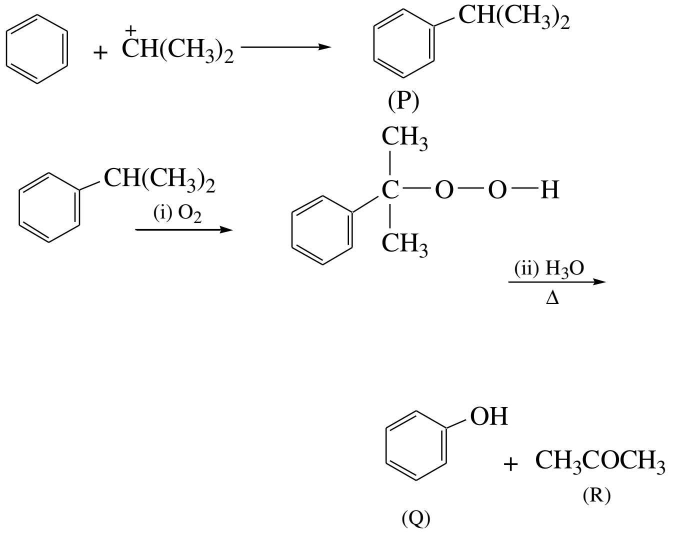
41. The activating effect is $—O^- > —OH > —OCOCH_3$. This follows from the fact that the negative charge in $—O^-$ pushes electron pair toward benzene ring more strongly than —OH group. The attachment of $COCH_3$ group with oxygen is  $—O\overset{\delta+}{\underset{\underset{O\,\delta-}{\|}}{C}}CH_3$ decreases this effect.

42. The attachment of two oxygen atoms with sulphur makes the group electron attracting, hence, *meta* director.

43. The given reaction proceeds as follows.

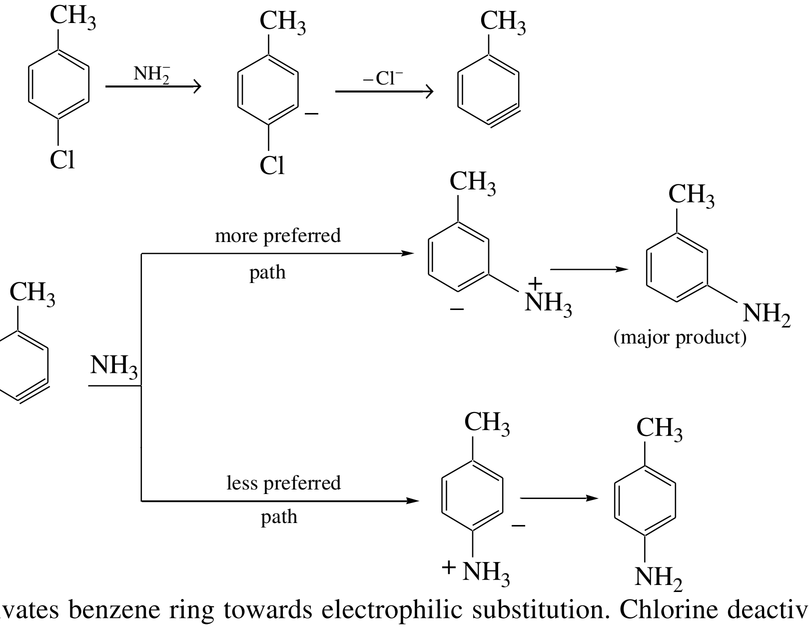
$$CH_3CH_2CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2\overset{+}{C}H_2 + AlCl_4^-$$

$$CH_3CH_2\overset{+}{C}H_2 \xrightarrow[\text{Rearrangement}]{} CH_3\overset{+}{C}HCH_3$$



44. The benzene ring attached to—NH— group gets activated and thus will undergo nitration at the *para* position in preference to ring attached to —CO— group.

45. The reaction proceeds via elimination-addition mechanism



46. Methyl group activates benzene ring towards electrophilic substitution. Chlorine deactivates benzene ring less than the nitro group.

47. The phenyl group attached to the —NH— group gets activated and thus bromination at the *para* position occurs in this phenyl group.

48. In 1-nitronaphthalene, the ring containing —NO_2 group is deactivated towards oxidation and the ring without —NO_2 group is thus oxidized to give 3-nitrophthalic acid. In α-naphthylamine, the ring containing —NH_2 group is activated towards oxidation and thus this ring gets oxidized to give phthalic acid.

49. CrO_3/acetic acid is mild oxidizing agent, it oxidizes naphthalene to 1,4-naphthaquinone whereas O_2/V_2O_5, heat causes the complete oxidation of one of the rings of naphthalene to give phthalic acid.

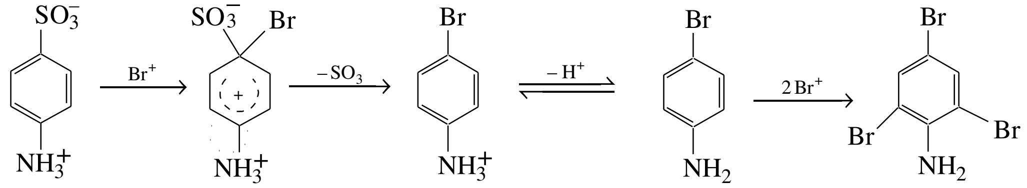
50. At higher temperature, thermodynamic-controlled product of *p*-toluenesulphonic acid (which is relatively sterically unhindered isomer as compared to *ortho* product) is formed in larger amounts.

51. Ph is an activating *o*, *p* group. Thus, p-$\mathrm{O_2NC_6H_4Ph}$ is formed as the major product.

52. Larger the —$\mathrm{NO_2}$ group, more the ring is deactivated and thus reactivity towards the eletrophile $\mathrm{E^+}$ is decreased.

53. —$\mathrm{NH_2}$ group is the ring activator. Its activating power is reduced when it is converted into —$\mathrm{NHCOCH_3}$. The group —$\mathrm{COCH_3}$ deactivates the ring towards the electrophile $\mathrm{E^+}$.

54. The compound p-$\mathrm{H_2NC_6H_4SO_3H}$ exists as the dipolar ion p-$\mathrm{H_2\overset{+}{N}C_6H_4SO_3^-}$. $\mathrm{Br^+}$ first attack at the carbon bearing $\mathrm{SO_3^-}$ group and thus replaces this group. The formed p-bromoanilinium ion is converted into *p*-bromoaniline. The —$\mathrm{NH_2}$ group activates the ring so as to cause the introduction Br at the two *ortho* positions. The reactions are



55. Electron-releasing group helps the removal of $\mathrm{Cl^-}$ while electron-attracting group makes the removal more difficult. Hence, the order is *p*-methoxybenzyl chloride > benzyl chloride > *p*-nitrobenzyl chloride.

56. Methyl group is electron-releasing, it helps releasing $\mathrm{Cl^-}$. Hence, the order is

$$\mathrm{PhCH_2Cl < PhCHClCH_3 < PhCCl(CH_3)_2.}$$

57. For $\mathrm{S_N2}$ reaction, the reverse order as described in Q. 56 is observed.

58. The addition of HBr proceeds via ionic mechanism. The electrophilic addition of $\mathrm{H^+}$ across the double bond produces $\mathrm{Ph\overset{+}{C}H\,CH_2CH_2CH_3}$ (which is more stable benzylic ion) followed by the addition of $\mathrm{Br^-}$.

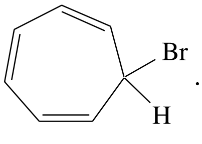
$$\mathrm{PhCH\overset{\curvearrowleft}{=}CHCH_2CH_3 \xrightarrow{H^+} Ph\overset{+}{C}HCH_2CH_2CH_3 \xrightarrow{Br^-} PhCH(Br)CH_2CH_2CH_3}$$

In the presence of peroxide, the reaction proceeds via free radical. Here $\mathrm{Br^\bullet}$ adds to the β-C forming the more stable benzylic $\mathrm{Ph\overset{\bullet}{C}H\,CH(Br)CH_2CH_3}$ intermediate which then removes $\mathrm{H^\bullet}$ from HBr to propagate the chain.

$$\mathrm{PhCH{=}CHCH_2CH_3 \xrightarrow{Br^\bullet} Ph\overset{\bullet}{C}H\,CH(Br)CH_2CH_3 \xrightarrow{HBr} PhCH_2CH(Br)CH_2CH_3 + Br^\bullet}$$

59. —$\mathrm{N(CH_3)_2}$ is stronger ring activator than —$\mathrm{CH_3}$ group. —$\mathrm{N(CH_3)_3^+}$ is the ring deactivator.

60. The structure of 7-bromo-1,3,5-cycloheptatriene is



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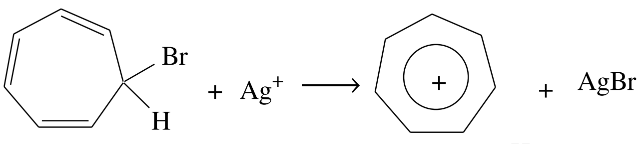
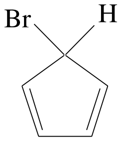
In the presence of $\mathrm{Ag^+}$ in solution, bromine gets precipitated as AgBr giving a stable cycloheptatrienyl carbocation due to its aromatic character (six π electrons delocalised in seven overlapping p orbitals)



The structure of 5-bromo-1,3-cyclopentadiene is



The bromine in this case is not precipitated in the presence of $\mathrm{Ag^+}$ ions because the cyclopentadiene carbocation will not be stable as it is not aromatic (4π electrons distributed over 5p orbitals). It is for this reason, the carbocation is not formed.

61. Electron-releasing group makes benzoic acid lesser acidic; larger the electron-releasing effect, more weaker the acid. Hence, the expected trend is benzoic acid > *p*-toluic acid > *p*-hydroxybenzoic acid

62. Electron-attracting group makes benzoic acid more acidic and electron-releasing group makes it less acidic. Hence, the expected trend is *p*-nitrobenzoic acid > benzoic acid > *p*-anthranilic acid

63. Electron-attracting group makes aniline less basic while electron-releasing group makes it more basic. Thus, the expected trend is *p*-nitroaniline < aniline < *p*-toluidine

64. The expected trend is *p*-hydroxybenzoic acid < *p*-methoxybenzoic acid < *p*-toluic acid.

65. The expected trend is *p*-nitrobenzoic acid > *p*-cyanobenzoic acid > *p*-chlorbenzoic acid.

66. Larger the activating group, more strong the base. Hence, the expected trend is
p-methylaniline < *p*-methoxyaniline < *p*-aminoaniline.

67. The expected trend is *p*-nitroaniline < *p*-cyanoaniline < *p*-methylaniline

68. Electron attracting group makes phenol more acidic while electron releasing makes it less basic.
p-aminophenol < *p*-chlorophenol < *p*-nitrophenol

Multiple Correct Choice Type

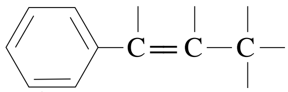
1. The electron density on *meta* carbon is more than that on *ortho* and *para* positions (choice a). Also choice d is correct which states that loss of H^+ is easier to regain aromaticity from the *meta* position than from *ortho* and *para* positions.

5. (a) Benzene gets stabilised because of resonance. (b) Both represent one and the same compound.
(c) Each carbon in benzene is sp^2 hybridized.
(d) An electron attracting group directs the incoming electrophilic group to the *meta* position.

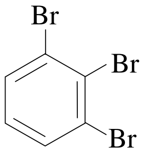
6. (a) Benzene is more stable due to resonance.
(b) Benzene undergoes electrophilic substitution reactions.
(d) Cycloheptatrienyl cation contains six π electrons and thus behaves like an aromatic molecule.

7. (a) One of the structures having molecular formula C_6H_6 is $CH{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$. It will have two isomers: $CH{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_3$ and $CH{\equiv}C{-}C{\equiv}C{-}CH_2CH_3$.
(d) $AlCl_3$ acts as a Lewis acid.

8. (b) An activating group activates all positions in the benzene ring; *ortho* and *para* positions are activated much more than the *meta* position.
(c) A deactivating group deactivates all positions in benzene ring; *ortho* and *para* positions are deactivated much more than the *meta* position.

9. (a) It proceeds faster as $—NHCOCH_3$ is benzene-activating group.
(b) The group $—COCH_3$ is benzene-deactivating group, hence bromination occurs slower.
(c) In Clemmensen reduction, amalgamated zinc and HCl is used.
(d) The structure  is more stable as it contains a double bond in conjugation with ring.

10. (c) There are three isomers.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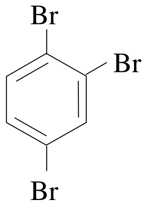
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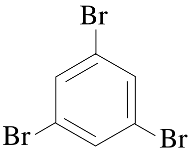
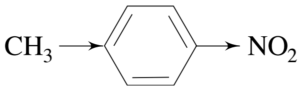
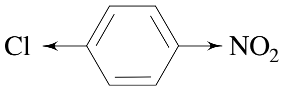
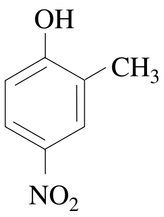


1, 2, 3-tribromobenzene 1, 2, 4-tribromobenzene 1, 3, 5-tribromobenzene

(d) In *p*-nitrotoluene, both group moments act in the same direction while in *p*-chloronitrobenzene they act in the opposite directions:



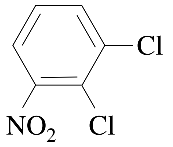


11. (a) The product is 

A strongly activating group, competing with a weakly activating group, controls the orientation. The position 6 will be sterically hindered.

(b) The C—H bond in benzene involves sp^2–s character while in cyclohexane it is sp^3–s. The bond C—H in benzene is expected to be shorter and thus stronger than in cyclohexane.

(c) There are only two isomers.



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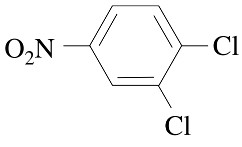
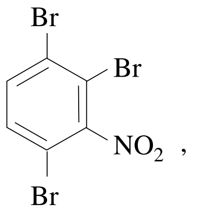


(d) 1,2,4-tribromobenzene gives three isomers.



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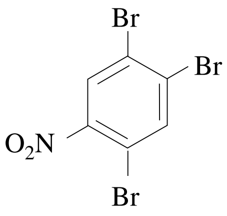

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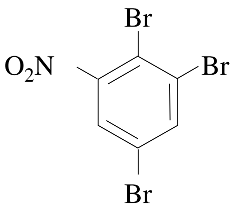
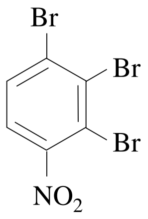
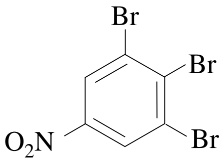


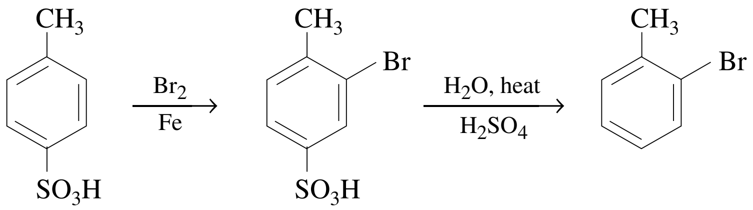
The compound 1, 2, 3-tribromobenzene gives two isomers.



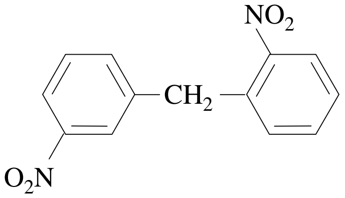
and

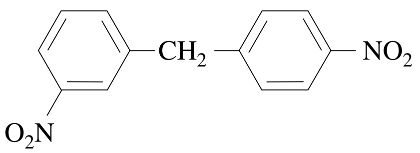


12. (a) The product is *o*-bromotoluene.



(b) Substitution is faster in the ring that is not deactivated by —NO_2. Thus, the compounds obtained will be





(c) In 2,4-dinitrotoluene, there are two deactivating (NO_2) groups and one activating (CH_3) group while in *m*-dinitrobenzene, there are only two deactivating groups.

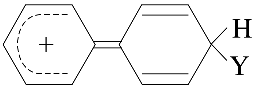
(d) 2,4-dinitrophenol contains a strongly activating group (—OH) while 2,4-dinitrochlorobenzene contains weak deactivating group (—Cl).

13. (a) *p*-xylene contains two activating group, toluene contains one activating group, *p*-toluic acid contains one activating group (CH_3) and one deactivating group (COOH) and terephthalic acid contains two deactivating groups (COOH).

(b) The farther away a deactivating group from the ring, the less effective it is .

(c) The more electron-withdrawing groups in benzene, the greater the deactivation.

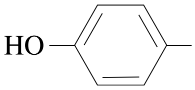
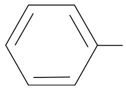
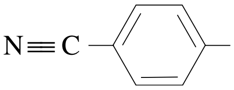
(d) The positive charge of the intermediate can be dispersed by the second phenyl group when the latter is attached to *ortho* or *para*, but not to *meta*.

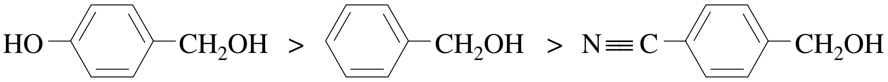


Intermediate

14. (a) The two hydrogens are in the same plane as the ring. This arrangement permits overlap of π cloud with the p orbital of the side carbon.

(b) Resonance stabilisation of the anion, with dispersal of negative charge, increases the acidity.

(c) The reactivity is largely determined by the stability of the carbocations being formed. The electron releasing group stabilises the carbocation. The group  is most strongly electron releasing group, followed by  and then  (in fact, the latter is electron withdrawal group). Hence, the correct order is

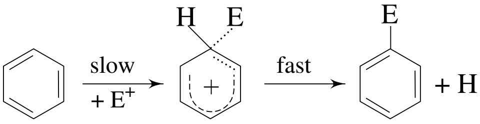


(d) The reactivity is largely determined by the stability of the carbocation being formed.

15. (a) The formation of intermediate arenium cation is slow while the elimination of H$^+$ from this cation is fast. The former involves the removal of aromaticity while the latter restores aromaticity.

(b) The C—D bonds are stronger than C—H bonds. In fact, the bond with the heavier isotope is slightly stronger than that with the lighter isotope.

(c) In electrophilic substitution reactions, the rate-determining step is the formation of arenium cation.



In this step, E$^+$ bonds to the aromatic ring without cleavage of a C—H bond. The latter is broken in the second step, which is fast as it restores the stable aromatic system. Since C—H or C—D bond is not broken in the rate-determining step, the overall rates of reaction are identical.

16. (b) In sulphonation reaction, both steps involving the formation of arenium cation and its conversion to the substituted benzene determine the overall rate of reaction. In the second step, the loss of D$^+$ from the deuterated σ complex is a little slower than the loss of H$^+$ from the ordinary σ complex.

(d) The product contains both $PhCH_2CH_2CH_3$ and $PhCH(CH_3)_2$.

17. (a) ICl is more electrophilic than I_2 because it is polarised as $^{\delta+}$I—Cl$^{\delta-}$.

(b) In —NH_2COCH_3, the C of the $^{\delta+}$C=O$^{\delta-}$ has a positive charge and this diminishes the ability of —$\ddot{N}$— to donate a pair of electrons to the arenonium ion.

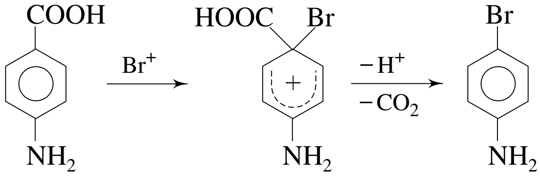
(d) In acidic medium, $PhN(CH_3)_2$ exists as $\mathrm{Ph\overset{+}{N}H(CH_3)_2}$ which is a *meta* director.

18. (a) At low temperature, kinetic control prevails for formation of the rate-determining transition state while at higher temperature, the thermodynamically more stable product (*p*-toluenesulphonic acid) predominates.

(b) Benzene is more reactive than bromobenzene in the Friedel-Crafts reaction and thus benzene is alkylated in preference to bromobenzene. Nitrobenzene is a suitable solvent as it is not alkylated due to the presence of nitro-group which has a deactivating effect.

(c) In attack at the *o*, *p*-positions the unreacted ring can stabilise the +charge on the attached C of the σ complex by electron-releasing delocalisation that results in delocalising the +charge to both rings.

(d) One of the examples is



19. (a) $C_6H_5^+$ is a vinyl carbocation and $C_6H_{11}^+$ is a 2° carbocation. Vinyl carbocation is less stable as compared to 2° carbocation.

(b) The electron pair in $C_6H_5^-$ is present in the sp^2 hybrid orbital where as in $C_6H_{11}^-$ it is present in the sp^3 hybrid orbital. The phenyl carbanion has more s-character, therefore, it is more stable.

(c) The 1, 4-isomer has a more symmetrical structure, allowing it to fit better into the crystal lattice than either of its isomers.

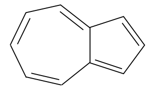
(d) Benzene-water forms a lower boiling azeotrope because the attractive forces between benzene and benzene, and water and water are more strong than that existing between benzene and water.

20. (a) Amino group has priority over nitro; the correct name is 4-nitroaniline.

(b) Substituents should be listed in alphabetical order. The correct name is 1-butyl-4-ethylbenzene.

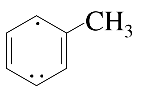
(c) The removal of H^+ from cyclopentadiene gives the resonance stabilised aromatic cyclopentadienyl anion. This is not so in case of 1,3-cyclohexadiene.

(d) The two phenyl groups are not in the same plane. They are joined by a single bond and have free rotation about it.

21. (a) The structure of azulene is 

Neither the seven-carbon ring nor five-carbon is aromatic, but the cycloheptatriene cation and cyclopentadiene anion are aromatic. The charge separation gives considerable dipole moment to azulene.

(d) Birch reduction involves the addition of an electron (from alkali metal in liquid NH_3) to form the benzene radical anion. The CH_3 group is electron-donating and it will destabilise a negatively charged carbon of the ring bound to this group. Thus, the stable intermediate formed is



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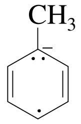
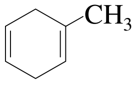


. Hence, the product obtained is


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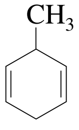
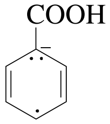
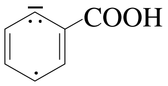
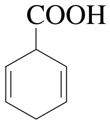


.

22. (a) The —COOH group is electron-attracting and it will stabilise a negatively charged carbon of the ring bound to this group. Thus, the stable intermediate formed is


and not


. Hence, the product is


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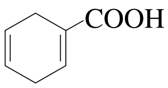
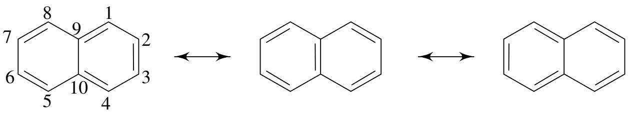


.

(b) Naphthalene has three resonating structures:



(I) (II) (III)

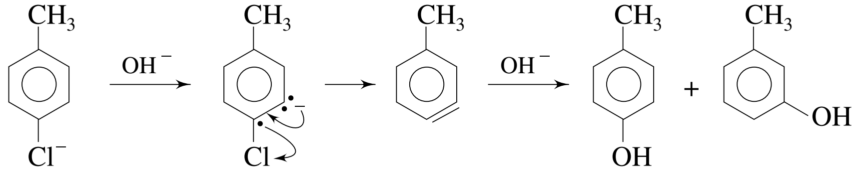
Resonance structures (I) and (III) have the Kekule structure in only one ring while the structure (II) has in both the rings. The major contributor to the hybrid is from the structure (II). Hence, the bond length $C^1—C^2$ is expected to be shorter than $C^2—C^3$ and so on.

23. (a) The resonance stabilisation of benzene is 151 kJ mol^{-1} while that of naphthalene is 255 kJ mol^{-1}.

(b) One ring of naphthalene has lesser resonance stabilisation (255 kJ mol^{-1} – 151 kJ mol^{-1} = 104 kJ mol^{-1}). Thus, it is easily oxidisable.

(c) The electron-attracting —NO_2 group stabilises the ring to which it is attached towards oxidation. Thus, it is the other ring which gets oxidised. The product is 3-nitrophthalic acid.
(d) The electron-releasing —NH_2 group destabilises the ring to which it is attached towards oxidation. Thus, it is this ring which gets oxidised.

24. (a) The product is 1, 4-naphthaquinone. (b) The product is phthalic acid.
(c) Two products namely *p*-hydroxytoluene and *m*-hydroxytoluene are obtained. This reaction proceeds through the formation of benzyne and is known as elimination-addition reaction



(d) There is no *ortho*-H, thus benzyne cannot form.

25. (b) The product is $PhCH{=}CHCH_2CH_2CH_3$. This is formed due to the extended conjugation with Ph group.

26. (a) The intermediate is $C_6H_5CH(OCOCH_3)_2$, benzylidene acetate
(c) Cyclopentadienyl anion has high stability

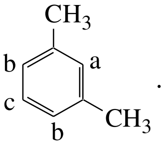
27. (c) —CH_3 group is an activator group, it causes nitration to proceed faster in toluene.
(d) Chlorobenzene is less reactive than benzene towards nitration.

28. (c) The product is isopropylbenzene. (d) The product is 4-nitro-1,3-dibromobenzene.

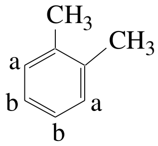
30. (b) The side chain halogenation requires heating or the use of light.
(d) Benzylic hydrogen is easier to abstract as compared to 3° hydrogen.

31. (a) The product is $C_6H_5CH(Br)CH_2CH_3$. (b) The product is $C_6H_5CH_2CH(Br)CH_3$.

32. (c) *m*-Xylene will give three products



. (d) *o*-Xylene will give two products



33. (a) If an *ortho-para* director and an *m*-director are not reinforcing, the former controls the orientation.
(c) (Substitution is faster in the ring that is not deactivated by nitro group.)
(d) (Substitution is faster in the ring that is activated by phenolic oxygen.)

34. —CH_3 group is *para* directing as it activates the benzene ring by hyperconjugation.

Linked Comprehension Type

1. **(i)** In sulphonation, the electrophile is : SO_3.
(ii) Sulphonation is a reversible reaction.
(iii) Nitrobenzene does not undergo the Friedel-Crafts reaction owing to the deactivating effect of the —NO_2 group.

2. **(i)** Methyl group has a weak electron-donating inductive effect with none resonance effect.
(ii) Chlorine has a strong electron-withdrawing inductive effect with weak electron-donating resonance effect
(iii) —CHO group has strong electron-withdrawing inductive effect with strong electron-donating resonance effect.

3. **(i)** The $\Delta_c H$'s in kJ/mol are as follows.

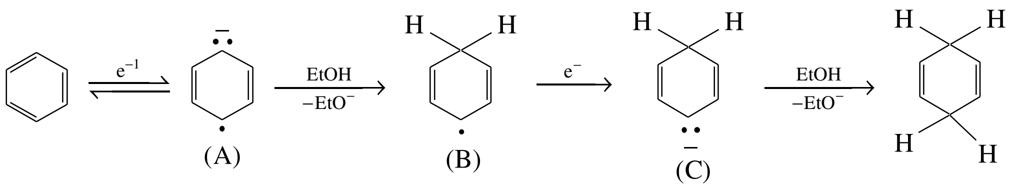
cyclopropane	– 2090	cyclopentane	– 3288
cyclobutane	– 2718	cyclohexane	– 3918

(ii) The $\Delta_c H$'s in kJ/mol per mole of CH_2 is

cyclopropane	– 697	cyclopentane	– 658
cyclobutane	– 680	cyclohexane	– 653

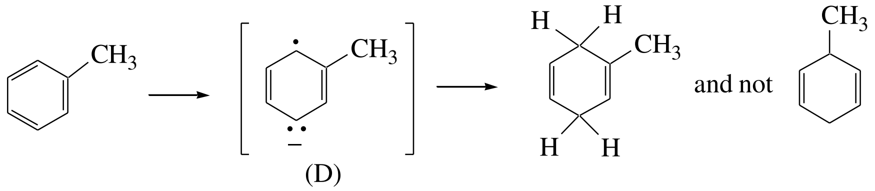
(iii) Minimum strain energy is possessed by cyclohexane.

4. **(i)** An alkali metal in liquid NH_3 is a source of solvated electron. The first step in Birch reduction is the addition of an e^- to form a benzene radical anion along with acceptance of H^+ (from EtOH or NH_3). The resulting radical then accepts another e^- to form an anion followed by protonation.

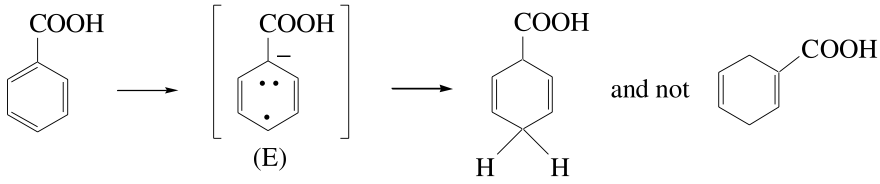


The intermediates A, B and C also exist in other resonating structures. The protonation of C occurs more rapidly than the other resonating structures. The product is unconjugated product which is the rate-controlled product. The thermodynamic more stable product is 1, 3-cyclohexadiene.

(ii) The —CH_3 group is electron-donating and thus will destabilize a (–) on the ring carbon bonded to it. Consequently, the more stable intermediate radical anion D form the product in which —CH_3 group is attached to the double bond.



(iii) The —COOH group is electron-withdrawing and the more stable intermediate radical anion (E) leads to the product in which —COOH is attached to the negatively-charged C.



CHAPTER 25

ALKYL AND ARYL HALIDES

ALKYL HALIDES

METHODS OF PREPARATION

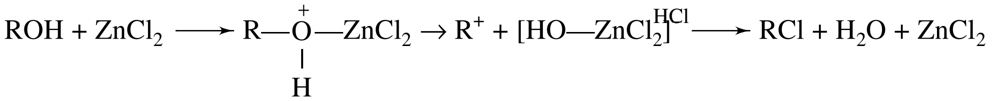
1. Replacement of hydroxyl group in alcohols The reagents used are:

For primary and secondary alcohol—hydrogen chloride in the presence of zinc chloride.

For tertiary alcohol—concentrated hydrochloric acid in the presence of zinc chloride.

The reaction proceeds as follows.

S_N1 mechanism



$$\mathrm{ROH + ZnCl_2 \longrightarrow R{-}\overset{+}{\underset{\underset{H}{|}}{O}}{-}ZnCl_2 \rightarrow R^+ + [HO{-}ZnCl_2] \xrightarrow{HCl} RCl + H_2O + ZnCl_2}$$

S_N2 mechanism $\mathrm{ROH + ZnCl_2 + HCl \longrightarrow ZnCl_3^- + ROH_2^+ \longrightarrow ZnCl_2 + RCl + H_2O}$

Tertiary alcohol follows S_N1 mechanism.

Straight chain primary alcohols favour S_N2 mechanism.

Secondary alcohol may react via both the mechanisms.

For alkyl bromides, constant boiling hydrobromic acid (48%) is used. For primary alcohols, a little concentrated sulphuric acid is used as a catalyst. For secondary and tertiary alcohols, sulphuric acid is not used as these alcohols tend to dehydrate to give alkenes. HBr can be generated in situ by the action of concentrated sulphuric acid on potassium bromide.

For alkyl iodides, constant boiling HI(57%) is used. It may be generated in situ by the action of 95% phosphoric acid on KI.

The convenient reagents to replace —OH by —Cl are phosphorus chloride and thionyl chloride ($SOCl_2$). The latter is preferred as the end products are gaseous products which escape in air giving almost pure alkyl chloride.

2. Addition of halogen acids to an alkene The addition occurs in accordance with Markovnikov's rule. HBr in the presence of peroxide adds according to anti-Markovnikov's rule.

PHYSICAL PROPERTIES

The C—X bond in alkyl halides is a polar bond. The dipole moment of methyl halides follows the order:

$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$

The bond strength of C—X decreases with increasing size of halogen atom, i.e.

$$\varepsilon(C{-}F) > \varepsilon(C{-}Cl) > \varepsilon(C{-}Br) > \varepsilon(C{-}I)$$

The boiling points of alkyl halides are higher than those of the corresponding alkanes. The boiling point of alkyl halides increases with increasing size of the halogen atom.

Alkyl chlorides are lighter than water while alkyl bromides and iodides are heavier than water.

CHEMICAL REACTIONS

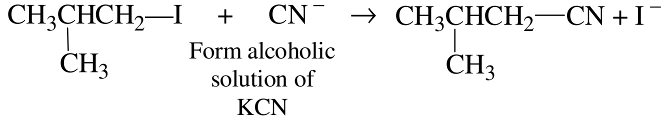
The alkyl halides undergo nucleophilic substitution reactions in which a stronger nucleophile replaces a weaker nucleophile. Some alkyl halide can undergo elimination reactions producing an alkene.

Nucleophilic substitution reactions A few typical nucleophilic substitution reactions are as follows.

1. $CH_3—Cl \; + \; OH^- \xrightarrow[\Delta]{} CH_3OH + Cl^-$

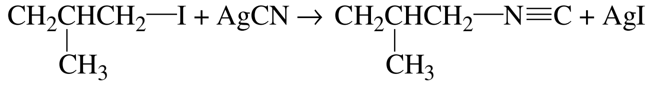
   form aq
   KOH or Ag_2O
   in boiling water

2. $CH_3CH_2—I + CH_3O^- \rightarrow CH_3CH_2OCH_3 + I^-$

3. 

   $\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCH_2}—I \; + \; \underset{\text{Form alcoholic solution of KCN}}{CN^-} \rightarrow \underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCH_2}—CN + I^-$

   When silver cyanide is used, the product is isocyanide.

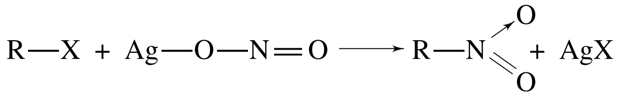
   

   $\underset{\displaystyle CH_3}{CH_2\underset{|}{C}HCH_2}—I + AgCN \rightarrow \underset{\displaystyle CH_3}{CH_2\underset{|}{C}HCH_2}—N{\equiv}C + AgI$

4. $CH_3CH_2I + :NH_3 \rightarrow CH_3CH_2NH_3^+ + I^-$

5. $RX + KNO_2 \rightarrow \underset{\text{alkyl nitrite}}{R—O—N{=}O} + RX$

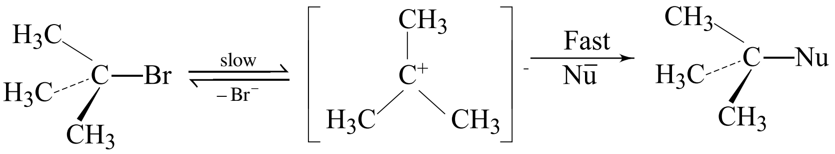
   If silver nitrite is used, the product is mainly nitroalkane.

   $R—X + Ag—O—N{=}O \longrightarrow R—N\overset{\nearrow O}{\underset{\searrow O}{}} + AgX$

The nucleophilic substitution reaction proceeds via either S_N1 or S_N2 mechanism.

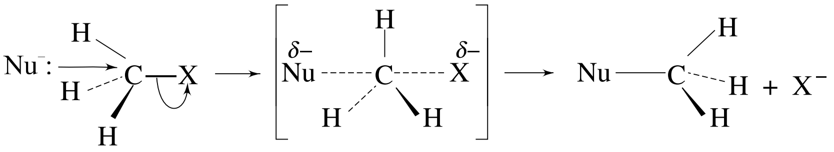
S_N1 Mechanism



Main characteristics

1. The more stable the carbocation intermediate, the faster the S_N1 mechanism.
2. The nucleophilie plays no role in the mechanism.
3. The weaker bases are the better leaving groups and thus favour S_N1 mechanism.
4. Polar solvents accelerate the S_N1 reaction because it favours the formation of polar transition state.
5. The S_N1 reaction on a chiral starting material ends up with the racemization of the product.

S_N2 Mechanism



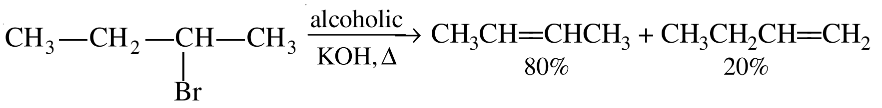
Main Characteristics

1. The conversion of reactants to transition state is the rate determining step.
2. The S_N2 reaction involves the inversion of stereochemistry around carbon atom of the substrate. This inversion is known as Walden inversion.
3. The rate of reaction depends on the steric bulk of the alkyl group.
   The kinetics study have shown that the methyl halides are the most reactive in S_N2 reactions. The increase in the length of chain of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically. The reactivity order for S_N2 reactions follows the following order.

   $CH_3 > 1° > 2° >> \text{neopentyl} > 3°$

4. Aprotic solvents increase the rate of S_N2 reactions.
5. The replacement of halide group follows the order $I^- > Br^- > Cl^-$

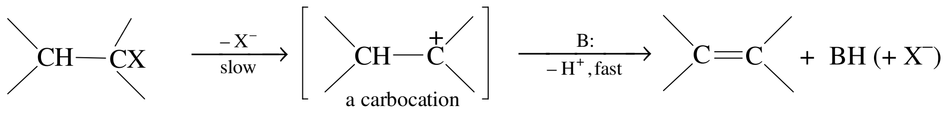
Elimination Reactions In the presence of alcoholic KOH and heating, the elimination reaction occurs which results into a double bond. If more than one product is possible, the major product is of more substituted alkene (Saytzeff rule).



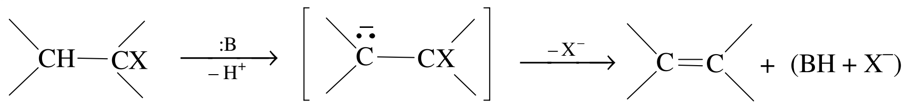
$$CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3 \xrightarrow[KOH,\Delta]{alcoholic} \underset{80\%}{CH_3CH{=}CHCH_3} + \underset{20\%}{CH_3CH_2CH{=}CH_2}$$

Elimination reaction may proceed through the following mechanisms

E1 (elimination, unimolecular) X^- leaves first, then the remaining R^+ loses the adjacent H^+ to $:B^-$



E1$_{cb}$ (elimination, unimolecular of the conjugate base)



If the substrate does not have high acidic H^+, the first step is slow.

E2 (elimination, bimolecular) This involves one step where both X^- and H^+ are departed simultaneously.

Competition between substitution and elimination reactions The relative proportion of products depends on mainly three factors, namely, basicity of the nucleophile, hindrance in the haloalkane, and steric bulk around the nucleophilic atom.

Factor 1. Base strength of the nucleophile

Weak bases (H_2O, ROH, halides, RS^-, N_3^-, NC^-, $RCOO^-$) lead to more substitution.

Strong bases (HO^-, RO^-, H_2N^-, R_2N^-) lead to more elimination.

Factor 2. Steric hindrane around the reacting carbon

Sterically unhindered (primary) haloalkanes lead to more substitution.

Sterically hindered (branched primary, secondary, tertiary) haloalkanes lead to more elimination.

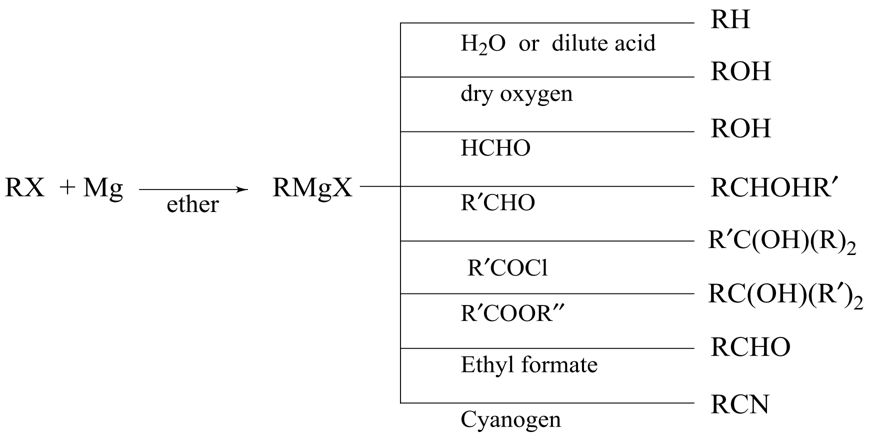
Factor 3. Steric hindrance in the nucleophile

Sterically unhindred (OH^-, CH_3O^-, $CH_3CH_2O^-$, H_2N^-) nucleophile lead to more substitution

Sterically hindered $(CH_3)_3CO^-$, $[(CH_3)_2CH_2N^-]$ nucleophiles lead to more elimination

Formation Grignard Reagent

Haloalkanes react with magnesium turnings in dry ether to form alkyl magnesium halide, known as Grignard reagent. The latter is most versatile compound as it can be used in the preparation of many different types of compounds.



Cyanides can also be prepared by treating alkyl halides with alcoholic solution of potassium cyanide. These, in turn, can be converted to amide, carboxylic acid and amine.

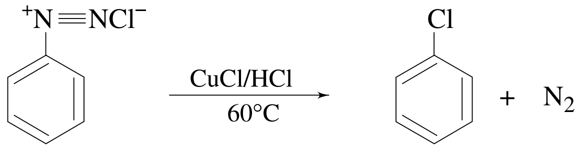
$$\mathrm{R{-}C{\equiv}N + H_2O \xrightarrow[\text{or } H_2O_2\,-\,NaOH]{\text{conc. HCl}} RCONH_2;} \qquad \mathrm{R{-}C{\equiv}N + H_2O \xrightarrow[\text{or alkali}]{\text{Mineral acid}} RCOOH + NH_3}$$

$$\mathrm{R{-}C{\equiv}N + 4H \xrightarrow[\text{or } H_2/Ni \text{ or } LiAlH_4]{Na/C_2H_5OH} RCH_2NH_2}$$

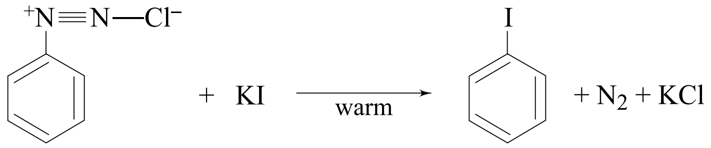
Alkyl Halides

Methods of preparation

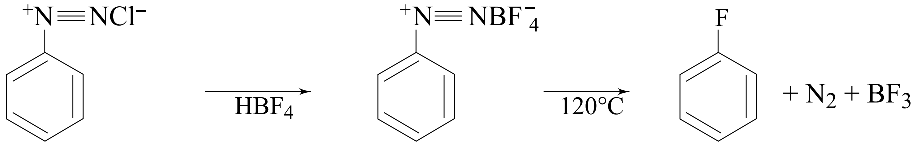
These can be prepared by Friedel-Crafts halogenation. Iodination cannot be carried out by this method as the reaction is endothermic. Aryl halides can also be prepared by Sandmeyer reaction. In this reaction, benzenediazonium chloride is treated with cuprous chloride or cuprous bromide dissolved in the corresponding acid.



Iodobenzene is obtained by warming diazonium salt solution with aq. KI solution.

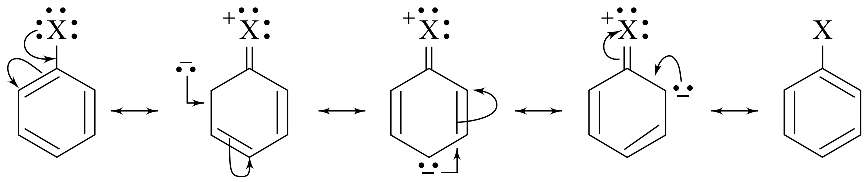


Fluorination is carried out by warming diazonium salt solution with HBF_4. This reaction is known as Schiemann reaction.



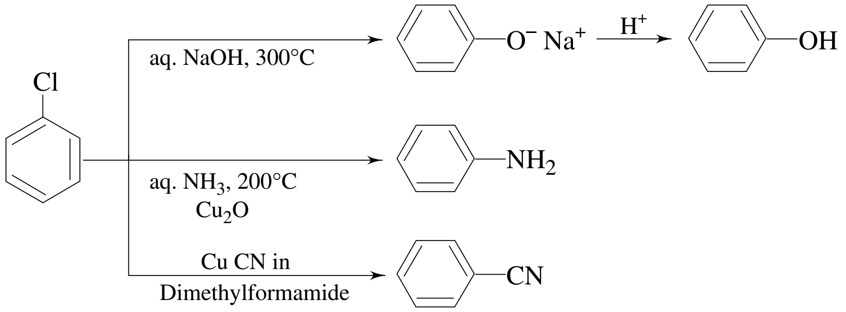
Chemical Reactions

In general, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions. This is due to the resonance effect in which lone pair of electron on halogen atom is delocalized to benzene ring imparting a partial double bond character to C—X bond.

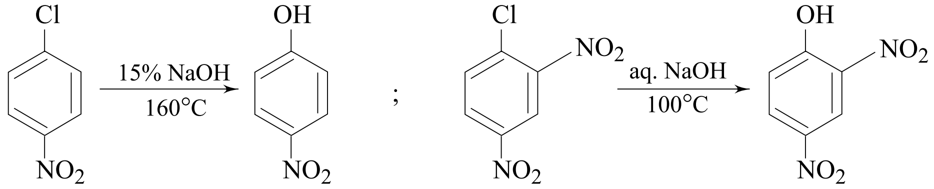


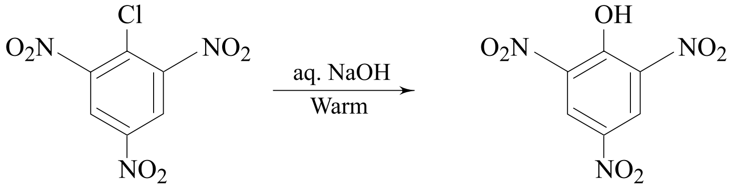
In alkyl halide, the C—X bond involves sp^3(C) whereas in aryl halide, sp^2(C) is involved. Since the sp^2(C) is more electronegative than the sp^3(C), the C—X bond in aryl halide is shorter than in alkyl halides. This makes C—X bond more strong in aryl halides.

Under normal conditions, halobenzenes are inert to nucleophiles. However, chlorobenzene can be made to react if the experimental conditions are drastic, i.e. high temperature and high pressure.



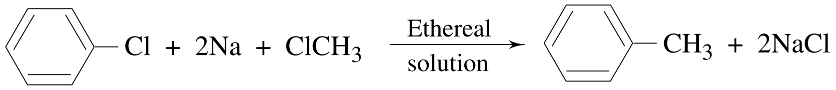
The presence of electron-withdrawing substituent at *ortho* and/or *para* positions is a favourable factor for the nucleophilic substitution reaction. More are such substituents, the faster is the reaction.



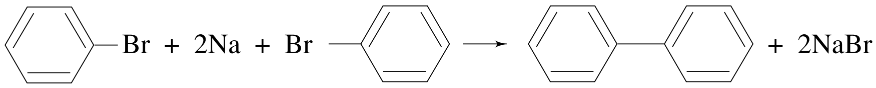


The factors responsible for the nucleophilic substitution reaction is due to (1) decrease in electron density in the ring, thereby favouring the nucleophilic attack, and (2) the stabilisation of intermediate anion by resonance. No such resonance is possible if the electron-withdrawing substituent occupies *meta* position.

Wurtz-Fittig Reaction The combination of aryl halide with alkyl halide in an ethereal solution in the presence of sodium to give alkyl substituted benzene is known as Wurtz-Fittig reaction



Fittig Reaction Treatment of ethereal solution of bromobenzene with sodium gives biphenyl.



Chloro substituent in chlorobenzene is *ortho* and *para* director, since resonance effect of Cl predominates over its inductive effect.

Straight Objective Type

General Characteristics

1. The bond dissociation enthalpy C—X in CH_3X (where X is halogen) follows the order
   (a) $CH_3—Cl > CH_3—Br > CH_3—I$ (b) $CH_3—Cl < CH_3—Br < CH_3—I$
   (c) $CH_3—Cl > CH_3—Br < CH_3—I$ (d) $CH_3—Cl < CH_3—Br > CH_3—I$
2. The dipole moment of CH_3X (where X is a halogen) follows the order
   (a) $CH_3F > CH_3Cl > CH_3Br$ (b) $CH_3F > CH_3Br > CH_3Cl$
   (c) $CH_3Cl > CH_3F > CH_3Br$ (d) $CH_3F < CH_3Cl < CH_3Br$
3. Which of the following molecules is expected to have maximum boiling point?
   (a) CH_3Cl (b) CH_3CH_2Cl (c) $CH_3(CH_2)_2Cl$ (d) $CH_3(CH_2)_3Cl$

4. Which of the following molecules is expected to have minimum boiling point?
(a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I

5. Which of the following orders regarding the boiling points of the given alkyl chloride is correct?
(a) $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3 > (CH_3)_3CCl$
(b) $CH_3(CH_2)_3Cl < CH_3CH_2CHClCH_3 < (CH_3)_3CCl$
(c) $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3 < (CH_3)_3CCl$
(d) $CH_3(CH_2)_3Cl < CH_3CH_2CHClCH_3 > (CH_3)_3CCl$

6. The number of isomers excluding optical isomers of dibromobutane is
(a) 4 (b) 5 (c) 6 (d) 8

7. Which of the following reagents is most effective in replacing —OH group in an alcohol by —Cl group?
(a) HCl gas (b) Concentrated HCl (c) SOCl (d) $SOCl_2$

8. Which of the following molecules have tetrahedral structures is expected to have maximum value of dipole moment?
(a) CH_3Cl (b) CH_2Cl_2 (c) $CHCl_3$ (d) CCl_4 (2003)

Nucleophilic Substitution Reactions in Alkyl Halides

9. Which of the following statements regarding the S_N1 reaction shown by alkyl halide is **not** correct?
(a) The added nucleophile plays no kinetic role in S_N1 reaction
(b) The S_N1 reaction involves the inversion of the sterochemistry around carbon atom of the substrate
(c) The S_N1 reaction on the chiral starting material ends up with the racemization of the product.
(d) The more stable the carbocation intermediate, the faster the S_N1 reaction

10. Which of the following statements regarding S_N2 reaction shown by alkyl halide is **not** correct?
(a) The conversion of reactants to transition state is the rate determining step.
(b) The S_N2 reaction involves the inversion of the stereochemistry around carbon atom of the substrate.
(c) The rate of reaction depends on the steric bulk of the alkyl group.
(d) The nucleophilicity of halides follows the order $Cl^- > Br^- > I^-$

11. The order of reactivity of S_N2 reactions shown by isomers of chlorobutane is
(a) $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3 > (CH_3)_2CHCH_2Cl$
(b) $CH_3(CH_2)_3Cl > (CH_3)_2CHCH_2Cl > CH_3CH_2CHClCH_3$
(c) $(CH_3)_2CHCH_2Cl > (CH_3)_3CCl > CH_3CH_2CHClCH_3$
(d) $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl > CH_3CH_2CHClCH_3$

12. The relative nucleophilicity of H_3N, H_2O and HF towards bromoethane is
(a) $H_3N < H_2O < HF$ (b) $H_3N > H_2O > HF$ (c) $H_3N > H_2O < HF$ (d) $H_3N < H_2O > HF$

13. Which of the following statements regarding the replacement of —Br by a nucleophilic reagent via S_N1 is not correct?
(a) It involves a carbocation as the intermediate
(b) The intermediate involves sp^2 carbon
(c) Polar solvents deccelerate the reaction
(d) The replacement at chiral carbon atom leads to the racemization of the product

14. The order of reactivity for the S_N2 reaction involving replacement of —X by a nucleophile in alkyl halides is
(a) $CH_3 < 1° < 2°$ (b) $CH_3 > 1° > 2°$ (c) $CH_3 < 1° > 2°$ (d) $CH_3 > 1° < 2°$

15. In the following groups

—OAc	—OMe	$—OSO_2Me$	$—OSO_2CF_3$
I	II	III	IV

the order of leaving group ability is
(a) I > II > III > IV (b) IV > III > I > II
(c) III > II > I > IV (d) II > III > IV > I (1997)

16. Which of the following has the highest nucleophilicity?
(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^- (2000)

17. The order of reactivities of the following alkyl halides for a S_N2 reaction is
(a) RF > RCl > RBr > RI (b) RF > RBr > RCl > RI
(c) RCl > RBr > RF > RI (d) RI > RBr > RCl > RF (2000)

18. The hydrolysis of 2-bromo-3-methylbutane yields.
(a) 3- methyl-2-butanol (b) 2- methyl-2-butanol (c) 3-methylbutanol (d) 2-methylbutanol

19. Which of the following orders regarding nucleophilicity is correct?
(a) $HO^- > H_2O$ and $H_2N^- > NH_3$ (b) $HO^- > H_2O$ and $H_2N^- < NH_3$
(c) $HO^- < H_2O$ and $H_2N > NH_3$ (d) $HO^- < H_2O$ and $H_2N < NH_3$

20. Which of the following orders regarding nucleophilicity is correct?
(a) $H_3C^- < H_2N^- < HO^-$ (b) $H_3C^- < HO^- < H_2N^-$ (c) $HO^- < H_2N^- < H_3C^-$ (d) $HO^- < H_3C^- < H_2N^-$

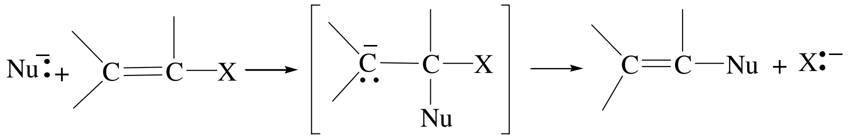
21. Which of the following orders regarding nucleophilicity is correct?
(a) $I^- > Br^- > Cl^-$ (b) $I^- > Cl^- > Br^-$ (c) $Cl^- > I^- > Br^-$ (d) $Cl^- > Br^- > I^-$

22. Which of the following orders regarding nucleophilicity is correct?
(a) $CH_3O^- > CH_3COO^- > HO^-$ (b) $CH_3O^- > HO^- > CH_3COO^-$
(c) $HO^- > CH_3O^- > CH_3COO^-$ (d) $HO^- > CH_3COO^- > CH_3O^-$

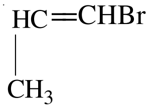
23. The rate of formation of alcohols from CH_3Br, CH_3CH_2Br, $(CH_3)_2CHBr$ in H_2O/EtOH which follow S_N2 mechanism is
(a) $CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$ (b) $CH_3Br > (CH_3)_2CHBr > CH_3CH_2Br$
(c) $(CH_3)_2CHBr > CH_3CH_2Br > CH_3Br$ (d) $(CH_3)_2CHBr > CH_3Br > CH_3CH_2Br$

24. The reaction of $CH_3CH{=}CHCH_2Cl$ with CN^- produces
(a) $CH_3CH{=}CHCH_2CN$ only
(b) $CH_3CH(CN)CH{=}CH_2$ only
(c) a mixture of $CH_3CH{=}CHCH_2CN$ and $CH_3CH(CN)CH{=}CH_2$
(d) $CNCH_2CH_2CH{=}CH_2$ only

25. Nucleophilic displacement on a vinyl halide may be represented as



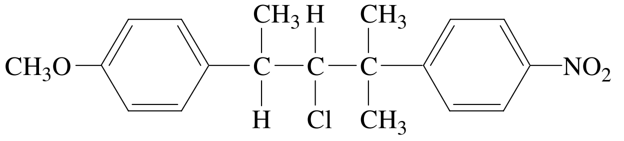
Which of the following vinyl halide is expected to follow this mechanism?
(a) $H_2C{=}CHBr$ (b)



$\underset{CH_3}{\underset{|}{HC}}{=}CHBr$

(c) $(CH_3)_2{=}CHBr$ (d) $F_2C{=}CHBr$

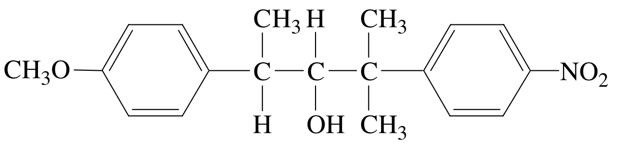
26. The hydrolysis of



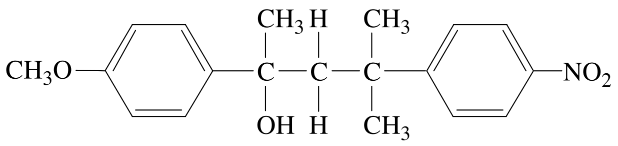
in aqueous acetone gives

(a) K and L (b) only K (c) L and M (d) only M
where

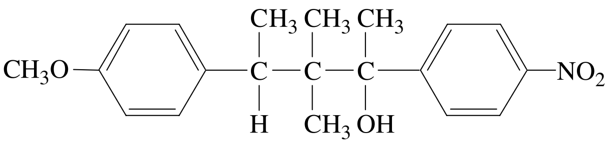
K is



L is

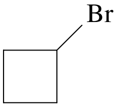


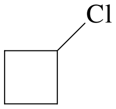
and M is

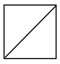


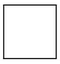
(2005)

27. 1-Bromo-3-chlorocyclobutane when treated with two equivalents of Na in the presence of ether results into

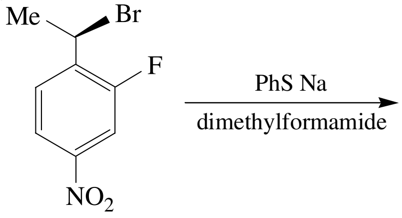
(a) 

(b) 

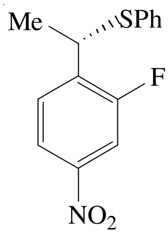
(c) 

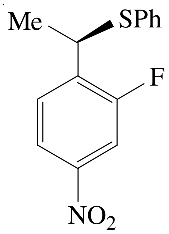
(d) 

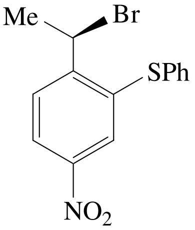
(2005)

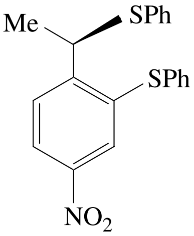
28. The major product of the reaction 

is

(a) 

(b) 

(c) 

(d) 

(2008)

Reactions of Grignared Reagent

29. The reaction of RMgX with R′CHO produces
(a) ROH (b) RCH(OH)R (c) RCH(OH)R′ (d) R′CH(OH)R′

30. The treatment of RMgX with ethyl formate leads to the formation of
(a) RCHO (b) CH_3CH_2OR (c) $RCHOHC_2H_5$ (d) C_2H_5OH

31. The treatment of RMgX with water leads to the formation of
(a) ROH (b) RH (c) RCHO (d) RCH_2OH

32. $(CH_3)_3CMgCl$ on reaction with D_2O produces:
(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$ (c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$ (1997)

33. The treatment of RMgX with the ester R′COOR″ produces
(a) $R'C(OH)(R')_2$ (b) $R'C(OH)(R)_2$ (c) RC(OH)(R’)R” (d) $RC(OH)(R'')_2$

34. The treatment of RMgX with R′COCl produces
(a) $R'C(OH)R_2$ (b) $RC(OH)R'_2$ (c) RC(OH)(R)R′ (d) $RC(OH)R_2$

Elimination Reactions of Alkyl Halides

35. The relative order of elimination reactions of
(A) $CH_3CH_2CH_2CH_2Br$ (B) $CH_3CH_2CHBrCH_3$ and (C) $(CH_3)_3CBr$ with alcoholic KOH is
(a) A > B > C (b) A > C > B (c) C > A > B (d) C > B > A

36. Which of the following products is obtained in highest yield when 2-bromopentane is treated with $CH_3CH_2O^-$ Na^+?
(a) *trans*- $CH_3CH{=}CHCH_2CH_3$ (b) *cis*- $CH_3CH{=}CHCH_2CH_3$
(c) $H_2C{=}CHCH_2CH_2CH_3$ (d) 2-pentanol

37. The order of reactivity of elimination in RX with strong base follows the order
(a) RI < RBr < RCl (b) RI < RCl < RBr (c) RCl < RBr < RI (d) RCl < RI < RBr

38. The major product when 2-bromobutane is treated with ethanolic KOH is
(a) 2-hydroxybutane (b) butanol (c) 1-butene (d) 2-butene

39. The E2 dehydrobromination of (*R*, *R*)-2,3-dibromobutane and (*R*, *S*)-2,3-dibromobutane respectively give
(a) *trans*-2-bromo-2-butene, *trans*-2-bromo-2-butene (b) *trans*-2-bromo-2-butene, *cis*-2-bromo-2-butene
(c) *cis*-2-bromo-2-butene, *trans*-2-bromo-2-butene (d) *cis*-2-bromo-2-butene, *cis*-2-bromo-2-butene

40. Dehalogenation of *vic*-dihalides with active metals or I^- involve *anti* elimination of halogens. The products obtained in dehalogenation of *meso*-2,3-dibromobutane and (*S*, *S*) – 2,3-dibromobutane, respectively are
(a) *trans*-2-butene, *cis*-2-butene (b) *trans*-2-butene, *trans*-2-butene
(c) *cis*-2-butene, *trans*-2-butene (d) *cis*-2-butene, *cis*-2-butene

41. Which of the following compounds reacts rapidly with the cold $AgNO_3$ solution?
(a) $CH_3CH{=}CHCl$ (b) $CH_3CH_2CH_2Cl$ (c) $CH_2{=}CHCH_2Cl$ (d) $CH_3CH_2CH(Cl)_2$

Aryl Halides

42. Fittig reaction involves
(a) two molecules of alkyl halides
(b) two molecules of aryl halides
(c) one molecule of each of alkyl and aryl halide
(d) one molecule of alkyl halide and one molecule of aldehyde

43. Chlorination of toluene with excess of chlorine under the condition of light and heat produces
(a) *o*-chlorotoluene (b) *p*-chlorotoluene (c) benzyl chloride (d) benzotrichloride

44. Chlorination of benzene proceeds via
(a) nucleophilic substitution mechanism (b) electrophilic substitution mechanism
(c) elimination-addition mechanism (d) addition-elimination mechanism

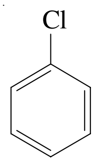
45. Which of the following reactions is highly exothermic?
(a) Fluorination of benzene (b) Chlorination of benzene
(c) Bromination of benzene (d) Iodination of benzene

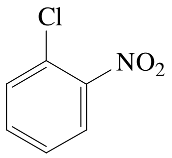
46. Which of the following reactions is an endothermic reaction?
(a) Fluorination of benzene (b) Chlorination of benzene
(c) Bromination of benzene (d) Iodination of benzene

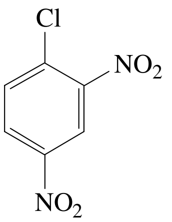
47. Which of the following statements is correct?
(a) Alkyl halides are more reactive than aryl halides towards nucleophilic substitution reactions
(b) Alkyl halides are less reactive than aryl halides towards nucleophilic substitution reactions
(c) The presence of an electron-withdrawing substituent at *ortho* and/or *para* position decreases the reactivity of nucleophilic substitution of chlorine in the substituted chlorobenzene
(d) The replacement of chlorine in chlorobenzene by strong bases proceeds via elimination-addition reaction

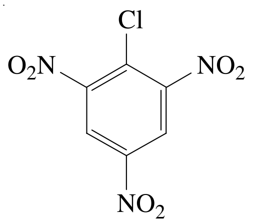
48. The Wurtz-Fittig reactions involves
(a) two molecules of aryl halides
(b) two molecules of alkyl halides
(c) one molecule of each of aryl halide and alkyl halide
(d) one molecule of each of aryl halide and phenol

49. Which of the following compounds undergoes replacement of —Cl by —OH by merely warming the compound with aqueous NaOH?

(a)


(b)


(c)


(d)


50. The chlorine atom in chlorobenzene is *ortho* and *para* director because
(a) resonance effect predominates over inductive effect
(b) inductive effect predominates over resonance effect
(c) both inductive and resonance effects are evenly matched
(d) only resonance effect and not inductive effect is operating

51. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to
(a) the formation of less stable carbonium ion (b) resonance stabilization
(c) longer carbon-halogen bond (d) inductive effect

52. In the reaction *p*-chlorotoluene with KNH_2 in liquor NH_3, the major product is
(a) *o*-toluidine (b) *m*-toluidine (c) *p*-toluidine (d) *p*-chloroaniline

Multiple Correct Choice Type

1. Aryl halides are less reactive towards nucleophilic substitution as compared to alkyl halides due to
(a) the formation of less stable carbonium ion (b) resonance stabilization
(c) the inductive effect (d) sp^2-hybridized carbon attached to the halogen

2. Which of the following factors favour S_N1 elimination in alkyl chloride?
(a) Stability of R^+ (b) Steric hindrance (c) Protic solvent (d) Aprotic solvent

3. Which of the following statements is correct for S_N1 reactions?
(a) The reaction follows first-order kinetics
(b) The nucliophile plays no role in the mechanism
(c) The rate determinig step is the conversion of transition state to the product.
(d) The rate of reaction does not depend on the steric bulk of the alkyl group.

4. Which of the following statements is correct for S_N2 reactions?
(a) The conversion of reactant to transition state is the rate determining step.
(b) The rate depends on the concentration and nature of nucleophile.
(c) Protic solvents increase the rate of reaction.
(d) The weaker the leaving base, faster the rate of replacement.

5. Which of the following factors favour substitution reaction than elimination reaction in an alkyl halide?
(a) Strong base (b) Sterically unhindered haloalkane
(c) Sterically unhindered nucleophile (d) Aqueous solvent

6. Which of the following factors favour elimination reaction than substitution reaction in an alkyl halide?
(a) Low polarity of solvent (b) Strong base
(c) High concentration of base (d) Sterically unhindered haloalkene.

7. Which of the following factors are involved in S_N1 mechanism in haloalkane?
(a) No concentration effect of substrate
(b) Rearrangement of alkyl group.
(c) Use of catalyst helps increasing rate of reaction
(d) No solvent effect.

8. Which of the following factors are involved in S_N2 mechanism in haloalkane?
(a) Second-order kinetics
(b) Inversion of stereocentre
(c) Rearrangement of alkyl group
(d) Use of Lewis and Bronsted acids helps increasing the rate of reaction.

Linked Comprehension Type

1. Much of the chemistry of alkyl halides is dominated by their electrophilic behaviour. Identify the halomethane with maximum value of its physical properties.

(i) Maximum bond length is possessed by
(a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I

(ii) Maximum bond dissociation energy is possessed by
(a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I

(iii) Maximum value of dipole moment is possessed by
(a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I

2. Optically pure (*S*)-(+)–2-bromooctane, $[\alpha]_D^{25^\circ} = +35^\circ$, reacts with aqueous NaOH in acetone to give optically pure (*R*)-(–)-2-octanol, $[\alpha]_D^{25^\circ} = -10^\circ$. With partially racemized bromo compound whose $[\alpha]_D^{25^\circ} = +30^\circ$, the $[\alpha]_D^{25^\circ}$ of the alcohol product is -6.0°. Based on these informations answer the following three questions.

(i) The percentages of optical purity of partially racemized bromo and alcohol, respectively, are
(a) 85.7, 60 (b) 60, 85.7 (c) 75, 25 (d) 25, 75

(ii) The percentages of inversion and racemization of the conversion, respectively, are
(a) 30, 70 (b) 70, 30 (c) 33, 67 (d) 67, 33

(iii) The percentage of frontside and backside attack in the conversion, respectively, are
(a) 65, 35 (b) 67, 33 (c) 15, 85 (d) 83, 16

Assertion and Reason Type

Given below are questions, each containing two statements. Answer each question correctly using the following key.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct exsplanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement–1	**Statement–2**
1.	Aryl halides undergo nucleophilic substitution with ease.	The carbon-halogen bond in aryl halides has partial double bond character.
2.	Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.	CN^- is a strong nucleophile.
3.	The rate of solvolyses of an alkyl halide following S_N1 mechanism increases in the presence of $AgNO_3$.	The precipitation of AgX helps increasing the rate of reaction.
4.	The more acidic the nucleophlic solvent, the faster the rate of S_N1 solvolysis.	The greater the acidity of the H, the more effective is the hydrogen bonding which leads to acceleration of dissociation of alkyl halide.
5.	The rate of solvolysis $(CH_3)_3CBr$ decreases with increase in polarity of the solvent.	The formation of $(CH_3)_3C^+$ increase with increase in polarity of solvent.
6.	In E1cb mechanism, the rate of overall elimination reaction in RX is independent of the nature of X.	X is eliminated in the fast step from a carboc- -ation.
7.	The order of nucleophilic displacement of X follows the order RI > RBr > RCl >>RF.	The weaker the Brönsted basicity of X^-, the better leaving group is X^- and the more reactive is RX.
8.	The C—Cl bond of vinyl chloride is shorter and stronger than the C—Cl bond of alkyl chloride.	The vinyl chloride involves resonance $CH_2{=}CH_2{-}Cl \leftrightarrow + \overset{+}{C}H_2{-}CH{=}\overset{+}{C}l$.
9.	Vinyl chloride does not undergo S_N1 and S_N2 substitution reactions.	Vinyl cation is unstable species.
10.	Strong base leads to less elimination than substitution in alkyl halide.	Strong base helps extracting H^+ from the β-position.
11.	The E2 elimination in alkyl halide is stereospecific.	The transition state in E2 elimination in alkyl halide involves *cis*-coplanar conformation.
12.	*tert*-Butyl fluoride is solvolyzed only in very acidic conditions.	H- Bonding of F with a strong acid helps departuring F.
13.	*tert*-Butyl chloride is solvolyzed much slower than 2-chloro-1,1,1-trifluoro-2-methylpropane (A).	Carbocation formed in A is destabilized due to electron-withdrawing F_3C group.
14.	$(CD_3C^+$ is not stable as $(CH_3)_3C^+$.	CD_3 is as good an electron-donator as CH_3.

Matrix Match Type

1. Match the entries on the left with most appropriate choice(s) given on the right.

(a) $C_6H_5CH_2CD_2Br$ on reaction with $C_2H_5O^-$ gives $C_6H_5–CH{=}CD_2$	(p) E_1
(b) $C_6H_5CHBrCH_3$ and $C_6H_5CHBrCD_3$ both react with the same rate	(q) E_2
(c) $C_6H_5CHDCH_2Br$ on treatment with $C_2H_5O^-$ and C_2H_5OD gives $C_6H_5CD{=}CH_2$	(r) $E_{1,cb}$
(d) $C_6H_5CH_2CH_2Br$ reacts faster than $C_6H_5CD_2CH_2Br$ on reaction with $C_2H_5O^-$ in ethanol	(s) First order reaction

(2006)

2. Match the entries on the left with most appropriate choice(s) given on the right.

(a) Dehalogenation of *meso*-2,3-dibromobutane	(p) S_N2'
(b) (*S*, *S*)-2,3-dibromobutane	(q) *cis*-2-butene
(c) Hydrolysis of 2-bromo-3-methylbutane	(r) S_N1
(d) $CH_3CH{=}CHCH_2Cl + CN^-$	(s) *trans*-2-butene
	(t) *anti*-elimination

ANSWERS

Straight Objective Type

1. (a) **2.** (c) **3.** (d) **4.** (a) **5.** (a) **6.** (c) **7.** (d)
8. (b) **9.** (b) **10.** (d) **11.** (b) **12.** (b) **13.** (c) **14.** (b)
15. (b) **16.** (c) **17.** (d) **18.** (b) **19.** (a) **20.** (c) **21.** (a)
22. (b) **23.** (a) **24.** (c) **25.** (d) **26.** (a) **27.** (c) **28.** (a)
29. (c) **30.** (a) **31.** (b) **32.** (a) **33.** (b) **34.** (a) **35.** (d)
36. (a) **37.** (c) **38.** (d) **39.** (b) **40.** (a) **41.** (c) **42.** (b)
43. (a) **44.** (b) **45.** (c) **46.** (d) **47.** (a) **48.** (c) **49.** (d)
50. (a) **51.** (b) **52.** (b)

Multiple Correct Choice Type

1. (b), (d) **2.** (a), (b), (c) **3.** (a), (b) **4.** (a), (b), (d)
5. (b), (c) **6.** (a), (b), (c) **7.** (b), (c) **8.** (a), (b)

Linked Comprehension Type

1. **(i)** (d) **(ii)** (a) **(iii)** (b)
2. **(i)** (a) **(ii)** (b) **(iii)** (c)

Assertion and Reason Type

1. (d) **2.** (d) **3.** (a) **4.** (a) **5.** (d) **6.** (c) **7.** (a)
8. (b) **9.** (b) **10.** (d) **11.** (c) **12.** (a) **13.** (d) **14.** (c)

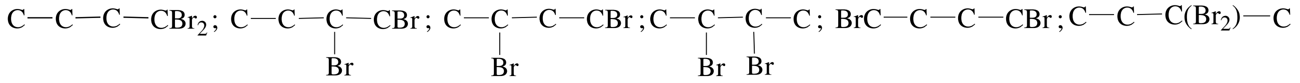
Matrix Match Type

1. (a) – (q); (b) – (p), (s); (c) – (q); (d) – (q) **2.** (a) – (s), (t); (b) – (q), (t); (c) – (r); (d) – (p)

Hints and Solutions

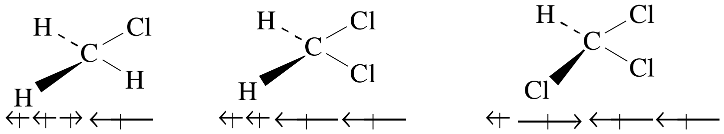
Straight Objective Type

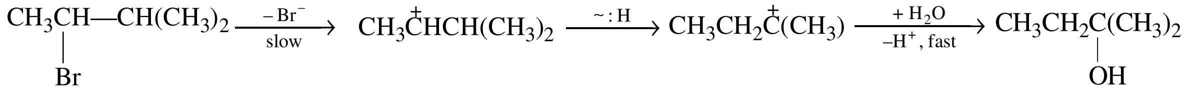
1. The bond dissociation enthalpy C — X (where X is halogen) is C — Cl > C — Br > C — I
2. The dipole moment of CH_3X (where X is halogen) follows the order $CH_3F < CH_3Cl > CH_3Br$
3. Longer the hydrocarbon chain, the larger the boiling point.
4. CH_3F has minimum boiling point amongst the given halomethanes.
5. Larger the branching of hydrocarbon chain, lesser the boiling point. Hence, the correct order is
   $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3 > (CH_3)_3CCl$
6. The skeleton of isomers are



$$\text{C—C—C—CBr}_2;\ \text{C—C—}\underset{\text{Br}}{\text{C}}\text{—CBr};\ \text{C—}\underset{\text{Br}}{\text{C}}\text{—C—CBr};\ \text{C—}\underset{\text{Br}}{\text{C}}\text{—}\underset{\text{Br}}{\text{C}}\text{—C};\ \text{BrC—C—C—CBr};\ \text{C—C—C(Br}_2\text{)—C}$$

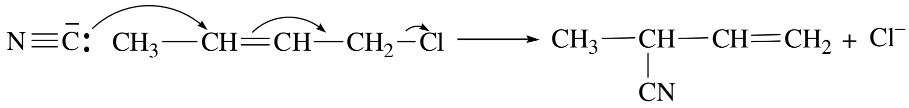
7. The reagent $SOCl_2$ is most effective.
8. In CH_2Cl_2 all bond moments reinforce each other, while in CH_3Cl and $CHCl_3$ only one CCl and CH bond moments reinforce each other as shown in the following figure.



9. The S_N1 reaction may or may not involve the inversion of stereochemistry around carbon atom of the substrate.
10. The nucleophilicity of halides follows the order $Cl^- < Br^- < I^-$
11. Crowding around the centre of reaction decreases rate of reaction. The correct order is
    $CH_3(CH_2)_3Cl > (CH_3)_2CHCH_2Cl > CH_3CH_2CHClCH_3$
12. The more electronegativity of atom, lesser the nucleophilicity. The correct order is $H_3N > H_2O > HF$.
13. Polar solvents accelerate the rate of S_N1 reaction.
14. The increase in bulkiness of alkyl group decreases reactivity for the S_N2 reaction. The correct order is
    $CH_3 > 1° > 2°$.
15. The weaker the base, larger the leaving group ability. The order of acid strength of the conjugate acids is
    $F_3CSO_2OH > CH_3SO_2OH > HOAc > MeOH$
    The order of corresponding conjugate bases is $F_3CSO_2O^- < CH_3SO_2O^- < {}^-OAc < MeO^-$
    The same will also be leaving group ability.
16. More the electronegativity of the atom to which H is attached, lesser the nucleophilicity of the anion. Thus CH_3^- has the highest nucleophilicity.
17. Stronger the C—X bond, lesser the reactivity of the alkyl halides for a S_N2 reaction. Thus, the correct order is $RI > RBr > RCl > RF$.
18. 

$$\underset{\text{Br}}{CH_3CH}\text{—}CH(CH_3)_2 \xrightarrow[\text{slow}]{-Br^-} CH_3\overset{+}{C}HCH(CH_3)_2 \xrightarrow{\sim:H} CH_3CH_2\overset{+}{C}(CH_3) \xrightarrow[-H^+,\ \text{fast}]{+H_2O} CH_3CH_2\underset{\text{OH}}{C}(CH_3)_2$$

19. Bases are better nucleophiles than their conjugate acids
20. In going from left to right across the periodic table, nucleophilicity decreases.
21. In going down a group in the periodic table, nucleophilicity increases.
22. When the nucleophilic and basic sites are the same, nucleophilicity parallels basicity.
23. The steric hindrance causes the decreases in the rate of S_N2 reaction.
24. $CH_3CH{=}CHCH_2Cl + CN^- \rightarrow CH_3CH{=}CHCH_2CN$



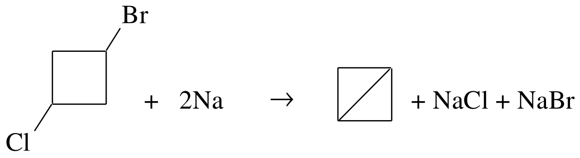
$$N{\equiv}\bar{C}\!:\ CH_3\text{—}CH{=}CH\text{—}CH_2\text{—}Cl \longrightarrow CH_3\text{—}\underset{\text{CN}}{CH}\text{—}CH{=}CH_2 + Cl^-$$

The second reaction is said to follow S_N2' mechanism.

25. The electron-attracting F atoms stabilizes the intermediate carbanion. Hence, $F_2C{=}CHBr$ will exhibit this mechanism.

26. With acetone as solvent, the reaction proceeds with the characteristics of both S_N1 and S_N2 mehanisms. The S_N1 involves hydride shift giving structure L.

27. The reaction involves intramolecular elimination of halogens by using sodium. (Wurtz reaction).



28. The reaction involves nucleophilic substitution of a halogen by PhS^-. It is easy to carry such substitution in alkyl halide than in aryl halide. The substitution will proceed via S_N2 mechanism, which results into the inversion of configuration of carbon atom at which substitution reaction occurs.

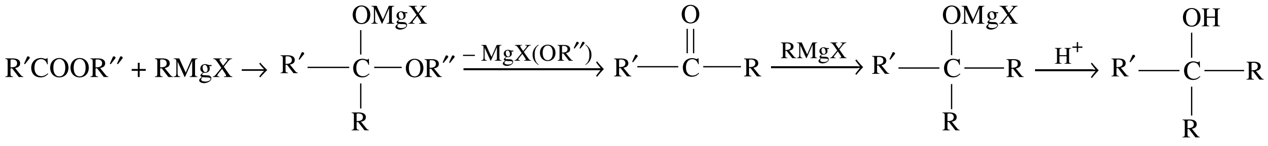
29. The reaction is $R'CHO + RMgX \longrightarrow R'CH(OMgX)R \xrightarrow{H_2O} R'CH(OH)R$

30. $HCOOC_2H_5 + RMgX \longrightarrow RCHO + Mg(OC_2H_5)X$

31. $H_2O + RMgX \longrightarrow RH + Mg(OH)X$

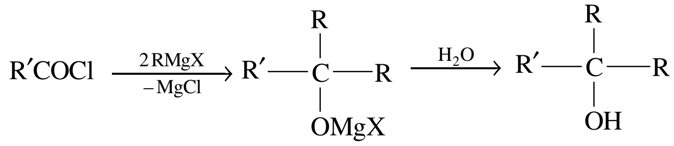
32. $(CH_3)_3CMgCl \xrightarrow{D_2O} (CH_3)_3CD$

33.



$$R'COOR'' + RMgX \rightarrow R'-\underset{R}{\overset{OMgX}{C}}-OR'' \xrightarrow{-MgX(OR'')} R'-\overset{O}{\overset{\|}{C}}-R \xrightarrow{RMgX} R'-\underset{R}{\overset{OMgX}{C}}-R \xrightarrow{H^+} R'-\underset{R}{\overset{OH}{C}}-R$$

34.



$$R'COCl \xrightarrow[-MgCl]{2RMgX} R'-\underset{OMgX}{\overset{R}{C}}-R \xrightarrow{H_2O} R'-\underset{OH}{\overset{R}{C}}-R$$

35. The relative order of reactivities of RBr's is 3° > 2° > 1°.

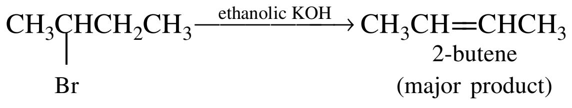
36. There are three possible products. These are

cis-$CH_3CH{=}CHCH_2CH_3$; *trans*-$CH_3CH{=}CHCH_2CH_3$ and $H_2C{=}CHCH_2CH_2CH_3$.

The most substituted alkene is produced with the highest yield as predicted by the Saytzeff's rule, with *trans* dominating over *cis*.

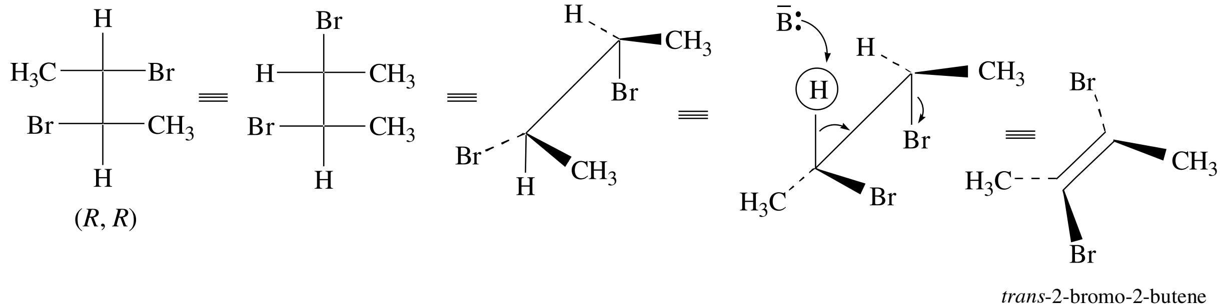
37. The rate of reaction depends directly on the leavability of X^-. The weakest base is the best leaving group. Hence, the reactivities follow the order $RCl < RBr < RI$.

38. The reaction is



$$CH_3\underset{Br}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{\text{ethanolic KOH}} \underset{\substack{\text{2-butene}\\\text{(major product)}}}{CH_3CH{=}CHCH_3}$$

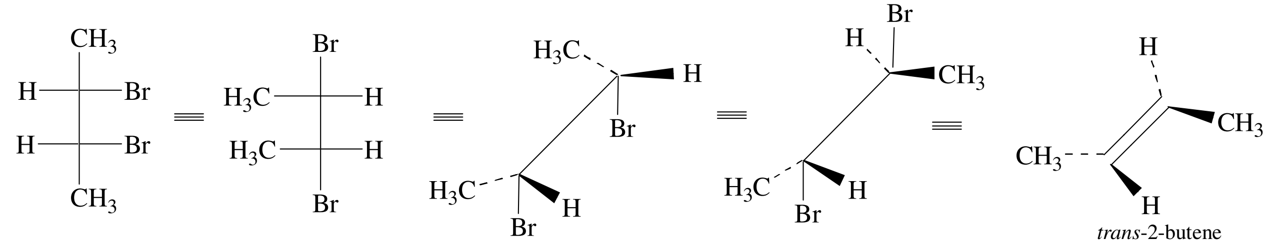
39.



trans-2-bromo-2-butene

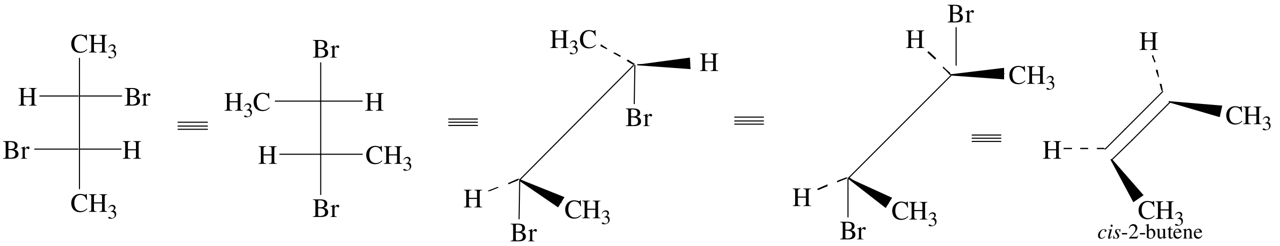
(*RS*)-isomer gives *cis*-2-bromo-2-butene.

40.



meso-2,3-dibromobutane

trans-2-butene

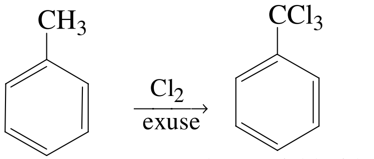


cis-2-butene

41. Allylic chloride ($CH_2{=}CHCH_2Cl$) reacts rapidly with $AgNO_3$ in the cold. $CH_3CH_2CH_2Cl$ is less reactive, it gives white precipitate only on warming. Vinyl chloride ($CH_3CH{=}CHCl$) is inert to $AgNO_3$.

42. Fittig reaction involves two molecules of aryl halides.

43. Under the condition of light and heat, chlorination of side chain occurs.



benzotrichloride

44. Chlorination of benzene proceeds via electrophilic substitution mechanism.

45. Fluorination of benzene is highly exothermic.

46. Iodination of benzene is an endothermic reaction.

47. Choice a is correct, i.e. alkyl halides are more reactive than aryl halides towards nucleophilic substitution reaction.

48. The Wurtz-Fittig reaction involves one molecule of each aryl halide and alkyl halide.

49. Trinitrotoluene requires mild condition for the replacement of —Cl by —OH.

50. The chlorine atom in chlorobenzene is *ortho* and *para* director because resonance effect predominates over inductive effect.

51. Resonance stabilization makes halogen less reactive in aryl halides as compared to alkyl halides.

52. The reaction proceeds via elimination-addition mechanism. The major product is *m*-toluidine.

Multiple Correct Choice Type

1. The choice b and d are correct. The lesser reactivitiy of aryl halide is due to resonance stabilization and sp^2-hybridized carbon attached to the halogen.

2. Stability of R^+, steric hindrance and protic solvent favour S_N1 reactions.

3. (a) The rate expression is $r = k$ [haloalkane]　(b) Nucleophile is involved in the fast reaction.
(c) Substrate → Transition state is the slow step.　(d) Steric bulk favours S_N1 mechanism.

4. (a) The first step involved　Haloalkane + nucleophile → Transition state　is the slow step.
(b) The reaction follows second-order kinetics;　rate = k[haloalkane][nucleophile]
(d) The weaker the base, faster the replacement.

5. Sterically unhindred haloalkane and nucleophile favour substitution reaction.

6. Low polarity of solvent, strong base and high concentration of base favour elimination reaction.

7. S_N1 may accompany with rearrangement of alkyl group. The catalyst helps removing halogen.

8. S_N2 follows second-order kinetics. This is accompanied with inversion of stereocentre.

Linked Comprehension Type

1. **(i)** Bond length is maximum for C—I, bond length increases as the size of halogen is increased.

(ii) C—F bond has maximum bond dissociation energy.

(iii) CH_3Cl has the maximum value of dipole moment.

2. **(i)** Percent purity of bromide = $\frac{30°}{35°}$ (100%) = 85.7%

Percent purity of alcohol = $\frac{-6°}{-10°}$ (100%) = 60%

(ii) Per centage inversion (S_N2 mechanism) = $\frac{60\%}{85\%}$ (100%) = 70%

Per centage racemization (S_N1 mechanism) = 100% – 70% = 30%

(iii) Inversion involves only backside attack, while racemization results from equal backside and frontside attacks. The percentage of backside attack is the sum of the inversion and one-half the percentage of racemization. The percentage of frontside attack is the one-half of the percentage of racemization. Hence,

Percentage of backside attack = 70% + $\frac{1}{2}$ (30%) = 85%

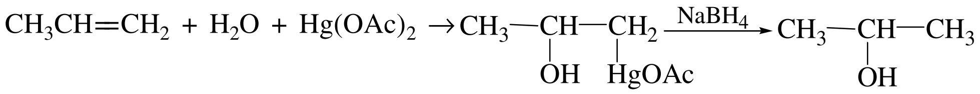
Percentage of frontside attack = $\frac{1}{2}$ (30%) = 15%

CHAPTER 26

ALCOHOLS AND ETHERS

METHODS OF PREPARATION

1. Oxymercuration-demercuration process Alkenes react with mercury acetate in the presence of water to give hydroxymercurial compounds which on reduction with sodium borohydride ($NaBH_4$) yield alcohol. The net result is the addition of H_2O to the double bond and the product obtained is in agreement with Markovnikov's rule. For example,



$$CH_3CH{=}CH_2 + H_2O + Hg(OAc)_2 \rightarrow CH_3{-}\underset{OH}{\underset{|}{C}H}{-}\underset{HgOAc}{\underset{|}{C}H_2} \xrightarrow{NaBH_4} CH_3{-}\underset{OH}{\underset{|}{C}H}{-}CH_3$$

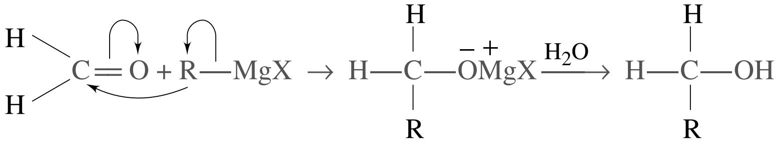
No rearrangement occurs in this reaction.

2. Hydroboration-oxidation process Alkenes undergo hydroboration with diborane to yield alkylboranes which on oxidation with alkaline H_2O_2 give alcohols. The net result is the addition of H_2O to the double bond and the product obtained is in accordance with the anti-Markovnikov's rule. For example,

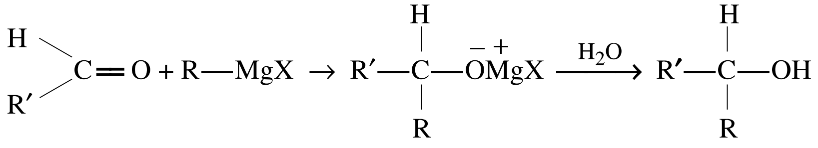
$$CH_3CH{=}CH_2 + BH_3 \rightarrow CH_3CH_2CH_2BH_2 \xrightarrow{H_2O_2,\ O\overline{H}} \underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH}$$

No rearrangement occurs during the hydroboration.

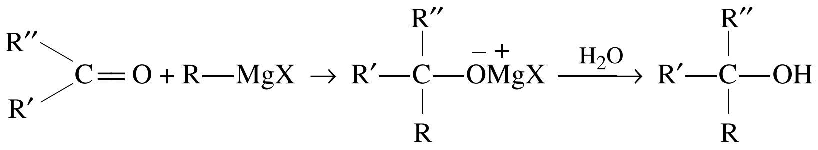
3. Grignard synthesis of alcohols Reaction of aldehyde or ketone with RMgX produces alcohol.



1° alcohol

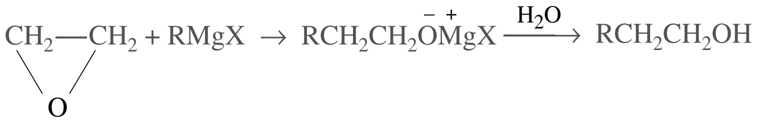


2° alcohol

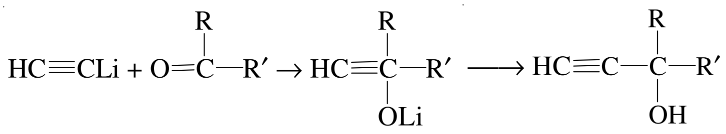


3° alcohol

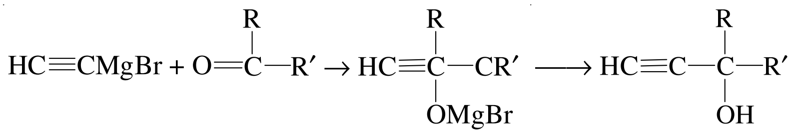
4. Reaction of ethylene oxide with RMgX



5. Reactions of lithium acetylides or alkynyl Grignard reagents with aldehyde or ketone



$$HC\equiv CLi + O=\overset{R}{C}-R' \rightarrow HC\equiv \underset{OLi}{\overset{R}{C}}-R' \longrightarrow HC\equiv C-\underset{OH}{\overset{R}{C}}-R'$$

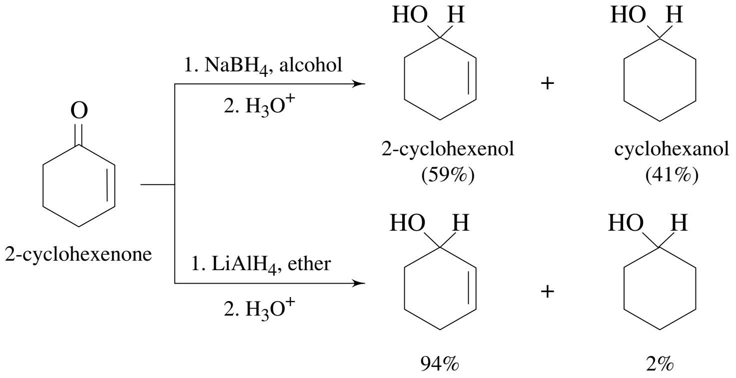


$$HC\equiv CMgBr + O=\overset{R}{C}-R' \rightarrow HC\equiv \underset{OMgBr}{\overset{R}{C}}-CR' \longrightarrow HC\equiv C-\underset{OH}{\overset{R}{C}}-R'$$

6. Reduction of aldehydes and ketones Sodium borohydride, $NaBH_4$, is the convenient reagent to carry out the reduction of aldehydes or ketones into alcohol.

$$RCHO \xrightarrow[2.\ H_3O^+]{1.\ Na\,BH_4 \text{ in alcohol}} RCH_2OH$$

$LiAlH_4$ in ether can also be used for reduction. It is particularly useful for reducing α, β-unsaturated ketones. The reduction of such a ketone gives a mixture of both unsaturated and saturated alcohols. For example,



PHYSICAL PROPERTIES

Due to the hydrogen bonding, alcohols have higher boiling points than their structural isomers. The boiling point decreases with increase in branching, i.e. the order of boiling point is primary > secondary > tertiary.

CHEMICAL PROPERTIES

The general formula of simple alcohol is ROH. The reactions shown by alcohols may be classified into two categories, namely, R ⋯ OH bond cleavage and RO ⋯ H bond cleavage.

Reactions Exhibiting R ⋯ OH Bond Cleavage

1. Reaction with hydrogen halides

$$R—OH + HX \rightarrow RX + H_2O$$

The mechanism is as follows

As such —OH is a poor leaving group. But its protonation converts into a good leaving group.

$$ROH + HX \xrightleftharpoons[\text{fast}]{} ROH_2^+ + X^-$$

ROH_2^+ reacts with X^- following either S_N1 or S_N2 mechanism.

1° alcohol (S_N2 mechanism) $X^- + ROH_2^+ \rightarrow XR + H_2O$

3° alcohol (S_N1 mechanism) $ROH_2^+ \xrightarrow[\text{slow}]{-H_2O} R^+ \xrightarrow[\text{fast}]{X^-} RX$

2° alcohol may proceed by both the mechanisms. Carbocation R^+ formed in S_N1 mechanism may undergo rearrangement.

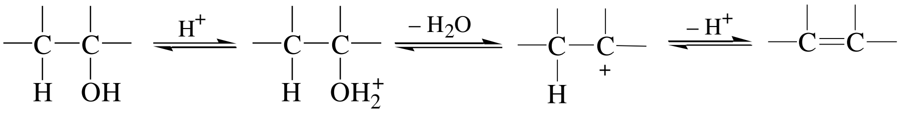
The order of reactivity is HI > HBr > HCl; allyl, benzyl > 3° > 2° > 1°

The reagents, used are concentrated HBr or NaBr + concentrated H_2SO_4, HCl + $ZnCl_2$ and concentrated HCl.

2. Dehydration

$$CH_3{-}CH_2{-}CH_2{-}CH_2OH \xrightarrow[\Delta]{H^+} \underset{\substack{\text{2-butene}\\\text{(main product)}}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene}}{CH_3CH_2\,CH{=}CH_2}$$

The mechanism is



The reaction may show rearrangement. Reactivity of ROH: 3° > 2° > 1°

The primary alcohol is dehydrated using concentrated H_2SO_4. The secondary and tertiary alcohols are dehydrated using dilue H_2SO_4 to avoid the polymerization of alkenes. Saytzeff's rules is applicable so as to get more substituted alkene.

3. Reaction with phosphorous trihalides

$$3R{-}OH + PX_3 \rightarrow 3R{-}X + H_3PO_3; \quad (PX_3 \equiv PBr_3,\ PI_3)$$

Reactions Exhibiting RO···H Bond Cleavage

4. Reaction with active metals

$$RO{-}H + M \rightarrow R\bar{O}M^+ + \tfrac{1}{2}H_2; \quad (M == \text{Na, K, Mg, Al, etc.})$$

Reactivity of alcohol CH_3OH > 1° > 2° > 3°

The above reaction shows alcohol as an acid. It is worth comparing the acid strength of alcohol with other species based on the following reactions.

$$\underset{\substack{\text{stronger base}\\\text{acid}}}{RO^-Na^+} + \underset{\substack{\text{stronger}\\\text{base}}}{H{-}OH} \rightarrow \underset{\substack{\text{weaker}\\\text{acid}}}{Na^+\,OH^-} + \underset{\substack{\text{weaker}\\\text{base}}}{RO{-}H}$$

$$\underset{\substack{\text{stronger}\\\text{acid}}}{HC{\equiv}\bar{C}Na^+} + \underset{\substack{\text{stronger}\\\text{base}}}{RO{-}H} \rightarrow \underset{\substack{\text{weaker}\\\text{acid}}}{R\bar{O}Na^+} + \underset{\text{weaker}}{HC{\equiv}C{-}H}$$

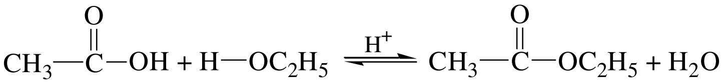
$$\underset{\substack{\text{stronger}\\\text{base}}}{H_2N^-\,Na^+} + \underset{\substack{\text{stronger}\\\text{acid}}}{RO^-\,H} \rightarrow \underset{\substack{\text{weaker}\\\text{base}}}{R\bar{O}Na^+} + \underset{\substack{\text{weaker}\\\text{acid}}}{H_2N{-}H}$$

$$\underset{\substack{\text{stronger}\\\text{acid}}}{ROH} + R'MgX \rightarrow \underset{\substack{\text{weaker}\\\text{acid}}}{R'H} + Mg(OR)X$$

Thus the relative order of acidity is $H_2O > ROH > HC{\equiv}CH > NH_3 > RH$

The relative order of basicity follows the reverse order, i.e. $OH^- < OR^- < HC{\equiv}C^- < NH_2^- < R^-$

5. Reaction with carboxylic acid This results in the formation of an ester.

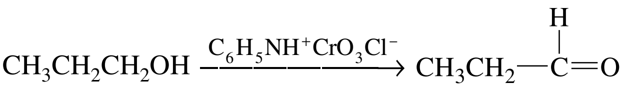


$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + H{-}OC_2H_5 \overset{H^+}{\rightleftharpoons} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5 + H_2O$$

ethyl acetate

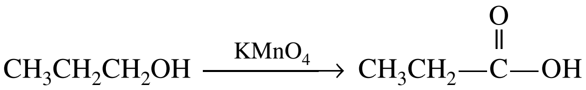
Instead of acetic acid, acetic anhydride or acetyl chloride can also be used.

6. Oxidation of alcohols The oxidation of an alcohol involves the loss of one or more α-hydrogens. 1° alcohol is changed to an aldehyde by using the reagent pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$) formed by the reaction between chromic acid and pyridinium chloride. For example,



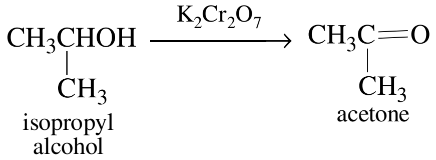
$$\underset{\text{1–propanol}}{CH_3CH_2CH_2OH} \xrightarrow{C_6H_5NH^+CrO_3Cl^-} \underset{\text{propanal}}{CH_3CH_2{-}\overset{\overset{\displaystyle H}{|}}{C}{=}O}$$

1° alcohol is directly converted into a carboxylic acid by the use of potassium permanganate. For example,



$$\underset{\text{1-propanol}}{CH_3CH_2CH_2OH} \xrightarrow{KMnO_4} \underset{\text{propanoic acid}}{CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

2° alcohol is changed into a ketone by the use of potassium dichromate or CrO_3 in glacial acetic acid or CrO_3 in pyridine. For example,



$$\underset{\text{isopropyl alcohol}}{CH_3\underset{|}{\overset{}{C}}HOH\ (CH_3)} \xrightarrow{K_2Cr_2O_7} \underset{\text{acetone}}{CH_3C(=O)CH_3}$$

3° alcohol is not oxidizable as it does not contain α-hydrogen.

The Jones reagent (a chromic acid in aqueous acetone solution) is a mild oxidizing agent. It oxidizes –OH without affecting or rearranging the double bond (if present). For example,

$$CH_3CH{=}CHCH(OH)CH_3 \xrightarrow{\text{Jones reagent}} CH_3CH{=}CHCOCH_3$$

MnO_2, a milder oxidizing agent, oxidizes allylic and benzylic — OH group without affecting double bond, if present. For examples

$$CH_3CH_2CH{=}CHCH_2OH \xrightarrow{MnO_2} CH_3CH_2CH{=}CHCHO.$$

$$PhCH_2OH \xrightarrow{MnO_2} PhCHO$$

$$PhCH(OH)CH_2CH_2OH \xrightarrow{MnO_2} PhCOCH_2CH_2OH$$

CHARACTERIZATION OF ALCOHOLS

1. Oxidation Method

$$1°\text{ alcohol} \xrightarrow{[O]} \text{aldehyde} \xrightarrow{[O]} \text{carboxylic acid}$$

$$2°\text{ alcohol} \xrightarrow{[O]} \text{ketone}$$

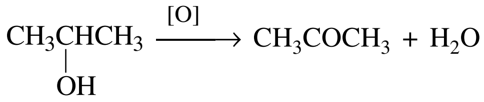
$$3°\text{ alcohol} \xrightarrow{[O]} \text{no reaction}$$

However, drastic oxidation will convert ketone (formed from 2° alcohol) and 3° alcohol into carboxylic acid containing fewer carbon atoms.

When the vapours of alcohols are passed over hot metallic Cu at 570 K, limited oxidation takes place.

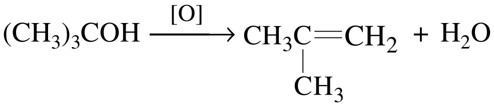
1° alcohol : $CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$

2° alcohol :



$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow{[O]} CH_3COCH_3 + H_2O$$

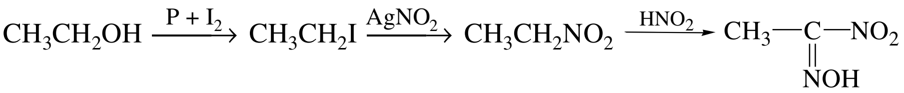
3° alcohol :



$$(CH_3)_3COH \xrightarrow{[O]} CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

2. Victor-Meyer Method The alcohols are treated with P_4 and I_2 to form an alkyliodide. This on treatment with $AgNO_2$ yields nitroalkanes. On treating the latter with aqueous $NaNO_2$ acidified with HCl and then alkaline with NaOH produces different colouration.

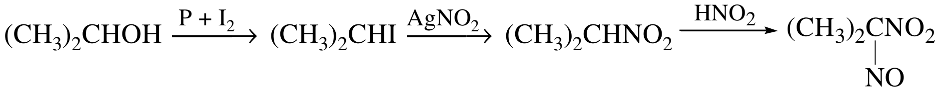
1° alcohol



$$CH_3CH_2OH \xrightarrow{P + I_2} CH_3CH_2I \xrightarrow{AgNO_2} CH_3CH_2NO_2 \xrightarrow{HNO_2} CH_3{-}\underset{\underset{NOH}{||}}{C}{-}NO_2$$

nitrolic acid
(Blood red colour)

2° alcohol



$$(CH_3)_2CHOH \xrightarrow{P + I_2} (CH_3)_2CHI \xrightarrow{AgNO_2} (CH_3)_2CHNO_2 \xrightarrow{HNO_2} (CH_3)_2\underset{\underset{NO}{|}}{C}NO_2$$

pseudo nitrol
(Blue colour)

3° alcohol $(CH_3)_3COH \xrightarrow{P + I_2} (CH_3)_3CI \xrightarrow{AgNO_2} (CH_3)_3CNO_2 \xrightarrow{HNO_2}$ no reaction

3. Lucas Test Lucas reagent is a mixture of concentrated hydrochloric acid and zinc chloride. It converts alcohol into chloride and the formation of the latter is indicated by the appearance of cloudiness which marks the separation of chloride from the solution.

A tertiary alcohol reacts immediately, a secondary alcohol reacts within five minutes and a primary alcohol does not react appreciably at room temperature.

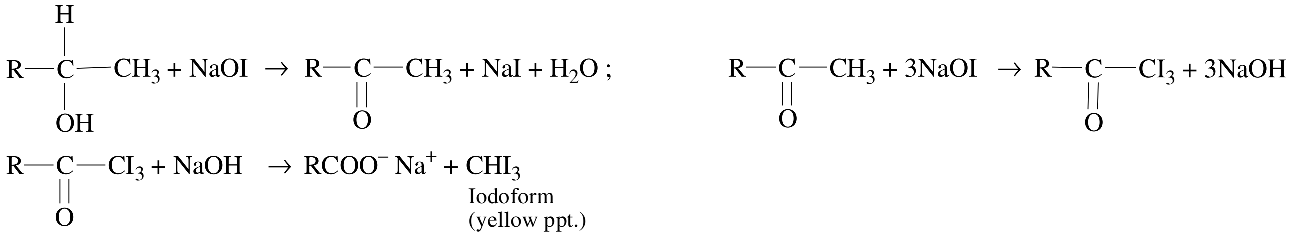
Allyl alcohol reacts as rapidly as tertiary alcohols but it remains in the solution.

Characteristic Test of CH_3CO— Group

An alcohol of the type $R-\underset{\underset{CH_3}{|}}{CH}-OH$ is oxidized to $R-\underset{\underset{O}{\|}}{C}-CH_3$ which gives iodoform test.

The reagent used is iodine and sodium hydroxide (sodium hypoiodite, NaOI).

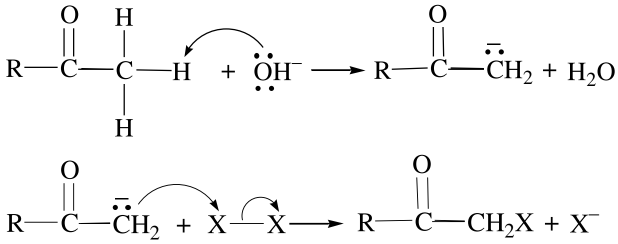
The reactions involved are



$$R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + NaOI \rightarrow R-\underset{\underset{O}{\|}}{C}-CH_3 + NaI + H_2O\ ; \qquad R-\underset{\underset{O}{\|}}{C}-CH_3 + 3NaOI \rightarrow R-\underset{\underset{O}{\|}}{C}-CI_3 + 3NaOH$$

$$R-\underset{\underset{O}{\|}}{C}-CI_3 + NaOH \rightarrow RCOO^- Na^+ + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt.)}}}{CHI_3}$$

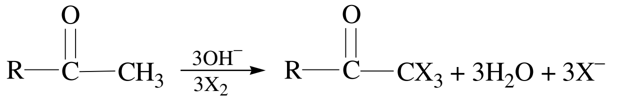
Mechanism The H atoms of the —CH_3 groups are replaced by halogens in alkali solution. A three step α–C halogenation, proceeding through carbanion – enolate intermediate, results in the intermediate $RCOCX_3$ (where X is halogen).



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H + \ddot{\underset{\cdot\cdot}{O}}H^- \longrightarrow R-\overset{\overset{O}{\|}}{C}-\ddot{C}H_2^- + H_2O$$

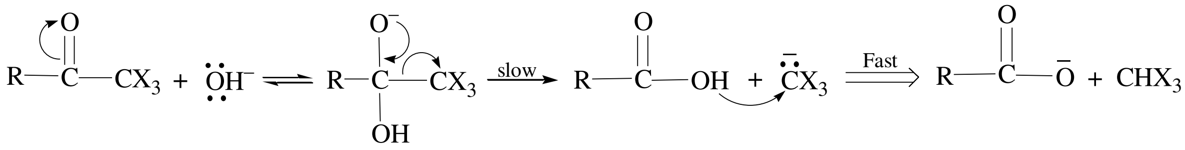
$$R-\overset{\overset{O}{\|}}{C}-\ddot{C}H_2^- + X-X \longrightarrow R-\overset{\overset{O}{\|}}{C}-CH_2X + X^-$$

This is continued till all the three H's of CH_3 are replaced.



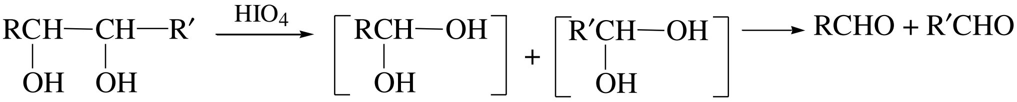
$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[3X_2]{3OH^-} R-\overset{\overset{O}{\|}}{C}-CX_3 + 3H_2O + 3X^-$$

Due to the inductive effects of the X atoms and —CO group, nucleophilic attack on C of C=O helps breaking the intermediate.

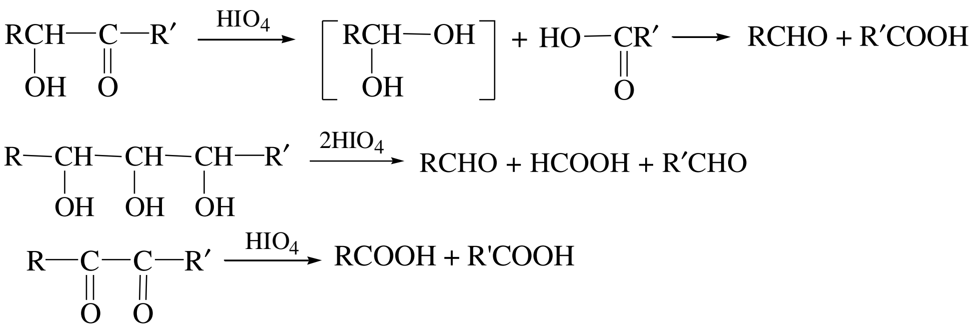


$$R-\overset{\overset{O}{\|}}{C}-CX_3 + \ddot{\underset{\cdot\cdot}{O}}H^- \rightleftharpoons R-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-CX_3 \xrightarrow{\text{slow}} R-\overset{\overset{O}{\|}}{C}-OH + \ddot{C}X_3^- \xRightarrow{\text{Fast}} R-\overset{\overset{O}{\|}}{C}-\bar{O} + CHX_3$$

Analysis of molecules containing —OH or =O groups attached to adjacent carbon atoms Molecules containing —OH or =O groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon-carbon bonds when treated with periodic acid. For example,



$$\underset{\underset{OH}{|}}{RCH}-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{HIO_4} \left[\underset{\underset{OH}{|}}{RCH}-OH\right] + \left[\underset{\underset{OH}{|}}{R'CH}-OH\right] \longrightarrow RCHO + R'CHO$$



$$\underset{OH}{\underset{|}{RCH}}-\underset{O}{\underset{\|}{C}}-R' \xrightarrow{HIO_4} \left[\underset{OH}{\underset{|}{RCH}}-OH\right] + HO-\underset{O}{\underset{\|}{C}}R' \longrightarrow RCHO + R'COOH$$

$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow{2HIO_4} RCHO + HCOOH + R'CHO$$

$$R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R' \xrightarrow{HIO_4} RCOOH + R'COOH$$

The amount of HIO_4 consumed is equal to the amount of carbon-carbon bond broken in the molecule.

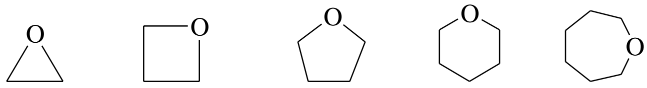
ETHERS

Ethers have two hydrocarbon groups attached to an oxygen (R — O — R).

In common system of nomenclature, ethers are named by the alkyl groups attached to the oxygen atom followed by the word ether, e.g., dimethyl ether, methyl ethyl ether.

In IUPAC nomenclature, ethers are considered to be alkoxy derivatives of alkanes, e.g., methoxyethane ($CH_3OC_2H_5$), ethoxyethane ($C_2H_5OC_2H_5$). The more complex R group is made the base hydrocarbon. If other substituents like —CHO, —OH, etc. are present, the compound is named as the derivative of that substance, e.g., 2-ethoxyethanol ($C_2H_5OCH_2CH_2OH$), 4-ethoxynitrobenzene.

The three membered cyclic ethers are called epoxide, e.g., 1,2-butene oxide may be named as 1,2-epoxybutane. The IUPAC amnes for the cyclic ethers $(CH_2)_nO$ are as follows:

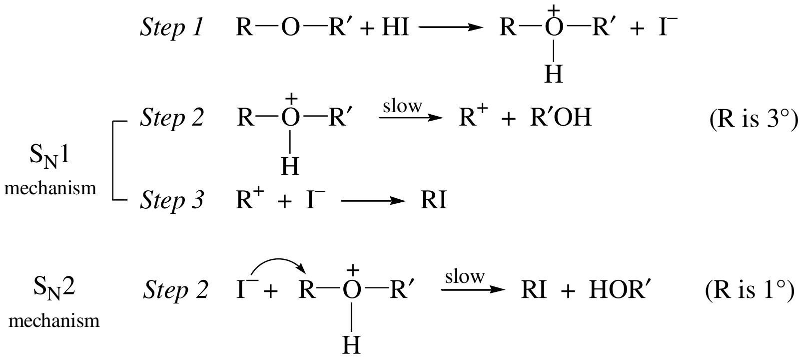


$n = 2$ Oxirane, $n = 3$ Oxetane, $n = 4$ Oxolane, $n = 5$ Oxane, $n = 6$ Oxepane

Ethers can be prepared by the dehydration of *n*-alcohols for which concentrated H_2SO_4 at 410 K is used. 2° and 3° alcohols canot be used as these mainly give alkenes.

Unsymmetrical ethers can be prepared by using Williamson synthesis in which alkyl halide is heated with sodium alkoxide. However, tertiaty halide produces alkenes with the elimination of HX.

Ethers are chemically inert substances. With concentrated acids, they form oxonium salts. Ether linkage is cleaved by heating with HI producing alcohol and alkyl iodide.



$$\text{Step 1}\quad R-O-R' + HI \longrightarrow R-\underset{H}{\underset{|}{\overset{+}{O}}}-R' + I^-$$

$$\text{Step 2}\quad R-\underset{H}{\underset{|}{\overset{+}{O}}}-R' \xrightarrow{slow} R^+ + R'OH \qquad (\text{R is } 3^\circ)$$

$$\text{Step 3}\quad R^+ + I^- \longrightarrow RI$$

$$S_N2 \text{ mechanism}\quad \text{Step 2}\quad I^- + R-\underset{H}{\underset{|}{\overset{+}{O}}}-R' \xrightarrow{slow} RI + HOR' \qquad (\text{R is } 1^\circ)$$

The solvent also plays important role in deciding the formation of products. For example, in ether

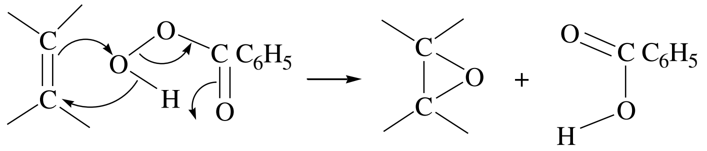
$$(CH_3)_3COCH_3 \xrightarrow{\text{anhyd HI}} CH_3I + (CH_3)_3COH \qquad (S_N2 \text{ mechanism})$$

In water,

$$(CH_3)_3COCH_3 \xrightarrow{\text{Conc. HI}} CH_3OH + (CH_3)_3CI \qquad (S_N1 \text{ mechanism})$$

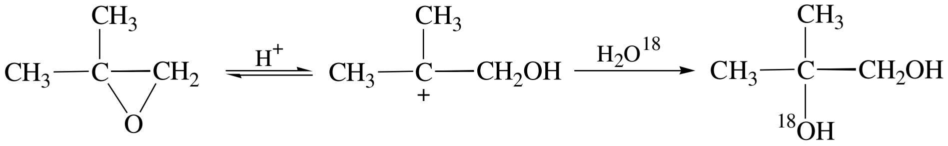
The ether of the type ArOR always gives ArOH and RI.

Oxiranes are prepared by the action of peroxyacid (usually peroxybenzoic acid or *m*-chloroperoxybenzoic acid) on alkenes.

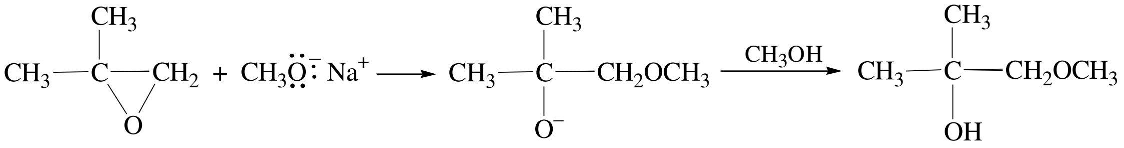


The cleavage of ether linkage in oxiranes is catalysed both by acids and bases.

The acid catalysed reaction proceeds with the protonation of epoxide oxygen followed by the nucleophilic attack at the more substituted carbon. The reaction follows S_N2 mechanism with the nucleophile attacking from the face opposite to the epoxide ring.

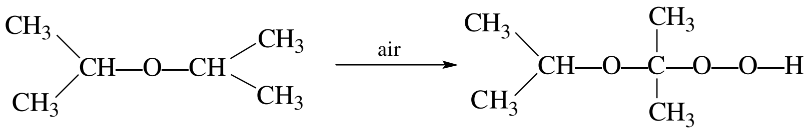


The base catalysed reaction also involves S_N2 mechanism with the base attacking the less substituted carbon.



Ether linkage in aromatic compound is *ortho* and *para* directing group.

Ether when exposed to air for a long time produces compound comtaining peroxide linkage. For example,



This perioxide linkage can be detected by treating the sample with ferrous ammonium sulphate followed by the addition of ammounium thiocynate. Ferrous ions is oxidized to ferric ions which produces red coloration with NH_4CNS.

Straight Objective Type

General Characteristics

1. An industrial method of preparation of methanol is
   (a) catalytic reduction of carbon monoxide in presence of $ZnO\text{-}Cr_2O_3$.
   (b) by reacting methane with steam at 900 °C with a nickel catalyst
   (c) by reducing formaldehyde with lithium aluminium hydride
   (d) by reacting formaldehyde with aqueous sodium hydroxide solution (1984)

2. Wood alcohol is
   (a) CH_3OH (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_2CHOH$

3. Grain alcohol is
   (a) CH_3OH (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_2CHOH$

4. Rubbing alcohol is
   (a) CH_3OH (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_2CHOH$

5. Absolute alcohol is
   (a) CH_3OH (b) C_2H_5OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_2CHOH$

6. The increasing order of boiling point of the given alcohols is
(a) 1-pentanol > 3-methyl-2-butanol > 2-methyl-2-butanol
(b) 1-pentanol > 2-methyl-2-butanol > 3-methyl-2-butanol
(c) 3-methyl-2-butanol > 2-methyl-2-butanol > 1-pentanol
(d) 2-methyl-2-butanol > 3-methyl-2-butanol > 1-pentanol

7. Which of the following sequences regarding the acidic nature of alcohols is correct?
(a) $CH_3OH > 1° > 2° > 3°$ (b) $CH_3OH < 1° < 2° < 3°$
(c) $1° > CH_3OH > 2° < 3°$ (d) $1° < CH_3OH < 2° < 3°$

8. The correct sequence regarding the Brönsted basicity of alcohols is
(a) $1° > 2° > 3°$ (b) $1° < 2° < 3°$ (c) $1° < 2° > 3°$ (d) $1° > 2° < 3°$

9. A 2° ROH can undergo
(a) via S_N1 nucleophilic substitution only (b) via S_N2 nucleophilic substitution only
(c) both S_N1 and S_N2 nucleophilic substitution (d) neither S_N1 nor S_N2 nucleophilic substitution

10. Hydrogen bonding is maximum in
(a) ethanol (b) diethylether (c) ethyl chloride (d) triethylamine (1987)

11. Which of the following alcohols is expected to have minimum boiling point?
(a) 1-Butanol (b) 2-Butanol (c) 2-Methyl-2-propanol (d) 1-Pentanol

12. The relative order of acidity of alcohols in comparison to H_2O and $HC\equiv CH$ is
(a) $H_2O > ROH > HC\equiv CH$ (b) $H_2O > HC\equiv CH > ROH$
(c) $ROH > H_2O > HC\equiv CH$ (d) $ROH > HCOOH > H_2O$

13. The relative order of basicity of conjugate bases is
(a) $OH^- < OR^- < HC\equiv C^-$ (b) $OH^- < HC\equiv C^- < OR^-$
(c) $HC\equiv C^- < OH^- < OR^-$ (d) $HC\equiv C^- < OR^- < OH^-$

14. Glycerine is a/an
(a) secondary alcohol (b) tertiary alcohol (c) ester (d) trihydric alcohol

15. Among the following compounds, the strongest acid is
(a) $HC\equiv CH$ (b) C_6H_6 (c) C_2H_6 (d) CH_3OH (1998)

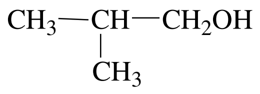
16. The compound that will react most readily with NaOH to form methanol is
(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3 (c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCI$ (2001)

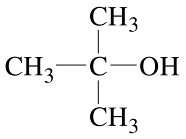
Cleavage of R···OH Bond

17. The compound which reacts fastest with Lucas reagent at room temperature is
(a) 1-butanol (b) 2-butanol (c) 2-methylpropanol (d) 2-methylpropan-2-ol (1981)

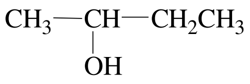
18. HBr reacts fastest with
(a) 2-methylpropan-2-ol (b) propan-1-ol
(c) propan-2-ol (d) 2-methylpropan-1-ol (1984)

19. The compound which gives the most stable carbonium ion on dehydration is

(a) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(b) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(c) $CH_3CH_2CH_2CH_2OH$

(d) 
$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_3$ (1988)

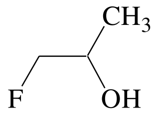
20. Butanonitrile may be prepared by heating
(a) propyl alcohol with KCN (b) butyl alcohol with KCN
(c) butylchloride with KCN (d) propyl chloride with KCN (1992)

21. The order of reactivity of HX towards ROH is
(a) HI > HBr > HCl (b) HI < HBr < HCl (c) HI > HBr < HCl (d) HI < HBr > HCl

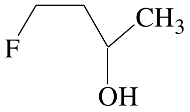
22. The order of reactivity of alcohols towards hydrogen halide is
(a) benzyl > 3° > 2° > 1° (b) benzyl < 3° < 2° < 1°
(c) 3° > 2° > 1° > benzyl (d) 3° > 2° > benzyl > 1°

23. The dehydration of 1-butanol gives
(a) 1-butene as the main product (b) 2-butene as the main product
(c) equal amounts of 1-butene and 2-butene (d) 2-methylpropene

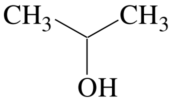
24. The order of reactivity of the following alcohols



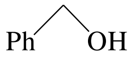
I



II



III



IV

towards concentrated HCl is
(a) I > II > III > IV (b) I > III > II > IV (c) IV > III > II > I (d) IV > III > I > II (1997)

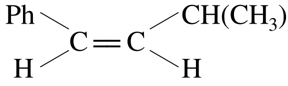
25. 3, 3-Dimethyl-2-butanol, on reacting with concentrated HCl, gives
(a) 3,3-dimethyl-2-chlorobutane
(b) 2,3-dimethyl-2-chlorobutane
(c) a mixture of 3,3-dimethyl-2-chlorobutane and 2,3-dimethyl-2-chlorobutane.
(d) 3,3-dimethyl-1-chlorobutane

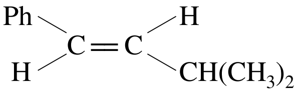
26. The reaction of neopentyl alcohol with concentrated HCl gives
(a) neopentyl chloride
(b) 2-chloro-2-methylbutane
(c) 2-methyl-2-butene
(d) a mixture of neopentyl chloride and 2-methyl-2 butene.

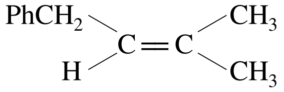
27. The reaction of neopentyl alcohol with $SOCl_2$ gives
(a) neopentyl chloride
(b) 2-chloro-2-methylbutane
(c) 2-methyl-2-butene
(d) a mixture of neopentyl chloride and 2-methyl-2-butene

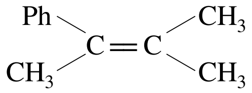
28. The reaction of 3-buten-2-ol with aqueous HBr gives
(a) 3-bromo-1-butene only
(b) 1-bromo-2-butene only
(c) a mixture of 3-bromo-1-butene and 1-bromo-2-butene
(d) 4-bromo-1-butene.

29. The major product in the reaction of $PhCH_2CH(OH)CH(CH_3)_2$ with concentrated H_2SO_4 is

(a)


(b)


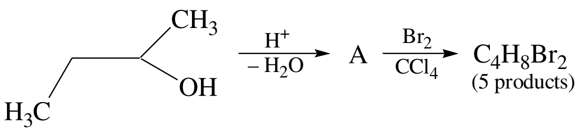
(c)


(d)


30. HBr reacts fastest with
(a) $C_6H_5CH_2OH$ (b) p-$O_2NC_6H_4CH_2OH$ (c) p-$CH_3OC_6H_4CH_2OH$ (d) p-$ClC_6H_4CH_2OH$

31. HBr reacts slowest with
(a) $C_6H_5CH_2OH$ (b) p-$O_2NC_6H_4CH_2OH$ (c) p-$CH_3OC_6H_4CH_2OH$ (d) p-$ClC_6H_4CH_2OH$

32. In the reaction



The number of structures of A is
(a) 2 (b) 3 (c) 5 (d) 6 (2003)

33. Which of the following reagents can be used to convert cyclohexanol to cyclohexene?
(a) Al_2O_3, 350 °C (b) Conc. $HCl/ZnCl_2$ (c) Conc. HCl (d) Conc. HBr (2005)

34. The treatment of 3-pentanol with HBr results into
(a) 3-bromopentane only
(b) 2-bromopentane only
(c) a mixture of 2-bromopentane and 3-bromopentane
(d) 2-pentane.

35. The treatment of Ph_2CHCH_2OH with HBr produces
(a) Ph_2CHCH_2Br (b) $PhCHBrCH_2Ph$ (c) $Ph_2C = CH_2$ (d) $PhCH = CH Ph$

36. The reaction rates of benzyl alcohols *p*-$CH_3OC_6H_4CH_2OH$ (A), *p*-$ClC_6H_4CH_2OH$ (B) and *p*-$O_2NC_6H_4CH_2OH$ (C) with HBr follows the order
(a) A > B > C (b) A > C > B (c) C > A > B (d) C > B > A

Cleavage of RO···H Bond

37. Which of the following compounds is oxidised to prepare methyl ethyl ketone?
(A) 2-Propanol (B) 1-Butanol (C) 2-Butanol (D) *tert*-Butyl alcohol (1987)

38. The reactivity of alcohols towards active metals is
(A) $3° > 2° > 1°$ (B) $3° < 2° < 1°$ (C) $3° < 1° < 2°$ (D) $2° < 3° < 1°$

39. 1° Alcohol can be changed to 1° aldehyde by using the reagent
(A) pyridinium chlorochromate (B) potassium dichromate
(C) potassium permanganate (D) hydrogen peroxide

40. The reaction of ROH with R′MgX produces
(A) RH (B) R′H (C) R — R (D) R′ — R′

41. When vapours of 2-propanol is passed over hot metallic Cu at 570 K, the product formed is
(A) 1-propanol (B) propanone (C) propanal (D) propene

42. When dissolved in H_2SO_4, 1,4-hexadien-3-ol
(a) remains as such
(b) is converted into 3,5-hexadien-2-ol
(c) is converted into 2,4-hexadien-1-ol
(d) is converted into a mixture of 3,5-hexadien-2-ol and 2,4-hexadien-1-ol

43. The reaction of ethanol with concentrated H_2SO_4 at 0 °C gives
(a) $CH_3CH_2OH_2^+ HSO_4^-$ (b) $CH_3CH_2OSO_2OH$ (c) $CH_3CH_2OCH_2CH_3$ (d) $H_2C{=}CH_2$

44. The reaction of ethanol with concentrated H_2SO_4 at room temperature gives
(a) $CH_3CH_2OH_2^+HSO_4^-$ (b) $CH_3CH_2OSO_2OH$ (c) $CH_3CH_2OCH_2CH_3$ (d) $H_2C{=}CH_2$

45. The reaction of ethanol with concentrated H_2SO_4 at 130 °C gives
(a) $CH_3CH_2OH_2^+HSO_4^-$ (b) $CH_3CH_2OSO_2OH$ (c) $CH_3CH_2OCH_2CH_3$ (d) $H_2C{=}CH_2$

46. The reaction of ethanol with concentrated H_2SO_4 at 180 °C gives
(a) $CH_3CH_2OH_2^+ HSO_4^-$ (b) $CH_3CH_2OSO_2OH$ (c) $CH_3CH_2OCH_2CH_3$ (d) $H_2C{=}CH_2$

47. The reaction of phenyl magnesium bromide with tertiary butanol results in the formation of
(a) benzene (b) phenol
(c) *tert*-butylbenzene (d) *tert*-butylmethyl ether (2005)

48. Given are the following reactions:

$$RSH + OH^- \rightleftharpoons RS^- + H_2O$$
$$ROH + OH^- \rightleftharpoons RO^- + H_2O$$

Which of the following order of acid strength and base strength is correct?
(a) $RSH > H_2O > ROH$ and $RS^- > OH^- > RO^-$
(b) $RSH > H_2O > ROH$ and $RO^- > OH^- > RS^-$
(c) $RSH < H_2O < ROH$ and $RS^- < OH^- < RO^-$
(d) $RSH < H_2O < ROH$ and $RO^- < OH^- < RO^-$

Characteristic of Alcohols

49. In the Victor-Meyer test, blue colouration is shown by
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) diol

50. Reaction of tertiary butyl alcohol with hot Cu at 350 °C produces
(A) butanol (B) butanal (C) 2-butene (D) 2-methylpropene

51. Lucas reagent is
(A) anhydrous $AlCl_3$ with concentrated HCl (B) anhydrous $ZnCl_2$ and concentrated H_2SO_4
(C) anhydrous $ZnCl_2$ and concentrated HCl (D) anhydrous $CaCl_2$ and concentrated HCl

52. The compound that does not react with Lucas reagent is
(A) *n*-butanol (B) *sec*-butyl alcohol (C) isobutyl alcohol (D) *tert*-butyl alcohol

53. In the Victor-Meyer test, red colouration is shown by
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) phenol

54. In the Lucas test of alcohols, appearance of cloudiness is due to the formation of
(A) aldehydes (B) ketones (C) acid chlorides (D) alkyl chlorides

55. Which of the alcohols does not give iodoform test?
(a) $(CH_3)_2CH(OH)CH_3$ (b) $PhCH(OH)CH_2CH_3$
(c) 1-methylcyclohexanol (d) $CH_3CH_2CH(OH)CH_3$

56. 1-propanol and 2-propanol can be best distinguished by
(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution.
(b) oxidation with acidic dichromate followed by reaction with Fehling solution.
(c) oxidation by heating with copper followed by reaction with Fehling solution.
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution. (2001)

Ethers

57. Which of the following is expected to have the lowest boiling point?
(a) CH_3CH_2OH (b) CH_3CHO (c) CH_3COOH (d) CH_3OCH_3

58. Which of the following does not react with sodium metal?
(a) $CH_3CH_2OCH_2CH_3$ (b) CH_3OH (c) CH_3COOH (d) HCOOH

59. The heating of phenyl methyl ether with HI produces
(a) ethyl chloride (b) iodobenzene (c) phenol (d) benzene

60. The IUPAC amne of $CH_3CH_2OCH_2CH_2CH_3$ is
(a) diethyl ether (b) ethyl propyl ether (c) ethoxypropane (d) propoxyethane

61. The reaction $CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaI$ is an example of
(a) Wurtz synthesis (b) Clemenson reaction (c) Williamson synthesis (d) Dow reaction

62. Which of the following compounds does not fit into the phenomenon of metamerism?
(a) $C_2H_5OC_2H_5$ (b) $CH_3OCH(CH_3)_2$ (c) $CH_3OCH_2CH_2CH_3$ (d) $CH_3CH_2CH_2CH_2OH$

63. The alkoxy group in benzene is
(a) *ortho* directing (b) *para* directing
(c) *ortho* and *para* directing (d) *meta* directing

64. The formation of peroxide linkage in ether due to the exposure in air can be detected by treating it with
(a) sodium
(b) dilute hydrochloric acid
(c) aqueous ferrous ammonium sulphate followed by addition of ammonium thiocynate
(d) dilute sodium hydroxide

65. The exposure of ether in air for a long time may cause
(a) oxidation to carboxylic acid (b) the formation of peroxide linkage
(c) oxidation to produce aldehyde or ketone (d) the degradation of the molecule

66. Ethers
(a) are soluble in concentrated acids
(b) are insoluble in concentrated acids
(c) have unpleasant smell
(d) have higher boiling point in comparison to the alcohol of comparable molecular mass

67. Given are the two cleavage reactions:
(i) $(CH_3)_3COCH_3 \rightarrow CH_3I + (CH_3)_3COH$
(ii) $(CH_3)_3COCH_3 \rightarrow CH_3OH + (CH_3)_3Cl$
Which of the following statements is correct?
(a) The reagent used in reaction (i) is anhydrous HI in either and in reaction (ii) is concentrated HI
(b) The reagent used in reaction (i) is concentrated HI and in reaction (ii) is anhydrous HI in ether
(c) The reagent used both in reactions (i) and (ii) is concentrated HI
(d) The reagent used both in reactions (i) and (ii) is anhydrous HI in ether

68. The word epoxide represents
(a) cyclic ether (b) noncyclic ether (c) unsaturated ether (d) branched ether

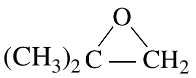
69. The word oxiranes represents
(a) cyclic ether (b) noncyclic ether (c) unsaturated ether (d) branched ether

70. The correct order of bond angles H—O—H, CH_3—O—H and CH_3—O—CH_3 is
(a) H—O—H < CH_3—O—H < CH_3—O—CH_3 (b) H—O—H < CH_3—O—CH_3 < CH_3—O—H
(c) CH_3—O—H < H—O—H < CH_3—O—CH_3 (d) CH_3—O—H < CH_3—O—CH_3 < H—O—H

71. Starting materials for Williamson synthesis of an ether are
(a) RONa + R′OH (b) RONa + R′X (c) ROH + R′OH (d) ROH + R′X

72. The ether $(CH_3)_3COCH_3$ is cleaved with (i) anhydrous HI, and (ii) concentrated HI. The products obtained, respectively, are
(a) $CH_3I + (CH_3)_3COH$; $CH_3I + (CH_3)_3COH$ (b) $CH_3I + (CH_3)_3COH$; $CH_3OH + (CH_3)_3CI$
(c) $CH_3OH + (CH_3)_3CI$; $CH_3I + (CH_3)_3COH$ (d) $CH_3OH + (CH_3)_3CI$; $CH_3OH + (CH_3)_3CI$

73. Acid-catalysed reaction of proplene oxide with MeOH gives
(a) $CH_3CH(OH)CH_2OMe$ (b) $CH_3CH(OMe)CH_2OH$
(c) $CH_3CH(OH)CH_2OH$ (d) $CH_3CH(OMe)CH_2(OMe)$

74. The reaction of  with CH_3OH in (i) acid H^+, and (ii) base CH_3O^-, respectively, give
(a) $(CH_3)_2C(OCH_3)CH_2OH$ and $(CH_3)_2CH(OH)CH_2OCH_3$
(b) $(CH_3)_2C(OCH_3)CH_2OH$ and $(CH_3)_2C(OCH_3)CH_2OH$
(c) $(CH_3)_2C(OCH_3)CH_2OCH_3$ and $(CH_3)_2C(OH)CH_2OH$
(d) $(CH_3)_2C(OH)CH_2OH$ and $(CH_3)_2C(OCH_3)CH_2OCH_3$

75. Diethyl ether on heating with concentrated HI gives two moles of
(a) ethanol (b) ethyl iodide (c) iodoform (d) methyl iodide (1982)

Multiple Correct Choice Type

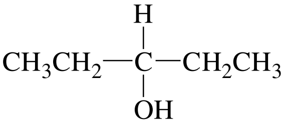
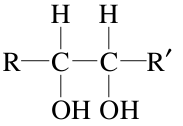
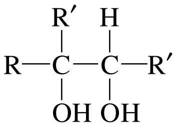
1. Which of the following alcoholas react with Lucas reagent at room temperature?
(a) CH_3CH_2OH (b) $CH_3CH(OH)CH_3$ (c) $(CH_3)_3COH$ (d) CH_3OH

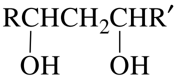
2. Which of the following statements are **not** correct?
(a) The branched isomer of an alcohol has lower boiling point than the unbranched alcohol.
(b) Ethylene glycol boils at a temperature lower than that of ethanol.
(c) The hydroboration-oxidation process gives product corresponding to Markovnikov addition of water to the carbon-carbon double bond.
(d) The oxymercuration-demercuration process gives products corresponding to anti-Markovnikov addition of water to the carbon-carbon double bond.

3. Which of the following statements are correct?
(a) The addition of water to the carbon-carbon double bond via hydroboration-oxidation process does not involve any rearrangement of carbon skeleton.
(b) The rearrangement of carbon skeleton may occur during the conversion of alcohol into alkene.
(c) The rearrangement of carbon skeleton may occur during the conversion of alcohol into alkyl halide.
(d) The cleavage of carbon-oxygen bond in alcohols is catalyzed in the presence of an acid.

4. Which of the following statements are correct?
(a) The substitution of hydroxyl group by a halogen group in alcohol is an electrophilic substitution reaction.

(b) Alcohols are weak acids as well as weak bases.
(c) A secondary alcohol on oxidation gives a carboxylic acid containing the same number of carbon atoms.
(d) A primary alcohol on oxidation gives a carboxylic acid containing the same number of carbon atoms.

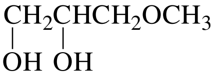
5. Which of the following statements are **not** correct?
(a) Tertiary butyl alcohol gives positive iodoform test.
(b)  $CH_3CH_2-\underset{OH}{\overset{H}{C}}-CH_2CH_3$ gives positive iodoform test.
(c) The carbon-carbon bond in  $R-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-R'$ can be broken by the use of periodic acid and the product obtained are two aldehydes.
(d) The carbon-carbon bond in  $R-\underset{OH}{\overset{R'}{C}}-\underset{OH}{\overset{H}{C}}-R'$ can be broken by the use of periodic acid giving two aldehydes.

6. Which of the following statements are correct?
(a) The molecule  $R\underset{OH}{CH}CH_2\underset{OH}{CH}R'$ is cleaved by HIO_4 giving RCHO and R′CHO.
(b) Tertiary alcohols are more readily dehydrated than the secondary alcohols.
(c) Tertiary butyl alcohol when passed over hot metallic Cu at 570 K produces isobutene.
(d) Primary alcohols show positive Lucas test.

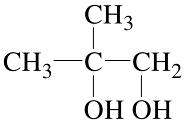
7. Which of the following statements are **not** correct?
(a) Tertiary alcohols show positive Lucas test with slower speed than in the case of secondary alcohols.
(b) The order of increasing acidity amongst 1°, 2° and 3° alcohols is

$$1^\circ \text{ alcohol} < 2^\circ \text{ alcohol} < 3^\circ \text{ alcohol}$$

(c) The reaction of glycerol with small amount of HI produces 2–iodopropane.
(d) The reaction of glycerol with excess of HI produces 1, 2, 3-triiodopropane.

8. Which of the following statements are correct?
(a) β-Chloroethyl alcohol is a stronger acid than ethyl alcohol.
(b) Benzyl alcohol is a stronger acid than *p*-nitrobenzyl alcohol.
(c) The amount of HIO_4 consumed when it is treated with one mol of  $\underset{OH}{CH_2}\underset{OH}{CH}CH_2OCH_3$ is 2 mol.
(d) The amount of HIO_4 consumed when it is treated with one mole of $CH_2OH(CHOH)_3CHO$ is 4 mol.

9. Which of the following statements are correct?
(a) An organic compound on treating with HIO_4 gives CH_3COCH_3 and HCHO. The compound is



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{CH_2}$$

(b) An organic compound on treating with HIO_4 gives 5HCOOH and one HCHO. The compound is  $\underset{OH}{H_2C}(CHOH)_4\underset{OH}{CH_2}$.
(c) Thiols are less soluble in water as compared to the corresponding alcohols.

10. Which of the following statements are **not** correct?
(a) Absolute alcohol can be obtained by distillation of ethanol and water mixture.
(b) Cyclohexanol is more soluble in water than 1-hexanol.

(c) The hydration of 3-phenyl-1-butene in dilute H_2SO_4 produces 3-phenyl-2-butanol.
(d) The hydration of cyclobutylethene in dilute H_2SO_4 gives 1-cyclobutylethanol.

11. Which of the following statements are correct?
(a) Alcohol is slightly more acidic than water.
(b) The reaction of HBr with *n*-butanol follows S_N1 mechanism.
(c) The reaction of HBr with *t*-butyl alcohol follows S_N1 mechanism.
(d) (*R*)-2-Hexanol on reacting with concentrated HBr gives (*S*)-2-bromohexane.

12. Which of the following statements are correct?
(a) (*R*)-3-Methyl-3-haxanol on reacting with concentrated HBr gives excess of *S*-3-bromo-3 methylhexane.
(b) S_N1 nucleophilic substitution in ROH may lead to the rearrangement of carbon skeleton.
(c) S_N2 nucleophilic substitution in ROH not only brings inversion of geometry but also the rearrangement of carbon skeleton.
(d) 3-Pentanol reacts with HBr to give a mixture of 3- and 2-bromopentane. The reaction follows S_N1 nucleophilic substitution mechanism.

13. Which of the following statements are correct?
(a) The product of the reaction Ph_2CHCH_2OH with HBr gives $PhCHBrCH_2Ph$.
(b) The reaction of 1° or 2° ROH with PBr_3 proceeds with the inversion giving BrR.
(c) The correct decreasing order of dehydration of the given alcohols with H_2SO_4 is

$$(CH_3)_2C(OH)CH(CH_3)_2 > CH_3CH_2CH(OH)CH(CH_3)_2 > CH_3(CH_2)_4CH_2OH$$

(d) The rate of dehydration of $(CH_3)_2C(OH)CH(CH_3)_2$ with H_2SO_4 is faster than that $(CH_3)_2C(OH)CH_2CH_2CH_3$.

14. Which of the following statements are correct?
(a) The rate of dehydration of $CH_3CH_2CH(OH)CH_2CH_2CH_3$ with H_2SO_4 is faster than $CH_3CH_2CH(OH)CH(CH_3)_2$.
(b) The dehydration of cyclobutylmethanol gives cyclobutylethene.
(c) The decreasing order of reactivity of benzyl alcohol with HBr is

$$p\text{-}CH_3OC_6H_4CH_2OH > C_6H_5CH_2OH > p\text{-}ClC_6H_4CH_2OH > p\text{-}O_2NC_6H_4CH_2OH$$

(d) MnO_2 is a milder oxidising agent than $KMnO_4$.

15. Which of the following statements are correct?
(a) MnO_2 can be used for selective oxidation of OH group of allylic and benzylic 1° and 2° alcohols to give aldehydes and ketones, respectively.
(b) The oxidation of $CH_3CH{=}CHCH_2OH$ with MnO_2 gives CH_3CHO and OHCCHO.
(c) The oxidation of $PhCH_2OH$ with MnO_2 gives PhCHO.
(d) The oxidation of $PhCH(OH)CH_2CH_2OH$ with MnO_2 gives

$PhC(=O)CH_2CHO$.

16. Which of the following statements are **not** correct?
(a) The reduction of $p\text{-}O_2NC_6H_4CH_2COOH$ with $LiAlH_4$ gives $p\text{-}O_2NC_6H_5CH_2CH_2OH$.
(b) The reaction of $Ph_2C{=}CHCH_3$ with BH_3 in tetrahydrofuran followed by H_2O_2/OH^- gives $Ph_2C(OH)CH_2CH_3$.
(c) Cyclopentylmethylcarbinol does not give iodoform test.
(d) An alcohol containing —$CH(OH)CH_3$ gives iodoform test.

17. Which of the following statements are correct?
(a) ROH is a stronger acid than RSH.
(b) The IUPAC name of $CH_3S^-Na^+$ is sodium methylmercaptide or sodium methanthiolate.
(c) ROH is a stronger base than RSH.
(d) The reaction $RSH + OH^- \rightleftharpoons RS^- + HOH$ lies far towards the left side.

18. Which of the following statements are **not** correct?
(a) The reaction $ROH + OH^- \rightleftharpoons RO^- + HOH$ lies far towards the left side.
(b) The reaction $ROH + R'S^-Na^+ \longrightarrow RO^-\ Na^+ + R'SH$ is feasible.

(c) RS^-, in a protic solvent, acts as a stronger nucleophile than RO^-.

(d) The bond angle R—O—H in methanol is smaller than that of R—S—H in methanethiol.

19. Which of the following statements are **not** correct?

(a) Ethanol vapour is passed over heated copper and the product is treated with aqueous sodium hydroxide. The final product is $CH_3CH(OH)CH_2CHO$.

(b) Aliphatic ethers are purified by shaking with a ferrous salt to remove peroxide which are formed on prolonged standing in contact with air.

(c) The catalyst octacarbonyldicobalt reduces the aldehyde RCHO to 2° alcohol.

(d) The treatment of CH_3CHO to RMgX followed by hydrolysis gives 1° alcohol.

20. Which of the following statements are **not** correct?

(a) The treatment of CH_3COCH_3 to RMgX followed by hydrolysis gives 2° alcohol.

(b) Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.

(c) Alkenes undergo hydroboration with diborane to yield alkyl boranes which on oxidation give alcohols.

(d) Hydroboration-oxidation of 1-butene gives isobutyl alcohol.

21. Which of the following statements are correct?

(a) Hydroboration-oxidation of 2-methyl-2-butene gives 3-methyl-2-butanol.

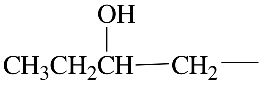
(b) The reaction of ethylene oxide with RMgX followed by hydrolysis gives RCH_2CH_2OH.

(c) The reaction $HC{\equiv}C^-\,Na^+ + ROH \rightarrow RO^-\,Na^+ + HC{\equiv}CH$ lies more to the right. From this, it follows that ROH is stronger acid than acetylene and $RO^-\,Na^+$ is a weaker base than $HC{\equiv}C^-\,Na^+$.

(d) The oxidation of an alcohol involves the loss of one or more hydrogen from the carbon bearing the —OH group.

22. Which of the following statements are **not** correct?

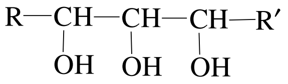
(a) The conversion of a primary alcohol to the aldehydic stage can be conveniently carried out by using the reagent alkaline $kMnO_4$.

(b) An alcohol giving positive iodoform test must contain the group  $CH_3CH_2\overset{\overset{OH}{|}}{C}H-CH_2-$.

(c) In the iodoform test perfomed by an alcohol, the first step is the oxidation of alcohol into ketone by sodium hypoiodite.

(d) The treatment of glycol with periodic acid gives HCHO.

23. Which of the following statements are **not** correct?

(a) The oxidation of  $R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R'$ with HIO_4 gives the products RCHO + HCHO + R′CHO and the amount of HIO_4 consumed is two mol.

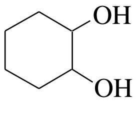
(b) The treatment of HIO_4 to 1,2-dihydrocyclohexane produces $OCH(CH_2)_4CHO$.

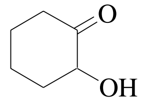
(c) The primary alcohols produce blue colour in the Victor-Meyer method.

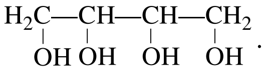
(d) The secondary alcohols produce red colour in the Victor-Meyer method.

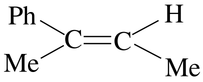
24. Which of the following statements are correct?

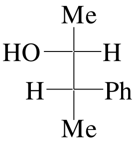
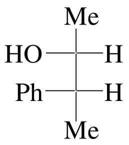
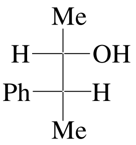
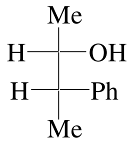
(a) The tertiary alcohols produce no colour in the Victor-Meyer method.

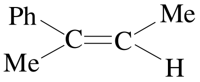
(b) An organic compound on treating with HIO_4 gives $OHC(CH_2)_4CHO$. The compound is  .

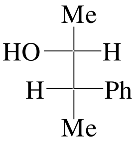
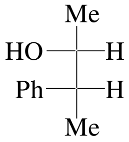
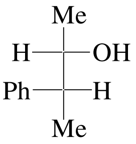
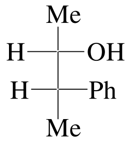
(c) An organic compound on treating with HIO_4 gives $HOOC(CH_2)_4CHO$. The compound is  .

(d) An organic compound on treating with HIO_4 gives 2HCOOH + 2HCHO. The compound is  $H_2\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$.

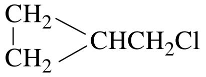
25. The products of hydroboration-oxidation of  produces

(a) 
(b) 
(c) 
(d) 

26. The products of hydroboratin – oxidation of  produces

(a) 
(b) 
(c) 
(d) 

27. The treatment of $H_2C{=}CHCH_2CH_2OH$ with conc. HCl results into the formation of

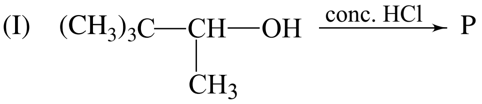
(a) $H_2C{=}CHCH_2CH_2Cl$
(b) 
(c) $H_3CCH(Cl)CH{=}CH_2$
(d) $H_3CCH{=}CHCH_2Cl$

28. Which of the following alcohols show the iodoform test?

(a) CH_3OH (b) CH_3CH_2OH (c) $CH_3CH(OH)CH_3$ (d) $CH_3CH_2CH_2OH$

Linked Comprehension Type

1. Given are the two reactions



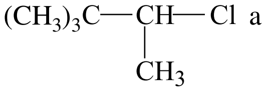
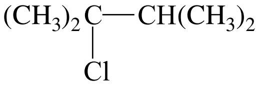
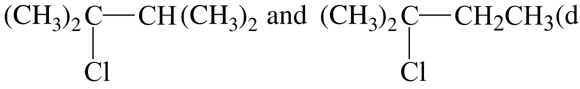
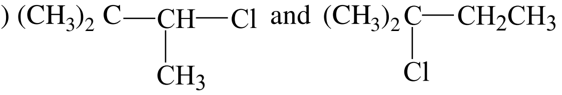
(I) $(CH_3)_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}OH \xrightarrow{\text{conc. HCl}} P$

(II) $(CH_3)_3C{-}CH_2OH \xrightarrow{\text{conc. HCl}} Q$

(i) The reactions (I) and (II), respectively, proceed via

(a) S_N1 and S_N1 mechanisms
(b) S_N1 and S_N2 mechanisms
(c) S_N2 and S_N1 mechanisms
(d) S_N2 and S_N2 mechanisms

(ii) The products P and Q, respectively, are

(a)  $(CH_3)_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}Cl$ and $(CH_3)_3C{-}CH_2{-}Cl$
(b)  $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH(CH_3)_2$ and $(CH_3)_3C{-}CH_2{-}Cl$
(c)  $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH(CH_3)_2$ and $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_2CH_3$
(d)  $(CH_3)_2\,C{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}Cl$ and $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_2CH_3$

(iii) The reactions I and II, respectively, follow

(a) first-order and first-order kinetics
(b) first-order and second-order kinetics
(c) second-order and first-order kinetics
(d) second-order and second-order kinetics

2. Given are the two reactions

(I) $n\text{-}C_4H_9OH + HBr \rightarrow C_4H_9Br + H_2O$

(II) $(CH_3)_3COH + HBr \rightarrow (CH_3)_3Br + H_2O$

(i) The reactions I and II, respectively, proceed via

(a) S_N1 and S_N1 mechanisms
(b) S_N1 and S_N2 mechanisms
(c) S_N2 and S_N1 mechanisms
(d) S_N2 and S_N2 mechanisms

(ii) The reactions I and II, respectively, follow

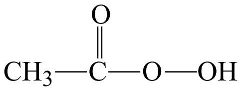
(a) first-order and first-order rate laws	(b) first-order and second-order rate laws
(c) second-order and first-order rate laws	(d) second-order and second-order rate laws

(iii) In both the reactions, the reactants react to give an intermediate, respectively, via

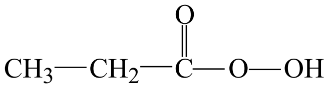
(a) reversible and irreversible steps	(b) reversible and reversible steps
(c) irreversible and reversible steps	(d) irreversible and irreversible steps

3. Oxiranes are synthesized by treating an alkene with an organic peroxy acid. This process is known as epoxidation. The highly strained three-membered ring in epoxide makes it much more reactive towards nucleophilic substitution than other ethers.

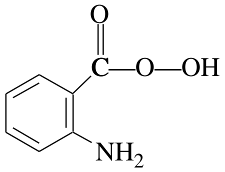
(i) The most commonly used peroxy acid is

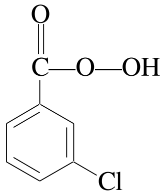
(a) 

$CH_3—C(=O)—O—OH$

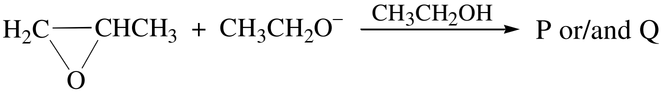
(b) 

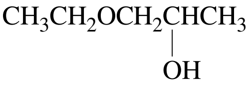
$CH_3—CH_2—C(=O)—O—OH$

(c) 

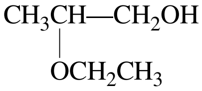
(d) 

(ii) The base-catalyzed ring opening of the epoxide is represented as follows.



where P is 

$CH_3CH_2OCH_2CH(OH)CH_3$

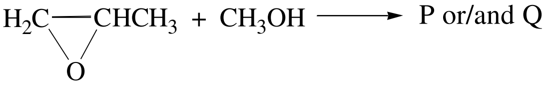
and Q is 

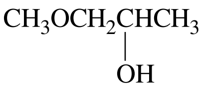
$CH_3CH(OCH_2CH_3)—CH_2OH$

Which of the following product(s) is/are obtained?

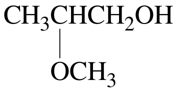
(a) P only	(b) Q only
(c) Equal mixture of P and Q	(d) Unequal mixture of P and Q

(iii) The acid-catalyzed ring opening of the expoxide is represented as follows.



where P is 

$CH_3OCH_2CH(OH)CH_3$

and Q is 

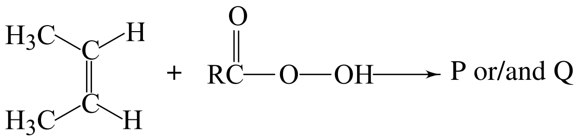
$CH_3CH(OCH_3)CH_2OH$

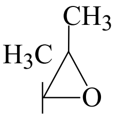
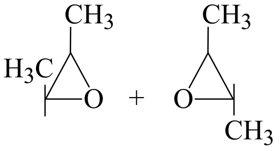
Which of the following product(s) is/are obtained?

(a) P only	(b) Q only
(c) Equal mixture of P and Q	(d) Unequal mixture of P and Q

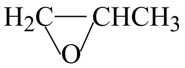
4. Oxiranes are synthesized by treating an alkene with an organic peroxy acid. This process is known as epoxidation. The highly strained three-membered ring in epoxide makes it much more reactive towards nucleophilic substitution than other ethers.

(i) In the reaction

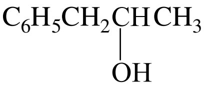
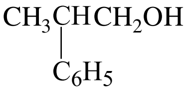


where P is  (*cis*-2,3-dimethyoxirane) and Q is  The product(s) obtained is/are

(a) P only
(b) Q only
(c) Equal mixture of P and Q
(d) Unequal mixture of P and Q

(ii) The reaction of C_6H_5MgBr with the oxirane  $H_2C\overset{O}{—}CHCH_3$ may be represented as

$$C_6H_5MgBr + H_2C\overset{O}{—}CH\,CH_3 \xrightarrow[H^+]{EtOH} \text{P or/and Q}$$

where P is  $C_6H_5CH_2CH(OH)CH_3$ and Q is  $CH_3CH(C_6H_5)CH_2OH$

Which of the following product(s) is/are obtained?

(a) P only
(b) Q only
(c) Equal mixture of P and Q
(d) Unequal mixture of P and Q

(iii) The acid-catalyzed hydrolysis of an epoxide gives

(a) an alcohol
(b) a glycol
(c) an aldehyde
(d) a ketone

Assertion and Reason Type

Given below are a few questions containing two statements. Based on the following key, answer correctly each question.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is incorrect and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	Solubility of *n*-alcohol in water decreases with increase in its relative molar mass.	The relative proportion of the hydrocarbon part in alcohols increases with increasing molar mass which permits enhanced hydrogen bonding with water.
2.	Cyclopentylmethylcarbinol does not give iodoform test.	An alcohol containing a methyl carbinol with at least one H atom on the carbinol C gives iodoform test.
3.	1,4-Hexadien-3-ol is converted into a mixture of 3,5-hexadien-2-ol and 2,4-hexadien-1-ol when dissolved in H_2SO_4.	H_2SO_4 helps removing OH as H_2O generating a carbocation which involves rearrangement to yield conjugated diene. The addition of —OH gives desire results.
4.	RSH is a weaker acid than ROH.	O is more electronegative than S.
5.	RS^- attracts H^+ less strongly than RO^-.	The –ve charge on S in RS^- is more spread out than the –ve charge on O in RO^-.
6.	Thiols have lower boiling point than the corresponding alcohols.	Thiols are less polar and form weaker intermolecular H–bonds.
7.	Acid catalysed dehydration of *tert*-butanol proceeds faster than that of *n*-butanol.	The acid catalysed dehydration of an alcohol proceeds via the formation of a carbocation.

ANSWERS

Straight Objective Type

1. (a)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (a)	**7.** (a)
8. (b)	**9.** (c)	**10.** (a)	**11.** (c)	**12.** (a)	**13.** (a)	**14.** (d)
15. (d)	**16.** (a)	**17.** (d)	**18.** (a)	**19.** (b)	**20.** (d)	**21.** (a)
22. (a)	**23.** (b)	**24.** (c)	**25.** (b)	**26.** (b)	**27.** (a)	**28.** (c)
29. (b)	**30.** (c)	**31.** (b)	**32.** (b)	**33.** (a)	**34.** (c)	**35.** (b)
36. (a)	**37.** (c)	**38.** (b)	**39.** (a)	**40.** (b)	**41.** (b)	**42.** (d)

43. (a) **44.** (b) **45.** (c) **46.** (d) **47.** (a) **48.** (b) **49.** (b)
50. (d) **51.** (c) **52.** (a) **53.** (a) **54.** (d) **55.** (b) **56.** (c)
57. (d) **58.** (a) **59.** (c) **60.** (c) **61.** (c) **62.** (d) **63.** (c)
64. (c) **65.** (b) **66.** (a) **67.** (a) **68.** (a) **69.** (a) **70.** (a)
71. (b) **72.** (b) **73.** (a) **74.** (a) **75.** (b)

Multiple Correct Choice Type

1. (b), (c) **2.** (b), (c), (d) **3.** (a), (b), (c), (d) **4.** (b), (d) **5.** (a), (b), (d)
6. (b), (c) **7.** (a), (b), (c), (d) **8.** (a), (d) **9.** (a), (c) **10.** (a), (c), (d)
11. (c), (d) **12.** (a), (b) **13.** (a), (b), (c), (d) **14.** (c), (d) **15.** (a), (c)
16. (a), (b), (c) **17.** (b), (c) **18.** (a), (b), (d) **19.** (c), (d) **20.** (a), (d)
21. (a), (b), (c), (d) **22.** (a), (b) **23.** (c), (d) **24.** (a), (b), (c), (d) **25.** (a), (c)
26. (b), (d) **27.** (a), (b), (c), (d) **28.** (b), (c)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (c) **(iii)** (d) **2.** **(i)** (c) **(ii)** (d) **(iii)** (b)
3. **(i)** (d) **(ii)** (a) **(iii)** (b) **4.** **(i)** (a) **(ii)** (a) **(iii)** (b)

Assertion Reason Type

1. (c) **2.** (d) **3.** (a) **4.** (d) **5.** (a) **6.** (a) **7.** (b)

Hints and Solutions

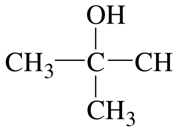
Straight Objective Type

1. Catalytic reduction of carbon monoxide in presence of $ZnO–Cr_2O_3$ constitutes industrial method of preparation of methanol.
2. Wood alcohol is CH_3OH.
3. Grain alcohol is C_2H_5OH
4. Rubbing alcohol is $(CH_3)_2CHOH$
5. Absolute alcohol is C_2H_5OH.
6. The order of boiling point is primary > secondary > tertiary. Hence, the correct oder is

1-pentanol > 3-methyl-2-butanol > 2-methyl-2-butanol

7. The acidic nature of alcohols follows the order $CH_3OH > 1° > 2° > 3°$.
8. As a Brönsted base, the order is reverse of its acidity. Hence, the correct order is $1° < 2° < 3°$.
9. A 2° alcohol can undergo both S_N1 and S_N2 substitutions.
10. Ethanol involves maximum hydrogen bonding amongst the given compounds.
11. More branched alcohol (2-methyl-2-propanol) has minimum boiling point.
12. The relative order of acidity is $H_2O > ROH > HC{\equiv}CH$.
13. The relative order of basicity follows reverse order as given in Q.12. The correct order is

$OH^- < OR^- < HC{\equiv}C^-$.

14. Glycerine is a trihydric alcohol.
15. CH_3OH is the strongest acid amongst the given compounds.
16. Positive charge on nitrogen makes $(CH_3)_4N^+I^-$ most reactive towards nucleophilic attack.
17. Tertiary alcohol reacts fastest with Lucas reagent. The compound is  $CH_3—\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CH_3$ (Choice d).
18. Tertiary alcohol (2-methylpropan-2-ol) reacts fastest with HBr.
19. 3° carbocation given by compound b is most stable.
20. $\underset{\text{propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow{KCN} \underset{\text{Butanonitrile}}{CH_3CH_2CH_2CN}$

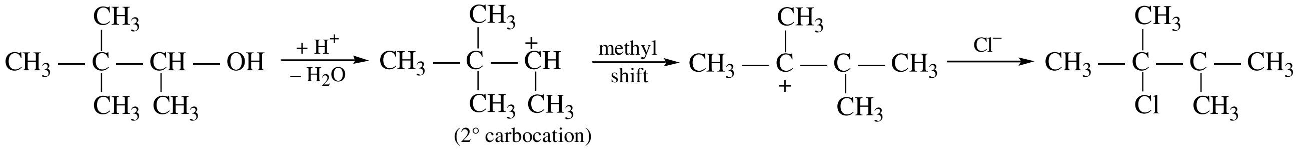
21. The order of reactivity of HX towards ROH is HI > HBr > HCl.

22. The order of reactivity of alcohols towards hydrogen halide is benzyl > 3° > 2° > 1°.

23. The reaction involves rearrangement $CH_3CH_2CH_2CH_2OH \xrightarrow{-H_2O} \underset{\text{main product}}{CH_3CH{=}CHCH_3}$

24. Electron releasing group makes the replacement faster. Hence, the correct order is IV > III > II > I.

25. The reaction involves rearrangement.

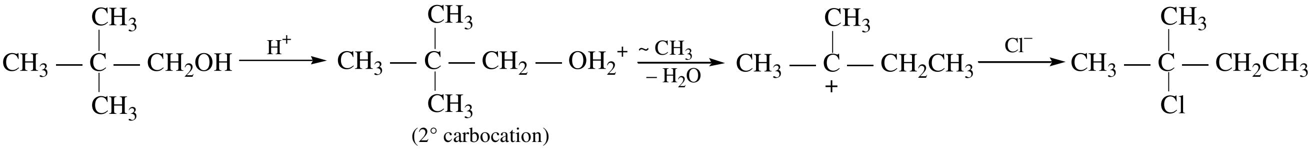


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-OH \xrightarrow[-H_2O]{+H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{\overset{+}{C}H} \xrightarrow[\text{shift}]{\text{methyl}} CH_3-\overset{CH_3}{\underset{+}{C}}-\underset{CH_3}{C}-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{Cl}{C}}-\underset{CH_3}{C}-CH_3$$

(2° carbocation)

The reaction proceeds via S_N1 mechanism. The intermediate carbocation undergoes rearrangement to give stable 3° carbocation.

26. The reaction involves rearrangement.

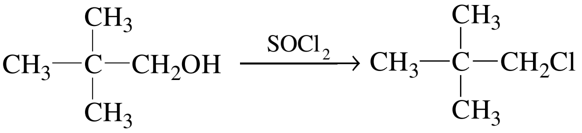


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH_2^+ \xrightarrow[-H_2O]{\sim CH_3} CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3$$

(2° carbocation)

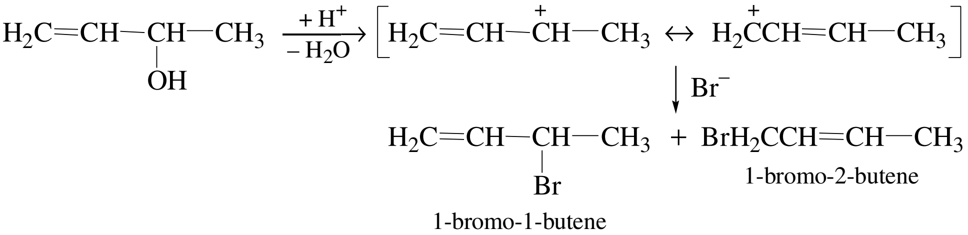
The reaction will proceed with very slow speed via S_N2 mechanism due to bulky neopentyl group. Here, methyl group acts as an intramolecular nucleophile which on migration removes H_2O. The result is 3° carbocation from which the final product is obtained.

27. The reaction is



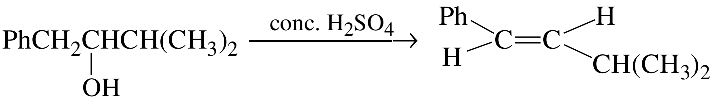
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \xrightarrow{SOCl_2} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl$$

28. The reaction involves rearrangement of carbocation.



$$H_2C{=}CH-\underset{OH}{CH}-CH_3 \xrightarrow[-H_2O]{+H^+} \left[H_2C{=}CH-\overset{+}{C}H-CH_3 \leftrightarrow H_2\overset{+}{C}CH{=}CH-CH_3\right] \xrightarrow{Br^-} \underset{\text{1-bromo-1-butene}}{H_2C{=}CH-\underset{Br}{CH}-CH_3} + \underset{\text{1-bromo-2-butene}}{BrH_2CCH{=}CH-CH_3}$$

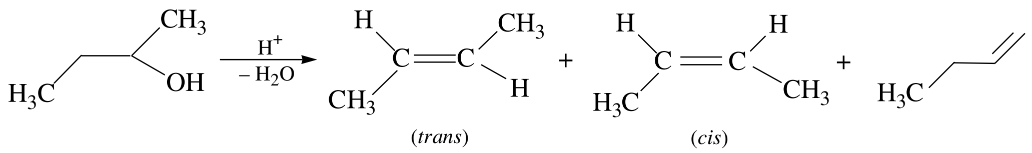
29. Mainly *trans* isomer is obtained as it more stable conjugated isomer.



$$PhCH_2\underset{OH}{CH}CH(CH_3)_2 \xrightarrow{\text{conc. }H_2SO_4} \overset{Ph}{\underset{H}{}}C{=}C\overset{H}{\underset{CH(CH_3)_2}{}}$$

30. The electron-releasing group makes the reaction fastest. Thus, *p*-$CH_3OC_6H_4CH_2OH$ reacts fastest with HBr.

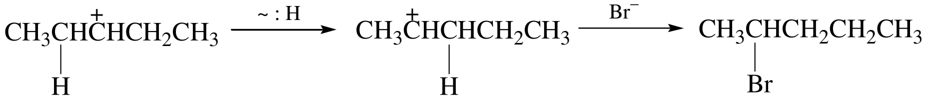
31. The electron-attracting group makes the reaction slowest. Thus, *p*-$O_2NC_6H_4CH_2OH$ reacts slowest.

32. 

The addition of Br_2 to *trans*-butene produces one compound, i.e. *meso*-2,3-dibromobutane.
The addition of Br_2 to *cis*-butene produces two compounds (racemic mixture of 2,3-dibromobutane).
The addition of Br_2 to but-1-ene produces two compounds (racemic mixture of 1,2-dibromobutane).

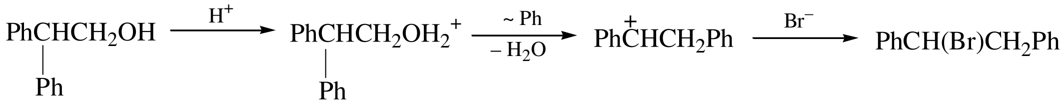
33. Al_2O_3 at elevated temperature converts cyclohexanol to cyclohexene.

34. A 2° ROH can undergo both S_N1 and S_N2 substitution. 3-Bromopentane can be formed from both these mechanism. However, in S_N1 mechanism, the intermediate carbocation undergoes a hydride (:H) shift to give some 2-bromopentane.



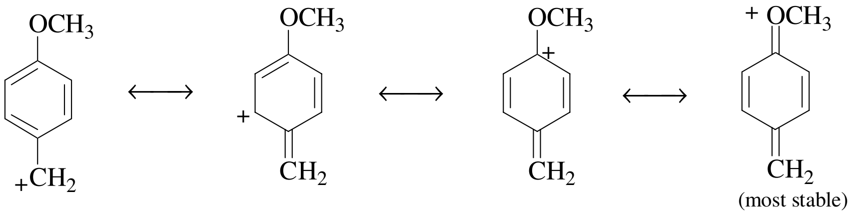
$$\mathrm{CH_3\underset{\displaystyle H}{C}H\overset{+}{C}HCH_2CH_3 \xrightarrow{\sim:H} CH_3\overset{+}{C}H\underset{\displaystyle H}{C}HCH_2CH_3 \xrightarrow{Br^-} CH_3\underset{\displaystyle Br}{C}HCH_2CH_2CH_3}$$

35. The reaction proceeds as

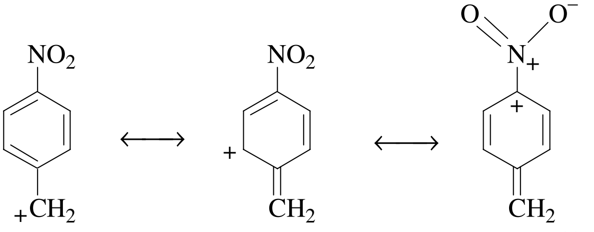


$$\mathrm{Ph\underset{\displaystyle Ph}{C}HCH_2OH \xrightarrow{H^+} Ph\underset{\displaystyle Ph}{C}HCH_2OH_2{}^+ \xrightarrow[-\,H_2O]{\sim Ph} Ph\overset{+}{C}HCH_2Ph \xrightarrow{Br^-} PhCH(Br)CH_2Ph}$$

36. The reaction proceeds with S_N1 mechanism. The +ve charge on the benzylic carbon is most effectively delocalized by the CH_3O— group and is thus most reactive. A similar stabilization places the +ve charge in the ring adjacent to the positively charged N of NO_2. This destabilizes the benzylic carbocation making it the least reactive. *p*–Cl destabilizes the +ve charge only by induction and not by resonance making it to be more reactive than *p*–$NO_2C_6H_4CH_2OH$.

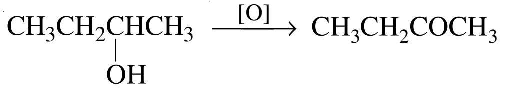


(most stable)



(Least stable)

37.



$$\mathrm{CH_3CH_2\underset{\displaystyle OH}{C}HCH_3 \xrightarrow{[O]} CH_3CH_2COCH_3}$$

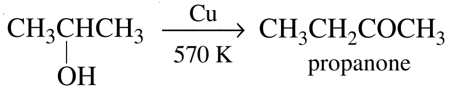
2-Butanol

38. The reactivity of alcohols with active metals is 3° < 2° < 1°.

39. Pyridinium chlorochromate is used to change 1° alcohol to 1° aldehyde.

40. $ROH + R'MgX \rightarrow R'H + Mg(RO)X$

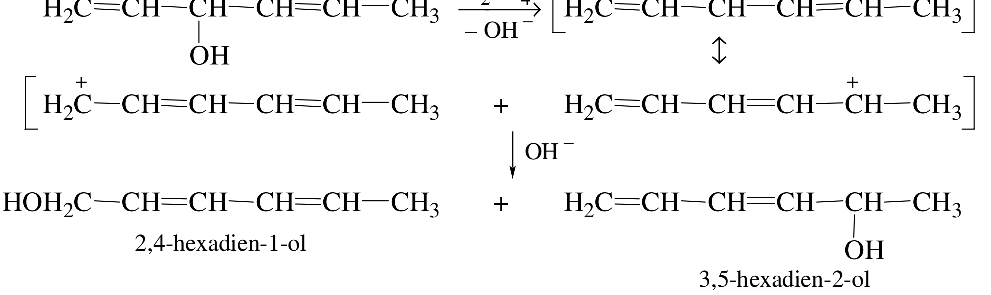
41.



$$\mathrm{CH_3\underset{\displaystyle OH}{C}HCH_3 \xrightarrow[570\,K]{Cu} CH_3CH_2COCH_3}$$

propanone

42. The reaction involves rearrangement of carbocation.



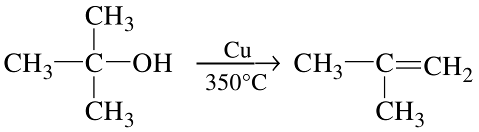
$$\begin{gathered}\mathrm{H_2C{=}CH{-}\underset{\displaystyle OH}{C}H{-}CH{=}CH{-}CH_3 \xrightarrow[-\,OH^-]{H_2SO_4} \left[H_2C{=}CH{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3\right]}\\ \updownarrow \\ \mathrm{\left[H_2\overset{+}{C}{-}CH{=}CH{-}CH{=}CH{-}CH_3 \quad + \quad H_2C{=}CH{-}CH{=}CH{-}\overset{+}{C}H{-}CH_3\right]}\\ \big\downarrow \mathrm{OH^-}\\ \mathrm{HOH_2C{-}CH{=}CH{-}CH{=}CH{-}CH_3 \quad + \quad H_2C{=}CH{-}CH{=}CH{-}\underset{\displaystyle OH}{C}H{-}CH_3}\end{gathered}$$

2,4-hexadien-1-ol

3,5-hexadien-2-ol

43. At 0°C, only salt formation takes place. The product is $CH_3CH_2OH_2^+\ HSO_4^-$.

44. At room temperature OH is replaced by —OSO_2OH. The product is $CH_3CH_2OSO_2OH$.

45. At 130°C, ether is formed. The product is $C_2H_5OC_2H_5$.
46. At 180°C, water is eliminated to give $H_2C{=}CH_2$.
47. The reaction is $(CH_3)_3COH + PhMgBr \rightarrow C_6H_6 + (CH_3)_3COMgBr$
48. Acid-base equilibrium lies toward the weaker acid and weaker base. Thus, we have $RSH > H_2O$ and $OH^- > RS^-$ and $H_2O > ROH$ and $RO^- > OH^-$.
49. 2° alcohol shows blue colouration in the Victor-Meyer test.
50. 

$$CH_3{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}OH \xrightarrow[350°C]{Cu} CH_3{-}\underset{\underset{\large CH_3}{|}}{C}{=}CH_2$$

3-methylpropene

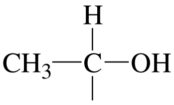
51. Lucas reagent is anhydrous $ZnCl_2$ and concentrated HCl.
52. Primary alcohol (*n*-butanol) does not react with Lucas reagent.
53. Red colouration is shown by 1° alcohol in the Victor-Meyer test.
54. The cloudiness is due to the formation of alkyl chloride.
55. A compound containing neither CH_3CO— nor $CH_3CH(OH)$— group does not show iodoform test. Thus, the compound $PhCH(OH)CH_2CH_3$ does not show iodoform test.
56. Heating with Cu causes dehydration. 1-Propanol gives propanal while 2-Propanol gives propanone. Only propanol reacts with Fehling solution.

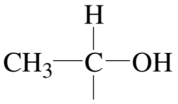
Multiple Correct Choice Type

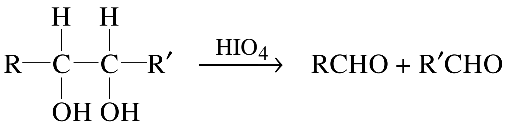
2. (b) Ethylene glycol ($HOCH_2CH_2OH$) has two centres of hydrogen bonding while ethanol has only one.
(c) Anti-Markovnikov addition of water takes place.
(d) Markovnikov addition of water takes place.

3. (b) This is because of the formation of carbocation as the intermediate.
(c) This is because of the formation of carbocation as the intermediate.
(d) In the presence of an acid, alcohol gives protonated alcohol. The latter readily loses the weakly basic water molecule leaving behind the carbocation. The unprotonated alcohol would have to lose the strongly basic hydroxide ion, which is difficult to take place.

4. (a) Replacement of —OH by a halogen in an alcohol is nucleophilic substitution reaction. It is the protonted alcohol which acts as a substrate.
(b) Alcohols are acidic enough to react with active metals to liberate hydrogen gas. They are basic enough to accept a proton from strong acids.
(c) It gives a ketone containing the same number of carbon atoms. Further oxidation will give carboxylic acid containing lesser number of carbon atoms.

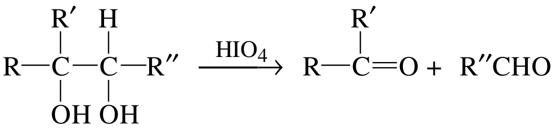
5. (a) *tert*-Butyl alcohol does not possess  $CH_3{-}\overset{\overset{\large H}{|}}{\underset{|}{C}}{-}OH$ group, hence it does not give iodoform test.

(b) The molecule does not possess  $CH_3{-}\overset{\overset{\large H}{|}}{\underset{|}{C}}{-}OH$ group.

(c) The reaction is 

$$R{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}R' \xrightarrow{HIO_4} RCHO + R'CHO$$

(d) The products are one aldehyde and one ketone.



$$R{-}\overset{\overset{\large R'}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}R'' \xrightarrow{HIO_4} R{-}\overset{\overset{\large R'}{|}}{C}{=}O + R''CHO$$

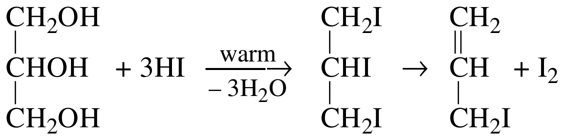
6. (a) The molecule does not contain —OH groups attached to adjacent carbon atoms.

(b) Tertiary alcohol gives 3° carbocation and secondary alcohol gives 2° carbocation. Since 3° carbocation is more stable than 2° carbocation, it is formed more readily.

7. (a) Tertiary alcohol reacts faster than secondary alcohol with Lucas reagent.

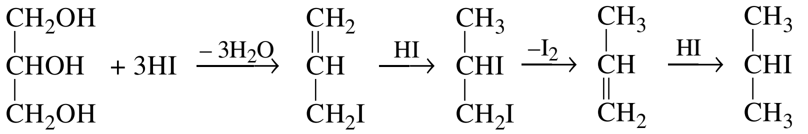
(b) The correct order is 1° > 2° > 3°.

(c) With small amount of HI, allyl iodide is obtained.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HI \xrightarrow[-3H_2O]{\text{warm}} \begin{array}{c} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} \rightarrow \begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array} + I_2$$

(d) With excess of HI, 2-iodopropane is obtained.

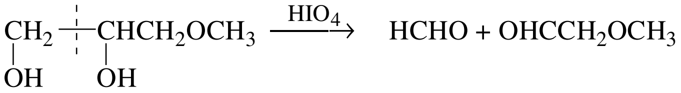


$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HI \xrightarrow{-3H_2O} \begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array} \xrightarrow{HI} \begin{array}{c} CH_3 \\ | \\ CHI \\ | \\ CH_2I \end{array} \xrightarrow{-I_2} \begin{array}{c} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} \xrightarrow{HI} \begin{array}{c} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array}$$

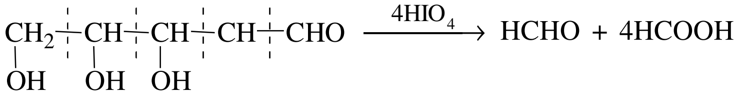
8. (a) Electron-withdrawing substituent increases acid strength by stabilising the anion.

(b) Nitro group is electron-withdrawing group. By withdrawing electrons, it stabilises the resultant anion and hence makes the acid stronger.

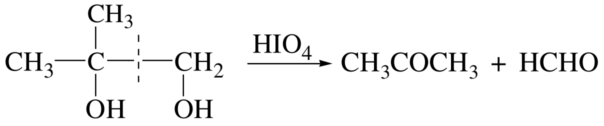
(c) Only one mole of HIO_4 will be consumed.



$$\underset{OH}{\underset{|}{CH_2}} \vdots \underset{OH}{\underset{|}{C}}HCH_2OCH_3 \xrightarrow{HIO_4} HCHO + OHCCH_2OCH_3$$

(d)


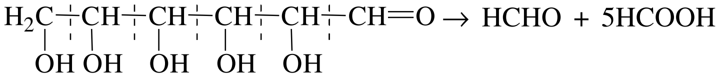
$$\underset{OH}{\underset{|}{CH_2}} \vdots \underset{OH}{\underset{|}{CH}} \vdots \underset{OH}{\underset{|}{CH}} \vdots CH \vdots CHO \xrightarrow{4HIO_4} HCHO + 4HCOOH$$

9. (a)


$$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\vdots-\underset{OH}{\underset{|}{CH_2}} \xrightarrow{HIO_4} CH_3COCH_3 + HCHO$$

(b) The compound is


$$H_2\underset{OH}{\underset{|}{C}}(CHOH)_4CHO.$$



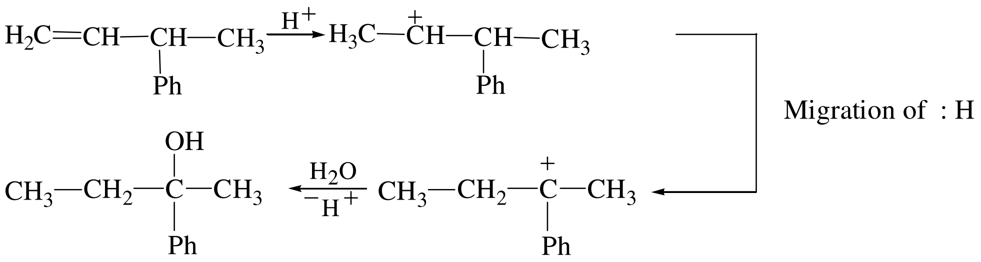
$$H_2\underset{OH}{\underset{|}{C}} \vdots \underset{OH}{\underset{|}{CH}} \vdots \underset{OH}{\underset{|}{CH}} \vdots \underset{OH}{\underset{|}{CH}} \vdots \underset{OH}{\underset{|}{CH}} \vdots CH{=}O \rightarrow HCHO + 5HCOOH$$

(c) Thiols are less polar than the alcohols.

10. (a) Ethanol forms a lower boiling azeotropic mixture containing 95.6 and 4.4 by volume of alcohol and water, respectively. Water can be remored by adding Mg metal to azeotropic mixture which reacts water forming $Mg(OH)_2$ and releasing H_2.

(b) The OH group of cyclohexanol is more exposed and available for H-bonding with water due to the more compactness of the remaining R group.

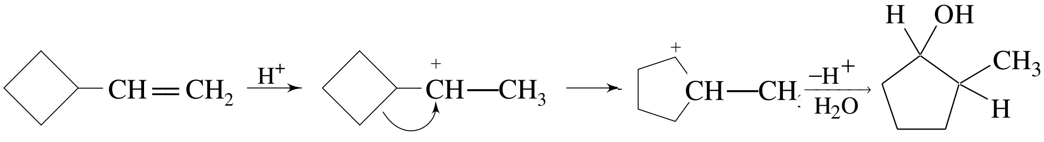
(c) The product is 2-phenyl-2-butanol.



$$H_2C{=}CH-\underset{Ph}{\underset{|}{CH}}-CH_3 \xrightarrow{H^+} H_3C-\overset{+}{C}H-\underset{Ph}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{Migration of : H}} CH_3-CH_2-\underset{Ph}{\underset{|}{\overset{+}{C}}}-CH_3 \xrightarrow[-H^+]{H_2O} CH_3-CH_2-\underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

(*Note*: Although phenyl is a better migrator than H, yet the hydride migrates so as to give a more stable 3° benzylic carbocation.)

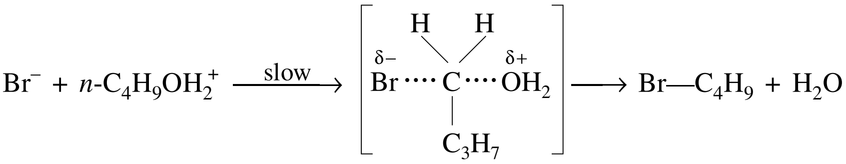
(d) The product is *cis*- and *trans*-2-methylcyclopentanol. In this reaction, addition of H^+ to C^1 gives a 2° carbocation which rearranges by ring expansion to give substituted cyclopentanol.



11. (a) The electron-releasing R group makes the alcohol less acidic than water.

(b) The reaction follows S_N2 mechanism.

$$n\text{-}C_4H_9OH + HBr \underset{}{\overset{\text{fast}}{\rightleftharpoons}} n\text{-}C_4H_9OH_2^+ + Br^-$$



$$Br^- + n\text{-}C_4H_9OH_2^+ \xrightarrow{\text{slow}} \left[\overset{\delta-}{Br} \cdots \underset{C_3H_7}{\overset{H\ \ H}{C}} \cdots \overset{\delta+}{OH_2} \right] \longrightarrow Br—C_4H_9 + H_2O$$

(c) The mechanism is

$$(CH_3)_3COH + HBr \overset{\text{fast}}{\rightleftharpoons} (CH_3)_3COH_2^+ + Br^-$$

$$(CH_3)_3COH_2^+ \xrightarrow[-H_2O]{\text{slow}} (CH_3)_3\,C^+ \xrightarrow[\text{fast}]{Br^-} (CH_3)_3CBr$$

(d) The reaction follows S_N2 mechanism which is brought about by inversion because Br^- bonds to the back side of the C, away from the departing H_2O.

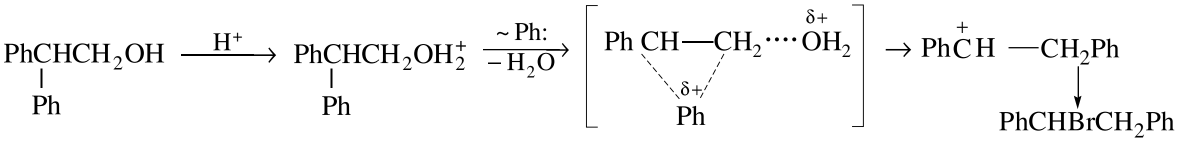
12. (a) The reaction follows S_N1 mechanism in which a carbocation is formed. Bonding with Br^- is equally probable by the flat carbocation. The H_2O shields the incipient C^+ to some extent from the frontal attack. Bonding from the rear side is not impeded and thus excess of *S*-isomer is formed.

(b) A carbocation is formed in S_N1 nucleophilic substitution reaction of ROH. The carbocation may involve rearrangement in going from a less stable to more stable carbocation.

(c) There is inversion but not rearrangement.

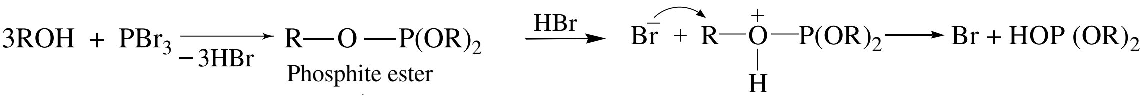
(d) The reaction may follow both types of S_N1 and S_N2 mechanisms.

13. (a) The reaction proceeds via the rearrangement of carbocation.



$$\underset{Ph}{PhCHCH_2OH} \xrightarrow{H^+} \underset{Ph}{PhCHCH_2OH_2^+} \xrightarrow[-H_2O]{\sim Ph:} \left[Ph\,CH—CH_2\cdots\overset{\delta+}{OH_2} \right] \rightarrow Ph\overset{+}{C}H—CH_2Ph \rightarrow PhCHBrCH_2Ph$$

(b) The reaction proceed as follows.



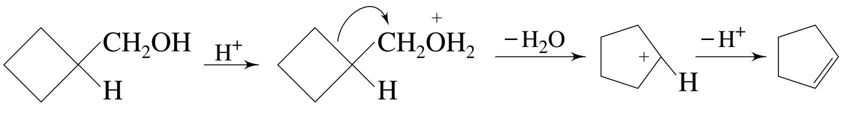
$$3ROH + PBr_3 \xrightarrow[-3HBr]{} \underset{\text{Phosphite ester}}{R—O—P(OR)_2} \xrightarrow{HBr} Br^- + R—\underset{H}{\overset{+}{O}}—P(OR)_2 \longrightarrow Br + HOP\,(OR)_2$$

(c) The decreasing order of dehydration follows 3° alcohol > 2° alcohol > 1° alcohol.

(d) Both alcohols are 3°. The alcohol $(CH_3)_2C(OH)CH(CH_3)_2$ produces more substituted alkene (Saytzeff rule).

14. (a) Both alcohols are 2°. The alcohol $CH_3CH_2CH(OH)CH(CH_3)_2$ produces more substituted alkene (Saytzeff rule).

(b) The product is cyclopentene. Expansion of a four to a five-membered ring relieves ring strain.



(c) The CH_3O group stabilises the benzylic carbocation by resonance where NO_2 group, being an electron attractant destabilises it. Chloro group destabilises inductively.

15. (b) MnO_2 oxidises only allylic OH group. The product is $CH_3CH{=}CHCHO$

(d) MnO_2 oxidises only benzylic OH group. The product is $PhCOCH_2CH_2OH$.

16. (a) Both NO_2 and COOH groups are reduced. The product is $p\text{-}H_2NC_6H_4CH_2CH_2OH$.

(b) The hydration involves anti-Markovanikov addition.

$$Ph_2C{=}CHCH_3 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ BH_3\cdot THF} Ph_2CHCH(OH)CH_3$$

(c) An alcohol containing a methyl carbinol with at least one H on the carbinol C gives iodoform test. Cyclopentylmethylcarbinol shows iodoform test and the product is cyclopentanecarboxylic acid.

17. (a) The sulphur atom has a larger size than the oxygen atom. The negative charge on S is more spread out in the conjugate base, RS^- as compared to the negative charge on O atom in RO^-. Thus, RS^- is less likely to attract on H^+ than RO^-. This, in turn, implies that RSH is a stronger acid than ROH.

(c) The O atom in ROH is more capable of attracting H^+ because of its smaller size (more charge density) as compared to S atom (less charge density).

(d) RSH is a much stronger acid than HOH and OH^- is a much stronger base than RS^-. Since the acid-base equilibrium lies toward the weaker acid and weaker base, the reaction lies far towards the right side.

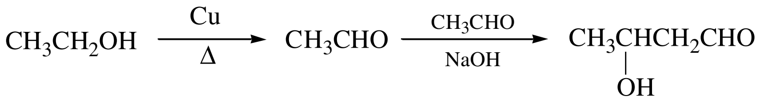
18. (a) The differences in acidities and basicities are slight, all species are present at equilibrium.

(b) ROH is a weak acid than R′SH and also $R'S^-$ is a weaker base than RO^-. Hence, the reaction will not be feasible as the reactants contain weaker acid and weaker base as compared to the products.

(c) Because of the bigger size of S, the negative charge on it is more easily polarised which makes it easier for the nucleophilic attack. The nucleophilic nature of RO^- is also diminished in a protic solvent because there will be more stronger hydrogen bonding due to the large negative charge density on the smaller sized O atom.

(d) The bond angles are 109° and 96° for C—O—H and C—S—H, respectively. The oxygen involves sp^3 hydrid orbitals while sulphur involves p orbitals for bonding with C and H atoms.

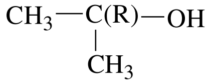
19. (a) The reaction is



$$CH_3CH_2OH \xrightarrow[\Delta]{Cu} CH_3CHO \xrightarrow[NaOH]{CH_3CHO} \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2CHO}$$

(c) The product is 1° alcohol

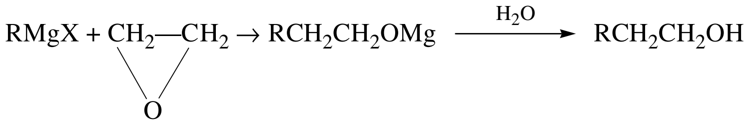
(d) The product is 2° alcohol. ($CH_3CH(R)OH$)

20. (a) The product is 3° alcohol 

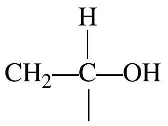
$$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{C}(R)—OH$$

(d) The product is *n*-butyl alcohol.

21. (b) The reaction is



22. (a) The reagent to be used is pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$)

(b) The alcohol must contain 

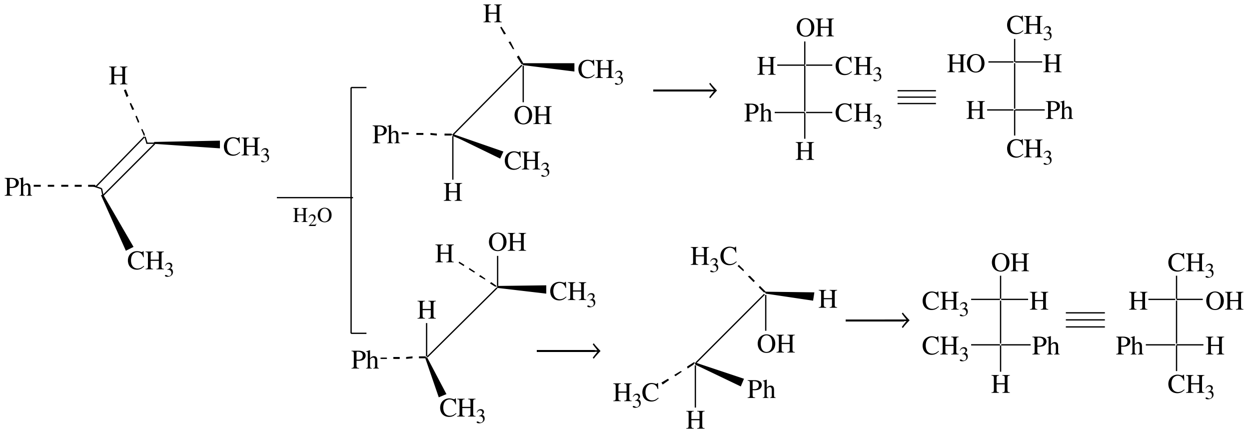
$$CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}—OH$$

group.

23. (c) The primary alcohol gives blood-red coloration.

(d) The secondary alcohol gives blue coloration.

25.

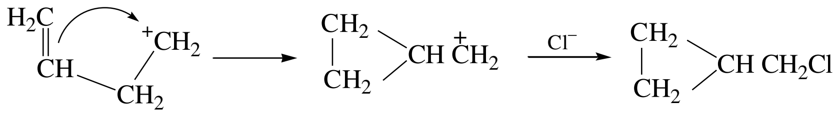


26. *Trans*-alkene produces compounds (b) and (d).

27. Let R ≡ —$CH_2CH{=}CH_2$. The reaction proceeds as follows.

$$RCH_2OH \xrightarrow{H^+} RCH_2-\overset{+}{O}H_2 \longrightarrow R\overset{+}{C}H_2$$

$$R\overset{+}{C}H_2 \xrightarrow{Cl^-} RCH_2Cl$$



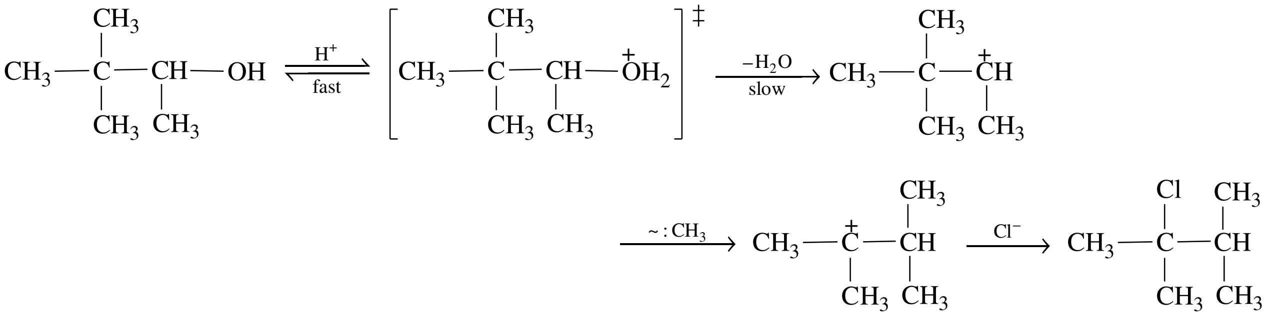
$$H_2C{=}CHCH_2\overset{+}{C}H_2 \xrightarrow{\sim H} H_2\overset{+}{C}\,CH{=}CHCH_3 \xrightarrow{Cl^-} ClH_2CCH{=}CHCH_3$$

$$H_2C{=}CHCH_2\overset{+}{C}H_2 \xrightarrow{\sim H} H_2C{=}CH\overset{+}{C}HCH_3 \longrightarrow H_2C{=}CH\,CH(Cl)CH_3$$

28. The compounds CH_3CH_2OH and $CH_3CH(OH)CH_3$ show positive iodoform test.

Linked Comprehension Type

1. (I)

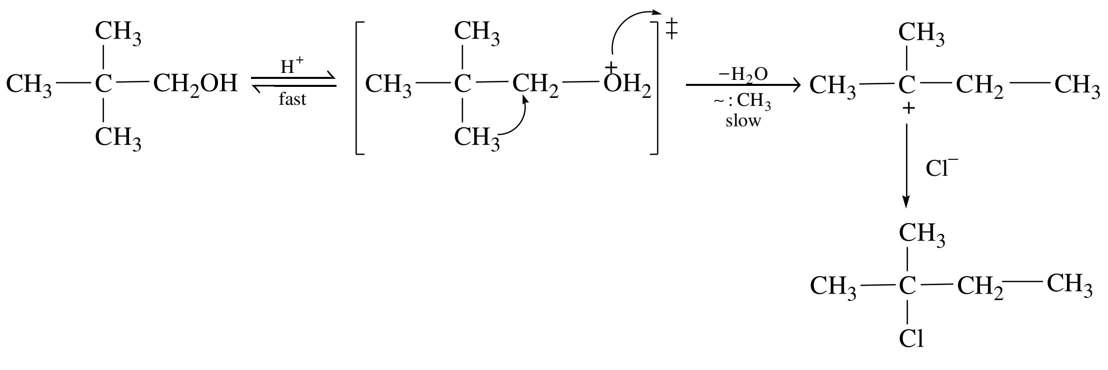


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-OH \underset{fast}{\overset{H^+}{\rightleftharpoons}} \left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-\overset{+}{O}H_2\right]^{\ddagger} \xrightarrow[slow]{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{\overset{+}{C}H}$$

$$\xrightarrow{\sim :CH_3} CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow{Cl^-} CH_3-\underset{CH_3}{\overset{Cl}{C}}-\underset{CH_3}{\overset{CH_3}{CH}}$$

2° R^+ formed via S_N1 rearranges by a : CH_3 shift to the more stable 3° C^+, which then gives the 3° chloride.

(II)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \underset{fast}{\overset{H^+}{\rightleftharpoons}} \left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{O}H_2\right]^{\ddagger} \xrightarrow[\substack{\sim :CH_3\\ slow}]{-H_2O} CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2-CH_3$$

Neopenty alcohol, though 1°, is extremely hindered and reacts very slowly by S_N2 displacement. Formation of neopentyl cation via S_N1 is also unlikely. Instead, a methyl group migrates intramolecularly and simultaneously displacing H_2O.

(i) The reactions (I) and (II) follow S_N1 and S_N2 mechanisms

(ii) The product P and Q are shown above

(iii) The reaction I follows the rate law

$$\text{rate} = k\,[(CH_3)_3CH(CH_3)\overset{+}{O}H_2] = k\,K_{eq}\,[(CH_3)_3CCH(CH_3)OH]\,[H^+]$$

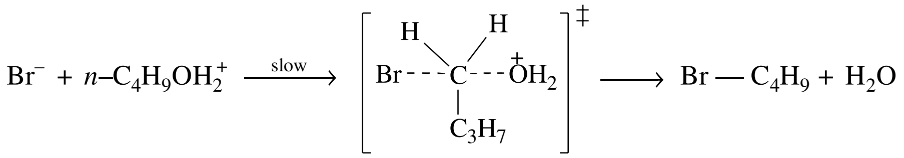
The reaction I follows the rate law

$$\text{rate} = k\,[(CH_3)_3CH_2\overset{+}{O}H_2] = k\,K_{eq}\,[(CH_3)_3CCH_2OH]\,[H^+]$$

Both follow second order kinetics.

2. The reactions proceed as follows.

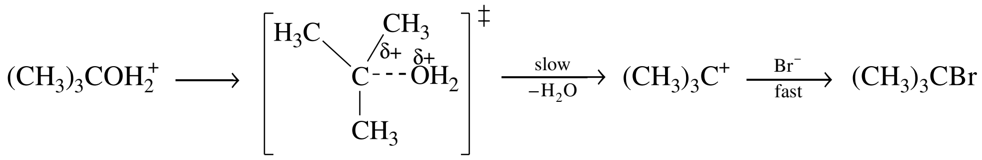
(I) $n\text{–}C_4H_9OH + H^+ \rightleftharpoons n\text{–}C_4H_9OH_2^+$ (fast)



$$Br^- + n\text{–}C_4H_9OH_2^+ \xrightarrow{\text{slow}} \left[Br\text{---}\underset{C_3H_7}{\overset{H\;\;H}{C}}\text{---}\overset{+}{O}H_2 \right]^{\ddagger} \longrightarrow Br—C_4H_9 + H_2O$$

S_N2 mechanism is followed.

(II) $(CH_3)_3COH + H^+ \rightleftharpoons (CH_3)_3COH_2^+$ (fast)



$$(CH_3)_3COH_2^+ \longrightarrow \left[\underset{CH_3}{\overset{H_3C\;\;CH_3}{\overset{\delta+}{C}}}\text{---}\overset{\delta+}{O}H_2 \right]^{\ddagger} \xrightarrow[-H_2O]{\text{slow}} (CH_3)_3C^+ \xrightarrow[\text{fast}]{Br^-} (CH_3)_3CBr$$

S_N1 mechanism is followed.

(i) The mechanism followed are S_N2 and S_N1, respectively.

(ii) For reaction I

$$\text{rate} = k\,[Br^-]\,[n\text{–}C_4H_9OH_2^+] \quad = k\,K_{eq}\,[n\text{–}C_4H_9OH]\,[H^+]$$

(iii) For reaction II

$$\text{rate} = k\,[\text{Intermediate complex}] \quad = k\,K_{eq}\,[(CH_3)_3COH]\,[H^+]$$

(iv) In both reactions, intermediate are formed via reversible paths.

3. (i) The most common peroxyacid is *m*-chloroperoxybenzoic acid.

(ii) In base-catalyzed ring opening of epoxide, the nucleophile attacks the less substituted carbon.

(iii) In acid-catalyzed ring opening of epoxide, the nucleophile attacks the most substituted carbon.

4. (i) The addition of oxygen is *syn* addition. The formation of three membered ring of epoxide requires that oxygen must add to both the carbons of the double bond from the same side of alkene.

(ii) The ring opening by the Grignard reagent is S_N2 reaction in which R group acts as nucleophile while MgBr part combines with oxygen. R group attaches to less hindred carbon.

(iii) The acid-catalyzed hydrolysis causes the formation of diol. Here OH^- from water acts as nucleophile.

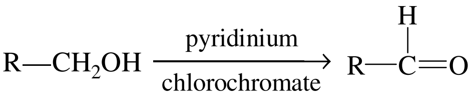
CHAPTER 27

ALDEHYDES AND KETONES

METHODS OF PREPARATION

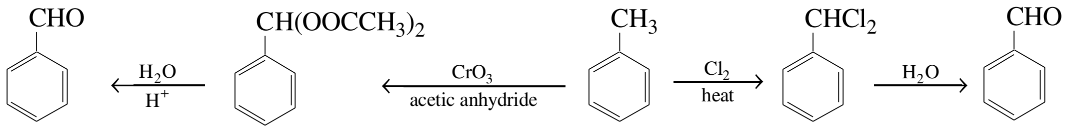
ALDEHYDES

1. Oxidation of primary alcohol



$$R{-}CH_2OH \xrightarrow[\text{chlorochromate}]{\text{pyridinium}} R{-}\overset{\displaystyle H}{\overset{|}{C}}{=}O$$

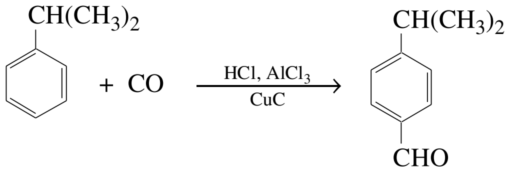
2. Oxidation of methylbenzenes



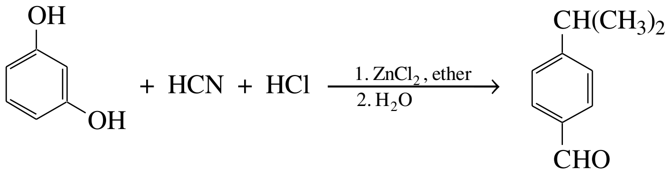
3. Reduction of acid chlorides

$$R{-}COCl \xrightarrow{LiAlH(OBu{-}t)_3} RCHO;\ R{-}COCl \xrightarrow[\text{ethyl acetate}]{H_2/Pd/BaSO_4} RCHO$$

4. Gatterman-Koch reaction



5. Gatterman reaction

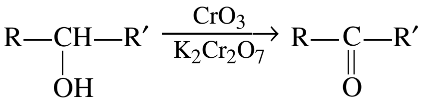


6. Heating a mixture of the calcium salts of formic acid and any one of its homologoues

$$(RCOO)_2Ca + (HCOO_2)_2Ca \rightarrow 2RCHO + 2CaCO_3$$

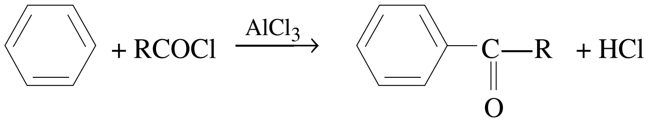
KETONES

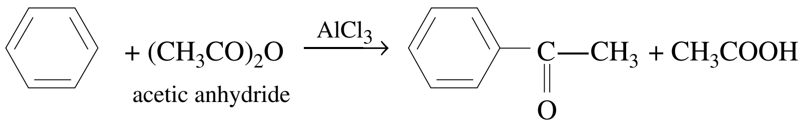
1. Oxidation of secondary alcohols



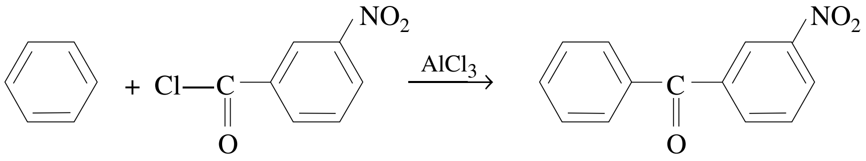
$$R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}R' \xrightarrow[K_2Cr_2O_7]{CrO_3} R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'$$

2. Friedel–Crafts acylation

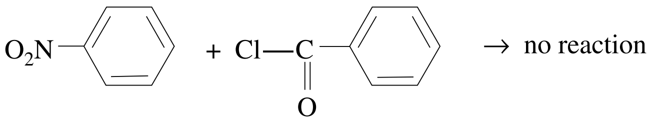




While preparing a ketone of the type ArCOAr′ containing deactivating group in one of the aromatic ring, it is important to select the proper combination of Ar and Ar′. For example, the preparation of *m*-nitrobenzophenone, one should proceeds as shown in the following.



The reaction



does not take place as the strongly deactivating nitro group prevents the acylation reaction.

3. Heating the calcium salt of any fatty acid other than formic acid

$$(RCO_2)Ca \rightarrow RCOR + CaCO_3$$

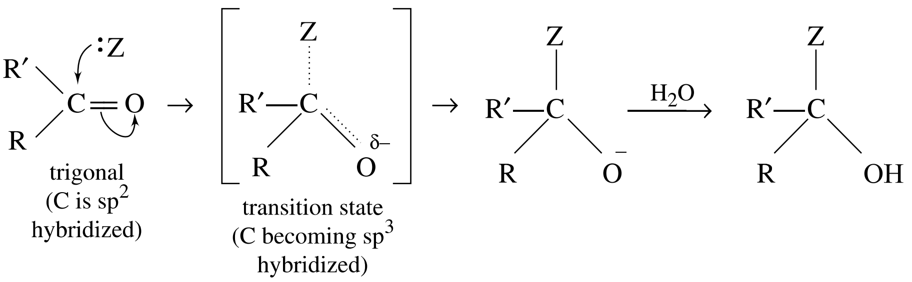
PHYSICAL PROPERTIES

Because of C═O group, aldehydes and ketones are polar compounds and their boiling points are higher than those of nonpolar compounds of comparable molar masses. However, they are not as polar as alcohols and carboxylic acids due to the absence of hydrogen bonding and thus their boiling points are lower than those of alcohols and carboxylic acids of comparable molar masses.

Formaldehyde is a gas, rest are liquids or solids. A 40% aqueous solution of formaldehyde is known as *formalin*. The lower aldehydes and ketones are soluble in water due to hydrogen bonding between solute and solvent.

CHEMICAL PROPERTIES

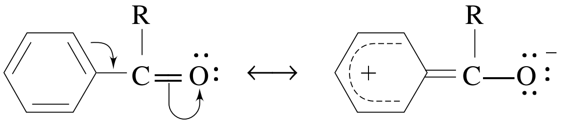
The carbonyl group, C═O, plays a dominating role in the chemistry of aldehydes and ketones. Because of the polarization $>\overset{\delta+}{C}=\overset{\delta-}{O}$ the addition reactions occurring across C═O bond is of nucleophilic type where the initiating step is the attack of nucleophile to carbon atom. The mechanism of addition reaction is



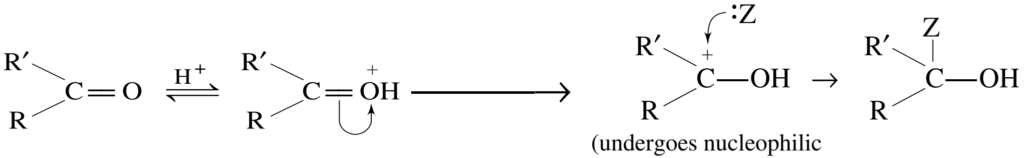
Aldehydes generally undergo nucleophilic addition more readily than ketones as the former involves lesser crowding at the transition state.

An alkyl group releases electrons and thus destabilises the transition state by intensifying the negative charge developing on oxygen. On the other hand, an aryl group, which is electron-withdrawing group, is expected to stabilise the transition state and thus speeds up the reaction.

However, an aryl group stabilises the reactant more than the transition state due to resonance and thus lowers down the speed of the reaction. The resonating structures are



The nucleophilic reaction involving >C=O group is catalyzed by acids. This is because carbon acquires more positive charge as depicted in the following.

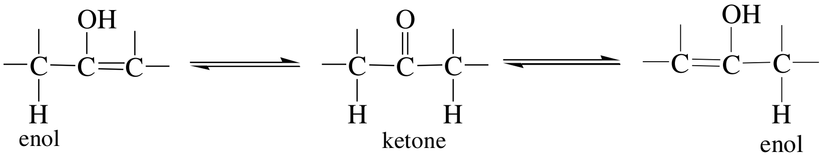

(undergoes nucleophilic attack more readily)

Typical reactions shown by aldehydes and ketones are as follows.

1. Oxidation The hydrogen atom attached to the carbonyl carbon is abstracted during oxidation. Hence, only aldehydes are oxidized easily and not ketones**:**

$$\text{R—CHO} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7]{\text{KMnO}_4} \text{R—COOH}$$

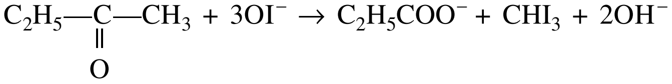
Ketones requires vigorous condition and the acids obtained contain fewer carbon atoms. Cleavage occurs at the double bond of the enol form**:**



Aldehydes are oxidized by even mild oxidizing reagents such as Tollens reagent (ammoniacal silver nitrate)**:**

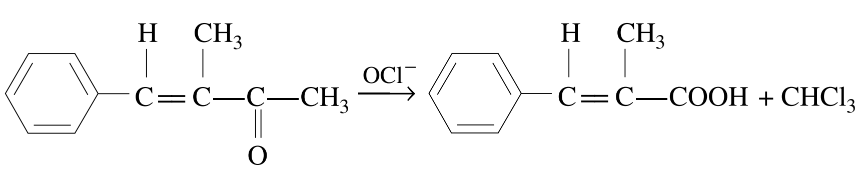
$$\text{CH}_3\text{CHO} + 2\text{Ag(NH}_3)_2^+ + 3\text{OH}^- \rightarrow \underset{\substack{\text{silver}\\\text{mirror}}}{2\text{Ag}} + \text{CH}_3\text{COO}^- + 4\text{NH}_3 + 2\text{H}_2\text{O}$$

Ketones containing $\text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}$ are oxidized by hypohalite to give carboxylic acid and haloform. For example,

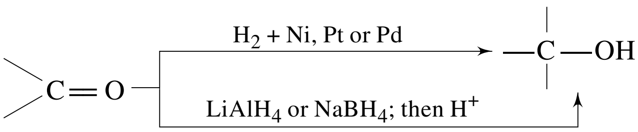


$$\text{C}_2\text{H}_5\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—CH}_3 + 3\text{OI}^- \rightarrow \text{C}_2\text{H}_5\text{COO}^- + \text{CHI}_3 + 2\text{OH}^-$$

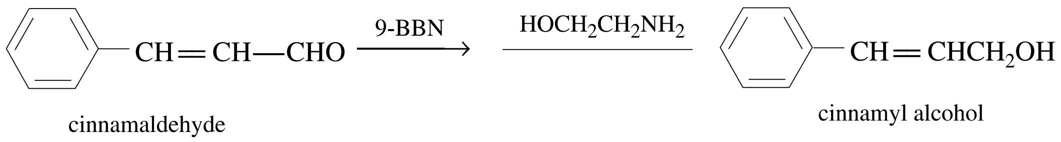
Hypohalite does not attack carbon-carbon double bond present in the molecules. For example,



2. Reduction Aldehydes are reduced to 1° alcohols whereas ketones to 2° alcohols. This can be achieved either by catalytic hydrogenation (H_2,Ni) or by the use of lithium aluminium hydride LiAlH_4**:**



If carbon-carbon double bond is also present in the carbonyl compound, it is also reduced alongwith. However, the use of the reagent 9-BBN (9-borabicyclo[3,3,1]nonane) prevents this and thus only the carbonyl group is reduced. For example,



cinnamaldehyde

cinnamyl alcohol

Reduction to Hydrocarbons Aldehydes and ketones are reduced to hydrocarbons by (a) Clemmensen reduction (amalgamated zinc and concentrated hydrochloric acid) and (b) Wolff-Kishner reduction (hydrazine, NH_2NH_2, and a strong base like KOH or potassium *tert*-butoxide). For example,

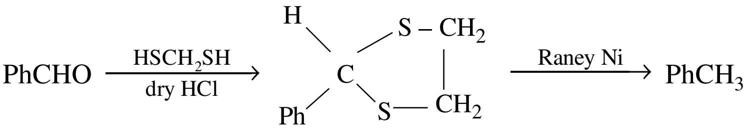
$$CH_3CH_2COCH_3 \xrightarrow[\text{conc. HCl}]{Zn(Hg)} CH_3CH_2CH_2CH_3$$

The Wolff-Kishner reaction proceeds as follows.

$$RCHO + H_2NNH_2 \longrightarrow RCH{=}N{-}NH_2 \xrightarrow{OH^-} [RCH{=}\ \ddot{N}{-}\ \overset{-}{\underset{\cdot\cdot}{\ddot{N}}}H \longleftrightarrow R\overset{-}{\ddot{C}}H{-}\ \ddot{N}{=}\ \ddot{N}H]$$

$$-\xrightarrow[\text{from } H_2O]{H^+} RCH_2\ \ddot{N}{=}\ \ddot{N}H \xrightarrow{OH^-} RCH_2\ \ddot{N}{=}\ \ddot{N}{:}^- \xrightarrow[\text{from } H_2O]{H^+} RCH_3 + N_2$$

Carbonyl group is also reducible by Raney Ni desulphurization method.



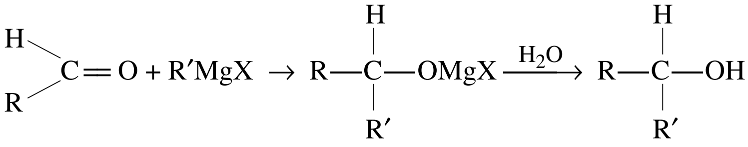
If a compound contains more than one CO group, the more reactive or unhindered CO group is reduced to CH_2.

Clemmenson method may be used if the compound is stable in acidic medium and contains a function group that reacts with strong base. For example, $BrCH_2CH_2CHO$.

Wolf-Kishner method may be used if the compound is sensitive to acid and stable in base. For example, $(CH_3)_2C(OH)CH_2CH_2COCH_3$.

Raney Ni desulphurization method cannot be used if the compound contains good leaving group because —SH is a nucleophilic group.

3. Action of Grignard reagents

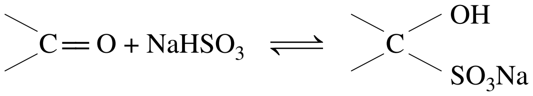


$$\underset{R}{\overset{H}{>}}C{=}O + R'MgX \rightarrow R{-}\underset{R'}{\overset{H}{\underset{|}{\overset{|}{C}}}}{-}OMgX \xrightarrow{H_2O} R{-}\underset{R'}{\overset{H}{\underset{|}{\overset{|}{C}}}}{-}OH$$

2° alcohol

Ketones produces 3° alcohol with Grignard reagent.

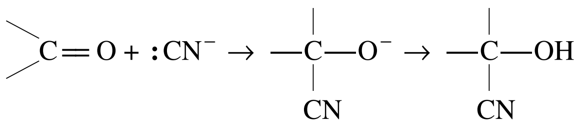
4. Reactions with sodium hydrogen sulphite



bisulphite

Most aldehydes form bisulphite compounds. Ketones of the type CH_3COR, where R is a primary alkyl group, form bisulphite compounds. If R is secondary or tertiary alkyl group, the formation of bisulphite is slow. Ketones of the type RCOR′ does not form bisulphite provided R is C_2H_5 or higher alkyl group.

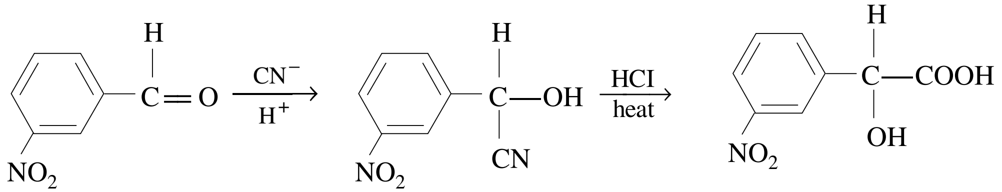
5. Addition of HCN (or sodium cyanide and mineral acid)



$$>C{=}O + {:}CN^- \rightarrow {-}\underset{CN}{\underset{|}{\overset{|}{C}}}{-}O^- \rightarrow {-}\underset{CN}{\underset{|}{\overset{|}{C}}}{-}OH$$

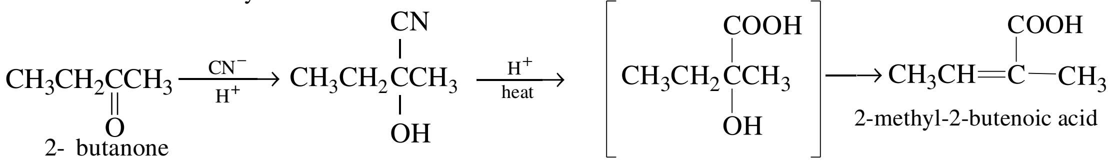
cyanohydrin

Cyanohydrin undergoes hydrolysis to give α-hydroxy acid or unsaturated acid. For example,



m-nitrobenzaldehyde

m-nitromandelic acid

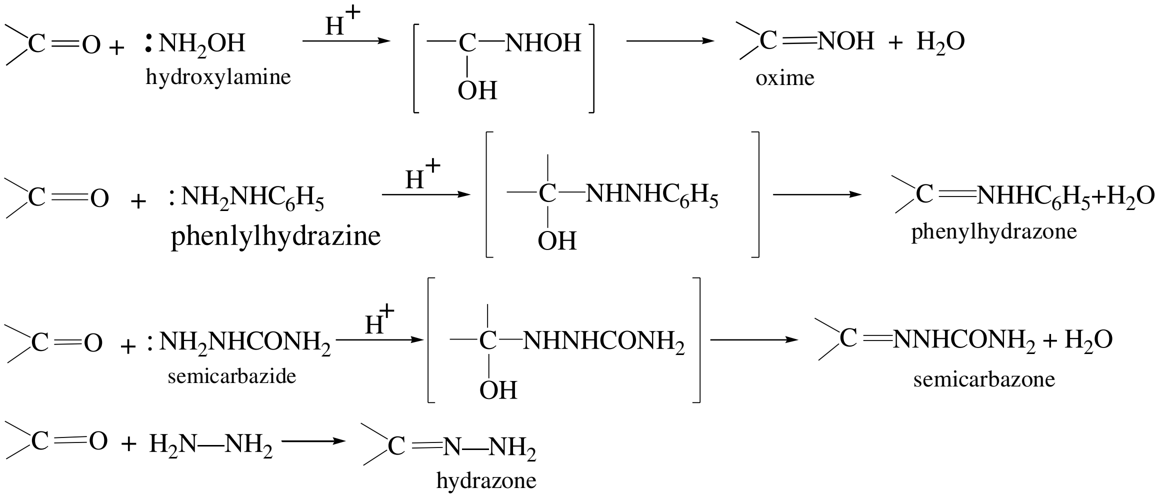


$$CH_3CH_2\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow[H^+]{CN^-} CH_3CH_2\overset{CN}{\underset{OH}{C}}CH_3 \xrightarrow[\text{heat}]{H^+} \left[CH_3CH_2\overset{COOH}{\underset{OH}{C}}CH_3\right] \longrightarrow CH_3CH{=}\overset{COOH}{C}{-}CH_3$$

2- butanone

2-methyl-2-butenoic acid

6. Addition of derivatives of ammonia The derivatives of ammonia which add on the carbonyl group are hydroxylamine, hydrazine, phenylhydrazine and semicarbazide. Their stable forms are available in the form of salts; hydroxylamine hydrochloride ($HONH_3^+Cl^-$), phenylhydrazine hydrochloride ($C_6H_5NHNH_3^+Cl^-$) and semicarbazide hydrochloride ($NH_2CONHNH_3^+Cl^-$). The addition of sodium acetate releases free base in solution which adds on the carbonyl group as follows.



$$>C{=}O + :NH_2OH \xrightarrow{H^+} \left[-\underset{OH}{C}-NHOH\right] \longrightarrow >C{=}NOH + H_2O$$

hydroxylamine — oxime

$$>C{=}O + :NH_2NHC_6H_5 \xrightarrow{H^+} \left[-\underset{OH}{\overset{|}{C}}-NHNHC_6H_5\right] \longrightarrow >C{=}NHHC_6H_5{+}H_2O$$

phenlylhydrazine — phenylhydrazone

$$>C{=}O + :NH_2NHCONH_2 \xrightarrow{H^+} \left[-\underset{OH}{\overset{|}{C}}-NHNHCONH_2\right] \longrightarrow >C{=}NNHCONH_2 + H_2O$$

semicarbazide — semicarbazone

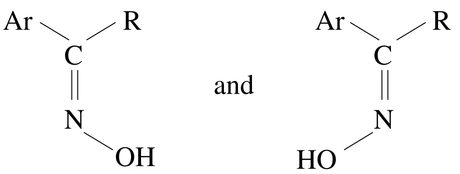
$$>C{=}O + H_2N{-}NH_2 \longrightarrow >C{=}N{-}NH_2$$

hydrazone

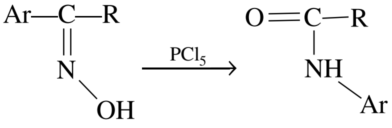
The adjustment of pH is necessary as in the low enough pH, bases may form protonated species $^+H_3N{-}G$ which inhibits the addition as these are no longer nucleophilic reagents. On the other hand, protonation of carbonyl oxygen makes the molecule more susceptible to nucleophilic attack at positively charged carbon.

The addition products are used to characterize the aldehyde or ketone as they have characteristic melting points.

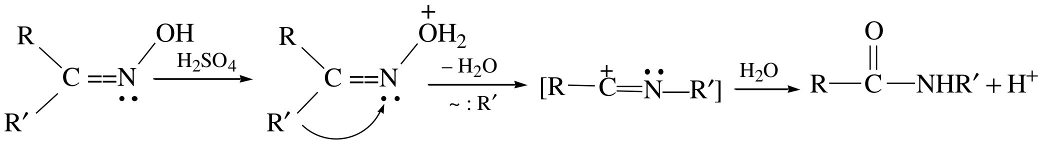
Configuration of Oximes Many aromatic aldoximes and ketoximes exist in two isomeric forms—*cis*-and *trans*-forms**:**



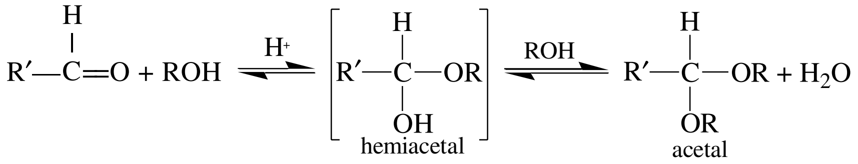
Aromatic ketoximes undergo *Beckmann rearrangement* when treated with PCl_5, H_2SO_4, etc. The exchange occurs in *anti*-position and the product obtained is *N*-substituted acetamide.



Mechanism of Beckmann Rearrangement The acidic reagent converts —OH into a better leaving group. Loss of H_2O occurs with simultaneous migration of the *trans* : R.

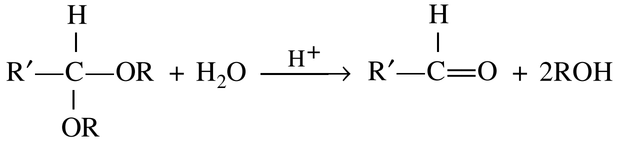


7. Addition of alcohols Aldehydes react with anhydrous ethanol in the presence of anhydrous acids (usually dry HCl) to form acetal. The reaction taking place is



$$R'—\overset{H}{\overset{|}{C}}=O + ROH \underset{}{\overset{H^+}{\rightleftharpoons}} \left[R'—\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}—OR\right]_{\text{hemiacetal}} \overset{ROH}{\rightleftharpoons} \underset{\text{acetal}}{R'—\overset{H}{\overset{|}{\underset{\underset{OR}{|}}{C}}}—OR} + H_2O$$

Hemiacetals are too unstable to be isolated. Acetals are readily cleaved by acids and are stable towards bases**:**

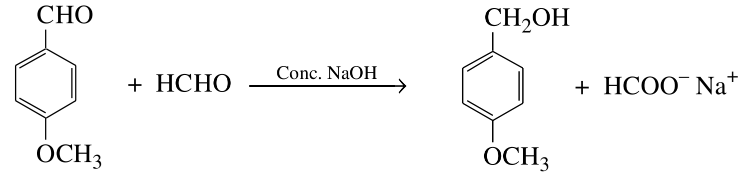


$$R'—\overset{H}{\overset{|}{\underset{\underset{OR}{|}}{C}}}—OR + H_2O \xrightarrow{H^+} R'—\overset{H}{\overset{|}{C}}=O + 2ROH$$

8. Cannizzaro reaction This reaction is shown by aldehydes containing no α-hydrogen. In the presence of concentrated alkali, two molecules of an aldehyde undergo self-oxidation-and-reduction to yield a mixture of an alcohol and a salt of a carboxylic acid. For example.

$$2HCHO \xrightarrow{50\%\ NaOH} \underset{\text{methanol}}{CH_3OH} + \underset{\text{sodium formate}}{HCOO^-Na^+}$$

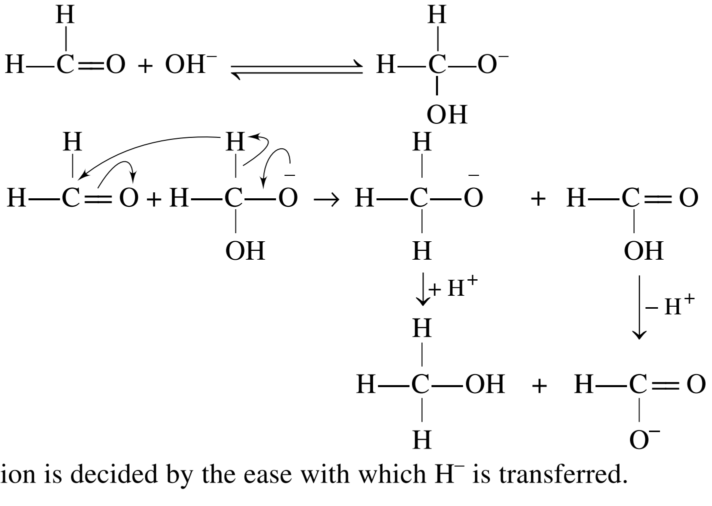
In the crossed Cannizzaro reaction, two different aldehydes are involved yielding all possible products. However, if one of the reactants is formaldehyde, it is always converted into sodium formate. For example,



anisaldehyde
(*p*-methyoxybenzaldehyde)

(*p*-methyoxybenzyl alcohol)

The Cannizzaro reaction involved two successive additions as depicted in the following.



$$H—\overset{H}{\overset{|}{C}}=O + OH^- \rightleftharpoons H—\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}—O^-$$

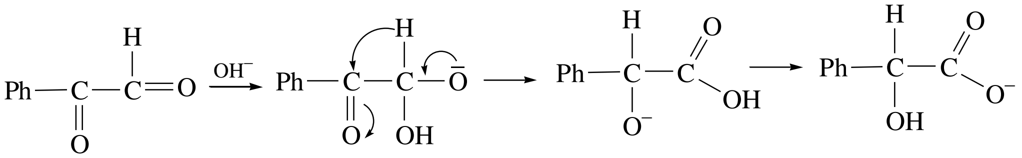
$$H—\overset{H}{\overset{|}{C}}=O + H—\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}—\overset{-}{O} \rightarrow H—\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}—\overset{-}{O} + H—\underset{\underset{OH}{|}}{C}=O$$

$$\downarrow +H^+ \qquad\qquad \downarrow -H^+$$

$$H—\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}—OH + H—\underset{\underset{O^-}{|}}{C}=O$$

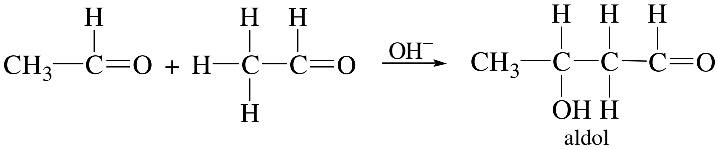
The rate of reaction is decided by the ease with which H^- is transferred.

The molecule of the type PhCOCHO shows internal crossed-Cannizzaro reaction.



$$\mathrm{Ph-\underset{O}{\overset{}{C}}-\overset{H}{C}=O \xrightarrow{OH^-} Ph-\underset{O}{C}-\underset{OH}{\overset{H}{C}}-O^- \longrightarrow Ph-\underset{O^-}{\overset{H}{C}}-C(=O)OH \longrightarrow Ph-\underset{OH}{\overset{H}{C}}-C(=O)O^-}$$

9. Aldol condensation This reaction is shown by aldehydes or ketones containing α-hydrogen. In the presence of a base, α-carbon of one molecule gets attached to the carbonyl carbon of the second molecule. For example,



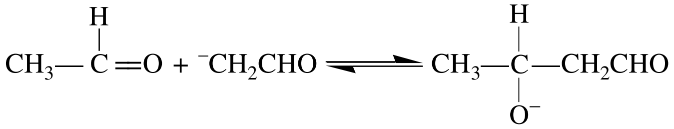
$$\mathrm{CH_3-\overset{H}{C}=O + H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O \xrightarrow{OH^-} CH_3-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O}$$

aldol

The mechanism involved is as follows.

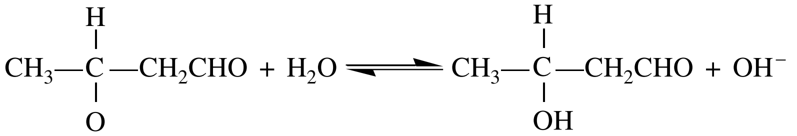
(a) Formation of carbanion—a nucleophilic reagent $\mathrm{CH_3CHO + OH^- \rightleftharpoons H_2O + {}^-CH_2CHO}$

(b) Attack of carbanion to the second molecule



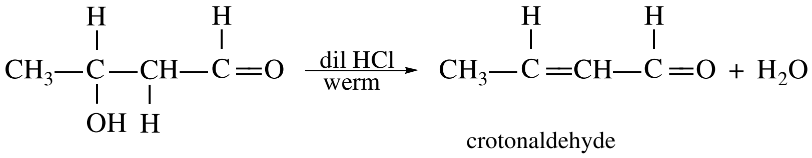
$$\mathrm{CH_3-\overset{H}{C}=O + {}^-CH_2CHO \rightleftharpoons CH_3-\underset{O^-}{\overset{H}{C}}-CH_2CHO}$$

(c) Transfer of H^+ from water



$$\mathrm{CH_3-\underset{\underline{O}}{\overset{H}{C}}-CH_2CHO + H_2O \rightleftharpoons CH_3-\underset{OH}{\overset{H}{C}}-CH_2CHO + OH^-}$$

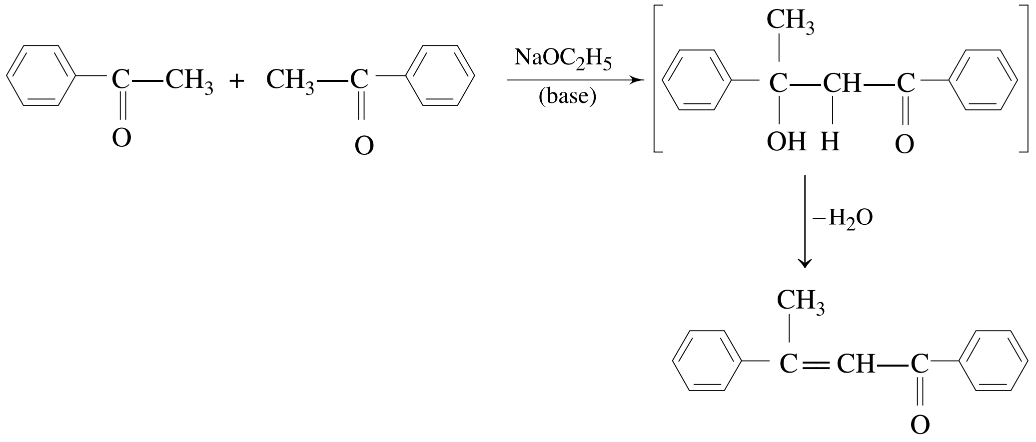
The product obtained in aldol reaction is β-hydroxyaldehyde or ketone. This is very easily dehydrated to form a double bond at α- and β- carbon atoms. For example,



$$\mathrm{CH_3-\underset{OH}{\overset{H}{C}}-\underset{H}{CH}-\overset{H}{C}=O \xrightarrow[werm]{dil\,HCl} CH_3-\overset{H}{C}=CH-\overset{H}{C}=O + H_2O}$$

crotonaldehyde

The resultant molecule contains a double bond in conjugation with the carbonyl group and it thus acquires extra stability. If the double bond is also in conjugation with an aromatic ring, the product is so stable that the product obtained in aldol reaction is unsaturated aldehyde or ketone instead of β-hydroxyaldehyde or ketone. For example,



1, 3-diphenyl-2-butene-1-one

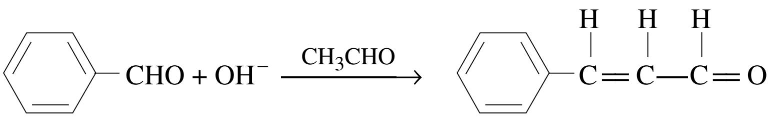
A crossed aldol condensation involves two different carbonyl compounds yielding a mixture of all the four possible products. However, a single product is obtained as shown in the following.

Aldehyde containing no α-hydrogen (e.g. benzaldehyde or formaldehyde) + catalyst OH^-

$$\Big\downarrow \text{carbonyl compound containing } \alpha\text{-hydrogen}$$

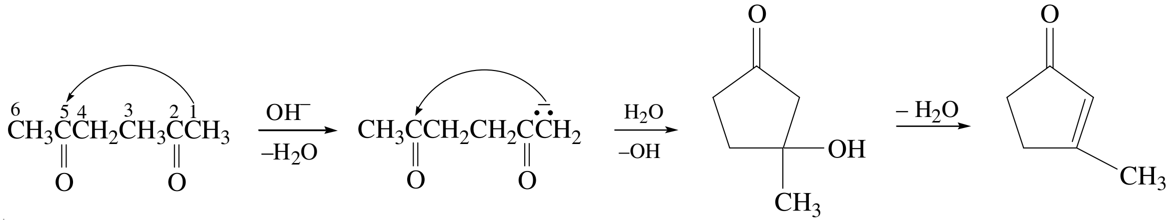
Only one cross aldol product

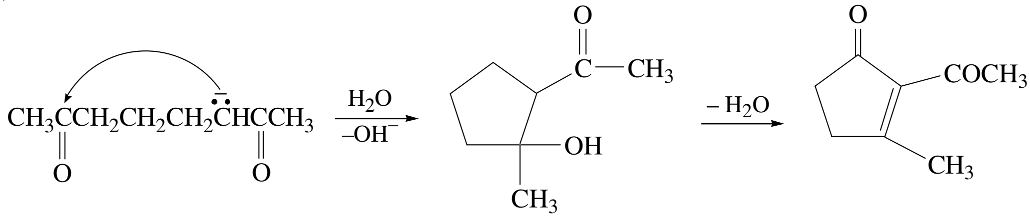
For example,



cinnamaldehyde

Properly constituted diketons give cyclic intramolecular aldol addition products.

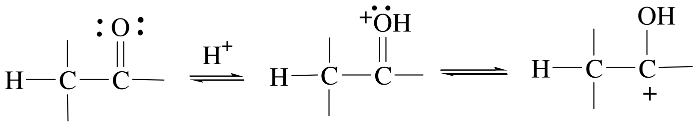




Acid-Catalysed Aldol Condensation

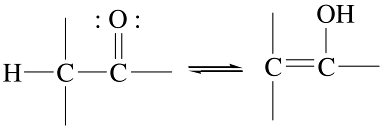
Aldol condensation also takes place in acidic conditions. The mechanism involved is as follows.

(a) Formation of Carbocation



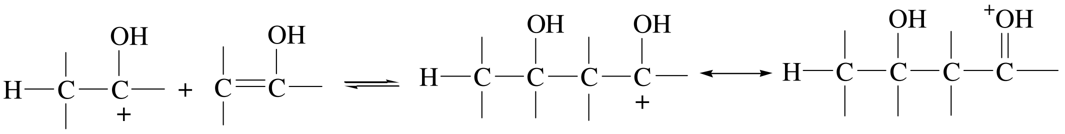
$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{:\ddot{O}:}{\overset{\|}{C}}{-}} \xrightleftharpoons{H^+} \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{{}^{+}\ddot{O}H}{\overset{\|}{C}}{-}} \rightleftharpoons \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{+}{C}}}{-}}$$

(b) Formation of Enol of Second Molecule



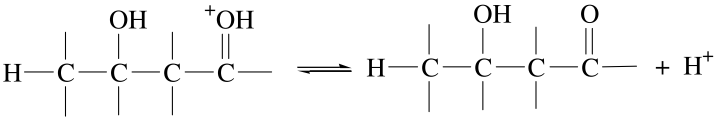
$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{:O:}{\overset{\|}{C}}{-}} \rightleftharpoons \mathrm{\overset{|}{\underset{|}{C}}{=}\overset{OH}{\overset{|}{C}}{-}}$$

(c) Condensation of Carbocation and Enol

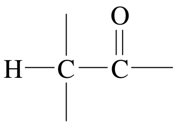
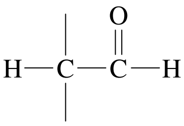


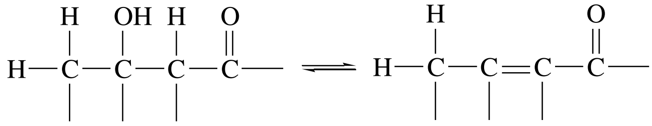
$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{+}{C}}}{-}} + \mathrm{\overset{|}{\underset{|}{C}}{=}\overset{OH}{\overset{|}{C}}{-}} \rightleftharpoons \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{+}{C}}}{-}} \longleftrightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}\overset{{}^{+}OH}{\overset{\|}{C}}{-}}$$

(d) Deprotonation of Intermediate



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}\overset{{}^{+}OH}{\overset{\|}{C}}{-}} \rightleftharpoons \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{OH}{\overset{|}{\underset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}} + H^+$$

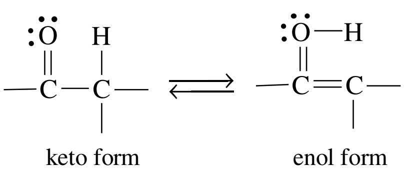
If the compound  $\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}}$ is  $\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H}$, then dehydration production is normally obtained



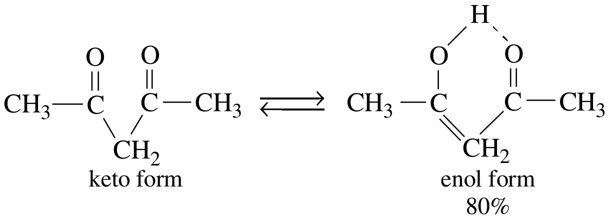
Note: The enol formed in step (b) is the stable enol. In general, more substituted enol is more stable. For example, in the compound $CH_3COCH_2CH_3$, the more stable enol is $CH_3(OH)C=CHCH_3$ and the less stable enol is $CH_2=C(OH)—CH_2CH_3$. For example, the aldol condensation between PhCHO and $CH_3COCH_2CH_3$ gives $PhCH=C(CH_3)\ COCH_3$ and not $PhCH=CH_2COCH_2CH_3$.

Keto-Enol Tautomerism A carbonyl compound with an acidic alpha hydrogen may exist in two forms called tautomers: a keto tautomer and an enol tautomer. The keto tautomer has the expected carbonyl group while the enol (from – ene + – ol) tautomer contains vinylic hydroxyl group which is formed by transfer of an acidic hydrogen from the α-carbon to the carbonyl oxygen.

Most simple aldehydes and ketones exist primarily in their keto forms. However, 2, 4-pentanedione exists in 80% enol form due to the formation of six membered ring involving the internal hydrogen bonding.



keto form enol form

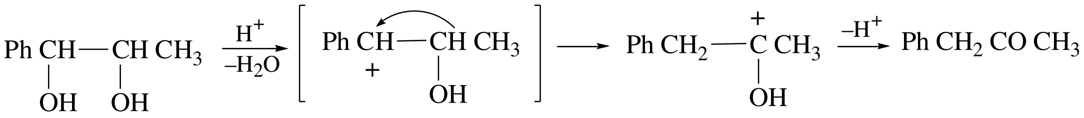


keto form enol form 80%

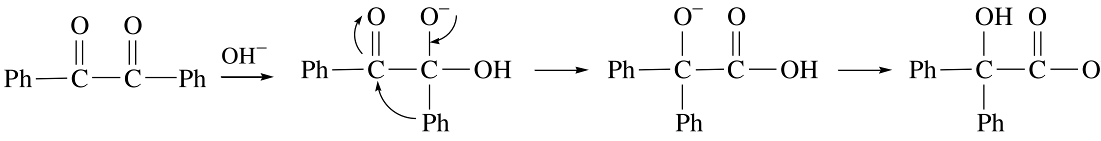
Pinacol-Pinacolone Rearrangement Pinacol may be prepared by the reduction of ketones with magnesium amalgam.

$$2CH_3COCH_3 \xrightarrow[(ii)\,H_2O]{(i)\,Mg-Hg} (CH_3)_2\ C(OH)\ C(OH)\ (CH_3)_2$$

Treatment of a compound with two vicinal —OH groups undergoes rearrangement in the presence of conc. H_2SO_4 as shown in the following

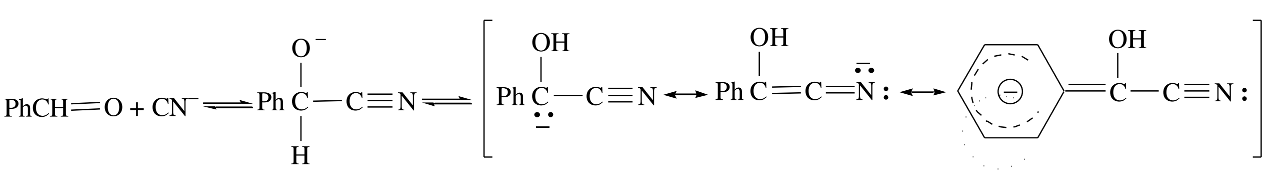


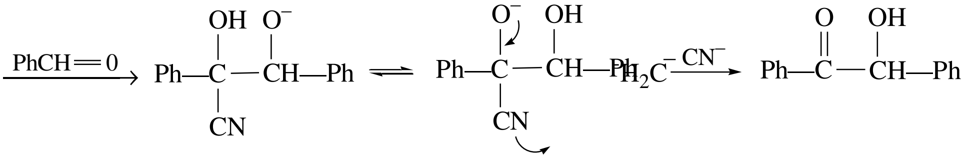
Benzilic Acid Rearrangement Diketo compounds of the type PhCOCOPh in $—OH^-$ medium shows benzilic acid rearrangement.



Benzoin Condensation

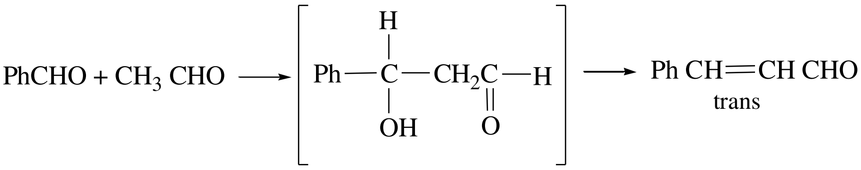
Aromatic aldehyde is dimerized in the presence of ethanolic KCN.





$$\xrightarrow{PhCH=0} Ph-\underset{CN}{\overset{OH}{C}}-\overset{O^-}{CH}-Ph \rightleftharpoons Ph-\underset{CN}{\overset{O^-}{C}}-\overset{OH}{CH}-Ph \xrightarrow{-CN^-} Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{CH}-Ph$$

Claisen-Schmidt Reaction In this reaction, benzaldehyde reacts with alkyl aldehyde or alkyl ketone



$$PhCHO + CH_3\,CHO \longrightarrow \left[Ph-\underset{OH}{\overset{H}{C}}-CH_2\underset{O}{\underset{\|}{C}}-H \right] \longrightarrow \underset{trans}{Ph\,CH=CH\,CHO}$$

Perkin Condensation Heating of aromatic aldehyde with acid anhydride in the presence of sodium acetate gives *α,β*-unsaturated carboxylic acid.

$$Ph\,CHO + (CH_3CO)_2O \xrightarrow[\Delta]{NaOAc} \textit{trans} - PhCH = CHCOOH$$

Distinction between Aldehydes and Ketones Aldehydes show the following characteristic tests. Ketones do not show these tests.

Tollens Test The Tollens reagent is an ammoniacal solution of silver nitrate. Aldehydes reduce Tollens reagent to a bright silver mirror.

Fehling's Test Fehling's solution consists of an equimolar mixture of Fehling's solution A and Fehling's solution B. Fehling's solution A is $CuSO_4$ solution and Fehling's solution B is a mixture of Rochelte salt (sodium potassium tartarate) and sodium hydroxide. Aliphatic aldehydes (but not aromatic) reduce Fehling's solution to red brown cuprous oxide.

Schiff's Test Schiff's reagent is rosaniline hydrochloride solution in water decolourized with SO_2. Aldehydes when warmed with Schiff's reagent restore pink colour of the reagent.

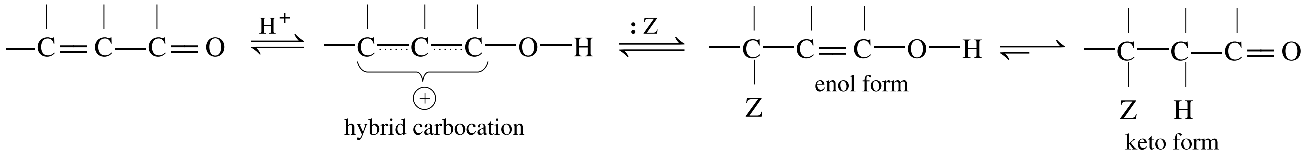
α, β-UNSATURATED CARBONYL COMPOUNDS

A compound containing the carbon-carbon and carbon-oxygen double bonds in conjugation is known as α,β-unsaturated carbonyl compound. Because of this conjugation $\left(>C=\overset{|}{C}-\overset{|}{C}=O \right)$, the molecule possesses not only the properties of the individual functional groups but also properties due to the interaction of functional groups.

Due to the electron-withdrawing nature of C=O group, the reactivity of carbon-carbon double bond towards electrophilic reagents is decreased as compared to an isolated double bond. At the same time, carbon-carbon double bond also becomes susceptible towards nucleophilic attack and thus undergoes nucleophilic addition reactions which are uncommon for simple alkenes.

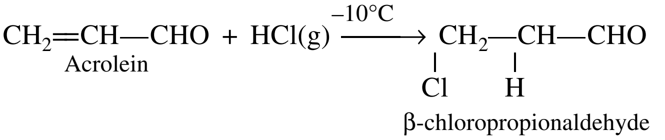
Electrophilic Addition

α, β-unsaturatred carbonyl compounds follow the following mechanism:

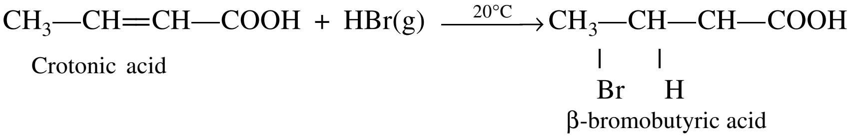


$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O \xrightleftharpoons{H^+} \underset{\substack{\oplus \\ \text{hybrid carbocation}}}{\underbrace{-\overset{|}{C}\cdots\overset{|}{C}\cdots\overset{|}{C}}}-O-H \xrightleftharpoons{:Z} -\underset{Z}{\overset{|}{C}}-\underset{\text{enol form}}{\overset{|}{C}=\overset{|}{C}-O-H} \rightleftharpoons \underset{\text{keto form}}{-\underset{Z}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-\overset{|}{C}=O}$$

Hence, in electrophilic addition, hydrogen gets attached to the α-carbon and the negative group gets attached to the β-carbon. For example,



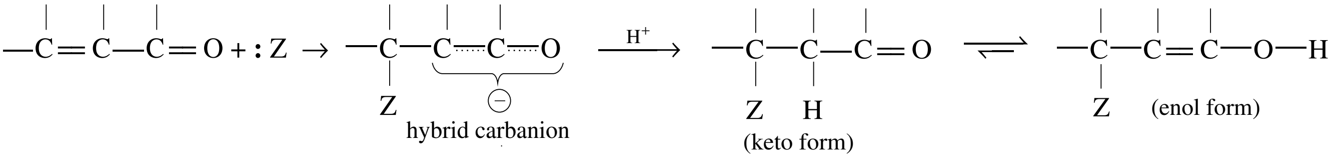
$$\underset{\text{Acrolein}}{CH_2{=}CH{-}CHO} + HCl(g) \xrightarrow{-10°C} \underset{\beta\text{-chloropropionaldehyde}}{\underset{Cl}{\underset{|}{CH_2}}{-}\underset{H}{\underset{|}{CH}}{-}CHO}$$



$$\underset{\text{Crotonic acid}}{CH_3{-}CH{=}CH{-}COOH} + HBr(g) \xrightarrow{20°C} \underset{\beta\text{-bromobutyric acid}}{CH_3{-}\underset{Br}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH}}{-}COOH}$$

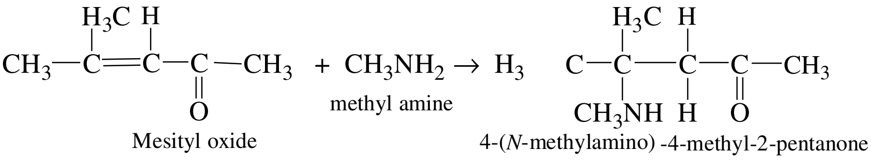
Nucleophilic Addition

The nucleophilic addition across the carbon-carbon double bond is believed to take place by the following mechanism.

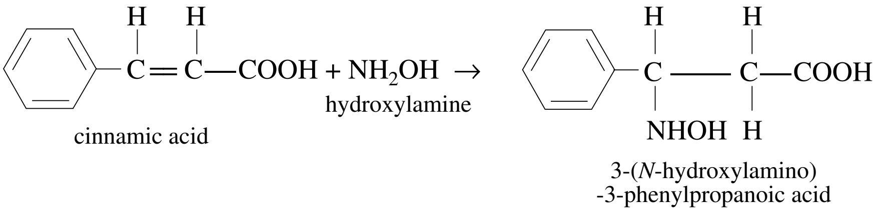


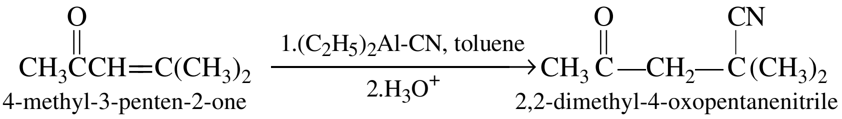
$$-\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O + :Z \rightarrow \underset{\text{hybrid carbanion}}{-\underset{Z}{\underset{|}{\overset{|}{C}}}{-}\underbrace{\overset{|}{C}{\cdots}\overset{|}{C}{\cdots}O}_{\ominus}} \xrightarrow{H^+} \underset{\text{(keto form)}}{-\underset{Z}{\underset{|}{\overset{|}{C}}}{-}\underset{H}{\underset{|}{\overset{|}{C}}}{-}\overset{|}{C}{=}O} \rightleftharpoons -\underset{Z}{\underset{|}{\overset{|}{C}}}{-}\overset{|}{C}{=}\overset{|}{C}{-}O{-}H \quad \text{(enol form)}$$

Thus, the tendency of nucleophilic addition is due to the formation of hybrid carbanion. Examples include the following reactions.



$$\underset{\text{Mesityl oxide}}{CH_3{-}\overset{H_3C}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}CH_3} + \underset{\text{methyl amine}}{CH_3NH_2} \rightarrow \underset{\text{4-(}N\text{-methylamino) -4-methyl-2-pentanone}}{H_3\ C{-}\overset{H_3C}{\overset{|}{\underset{CH_3NH}{\underset{|}{C}}}}{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}\underset{O}{\underset{\|}{C}}{-}CH_3}$$





$$\underset{\text{4-methyl-3-penten-2-one}}{CH_3\overset{O}{\overset{\|}{C}}CH{=}C(CH_3)_2} \xrightarrow[2.H_3O^+]{1.(C_2H_5)_2Al\text{-}CN,\ \text{toluene}} \underset{\text{2,2-dimethyl-4-oxopentanenitrile}}{CH_3\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{CN}{\overset{|}{C}}(CH_3)_2}$$

Two important reactions shown by α, β-unsaturated carbonyl compounds are as follows.

1. *The Michael Addition*

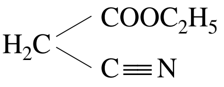
The Michael addition may be represented as

$$\begin{matrix}\alpha,\ \beta\text{-unsaturated} \\ \text{carbonyl compound}\end{matrix} + \begin{matrix}\text{a fairly acidic} \\ \text{substance}\end{matrix} \xrightarrow{\text{base}} \begin{matrix}\text{addition} \\ \text{product}\end{matrix}$$

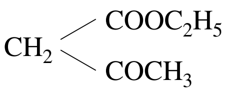
A fairly acidic substance contains a —CH_2 or CH— group flanked by two electron-withdrawing group which can help accommodate the negative charge of the anion which is formed by abstracting H^+ as a result of the presence of a base. Examples are

ethyl malonate $H_2C(COOC_2H_5)_2$

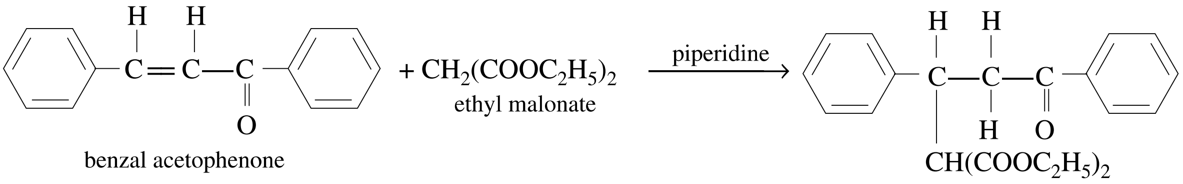
ethyl cyanoacetate

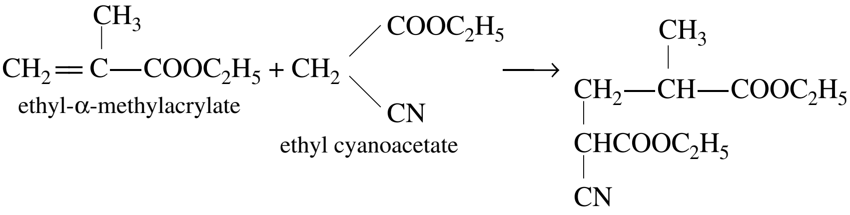


ethyl acetoacetate



Examples of the Michael addition are given below.

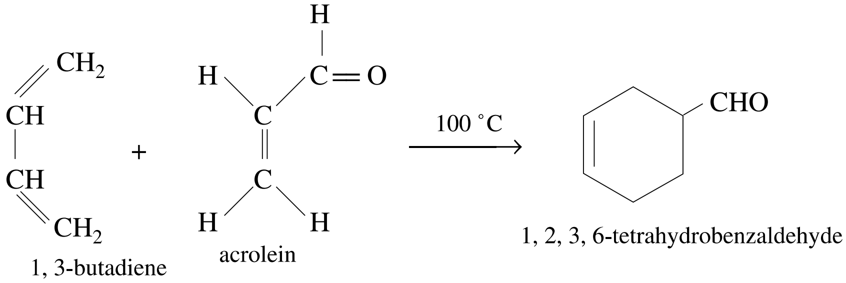




2. ***The Diels-Alder Reaction*** The Diels-Alder reaction may be represented as

α,β-unsaturated carbonyl compound + Conjugated diene → Adduct

The adduct contains six-membered ring formed due to the attachment of C-1 and C-4 of conjugated diene with the doubly bonded carbons of the unsaturated carbonyl compound. For example



Straight Objective Type

General Characteristics

1. Polarization of electrons in acrolein may be written as

(a) $\overset{\delta^-}{CH_2}=CH—\overset{\delta^+}{CH}=O$ (b) $\overset{\delta^-}{CH_2}=CH—CH=\overset{\delta^+}{O}$ (c) $\overset{\delta^-}{CH_2}=\overset{\delta^+}{CH}—CH=O$ (d) $\overset{\delta^+}{CH_2}=CH—CH=\overset{\delta^-}{O}$ (1988)

2. Formaline is an aqueous solution of

(a) 40% formaldehyde (b) 50% formaldehyde (c) 60% formaldehyde (d) 70% formaldehyde

3. Which of the following statements regarding aldehydes is **not** correct?

(a) The carbonyl functional group is planar
(b) The boiling points of aldehydes is greater than those of alkanes of comparable molar masses
(c) The boiling points of aldehydes is greater than those of alcohols of comparable molar masses
(d) Formaldehyde is gas at room temperature

4. Which of the following statements regarding aldehydes is **not** correct?

(a) The addition reactions occurring across the C=O bond is electrophilic type
(b) The addition reactions occurring across the C=O bond is nucleophilic type
(c) Aldehydes undergo addition reactions more readily than ketones
(d) The addition reactions shown by CO group is catalyzed by acids

5. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

(a) CH_3COCl (b) CH_3CHO (c) CH_3COOCH_3 (d) $CH_3COOCOCH_3$ (1997)

6. 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) $CD_2=\underset{OD}{\underset{|}{C}}—CD_3$ (1999)

7. The correct sequence of equilibrium constants for the reactions

$$H_2CO + H_2O \overset{K_1}{\rightleftharpoons} H_2C(OH)_2;\quad CH_3CH_2CHO + H_2O \overset{K_2}{\rightleftharpoons} CH_3CH_2CH(OH)_2$$

$$CH_3COCH_3 + H_2O \overset{K_3}{\rightleftharpoons} CH_3C(OH)_2CH_3$$

is

(a) $K_1 > K_2 > K_3$ (b) $K_1 < K_2 < K_3$ (c) $K_1 > K_3 > K_2$ (d) $K_1 < K_3 < K_2$

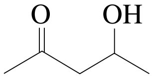
8. Which of the following compounds is expected to have maximum enol content in ethanol?

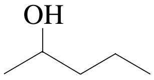
(a) $CH_3COCH_2CO_2CH_3$(b) $CH_3COCH_2CO_2C_2H_5$ (c) $CH_3COCH_2COCH_3$ (d) $CH_3COCH(CH_3)COCH_3$

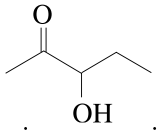
9. Which of the following has the most acidic hydrogen?

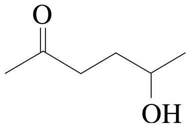
(a) 3-Hexanone (b) 2, 4-Hexanedione (c) 2, 5-Hexanedione (d) 2, 3-Hexanedione (2000)

10. Which one of the following will most readily be dehydrated in acidic condition?

(a) 

(b) 

(c) 

(d) 

(2000)

11. When acetaldehyde is heated with Fehling's solution it gives a precipitate of

(a) Cu (b) CuO (c) Cu_2O (d) Cu + Cu_2O + CuO (1983)

12. Which of the following will react with water?

(a) $CHCl_3$ (b) Cl_3CCHO (c) CCl_4 (c) $ClCH_2CH_2Cl$ (1998)

13. Which of the following statements regarding CO group is **not** correct?

(a) The carbon atom of CO group in aldehydes is sp^2 hybridized

(b) The carbon atom of CO group in the transition state formed during the addition reaction across CO group is sp^3 hybridized

(c) The aryl group in aromatic aldehydes speeds up the addition reaction across the CO group

(d) An aryl group stabilises an aldehyde more than the transition state

Oxidation and Reduction Reactions

14. The reaction $CH_3COCH_3 \xrightarrow[Zn(Hg),conc.HCl]{[H]} CH_3CH_2CH_3$ is known as

(a) Wolff-Kishner reduction (b) Clemmensen reduction

(c) Cannizzaro reaction (d) Rosenmund reduction

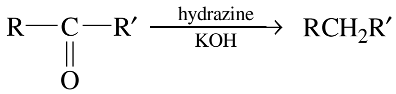
15. Benzaldehyde differs from acetaldehyde in that

(a) benzaldehyde does not react with Tollens reagent

(b) benzaldehyde does not react with Fehling's solution

(c) benzaldehyde does not react with HCN

(d) benzaldehyde does not react with $NaHSO_3$

16. The reduction reaction 

$$R{-}\underset{\underset{O}{\|}}{C}{-}R' \xrightarrow[KOH]{hydrazine} RCH_2R'$$

is known as

(a) Clemmensen reduction (b) Wolff- Kishner reduction

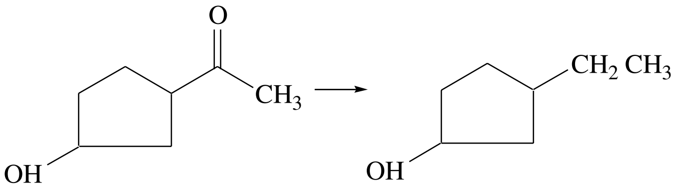
(c) Rosenmund reduction (d) Catalytic reduction

17. The reduction reaction $R{-}COCl \xrightarrow[ethyl\ acetate]{H_2/Pd/BaSO_4} RCHO$ is known as

(a) Clemmensen reduction (b) Wolff-Kishner reduction

(c) Rosenmund reduction (d) Catalytic reduction

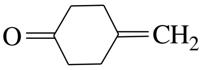
18. The appropriate reagent for the following transformation

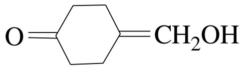
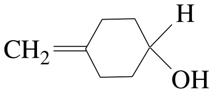
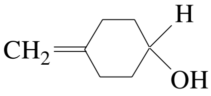
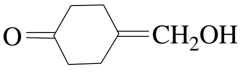


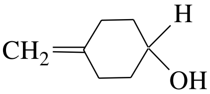
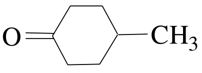
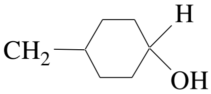
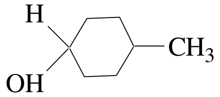
is

(a) Zn(Hg), HCl (b) NH_2NH_2, OH^-
(c) H_2/Ni (d) $NaBH_4$ (2000)

19. The correct order of reactivity of PhMgBr with PhCOPh, CH_3CHO and CH_3COCH_3 is
(a) PhCOPh > CH_3CHO > CH_3COCH_3 (b) PhCOPh > CH_3COCH_3 > CH_3CHO
(c) PhCOPh < CH_3COPh < CH_3CHO (d) PhCOPh < CH_3CHO < CH_3COCH_3 (2004)

20. The reductions of  with (i) BH_3/THF followed by H_2O_2, OH^- and (ii) $NaBH_4$, respectively, produce

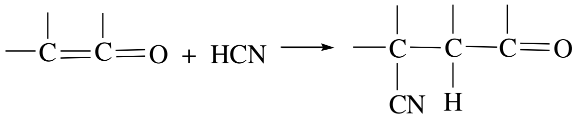
(a)  and  (b)  and 

(c)  and  (d)  and 

21. The reduction of $CH_2=CH\text{–}CHO$ by (i) Zn– Hg/HCl and (ii) H_2NNH_2/OH^-, respectively, yield
(a) $CH_2=CHCH_3$ and $CH_2=CHCH_3$ (b) CH_3CH_2CHO and $CH_3CH_2CH_3$
(c) $CH_3CH_2CH_3$ and $CH_2=CHCH_3$ (d) CH_3CH_2CHO and CH_3CH_2CHO

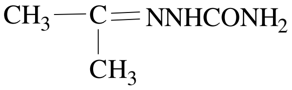
Nucleophilic Addition Reactions

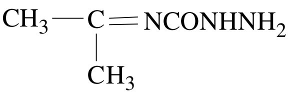
22. The formation of cyanohydrin from a ketone is an example of
(a) electrophilic addition (b) nucleophilic addition
(c) nucleophilic substitution (d) electrophilic substitution (1990)

23. The reaction  $-\overset{|}{C}=\overset{|}{C}=O + HCN \longrightarrow -\underset{CN}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}=O$ involves

(a) electrophilic addition across double bond (b) nucleophilic addition across double bond
(c) free radical addition across double bond (d) no effect of the CO group on the C=C bond

24. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2 \cdot HCl$ and sodium acetate gives a product 'C'. Identify the structure of 'C'.

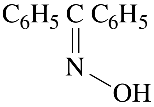
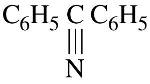
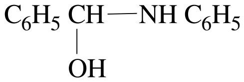
(a) $CH_3CH_2CH == NNHCONH_2$ (b)  $CH_3-\underset{CH_3}{\underset{|}{C}}=NNHCONH_2$

(c)  $CH_3-\underset{CH_3}{\underset{|}{C}}=NCONHNH_2$ (d) $CH_3CH_2CH == NCONHNH_2$ (2002)

25. The reagent that can be used to convert butan-2-one to propanoic acid is
(a) NaOH, NaI/H^+ (b) Fehling solution (c) Tollens reagent (d) NaOH, I_2/H^+ (2005)

26. The pH requirement for the addition of HCN to R_2CO is
(a) 4 to 5 (b) 6 to 7 (c) 9 – 10 (d) 13 – 14

27. In the reaction $C_6H_5COC_6H_5 \xrightarrow{NH_2OH} A \xrightarrow{PCl_5} B$ the product B is

(a)  $C_6H_5\underset{\underset{N\diagdown OH}{||}}{C}C_6H_5$ (b)  $C_6H_5\underset{\underset{N}{|||}}{C}C_6H_5$ (c) $C_6H_5CONHC_6H_5$ (d)  $C_6H_5\underset{\underset{OH}{|}}{CH}-NH\,C_6H_5$

28. The correct order of reactivities of nucleophilic addition across —C = O of the HCHO, RCHO and ArCHO is
(a) RCHO < RCOR < ArCHO (b) RCHO < ArCHO < RCOR
(c) ArCHO < RCOR < RCHO (d) ArCHO < RCHO < RCOR

Aldol Condensation and Cannizzaro Reaction

29. The Cannizzaro reaction is not given by
(a) trimethylactaldehyde (b) benzaldehyde
(c) acetaldehyde (d) formaldehyde (1983)

30. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol (1992)

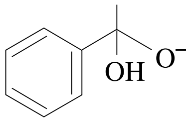
31. Which of the following compounds undergoes the Cannizzaro reaction?
(a) Acetaldehyde (b) Benzaldehyde (c) Acetone (d) Propanal

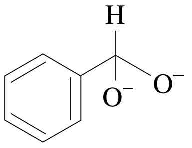
32. In the Cannizzaro reaction given below,

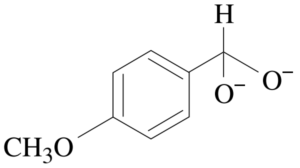
$$2\text{Ph—CHO} \xrightarrow{^-\text{OH}} \text{Ph—CH}_2\text{OH} + \text{PhCO}_2^-$$

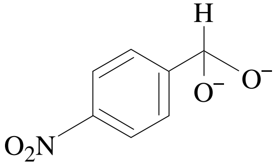
the slowest step is
(a) the attack of $^-$OH at the carbonyl group,
(b) the transfer of hydride to the carbonyl group,
(c) the abstraction of proton from the carboxylic acid,
(d) the deprotonation of Ph—CH_2OH (1996)

33. In a Cannizaro reaction, the intermediate that will be the best hydride donor is

(a) 

(b) 

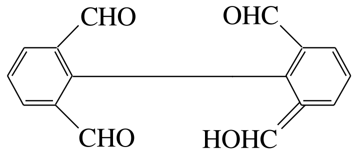
(c) 

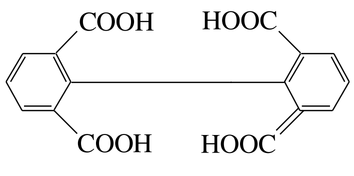
(d) 

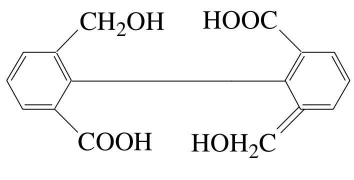
(1997)

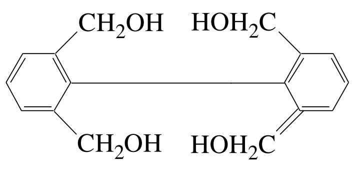
34. Which of the following compounds does not undergo aldol condensation?
(a) $C_6H_5CH_2CHO$ (b) C_6H_5CHO (c) CH_3COCH_3 (d) CH_3CH_2CHO

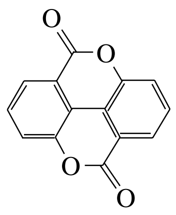
35. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate (b) sodium bezoate and methyl alcohol
(c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol (2001)

36. In the reaction  $\xrightarrow[\text{(ii) H}^+/\text{H}_2\text{O}]{\text{(i) NaOH/100°C}}$ A the product A is

(a) 

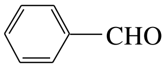
(b) 

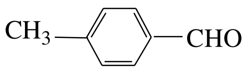
(c) 

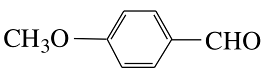
(d) 

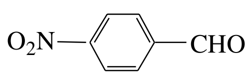
(2003)

37. Amongst the molecules


(I)


(II)


(III)


(IV)

the increasing order of rate of Cannizzaro reaction is

(a) IV < I < II < III (b) III < II < I < IV

(c) IV < III < II < I (d) IV < III < I < II

38. In the Cannizzaro's reaction $2PhCHO \xrightarrow{OH^-} PhCHO_2OH + PhCO_2^-$ the rate determining step is

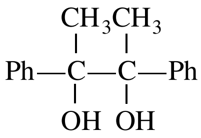
(a) attack of OH^- to PhCHO

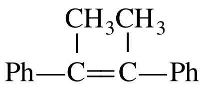
(b) the transfer of H^- from $PhCH(OH)O^-$ to PhCHO

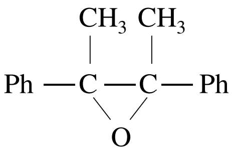
(c) the transfer of H^+ from PhCOOH to $PhCH_2O^-$

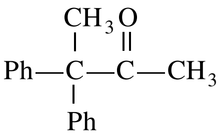
(d) the transfer of H^+ from PhCHO to $PhCH(OH)O^-$

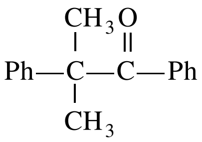
Pinacol-Pinacolone Rearrangement

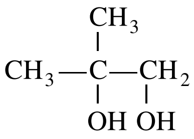
39. In the reaction  $Ph-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-Ph$ $\xrightarrow{\text{conc. } H_2SO_4}$ A, the product A is

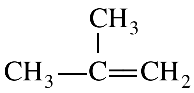
(a)  $Ph-\overset{CH_3}{C}=\overset{CH_3}{C}-Ph$

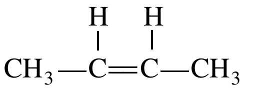
(b) 

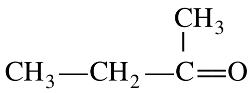
(c)  $Ph-\underset{Ph}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

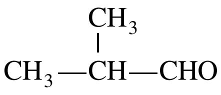
(d)  $Ph-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-Ph$

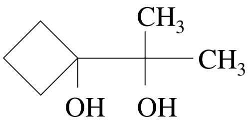
40. In the reaction  $CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{CH_2}$ $\xrightarrow{\text{conc. } H_2SO_4}$ A, the product A is

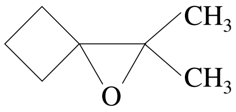
(a)  $CH_3-\overset{CH_3}{C}=CH_2$

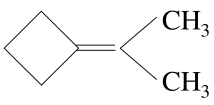
(b)  $CH_3-\overset{H}{C}=\overset{H}{C}-CH_3$

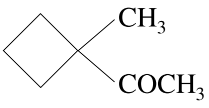
(c)  $CH_3-CH_2-\overset{CH_3}{C}=O$

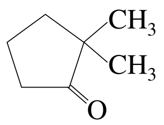
(d)  $CH_3-\overset{CH_3}{CH}-CHO$

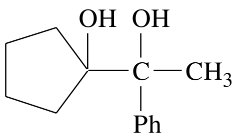
41. In the reaction  $\xrightarrow{\text{conc. } H_2SO_4}$ A, the product A is

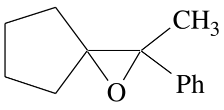
(a) 

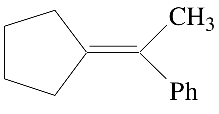
(b) 

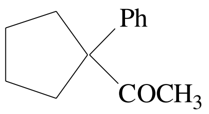
(c) 

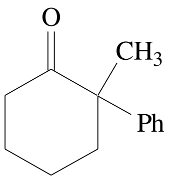
(d) 

42. In the reaction  $\xrightarrow{\text{Conc.} H_2SO_4}$ A, the product A is

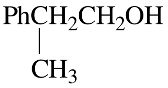
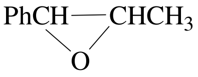
(a) 

(b) 

(c) 

(d) 

43. In the reaction $PhCH(OH)CH(OH)CH_3 \xrightarrow{H^+} D$, the compound D is

(a) 
$\underset{\displaystyle CH_3}{PhCH}CH_2CH_2OH$
(b) $PhCH_2COCH_3$
(c) 
(d) $PhCOCOCH_3$

Distinction Between Aldehydes and Ketones

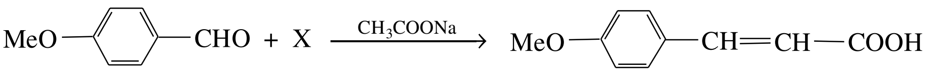
44. The reagent with which both acetaldehyde and acetone react easily is
(a) Fehling's reagent (b) Grignard reagent (c) Schiff's reagent (d) Tollens reagent (1981)

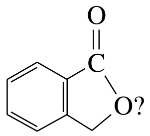
45. The compound that gives a positive iodoform test is
(a) 1-pentanol (b) 2-pentanone (c) 3-pentanone (d) pentanal (1982)

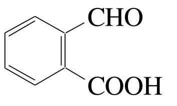
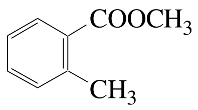
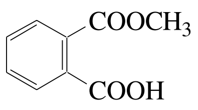
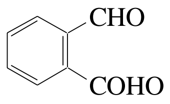
46. The compound that will not give iodoform on treatment with alkali and iodine is
(a) acetone (b) ethanol (c) diethyl ketone (d) isopropyl alcohol (1985)

47. The haloform reaction is not shown by the compound
(a) $C_2H_5COC_2H_5$ (b) CH_3CHO (c) CH_3COCH_3 (d) CH_3CH_2OH

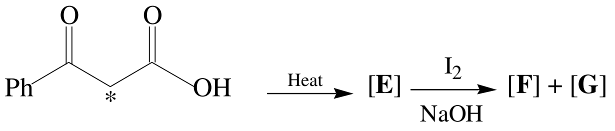
Additional Problems

48. In the reacion  the species X is
(a) CH_3COOH (b) $(CH_3CO)_2O$ (c) CHO—COOH (d) $BrCH_2COOH$ (2007)

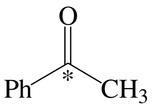
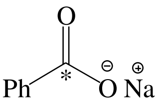
49. Which of the following compound(s) on treatment with aqueous alkali followed by acidification gives the lactone  ?

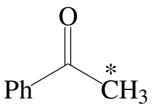
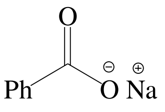
(a) 
(b) 
(c) 
(d) 
(2008)

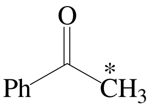
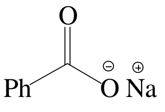
50. In the following reaction sequence, the correct structures of **E, F** and **G** are

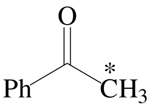
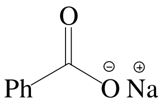


(* implies ^{13}C labelled carbon)

(A) **E** =  **F** =  **G** = CHI_3

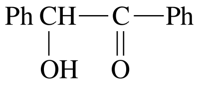
(B) **E** =  **F** =  **G** = CHI_3

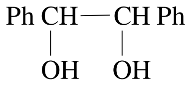
(C) **E** =  **F** =  **G** = $\overset{*}{C}HI_3$

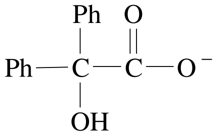
(D) **E** =  **F** =  **G** = $\overset{*}{C}H_3I$ (2008)

51. The treatment of PhCOCOPh in OH^- medium produces

(a) 2PhCOOH

(b) 
$PhCH(OH)-C(=O)-Ph$

(c) 
$PhCH(OH)-CH(OH)Ph$

(d) 
$Ph-C(Ph)(OH)-C(=O)-O^-$

52. The reduction of acetone with magnesium amalgam followed by hydrolysis produce
(a) $CH_3CH(OH)CH_3$ (b) $2CH_3CHO$
(c) $CH_3CH_2CH_3$ (d) $(CH_3)_2C(OH)C(OH)C(CH_3)_2$

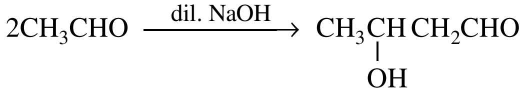
Multiple Correct Choice Type

1. Base catalysed aldol condensation occurs with
(a) propanal (b) benzaldehyde (c) 2-methylpropanal (d) 2,2-dimethylpropanal (1984)

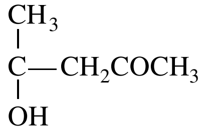
2. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) 2-Hydroxypropane (b) Acetophenone (c) Methylacetate (d) Acetamide (1984)

3. Which of the following compounds will react with ethanolic KCN?
(a) Ethyl chloride (b) Acetyl chloride (c) Chlorobenzene (d) Benzaldehyde (1989)

4. Which of the following are the examples of aldol condensation?

(a) 
$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$

(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3—$


$CH_3-C(CH_3)(OH)-CH_2COCH_3$

(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$ (d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$ (1989)

5. Which of the following statements regarding CO group are correct?
(a) The carbon atom of CO group in aldehydes is sp^2 hybridized
(b) The carbon atom of CO group in the transition state formed during the addition reaction across CO group is sp^3 hybridized
(c) The aryl group in aromatic aldehydes speeds up the addition reaction across the CO group
(d) An aryl group stabilises an aldehyde more than the transition state

6. A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction (b) Friedel-Crafts alkylation
(c) Clemmensen reduction (d) Reimer-Tiemann reaction (1998)

7. Among the following compounds, which will react with acetone to give a product containing $>C=N-$?
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$ (c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$ (1998)

8. Which of the following will undergo aldol condensation?
(a) Acetaldehyde (b) Propanaldehyde (c) Benzaldehyde (d) Trideuteroacetaldehyde (1998)

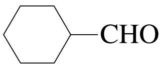
9. Which of the following compounds exhibit(s) positive iodoform test?
(a) Acetaldehyde (b) Methanol (c) Ethanol (d) Propanone

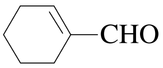
10. Which of the following compounds will not undergo aldol condensation when reacted with an alkali?
(a) Acetaldehyde (b) Benzaldehyde (c) Acetone (d) Formaldehyde

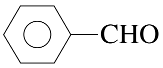
11. Which of the following compounds exhibit Fehling's test?
(a) Acetaldehyde (b) Benzaldehyde (c) Acetone (d) Propanal

12. Aldol condensation will not be observed in

(a) $CH_3CH_2CH_2CHO$

(b) 

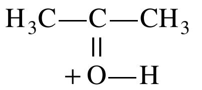
(c) 

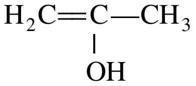
(d) 

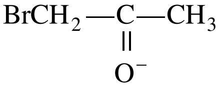
13. Benzaldehyde in the presence of alcoholic CN^- undergoes benzoin condensation to yield $C_6H_5COCOC_6H_5$ (benzoin). In this reaction only CN^- ions are effective because
   (a) cyanide is a good nucleophile.
   (b) cyanide is a weak base.
   (c) cyanide is an excellent electrophilic reagent.
   (d) cyanide poisons the base catalyst to force benzaldehyde to take a different course than forming cyanohydrin.

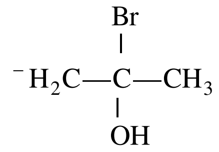
14. Which of the following statements is/are correct?
   (a) Acetamide on heating with P_2O_5 produces methanenitrile.
   (b) The structural formula of *meta* formaldehyde is $(CH_2O)_3$.
   (c) Benzaldehyde undergoes Cannizzaro reaction whereas acetaldehyde does not.
   (d) The reaction of formaldehyde with ammonia produces hexamethylenetetramine.

15. Which of the following species is/are not formed in the mechanisms of acid-catalysed halogenation of ketones?

(a) 
$H_3C-\underset{\underset{+O-H}{\|}}{C}-CH_3$

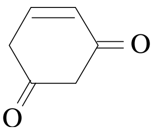
(b) 
$H_2C=\underset{\underset{OH}{|}}{C}-CH_3$

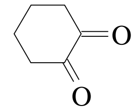
(c) 
$BrCH_2-\underset{\underset{O^-}{\|}}{C}-CH_3$

(d) 
$^-H_2C-\overset{\overset{Br}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

16. Ketene $H_2C=C=O$ is prepared industrially by heating
   (a) CH_3COOH (b) $CH_3COC_2H_5$ (c) $C_2H_5COC_2H_5$ (d) CH_3COCH_3

17. Tautomerism is exhibited by
   (a) $C_6H_5CH{=}CH{-}OH$ (b) *p*-benzoquinone

(c) 

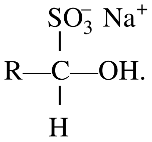
(d) 

(1998)

18. Which of the following statements are **not** correct?
   (a) Benzaldehyde undergoes aldol condensation in an alkaline medium.
   (b) Hydrazones of aldehydes and ketones are prepared in highly acidic medium.
   (c) The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol.
   (d) The part of an aldehyde or a ketone immediately surrounding carbonyl carbon is flat.

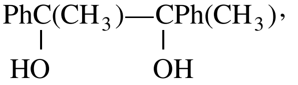
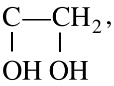
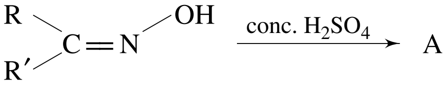
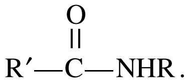
19. Which of the following statements are **not** correct?
   (a) Aldehydes or ketones have higher boiling points than comparable alcohols or carboxylic acids.
   (b) Lower aldehydes or ketones are soluble in water.
   (c) In the cross Cannizzaro reaction involving formaldehyde as one of the substrates, it is always converted into alcohol.
   (d) Benzaldehyde undergoes aldol condensation in an alkaline medium.

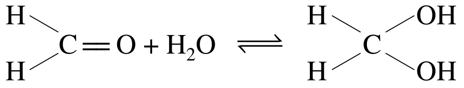
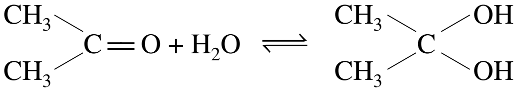
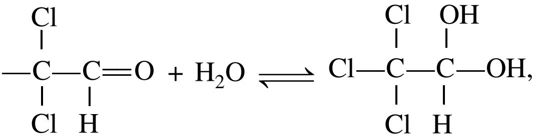
20. Which of the following statements are correct?
   (a) Ketones give red precipitate of Cu_2O with Benedict solution.
   (b) Formaldehyde does not form simple amine with NH_3 but forms urotropine.
   (c) Aldol condensation is shown by a carbonyl compound containing α-hydrogen atom(s).
   (d) $CH_3CH_2COCH_2CH_3$ shows positive iodoform test.

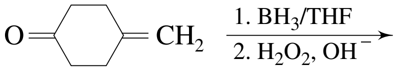
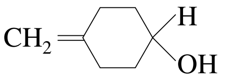
21. Which of the following statements are correct?
   (a) Toluene can be oxidized to benzaldehyde by using alkaline $KMnO_4$.
   (b) Phenolic aldehydes can be prepared by Reimer-Tiemann reaction.
   (c) $NaHSO_3$ reacts with RCHO in ethanol to give solid adduct having structure  $R-\overset{\overset{SO_3^-\,Na^+}{|}}{\underset{\underset{H}{|}}{C}}-OH$.
   (d) The formation of oximes is hindered at the very low pH.

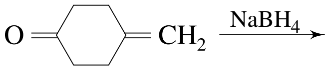
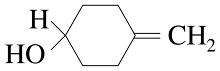
22. Which of the following statements are correct?
   (a) The magnitude of enthalpy of combustion of 2-butanone is lower than that of butanal.
   (b) 3-Penten-2-one is thermodynamically more stable than 4-pentene-2-one.
   (c) In the reaction $H_2 + PhCH_2CH_2COCl \xrightarrow[\text{S or quinoline}]{\text{Pd/C}} A$, the product A is $PhCH_2CH_2CH_2OH$.
   (d) In the reaction $CH_3CH(CH_3)COCl \xrightarrow{\text{LiAlH}_4} A$, the product A is $CH_3CH(CH_3)CHO$.

23. Which of the following statements are correct ?
   (a) Lithium-*t*-butoxyaluminium hydride is less strong reducing agent than lithium aluminium hydride.
   (b) LBAH stands for $Li(OCMe_3)_3AlH$.
   (c) DBAH stands for deuterium-*t*-butoxyaluminium hydride.
   (d) In the reaction $CH_3CH_2CH_2COOEt \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) DBAH at }-70^\circ\text{C}} A$, the product A is butanol.

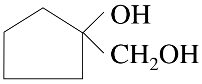
24. Which of the following statements are correct?
   (a) In pinacol-pinacolone rearrangement reaction involving  $\underset{\text{HO}}{\text{PhC}}(CH_3)—\underset{\text{OH}}{\text{CPh}}(CH_3)$, the phenyl group migrates in preference to methyl group.
   (b) In pinacol-pinacolone rearrangement reaction involving  $Me_2\underset{\text{OH}}{\text{C}}—\underset{\text{OH}}{\text{CH}_2}$, the 3° OH is lost, followed by :H migration.
   (c) Schiff base is N-substituted imine.
   (d) In the Beckmann rearrangement reaction  , the product A is  $R'—\overset{\text{O}}{\overset{\|}{\text{C}}}—NHR$.

25. Which of the following statements are correct?
   (a) The equilibrium constant of the hydration reaction  is lower than that of the reaction 
   (b) The equilibrium  $Cl—\underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}}—\underset{\text{H}}{\text{C}}{=}O + H_2O \rightleftharpoons Cl—\underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}}—\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}—OH$, lies more to the right side.
   (c) H_2CO is always oxidized to HCOOH in the crossed-Cannizzaro reactions.
   (d) The species PhCOCHO undergoes Cannizzaro reaction to give $PhCH(OH)COO^-$.

26. Which of the following statements are **not** correct?
   (a) The product obtained in the reaction of CH_3COCH_3 with one equivalent of Br_2 in H_3O^+ is $CH_3CBr(OH)CH_3$.
   (b) The reduction of $PhCH{=}CHCOCH_3$ with Li in NH_3 in ether solvent gives $PhCH{=}CHCH(OH)CH_3$.
   (c) The reduction of $PhCH{=}CHCOCH_3$ with hydrazine in alkaline medium gives $PhCH_2CH_2COCH_3$.
   (d) In the reaction  A, the product A is 

27. Which of the following statements are correct?
   (a) In the reaction  A , the product A is 

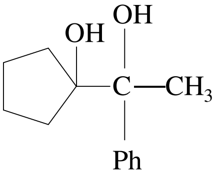
(b) An organic compound on treatment with HIO_4 gives cyclopentanone and formaldehyde. The compound is



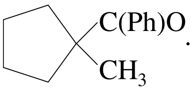
(c) The products obtained when CH_3COCHO is treated with HIO_4 are CH_3COOH and H_2CO.
(d) The product obtained when 1,2-cyclohexanedione is treated with HIO_4 is $OHC(CH_2)_4CHO$.

28. Which of the following statements are **not** correct?

(a) The treatment of



with concentrated H_2SO_4 gives

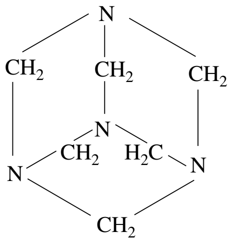


.

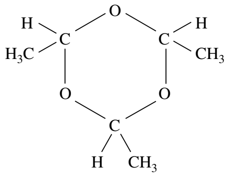
(b) The enol content of acetylacetone in water is greater than that of acetylacetone in hexane.
(c) The enol content of $C_6H_5COCH_2COC_6H_5$ in ethanol is greater than that of $CH_3COCH_2COCH_3$.

29. Which of the following statements are correct?

(a) The product obtained when methanal reacts with ammonia is urotropine having molecular structure



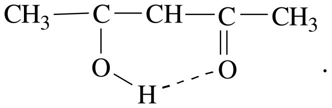
(b) Paraldehyde is a trimer of acetaldehyde and its structure is



(c) Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture is poured into water. The main product obtained in this process is $(C_2H_5)_3COH$.
(d) Fehling's solution A consists of an aqueous solution of copper sulphate while Fehling's solution B consists of an alkaline solution of Rochelte salt (sodium potassium tartrate — $NaKC_4H_4O_4 \, . \, 4H_2O$).

30. Which of the following statements are **not** correct?

(a) The structure of the enol form of $CH_3COCH_2COCH_3$ with intramolecular hydrogen bonding is



$$CH_3-\underset{\substack{|\\O}}{C}-CH-\underset{\substack{\|\\O}}{C}-CH_3 \quad .$$

(b) Carbonyl carbon of an aldehyde or a ketone is sp hybridized.
(c) Fomaldehyde is a liquid at room temperature.
(d) Formaline is 30% aqueous solution of formaldehyde.

31. Which of the following statements are **not** correct?

(a) The electrophile in the acylation of benzene is $RC\equiv O^+$, known as acylium ion.
(b) The Clemmensen reduction of —CO— to —CH_2— group is carried out by using Zn(Hg) and conc. HCl.
(c) The Wolff-Kisher reduction of —CO— to —CH_2— group is carried out by using $NaBH_+$.
(d) The addition across >C == O bond of an aldehyde or ketone is electrophilic addition.

32. Which of the following statements are **not** correct?

(a) Lithium aluminium hydride converts $>C=O$ group to $-\overset{|}{C}H-OH$.

(b) The addition of alcohol, ROH, across $>C=O$ bond of an aldehyde or ketone gives an acetal with the structure given as $-\underset{|}{C}(OR)_2$.

(c) Cannizzaro reaction is shown by an aldehyde or ketone containing alpha hydrogen atom.

(d) Tollens reagent is acidic solution of $AgNO_3$.

33. Which of the following statements are **not** correct?

(a) The —CHO group in benzaldehyde is *ortho-para* directing.

(b) The IUPAC name of $C_6H_5CH == CH—CHO$ is 3-phenylpropanal.

(c) The completes balanced equation of RCHO with Tollens reagent is

$$RCHO + 2Ag(NH_3)_2^+ + 3OH^- \rightarrow RCOO^- + 2H_2O + 4NH_3 + \underset{(mirror)}{2Ag(s)}$$

(d) The formation of oximes and other ammonia derivative requires slightly **basic** media for maximum rate.

34. Which of the following will give yellow precipitate with I_2/NaOH?

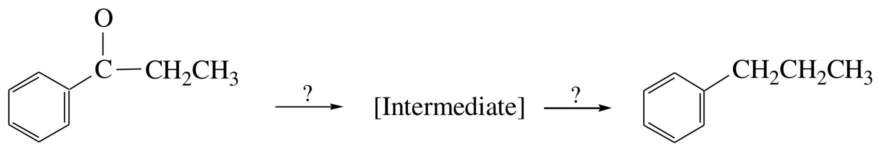
(a) $ICH_2COCH_2CH_3$ (b) $CH_3COOCOCH_3$ (c) CH_3CONH_2 (d) $CH_3CH(OH)CH_2CH_3$.

35. Which of the following compounds form(s) two isomeric oximes on reacting with NH_2OH?

(a) RCHO (b) RCOR′ (c) RCOR (d) HCHO

Linked Comprehension Type

1. The Wolff-Kishner reaction converts an aldehyde or ketone to the corresponding alkane.



(i) The reagent used in this conversion is

(a) Hydrazine in water

(b) Hydrazine in dimethyl sulphoxide followed by base treatment.

(c) Hydrazine in dimethyl sulphoxide followed by acid treatment.

(d) Hydrazine in dimethyl sulphoxide followed by strong heating.

(ii) The intermediate formed involves

(a) the formation of hydrazone leading direct to alkane

(b) the formation of hydrazone and acid-catalysed double bond migration

(c) the formation of hydrazone and base-catalysed double bond migration

(d) the formation of imine derivatives

(iii) The intermediate is converted to alkane by the release of

(a) N_2 (b) H_2O (c) NH_3 (d) H_2NNH_2

2. Haloform reaction may be depicted as follows.

$$RCOCH_3 \xrightarrow{A} \text{Intermediate} \longrightarrow RCOO^- + B$$

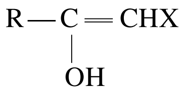
(i) The reagent A is

(a) X_2 and OH^- (b) X_2 and H^+ (c) X_2 and H_2O (d) only X_2

where X_2 is a halogen.

(ii) The intermediate formed is

(a) $RCOCH_2X$ (b) $RCOCHX_2$ (c) $RCOCX_3$ (d)


$R-\underset{OH}{\underset{|}{C}}=CHX$

(iii) The product B is

(a) CH_3X (b) CH_2X_2 (c) CHX_3 (d) CX_4

3. The aldol reaction is shown by aldehydes and ketones. Identify the correct statements in the following.

(i) Aldol reaction occurs in

(a) protic solvent with a basic catalyst (b) protic solvent with neutral medium

(c) aprotic solvent with a base catalyst (d) aprotic solvent with an acid catalyst

(ii) Aldol reaction involves

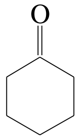
(a) irreversible reaction

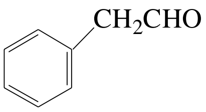
(b) reversible reaction

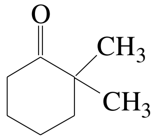
(c) aldehydes/ketones with no α-hydrogen atom(s)

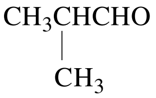
(d) a molecule of aldehyde and a ketone with no α-hydrogen atom

(iii) which of the following reactions gives the maximum percentage of aldol condensation product?

(a) 

(b) 

(c) 

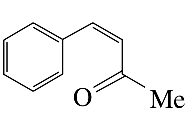
(d) 

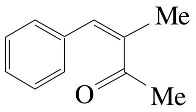
$$\underset{\displaystyle CH_3}{CH_3\overset{|}{C}HCHO}$$

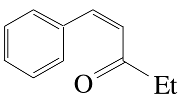
4. A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R which undergoes intramolecular aldol reaction to give predominately S.

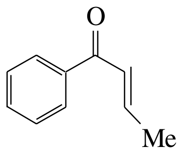
$$P \xrightarrow[\text{2. H}^+.\text{H}_2\text{O} \;\; \text{3. H}_2\text{SO}_4,\Delta]{\text{1. meMgBr}} Q \xrightarrow[\text{2. Zn, H}_2\text{O}]{\text{1. O}_3} R \xrightarrow[\text{2. }\Delta]{\text{1. OH}^+} S$$

(i) The structure of the carbonyl compound P is

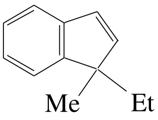
(a) 

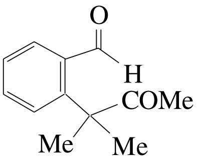
(b) 

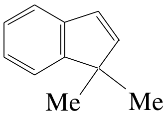
(c) 

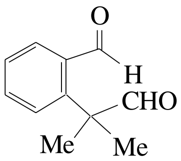
(d) 

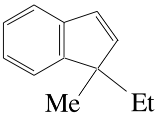
(ii) The structures of the products Q and R, respectively, are

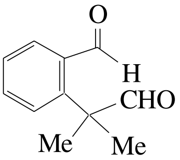
(a) 

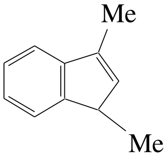
; 

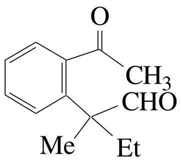
(b) 

; 

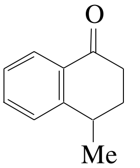
(c) 

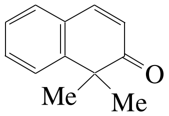
; 

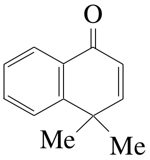
(d) 

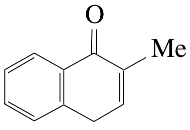
; 

(iii) The structure of product S is

(a) 

(b) 

(c) 

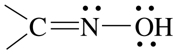
(d) 

(2009)

Assertion and Reason Type

Given below are a few questions containing two statements. Based on the following key, answer correctly each question.

- (a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
- (b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
- (c) Statements -1 is correct and Statement-2 is incorrect.
- (d) Statements-1 is incorrect and Statement-2 is correct.

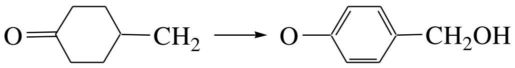
	Statement-1	**Statement-2**
1.	Acetic acid does not undergo haloform reaction	Acetic acid has no alpha hydrogen. (1998)
2.	Aliphatic carbonyl compounds are more reactive than the corresponding aryl compounds towards nuclephilic addition reaction.	The electron-donating resonance effect of benzene makes aryl compounds less reactive.
3.	Aldol equilibrium generally favours condensation product in the case of mono substituted acetaldehyde (RCH_2CHO). The equilibrium favours starting material for disubstituted acetaldehyde (R_2CHCHO) and for most ketones.	Steric factors seems to be responsible for this behaviour.
4.	An oxime  is a stronger acid than $NH_2\ddot{O}H$.	The conjugate base of oxime is stablilized due to delocalization of negative charge by extended π-bonding.
5.	Hydrazone of aldehydes are not prepared in highly acidic medium.	Nucleophicity of hydrazine is enchanced in highly acidic conditions.
6.	*o*-Hydroxybenzaldehyde is liquid at room temperature while *p*-hydroxy-benzaldehyde is a high melting solid.	*o*-Hydroxybenzaldehy involves inter-molecular hydrogen bonding while *p*-hydroxybenzaldehyde involves intra-molecular hydrogen bonding.
7.	CH_3COCH_2Cl shows enhanced reactivity towards S_N2 reaction as compared to $CH_3CH_2CH_2Cl$.	The transition state in CH_3COCH_2Cl is stabilized due to extended conjugation by CO group.

Matrix Match Type

1. Column I lists some of the methods employed for reduction and the reagents used in these methods are given in Column II. Match correctly the items in Column I and II.

Column I	**Column II**
(a) Wolff-Kishner reduction	(p) Pd/C (S or quinoline)
(b) Clemmensen reduction	(q) $HSCH_2CH_2SH$; Ni
(c) Rosenmund reduction	(r) H_2NNH_2 and strong base
(d) Raney Ni desulphurization	(s) Zn/Hg and HCl

2. Column I lists some of the reduction reactions and Column II lists the reducing agents. Match each entry in Column I with correct choice given in Column II.

Column I	**Column II**
(a) $CH_3CH(CH_3)COCl \rightarrow CH_3CH(CH_3)CHO$	(p) Lithium aluminium hydride
(b) $CH_3CH(CH_3)COCl \rightarrow CH_3CH(CH_3)CH_2OH$	(q) BH_3/THF followed by H_2O_2, OH^-
(c) 	(r) Lithium tri-*t*-butoxyaluminium hydride
(d) $CH_3CH=CHCH_2CHO \rightarrow$ $CH_3CH=CHCH_2CH_3$	(s) H_2NNH_2 and strong base

3. Column I names some typical organic reactions and Column II names the substrate in these reaction. Match the correct entries from Column I and Column II.

Column I	**Column II**
(a) Claisen - Schmidt	(p) PhCOPh + NaqOH
(b) Perkin condensation	(q) PhCHO + $(CH_3CO)_2O$
(c) Benzoin condensation	(r) PhCHO + CH_3CHO
(d) Benzilic acid rearrangement	(s) PhCHO + ethanolic CN^-

Straight Objective Type

1. (d) **2.** (a) **3.** (c) **4.** (a) **5.** (a) **6.** (a)
7. (a) **8.** (c) **9.** (b) **10.** (a) **11.** (c) **12.** (b)
13. (c) **14.** (b) **15.** (b) **16.** (b) **17.** (c) **18.** (b)
19. (c) **20.** (a) **21.** (c) **22.** (b) **23.** (b) **24.** (a)
25. (d) **26.** (c) **27.** (c) **28.** (d) **29.** (c) **30.** (d)
31. (b) **32.** (b) **33.** (c) **34.** (b) **35.** (a) **36.** (b)
37. (b) **38.** (b) **39.** (c) **40.** (d) **41.** (d) **42.** (d)
43. (b) **44.** (b) **45.** (b) **46.** (c) **47.** (a) **48.** (b)
49. (d) **50.** (c) **51.** (d) **52.** (d)

ANSWERS

1. (a), (c) **2.** (a), (b) **3.** (a), (d) **4.** (a), (b)
5. (a), (b), (d) **6.** (b), (d) **7.** (a), (d) **8.** (a), (b), (d)
9. (a), (c), (d) **10.** (b), (d) **11.** (a), (d) **12.** (c), (d)
13. (a), (b) **14.** (b), (c), (d) **15.** (c), (d) **16.** (a), (d)
17. (a), (c), (d) **18.** (a), (b), (c) **19.** (a), (b), (c), (d) **20.** (b), (c)
21. (b), (c), (d) **22.** (a), (b) **23.** (a), (b) **24.** (a), (b), (c)
25. (b), (c), (d) **26.** (a), (b), (c), (d) **27.** (a), (b) **28.** (a), (b)
29. (a), (b), (c), (d) **30.** (b), (c), (d) **31.** (c), (d) **32.** (c), (d)
33. (a), (b), (d) **34.** (a), (d) **35.** (a), (b)

Linked Comprehension Type

1. (i) (b) (ii) (c) (iii) (a)
2. (i) (a) (ii) (c) (iii) (c)
3. (i) (a) (ii) (b) (iii) (b)
4. (i) (b) (ii) (a) (iii) (b)

Assertion and Reason Type

1. (c) **2.** (a) **3.** (a) 4. (a)
5. (c) **6.** (c) **7.** (a)

Matrix Match Type

1. (a) – (r); (b) – (s); (c) – (p); (d) – (q)
2. (a) – (r); (b) – (p); (c) – (q); (d) – (s)
3. (a) – (r); (b) – (q); (c) – (s); (d) – (p)

Straight Objective Type

1. Polarization in acrolein may be represented as $\overset{\delta+}{CH_2}{=}CH{-}CH{=}\overset{\delta-}{O}$.

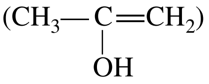
2. Formaline is 40% formaldehyde aqueous solution.

3. The boiling points of aldehydes are smaller than those of alcohols of comparable molar masses.

4. The addition reactions across the C=O bond is nucleophilic addition.

5. CH_3COCl is the most susceptible to nucleophilic attack at the carbonyl group. This is due to —Cl which stabilises the transition state.

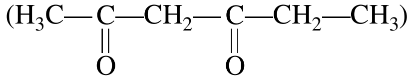
6. The enolic form of acetone ($CH_3{-}\underset{\large |\atop OH}{C}{=}CH_2$) contains active hydrogen, replaceable by deuterium.



7. The reactions are known as hydration of C = O group. Carbon of C = O changes from sp^2 to sp^3 hybrid state. The bulkier the groups attached to the C, the greater is the steric effect, the higher will be the energy the change in hybrid state, and during the equilibrium is to lie towards the unhydrated compound. The inductive effect of alkyl groups also decreases the reactivity of the C=O towards nucleophilic addition of water. Thus, the trend of equilibrium constants is $K_1 > K_2 > K_3$.

8. The compound $CH_3COCH_2COCH_3$ is expected to have maximum enol content. This is due to two carbonyl groups attached to CH_2 group.

9. 2,4-Hexanedione ($H_3C{-}\underset{\Vert\atop O}{C}{-}CH_2{-}\underset{\Vert\atop O}{C}{-}CH_2{-}CH_3$) has the most acidic hydrogen attached to C^3 carbon atom.



10. The compound $CH_3COCH_2CH(OH)\ CH_3$, a β-ketohydroxy compound, will be most readily dehydrated.

11. The red precipitates are due to Cu_2O.

12. Chloral, CCl_3CHO, reacts with water forming chloral hydrate, $CCl_3CH(OH)_2$

13. Aryl group lowers the speed of addition reaction across the C==O group due to the stabilization of the reactant more than the transition state via resonance effect.

14. The reaction $CH_3COCH_3 \xrightarrow[\text{Zn(Hg), conc. HCl}]{[H]} CH_3CH_2CH_3$ is known as Clemmensen reduction.

15. Benzaldehyde does not react with Fehling's solution.

16. The reduction reaction $RCR' \xrightarrow[\text{KOH}]{\text{hydrazine}} RCH_2R'$ is known as Wolff-Kishner reduction.

17. The reduction reaction $R{-}COCl \xrightarrow[\text{ethyl acetate}]{H_2/Pd/BaSO_4} RCHO$ is known as Rosenmund reduction.

18. The Wolff-Kishner reduction takes place in strongly basic solutions and can be used for those compounds that are sensitive to acid.

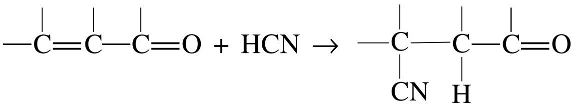
19. Aldehydes generally undergo nucleophilic addition more readily than ketones as the former involves lesser crowding at the transition state.

20. BH_3 reacts with the C = C faster than the C = O and the reverse is true for $NaBH_4$.

21. Zn–Hg/HCl reduces both C = C and —CHO groups while H_2NNH_2/OH^- reduces only —CHO group.

22. The formation of cyanohydrin from a ketone is an example of nucleophilic addition reaction.

23. The reaction $-\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O + HCN \rightarrow -\underset{\large |\atop CN}{\overset{|}{C}}{-}\underset{\large |\atop H}{\overset{|}{C}}{-}\overset{|}{C}{=}O$ involves nucleophilic addition reaction.

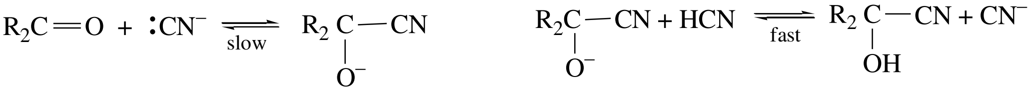


24. $\underset{(A)}{CH_3CH_2CH_2OH} \xrightarrow[K_2Cr_2O_7]{\text{acidified}} \underset{(B)}{CH_3CH_2CHO} \xrightarrow[\text{sodium acetate}]{H_2NCONHNH_2\cdot HCl} \underset{(C)}{CH_3CH_2CH{=}NNHCONH_2}$

25. Butanone is $CH_3CH_2COCH_3$. It contains —$COCH_3$ group which can be converted to —COOH by carrying out the iodoform test. The reagent used is NaOH, I_2/H^+.

$$CH_3CH_2COCH_3 + \underset{(\text{from } I_2 \text{ and } OH^-)}{3OI^-} \rightarrow CH_3CH_2COO^- + CHI_3 + 2OH^-$$

26. A small amount of base is necessary to convert some HCN to CN^- which intiates the addition reactions



$$R_2C{=}O + :CN^- \underset{\text{slow}}{\rightleftharpoons} R_2\underset{O^-}{\underset{|}{C}}{-}CN \qquad R_2\underset{O^-}{\underset{|}{C}}{-}CN + HCN \underset{\text{fast}}{\rightleftharpoons} R_2\underset{OH}{\underset{|}{C}}{-}CN + CN^-$$

With too much base the cyanohydrin is decomposed which causes the reversal of equilibrium. The optimum pH used in this reaction is 9 – 10.

27. The formation of A involves the addition of NH_2OH. The conversion of A to B is the Beckmann rearrangement.

28. Aliphatic aldehyde reacts faster than ketone. Aromatic aldehyde reacts slowest. This is mainly due to steric hindrance.

29. A ketone with no α-hydrogen shows Cannizzaro reaction. Acetaldehyde (CH_3CHO) contains α-hydrogen. It will not show this test.

30. *m*-Chlorobenzaldehyde in the presence of concentrated alkali will undergo Canizzaro reaction. The products will be potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.

31. Benzaldehyde undergoes Cannizzaro reaction.

32. The slowest step in Cannizzaro reaction is transfer of hydride to the carbonyl group.

33. The methoxy group being electron-releasing group makes the release of hydride group more easy.

34. Benzaldehyde does not undergo aldol condensation.

35. Formaldehyde is always converted into formic acid.

36. There occurs intramolecular Cannizzaro reaction.

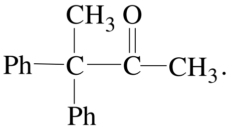
37. $—NO_2$ is electron-withdrawing group, it helps increasing positive charge on C of $—C{=}O$ group, thereby, facilitates the transfer of H^- in the rate determining step.

$—OCH_3$ is electron- releasing group, it decreases the positive charge on C of $—C{=}O$ group, thereby, retards the transfer of H^- in the rate determining step.

38. The rate determining step is the transfer of H^- from $PhCH(OH)O^-$ to PhCHO.

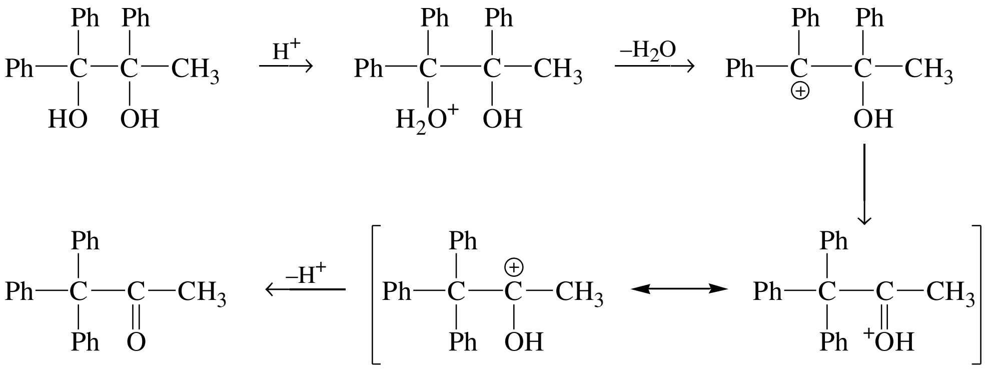
39. A phenyl group is migrated in preference to a methyl group.

The compound formed is



$$Ph{-}\overset{CH_3}{\overset{|}{\underset{Ph}{\underset{|}{C}}}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3.$$

The reaction, known as pinacol rearrangement, proceeds as follows.

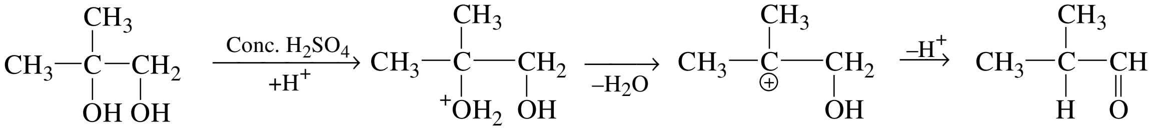


$$Ph{-}\overset{Ph}{\overset{|}{\underset{HO}{\underset{|}{C}}}}{-}\overset{Ph}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}CH_3 \xrightarrow{H^+} Ph{-}\overset{Ph}{\overset{|}{\underset{H_2O^+}{\underset{|}{C}}}}{-}\overset{Ph}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}CH_3 \xrightarrow{-H_2O} Ph{-}\overset{Ph}{\overset{|}{\underset{\oplus}{C}}}{-}\overset{Ph}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}CH_3$$

$$\downarrow$$

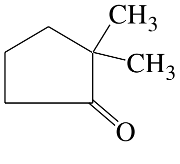
$$Ph{-}\overset{Ph}{\overset{|}{\underset{Ph}{\underset{|}{C}}}}{-}\underset{O}{\underset{\|}{C}}{-}CH_3 \xleftarrow{-H^+} \left[Ph{-}\overset{Ph}{\overset{|}{\underset{Ph}{\underset{|}{C}}}}{-}\overset{\oplus}{\underset{OH}{\underset{|}{C}}}{-}CH_3 \longleftrightarrow Ph{-}\overset{Ph}{\overset{|}{\underset{Ph}{\underset{|}{C}}}}{-}\underset{^+OH}{\underset{\|}{C}}{-}CH_3 \right]$$

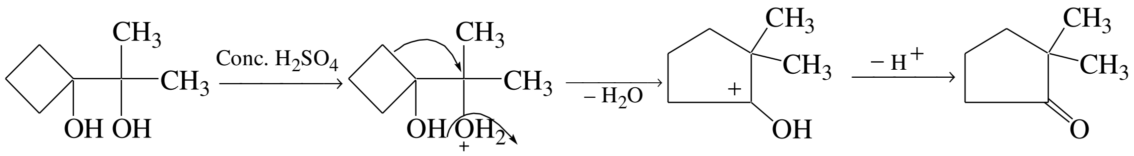
40. The product is $(CH_3)_2CHCHO$



$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}\underset{OH}{\underset{|}{CH_2}} \xrightarrow[+H^+]{\text{Conc. }H_2SO_4} CH_3{-}\overset{CH_3}{\overset{|}{\underset{^+OH_2}{\underset{|}{C}}}}{-}\underset{OH}{\underset{|}{CH_2}} \xrightarrow[-H_2O]{} CH_3{-}\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}{-}\underset{OH}{\underset{|}{CH_2}} \xrightarrow{-H^+} CH_3{-}\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}\underset{O}{\underset{\|}{CH}}$$

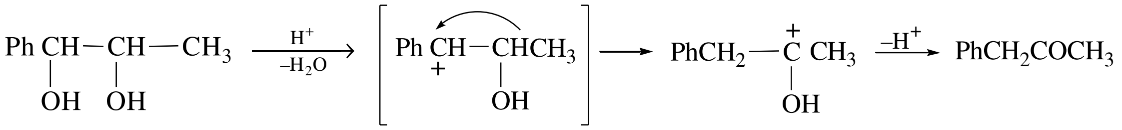
41. The product is





42. same as Q.41.

43.



$$Ph\,\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{H^+} \left[Ph\,\underset{+}{CH}-\underset{OH}{\underset{|}{C}}HCH_3\right] \longrightarrow PhCH_2-\overset{+}{\underset{OH}{\underset{|}{C}}}\,CH_3 \xrightarrow{-H^+} PhCH_2COCH_3$$

First step is the formation of more stable carbocation. In second step, H is migrated rather than CH_3.

44. Grignard reagent reacts both with acetaldehyde and acetone.

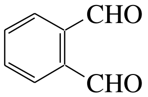
45. A compound containing CH_3CO— or $CH_3CH(OH)$— shows iodoform test. $CH_3CH_2CH_2COCH_3$ (2-pentanone) shows this test.

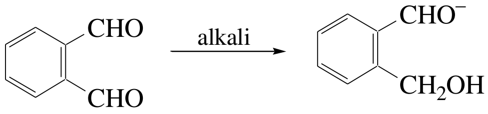
46. Diethyl ketone ($C_2H_5COC_2H_5$) will not show iodoform test.

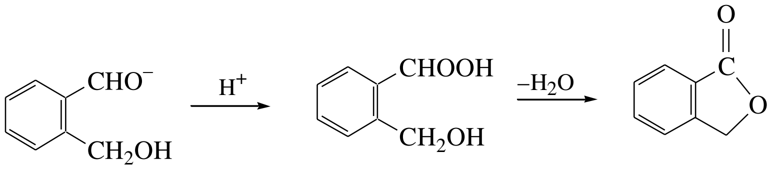
47. $C_2H_5COC_2H_5$ does not show iodoform test.

48. The reaction is called a Perkin condensation.

49. Carboxylic acid whose molecule has a hydroxyl group on a γ or δ carbon undergoes an intramolecular esterification to give cyclic esters known as γ- or δ-lactone. This reaction is acid catalysed.

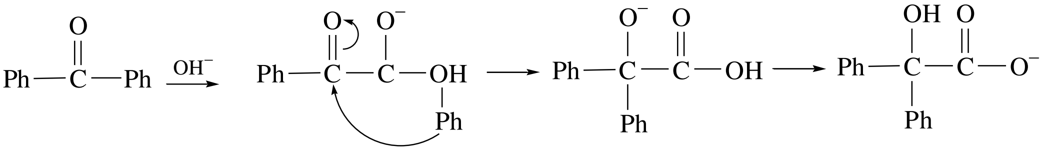
Of the given compounds,  will satisfy the above requirement after it has undergone intramolecular Cannizzaro reaction in the presence of alkali.





50. First reaction involves decarboxylation and the **E** is PhCO*CH_3. The second reaction is iodoform reaction giving $PhCOO^-$ Na^+ (**F**) and *CHI_3 (**G**).

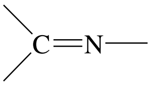
51. This is benzilic acid rearrangement.



Multiple Correct Choice Type

1. Aldol condensation is shown by an aldehyde or ketone with α-hydrogen atom. Propanal (CH_3CH_2CHO) and 2-methylpropanal ($CH_3CH(CH_3)CHO$) will show this condensation.
2. Acetophenone ($C_6H_5COCH_3$) contains CH_3CO— group. This will show iodoform test. Also 2-hydroxypropane ($CH_3CHOHCH_3$) which contains CH_3CHOH— group will show iodoform test.
3. Ethyl chloride and benzaldehyde will react with ethanolic KCN.
4. Aldehydes and ketones containing α-hydrogen atom show aldol condensation. Thus, the compounds CH_3CHO and CH_3COCH_3 show these condensation.
5. The aryl group in aromatic aldehyde retards the addition reaction across the CO group.
6. Friedel-Crafts alkylation and Reimer-Tiemann reaction involves the formation of C—C bond,.

7. Primary amines ($C_6H_5NH_2$ and $C_6H_5NHNH_2$) on reacting with acetone will give products containing



$>C{=}N—$ group.

8. Compounds containing α-hydrogen (or deuterium) undergo aldol condensation. Acetaldehyde, propanaldehyde and trideuteroacetaldehyde will undergo aldol condensation.

9. Iodoform test will be shown if the compound has CH_3CO—group.

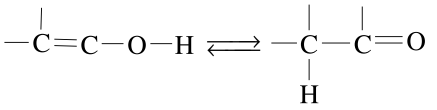
10. Aldol condensation occurs if the compound has *α*-hydrogen adjacent to —CO group.

11. Fehling's test is shown by aldehydes.

12. same as Q.10.

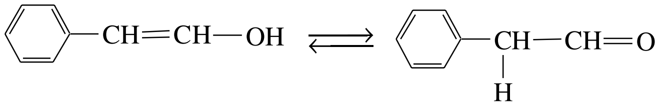
16. $CH_3COOH \xrightarrow[\Delta]{} H_2C{=}C{=}O + H_2O$ and $CH_3COCH_3 \xrightarrow[700\,°C]{} H_2C{=}C{=}O + CH_4$

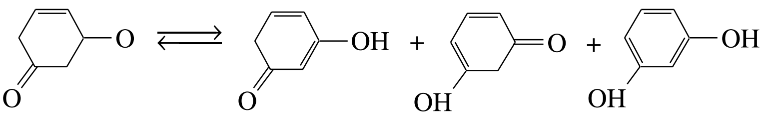
17. Keto-enol tautomerism involves the following equilibrium.

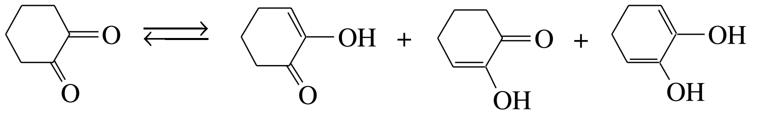


$$—\overset{|}{C}{=}\overset{|}{C}—O—H \rightleftharpoons —\underset{H}{\underset{|}{\overset{|}{C}}}—\overset{|}{C}{=}O$$

This equilibrium can exist in the following molecules



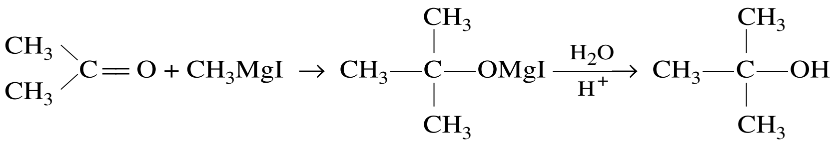




18. (a) Benzaldehyde does not possess α-hydrogen atom. It does not undergo aldol condensation but undergoes Cannizzaro reaction giving benzoic acid and benzyl alcohol.

(b) Hydrazine gets protonated in highly acidic medium. Due to this, its nucleophilicity is decreased.

(c) The product is tertiary butanol.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O + CH_3MgI \rightarrow CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OMgI \xrightarrow[H^+]{H_2O} CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OH$$

(d) Carbonyl carbon is sp^2 hybridized.

19. (a) Aldehydes or ketones as such have no hydrogen bonds but alcohols and carboxylic acids do have. Hence, the former have lower boiling points than the latter.

(b) The solubility is due to the hydrogen bonding between solute and solvent.

(c) Formaldehyde is always converted into sodium formate.

(d) Benzaldehyde does not contain α-hydrogen atom.

20. (a) Only aldehydes give red precipitate.

(b) The compound containing $CH_3—\underset{\underset{O}{\|}}{C}—$ shows positive iodoform test.

21. (a) With an alkaline $KMnO_4$, toluene is converted into benzoic acid. However, the use of CrO_3 in acetic anhydride followed by hydrolysis will convert toluene to benzaldehyde.

(b) At low pH, protonated aldehydes, ketones and hydroxylamines are formed.

22. (a) Alkyl substituents stabilize C==O group by releasing electrons towards the sp^2 hybridized C. The ehthalpy of the ketone is lowered because it has two alkyl groups while the aldehyde has only one.

(b) 3-Penten-2-one has conjugation which permits electron delocalization.

(c) The product A is $PhCH_2CH_2CHO$. The reduction stops at the aldehyde stage because the catalyst is poisoned (partially deactivated) by adding sulphur or quinoline.

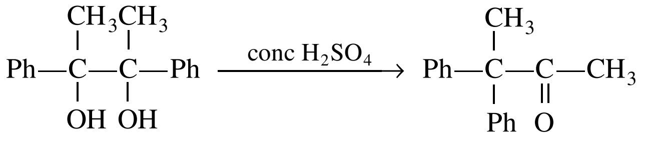
(d) The product A is $CH_3CH(CH_3)CH_2OH$.

23. (a) For example, in the reaction $CH_3CH(CH_3)COCl \xrightarrow[0°C]{LBAH} A$, the product is $CH_3CH(CH_3)CHO$.

(c) DBAH stands for diisobutylaluminium hydride.

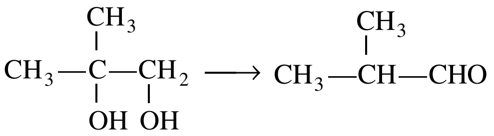
(d) The product is butanal. Diisobutylaluminium hydride is less reactive than lithium aluminium hydride. It reduces an ester to an aldehyde.

24. (a) The reaction is



$$\mathrm{Ph{-}\overset{CH_3}{\underset{OH}{C}}{-}\overset{CH_3}{\underset{OH}{C}}{-}Ph \xrightarrow{conc\ H_2SO_4} Ph{-}\overset{CH_3}{\underset{Ph}{C}}{-}\underset{\|\,O}{C}{-}CH_3}$$

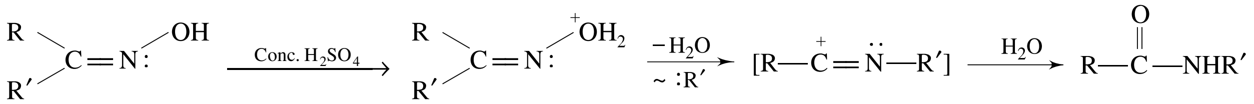
(b) The reaction is



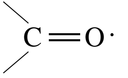
$$\mathrm{CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}\underset{OH}{CH_2} \longrightarrow CH_3{-}\overset{CH_3}{CH}{-}CHO}$$

(c) The general reaction for the formation of a Schiff base is $RCHO + R'NH_2 \xrightarrow{-H_2O} RCH{=}N{-}R'$

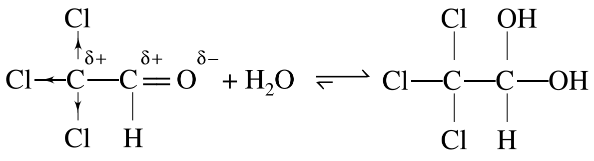
(d) It is the *trans* R′ group which migrates



25. (a) The equilibrium constant for the hydration of H_2CO is greater than that of $(CH_3)_2CO$. Two factors responsible for this trend are steric and inductive. Firstly, the addition of H_2O involves the change in the hybridization of C from sp^2 to sp^3. The alkyl groups in $(CH_3)_2CO$ will involve more steric hinderance and thus its hydration will be less effective than that of H_2CO. Secondly, the methyl group is an electron-releasing group. The presence of two methyl groups attached to C of CO group in $(CH_3)_2CO$ diminishes the positive charge on C causing the decrease in the reactivity of nucleophilic addition of H_2O across



(b) The chloral is less stable than chloral hydrate due to δ^+ charge on the C adjacent to the carbonyl C.



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}\underset{H}{C}{=}O + H_2O \rightleftharpoons Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}\overset{OH}{\underset{H}{C}}{-}OH}$$

(c) H_2CO is the most reactive aldehyde. It exists in aqueous OH^- solution mainly as the conjugate base of its hydrate $H_2C(OH)O^-$. The hydride shift from the anion occurs more readily giving formic acid.

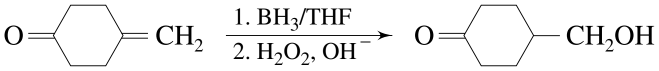
(d) PhCOCHO undergoes internal crossed-Cannizzaro reaction.

26. (a) The product is CH_3COCH_2Br

(b) The C=C of α, β-unsaturated carbonyl is reduced, instead of CO group. The product is thus $PhCH_2CH_2COCH_3$.

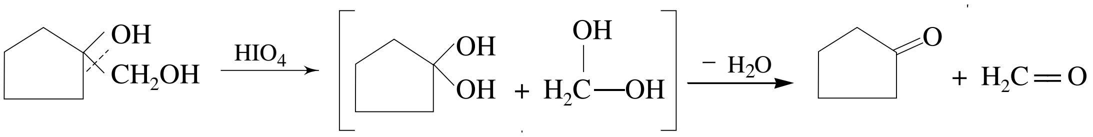
(c) The C=O group is reduced and this reaction is known as Wolff-Kishner reduction. The product is $PhCH{=}CHCH_2CH_3$.

(d) BH_3 reacts with the C═C faster than the C═O. The reaction is thus

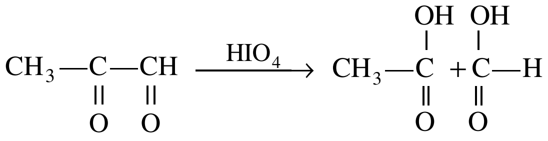


27. (a) $NaBH_4$ reacts with the C═O faster than C═C.

(b) The reaction is

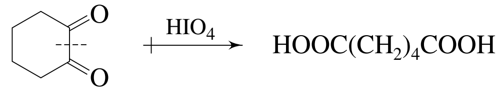


(c) The products are CH_3COOH and HCOOH.

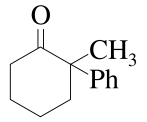


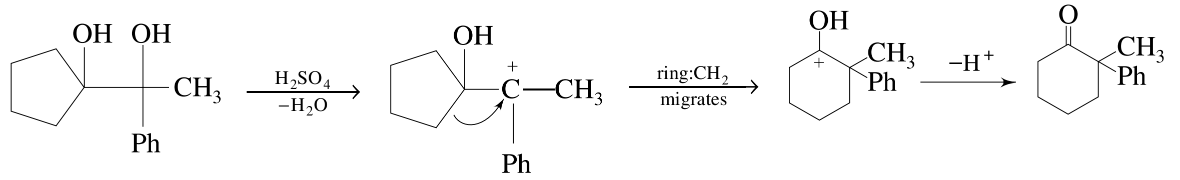
$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{CH} \xrightarrow{HIO_4} CH_3-\overset{OH}{\overset{|}{\underset{\underset{O}{\|}}{C}}} + \overset{OH}{\overset{|}{\underset{\underset{O}{\|}}{C}}}-H$$

(d) The product is adipic acid.



28. (a) The product is





(b) Any solvent that can form hydrogen bonds with the carbonyl group of the keto-form will cause an increase in the keto-content. The enol form involves intramolecular hydrogen bonding and its content is increased in a solvent not capable of forming hydrogen bonding. Thus, the enol content of acetylacetone will be greater in hexane.

30. (b) Carbon is sp^2 hybridized. (c) Formaldehyde is a gas at room temperature.

(d) Formaline is 40% aqueous solution of formaldehyde.

31. (c) Wolff-Kishner reduction is carried out by using hydrazine and a base. (d) The addition is nucleophilic

32. (c) Cannizzaro reaction is shown by an aldehyde or ketone with no alpha hydrogen atom

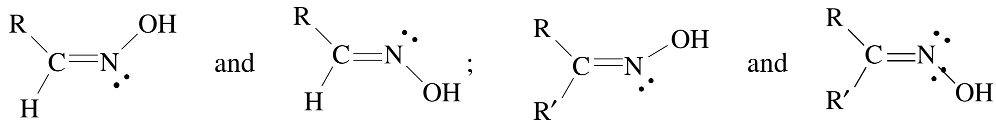
(d) Tollens reagent is ammoniacal solution of $AgNO_3$.

33. (a) The —CHO group is *meta* directing (b) The name is 3-phenylpropanal

(d) The required condition is slightly acidic.

In acidic medium, the carbonyl group becomes more electrophilic and reactive due to the formation of $>C^{+}—OH$. In more strongly acid solution (pH < 3.5), the unshared pair of electrons of N is protonated to give electrophile H_3NG^{+}, a species which cannot react. In basic medium, there is no protonation of C══O.

35. Two isomeric oximes are formed when an aldehyde (other than formaldehyde) or a nonsymmetrical ketone reacts with hydroxylamine.

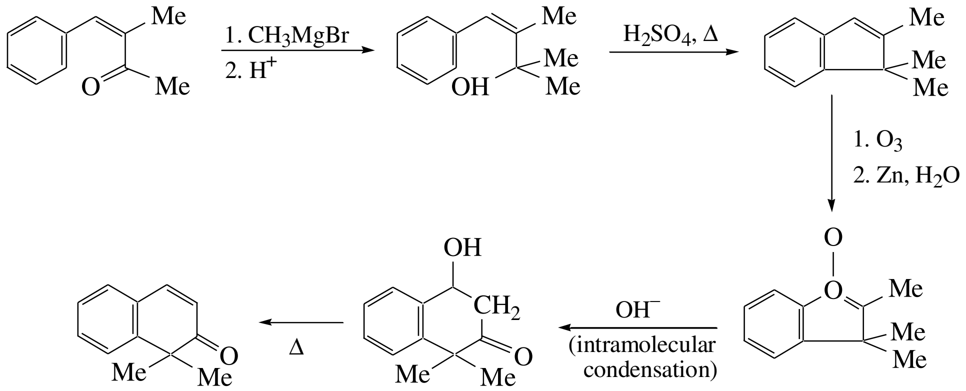


Linked Comprehension Type

(i) The choices (c) and (d) are excluded on the basis that these compounds will not exhibit iodoform test as there exists no —$COCH_3$ group.

Both the compounds (a) and (b) will exhibit the reactions P → Q → R. However, the reaction R → S will be shown only when a methyl group is present adjoining the CO group produced in the reaction Q → R. Hence, the **choice (b)** is correct.

The given reactions are as follows.



(S)

(ii) From the reactions shown in Q.(i), it follows that the **choice (a)** is correct.

(iii) From the reactions shown in Q.(i), it follows that the **choice (b)** is correct.

CHAPTER 28

CARBOXYLIC ACIDS

METHODS OF PREPARATION

1. Oxidation of primary alcohols $R—CH_2OH \xrightarrow{KMnO_4} R—COOH$

2. Oxidation of alkylbenzenes $C_6H_5—R \xrightarrow[\text{or } K_2Cr_2O_7]{KMnO_4} C_6H_5—COOH$

3. Carbonation of Grignard reagent $RMgX + O{=}C{=}O \rightarrow RCOO^-MgX^+ \xrightarrow{H^+} R—COOH + Mg^{2+} + X^-$

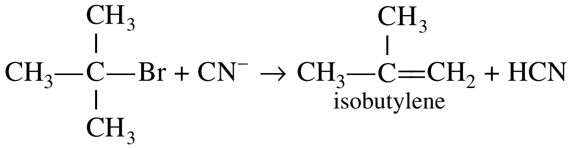
RMgX may be prepared from RX by adding Mg.

4. Hydrolysis of nitriles $R—C{\equiv}N + 2H_2O \xrightarrow[\text{or base}]{\text{acid}} R—COOH + NH_3$

Nitriles may be prepared by adding NaCN to the corresponding halides. For example,

$$CH_3CH_2CH_2Br + CN^- \rightarrow CH_3CH_2CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2CH_2COOH$$

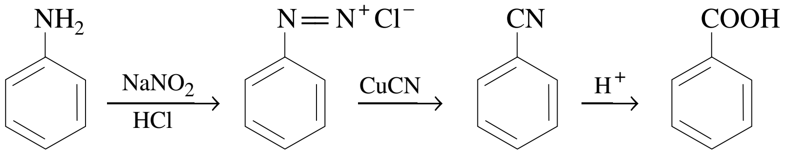
The above substitution of X with CN is applicable only when the halide is a primary halide. Tertiary halides yield alkene and for secondary halide, the yield of substitution product is poor.



$$CH_3—C(CH_3)_2—Br + CN^- \rightarrow \underset{\text{isobutylene}}{CH_3—C(CH_3){=}CH_2} + HCN$$

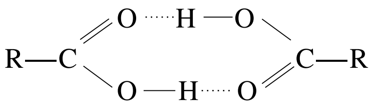
tert-butyl bromide

Aryl halides are unreactive towards substitution. Thus, aromatic nitriles are prepared via diazonium salt. For example,



PHYSICAL PROPERTIES

The molecules of carboxylic acids are polar and exhibit hydrogen bonding. The boiling point of a carboxylic acid is higher than that of an alcohol of comparable molar mass. This is due to the fact that the carboxylic acids exist as dimer.



CHEMICAL REACTIONS

1. Acidity Carboxylic acids are weak acids and their carboxylate anions are strong conjugate bases. The aqueous solutions of carboxylate salts are slightly alkaline due to the hydrolysis of carboxylate anion. Compared to other species, the orders of acidity and basicity of corresponding conjugate bases are as follows.

Acidity $RCOOH > HOH > ROH > HC\equiv CH > NH_3 > RH$

Basicity $RCOO^- < H\bar{O} < R\bar{O} < HC\equiv\bar{C} < NH_2^- < R^-$

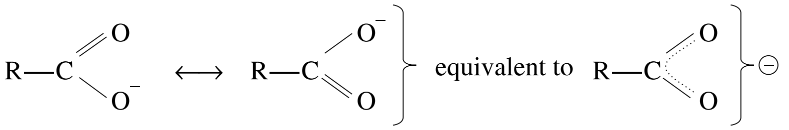
The carboxylic acids react with metals to liberate hydrogen and are soluble in both NaOH and $NaHCO_3$ solutions. For example

$2CH_3COOH + 2Na \rightarrow 2CH_3COO^-Na^+ + H_2$

$CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$

$CH_3COOH + NaHCO_3 \rightarrow CH_3COO^-Na^+ + H_2O + CO_2$

The acidity of a carboxylic acid is due to the resonance stabilization of its anion**:**



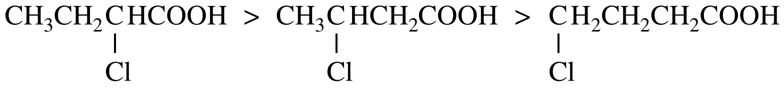
Because of the resonance, both the carbon-oxygen bonds in the carboxylate anion have identical bond length. In the carboxylic acid, these bond lengths are no longer identical. For example, in formic acid, one carbon-oxygen bond length is 136 pm (single bond) and another of 123 pm (double bond), whereas in the formate anion, both carbon-oxygen bonds have length equal to 127 pm (in between 123 pm and 136 pm).

The acidity of carboxylic acid depends very much on the substituent attached to —COOH group. Since acidity is due to the resonance stabilization of anion, any substituent which stabilizes the anion increases acidity whereas substituent causing destabilization of anion decreases acidity. For example, electron-withdrawing group disperses the negative charge of the anion and hence makes it more stable causing the increase in the acidity of the corresponding acid. On the other hand, electron-releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in the acidity. In the light of this, the following are the orders of a few substituted carboxylic acids.

1. Increase in the number of chlorine atoms on α-position increases the acidity, e.g.

   $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

2. Increase in the distance of Cl from —COOH decreases the acidity, e.g.

   $CH_3CH_2\underset{Cl}{C}HCOOH > CH_3\underset{Cl}{C}HCH_2COOH > \underset{Cl}{C}H_2CH_2CH_2COOH$

   This is due to the fact that inductive effect decreases with distance.

3. Increase in the electronegativity of halogen increases the acidity.

   $FCH_2COOH > BrCH_2COOH > ICH_2COOH.$

The aromatic acids are similarly affected by substituents.

Electron-releasing groups (—CH_3,—OH,—NH_2) make benzoic acid weaker.

Electron-withdrawing groups (—Cl, —NO_2) make benzoic acid stronger.

2. Conversion to acid chloride This may be carried out by using thionyl chloride ($SOCl_2$), phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5). Thionyl chloride is more convenient as the side products are only gaseous and thus the acid chloride can be easily separated; any excess of $SOCl_2$ can be easily removed as its boiling point is low (79°C).

$$RCOOH + SOCl_2 \xrightarrow[\text{reflux}]{} RCOCl + SO_2 + HCl; \qquad RCOOH + PCl_5 \xrightarrow[\text{heat}]{} RCOCl + POCl_3 + HCl$$

3. Conversion into esters

$$\underset{\text{acid}}{RCOOH} \xrightarrow{SOCl_2} \underset{\text{acid chloride}}{RCOCl} \xrightarrow{R'OH} \underset{\text{ester}}{RCOOR}$$

A direct reaction between acid and alcohol is a reversible one. Ester can be obtained either by using one of the reactants in excess or by removing one of the products.

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

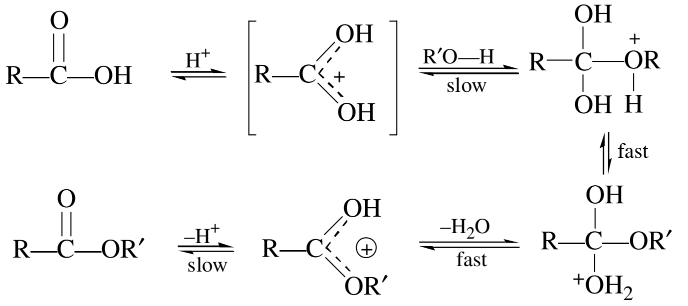
H^+ acts as a catalyst.

The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification as well as its hydrolysis. The relative order of esterification is

$CH_3OH > 1° > 2° > 3°$

$HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

The accepted mechanism is as follows.



Mineral acid speeds up both processes by protonating carbonyl oxygen and thus rendering carbonyl carbon more susceptible to nucleophilic attack. In esterification, the nucleophile is R′OH and leaving group is water and in the hydrolysis, the roles are reversed.

All steps are reversible. First slow step is slower than the second slow step and is the rate determining step.

4. Reduction of acids to alcohol Lithium aluminium hydride, $LiAlH_4$, is used to convert acids into alcohols. The initial product is an alkoxide which on hydrolysis gives an alcohol.

$$4R—COOH + 3LiAlH_4 \rightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4AlLi$$

$$(RCH_2O)_4AlLi \xrightarrow{H_2O} 4RCH_2OH$$

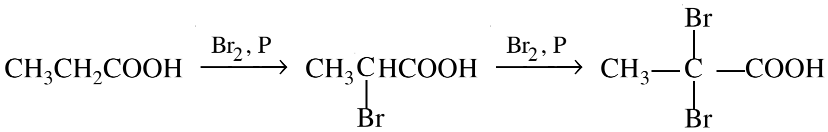
Alternatively, an ester may be converted into alcohol by the use of sodium metal and alcohol or $LiAlH_4$. For example,

$$\underset{\text{ethyl palmitate}}{CH_3(CH_2)_{14}COOC_2H_5} \xrightarrow[\text{(ii) } H^+]{\text{(i) } LiAlH_4} CH_3(CH_2)_{14}CH_2OH + C_2H_5OH$$

The reagent BH_3/THF followed by H_3O^+ also reduces —COOH to —CH_2OH.

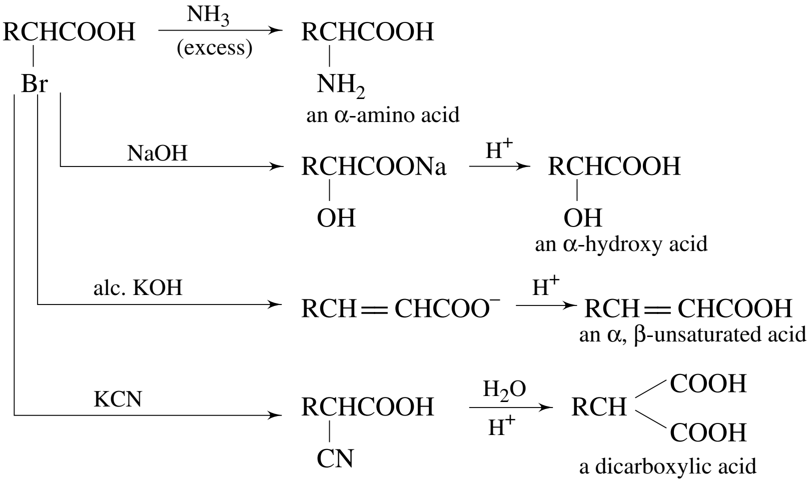
If the compound contains —CO—, —NO_2 and —Br groups, $LiAlH_4$ cannot be used as these are also reduced alongwith —COOH group. However, BH_3/THF can be used as this does not affect these groups. If the compound contains C═C group, then BH_3/THF cannot be used as this is rapidly reduced. However, $LiAlH_4$ can be used.

5. Halogenation of aliphatic acids (Hell-Volhard-Zelinsky reaction) In the presence of phosphorus, chlorine or bromine replaces α-hydrogen of an acid by halogen atom. For example,



$$CH_3CH_2COOH \xrightarrow{Br_2,\,P} CH_3\underset{|\\Br}{C}HCOOH \xrightarrow{Br_2,\,P} CH_3—\overset{Br}{\underset{Br}{C}}—COOH$$

The halogen atom in the *α*-position can be easily replaced by another nucleophilic reagent. This provides a method to convert carboxylic acid into many important substituted carboxylic acids. For example,



6. Decarboxylation Heating of sodium salt of carboxylic acid with soda lime (NaOH + CaO) produces alkane

$$\mathrm{RCOONa} \xrightarrow[\mathrm{CaO}]{\mathrm{NaOH}} \mathrm{RH} + \mathrm{Na_2CO_3}$$

Heating of calcium salt of carboxylic acid produces the compound containing CO group.

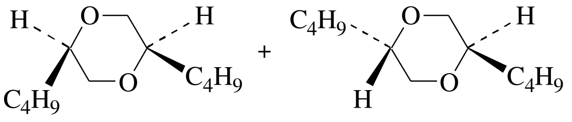
$$\mathrm{RCO_2(Ca/2) + R'CO_2(Ca/2) \rightarrow RCOR' + Ca_2CO_3}$$

If R is H, then aldehyde R′CHO is produced.

7. Action of Heat on Hydroxycarboxylic Acid

(i) *α-Hydroxyhexanoic acid*

$\mathrm{CH_3(CH_2)_3CHOHCOOH} \rightarrow$

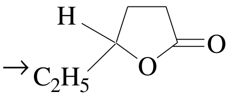


cis, racemic *trans*, meso

(ii) *β-Hydroxyhexanoic acid* $\mathrm{CH_3(CH_2)_2CHOHCH_2COOH \rightarrow CH_3(CH_2)_2CH{=}CHCOOH}$

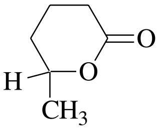
(stable conjugated molecule)
mainly *trans*

(iii) *γ-Hydroxyhexanoic acid* $\mathrm{CH_3CH_2CHOH(CH_2)_2COOH} \rightarrow$



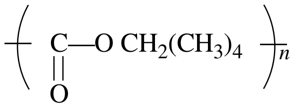
4-Ethyl-γ-butyrolactone

(iv) *δ-Hydroxyhexanoic acid* $\mathrm{CH_3CHOH(CH_2)_3COOH} \rightarrow$



5-Methyl-δ-valerolactone

(v) *∈-Hydroxyhexanoic acid* $n\ \mathrm{HOCH_2(CH_2)_4COOH} \rightarrow$



$$\left(\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{—O\ CH_2(CH_3)_4} \right)_n$$

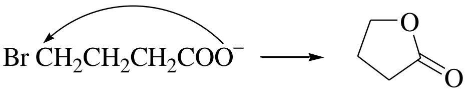
Linear polymeric ester

8. Action of Aqueous NaOH on Halocarboxylic Acid

(i) α-Haloacids (S_N2 displacement) $\mathrm{CH_3CH_2CHBrCOOH \xrightarrow{OH^-} CH_3CH_2CHOHCOOH}$

(ii) β-Haloacids (E2 dehydrohalogenation) $\mathrm{CH_3CHBrCH_2COOH \rightarrow CH_3{=}CHCOOH}$ (mostly *trans*)

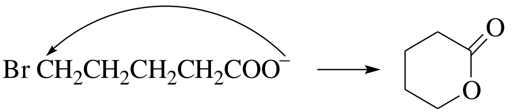
(iii) γ-Haloacids (Intramolecular S_N2 displacement)



$\mathrm{Br\,CH_2CH_2CH_2COO^- \longrightarrow}$

γ-Butyrolactone

(iv) δ-Haloacids (Intramolecular S_N2 displacement)



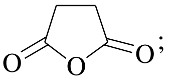
$\mathrm{Br\,CH_2CH_2CH_2CH_2COO^- \longrightarrow}$

δ-Valerolactone

9. Action of Heat on Dicarboxylic Acids

(i) $\mathrm{HOOCCOOH \rightarrow H_2O + CO + CO_2}$; (ii) $\mathrm{CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2}$

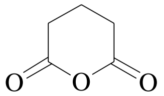
(iii) $\mathrm{HOOC(CH_2)_2COOH} \rightarrow$



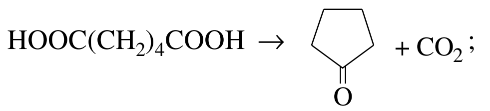
;

Succinic anhydride

(iv) $\mathrm{HOOC(CH_2)_3COOH} \rightarrow$

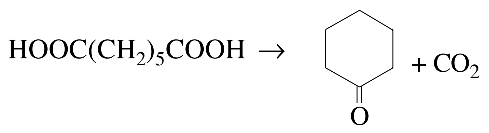


Glutaric anhydride

(v)


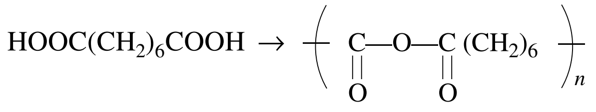
$HOOC(CH_2)_4COOH \rightarrow$ Cyclopentanone $+ CO_2$;

Cyclopentanone

(vi)


$HOOC(CH_2)_5COOH \rightarrow$ Cyclohexanone $+ CO_2$

Cyclohexanone

(vii)


$$HOOC(CH_2)_6COOH \rightarrow \left(\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}\,(CH_2)_6 \right)_n$$

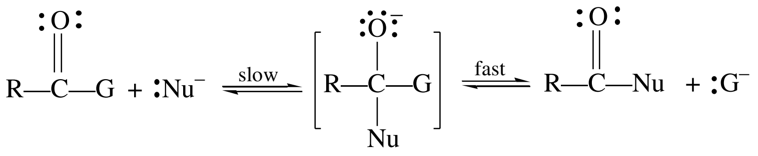
Linear polymeric anhydride

FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACIDS

The functional derivatives of carboxylic acids are acid chlorides (RCOCl), anhydride $\left(R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R\right)$, amides ($RCONH_2$) and esters $\left(R\underset{\underset{O}{\|}}{C}OR'\right)$. They all contain acyl group $\left(R-C\overset{\displaystyle O}{\diagup\!\!\diagdown}\right)$.

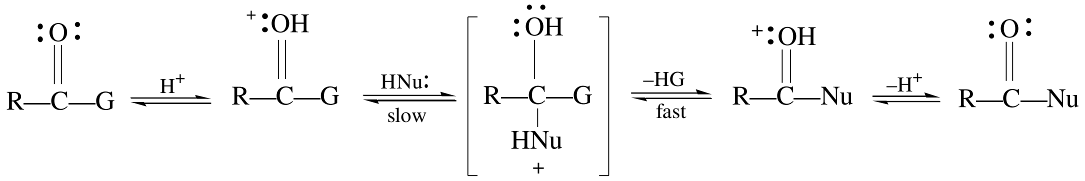
Nucleophilic Substitution Reactions The acyl derivatives undergo nucleophilic substitution reactions. Their mechanisms are as follows.

Basic medium



$$R-\overset{\overset{:O:}{\|}}{C}-G + :Nu^- \underset{}{\overset{slow}{\rightleftharpoons}} \left[R-\underset{\underset{Nu}{|}}{\overset{\overset{:\ddot{O}:^-}{|}}{C}}-G \right] \overset{fast}{\rightleftharpoons} R-\overset{\overset{:O:}{\|}}{C}-Nu + :G^-$$

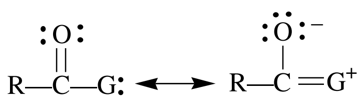
Acidic medium



$$R-\overset{\overset{:O:}{\|}}{C}-G \overset{H^+}{\rightleftharpoons} R-\overset{\overset{^+:OH}{\|}}{C}-G \underset{slow}{\overset{HNu:}{\rightleftharpoons}} \left[R-\underset{\underset{\overset{+}{HNu}}{|}}{\overset{\overset{:\ddot{O}H}{|}}{C}}-G \right] \underset{fast}{\overset{-HG}{\rightleftharpoons}} R-\overset{\overset{^+:OH}{\|}}{C}-Nu \overset{-H^+}{\rightleftharpoons} R-\overset{\overset{:O:}{\|}}{C}-Nu$$

Reactivity of Acyl Derivatives

The reactivity of RCOG depends on the resonance stabilization of the —CO—G group.



$$R-\overset{\overset{:O:}{\|}}{C}-G: \longleftrightarrow R-\overset{\overset{:\ddot{O}:^-}{|}}{C}=G^+$$

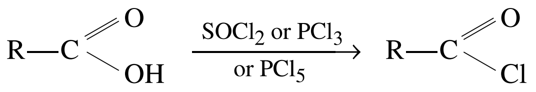
The greater the degree of delocalization, the lesser reactive is RCOG. NH_2 has the greatest degree of delocalization, thus $RCONH_2$ is least reactive, while X has little or no delocalization and thus RCOX is the most reactive.

Thus, the reactivity follows the order: Acid chloride > anhydride > ester > amide

A more reactive derivative may be used to prepare a less reactive derivative by reaction with appropriate nucleophile. Incidently, the reactivity decreases as the base strength of the leaving group increases i.e. $Cl^- < RCOO^- < RO^- < H_2N^-$.

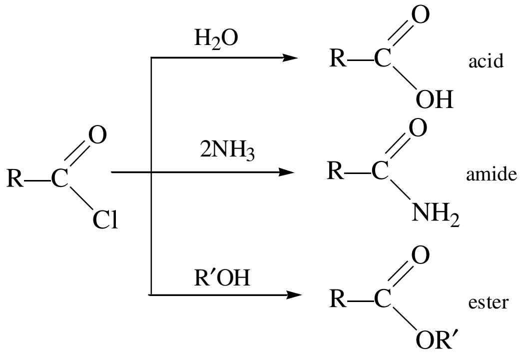
We describe in brief the method of preparation and the main reactions of the above functional derivatives.

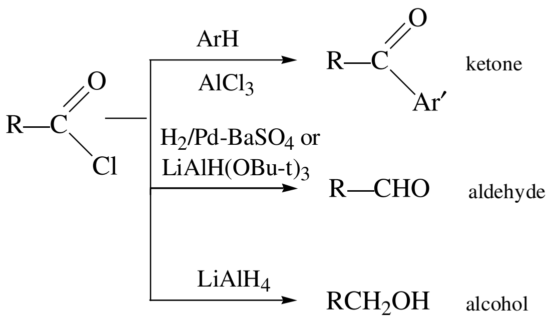
Acid Chlorides



$$R-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\!\!\diagdown}} \xrightarrow[\text{or } PCl_5]{SOCl_2 \text{ or } PCl_3} R-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\diagup\!\!\diagdown}}$$

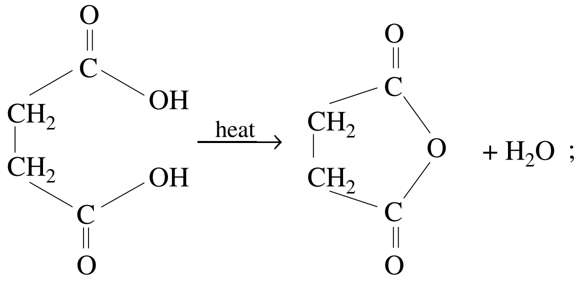
($SOCl_2$ is the best as the unwanted products are gases.)



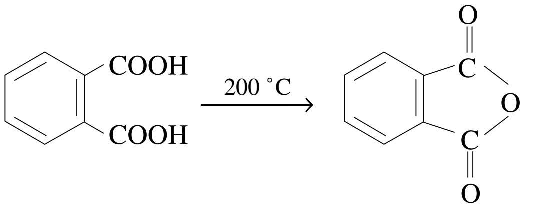


Acid Anhydrides

$$\underset{}{CH_3COOH} \xrightarrow[700\ ^\circ C]{AlPO_4} H_2O + \underset{\text{ketene}}{CH_2{=}C{=}O} \xrightarrow{CH_3COOH} \underset{\text{acetic anhydride}}{(CH_3CO)_2O}$$



succinic anhydride



phthalic anhydride

$$(RCO)_2O \xrightarrow{H_2O} 2RCOOH$$

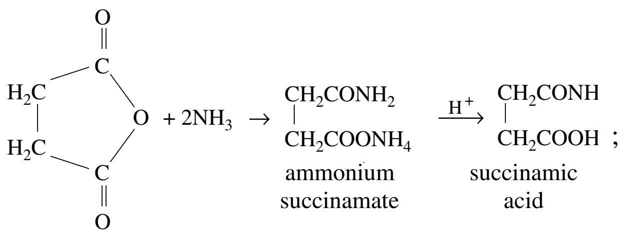
$$(RCO)_2O \xrightarrow{2NH_3} RCONH_2 + RCOO^-NH_4^+$$

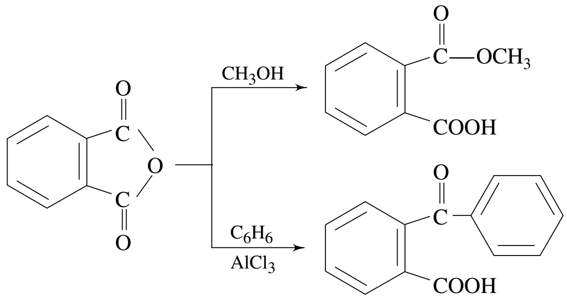
$$(RCO)_2O \xrightarrow{R'OH} 2RCOOR' + RCOOH$$

$$(RCO)_2O \xrightarrow[AlCl_3]{ArH} 2RCOAr + RCOOH$$

$$(RCO)_2O \xrightarrow{LiAlH_4} 2\text{ eq. of } RCH_2OH$$

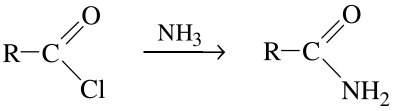
Cyclic anhydries with NH_3, R′OH and ArH/$AlCl_3$ gives only one product.

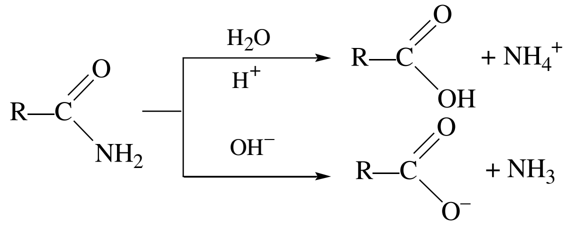


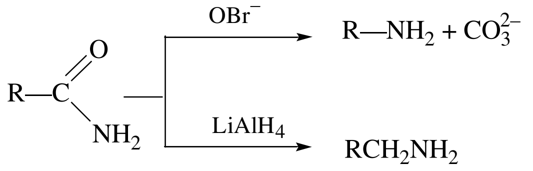


o-benzoylbenzoic acid

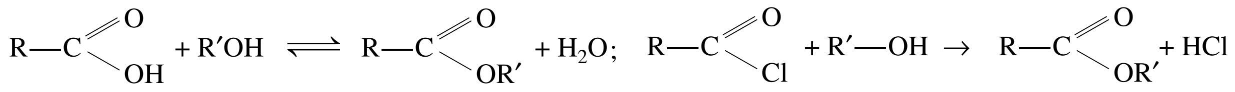
Amides

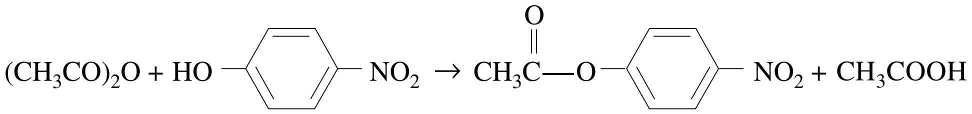




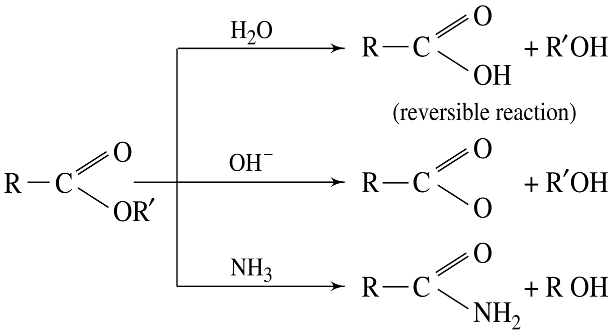


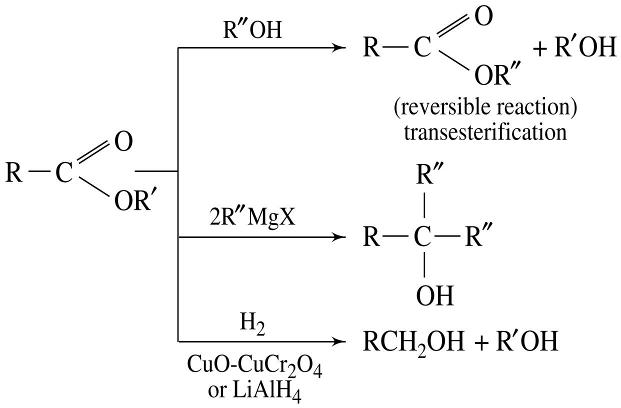
Esters



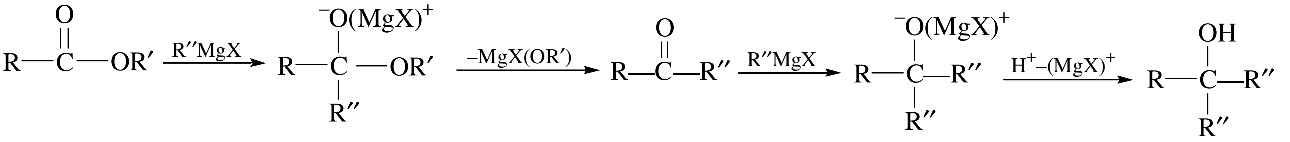


p-nitrophenyl acetate



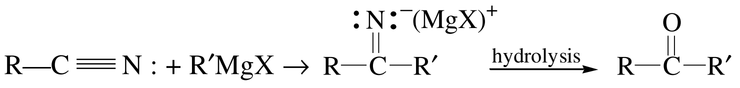


The reaction of RCOOR′ with R″MgX proceeds as follows



$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{R''MgX} R-\underset{R''}{\overset{^{-}O(MgX)^{+}}{C}}-OR' \xrightarrow{-MgX(OR')} R-\overset{O}{\overset{\|}{C}}-R'' \xrightarrow{R''MgX} R-\underset{R''}{\overset{^{-}O(MgX)^{+}}{C}}-R'' \xrightarrow{H^{+}-(MgX)^{+}} R-\underset{R''}{\overset{OH}{C}}-R''$$

The reaction of RCN with R′MgX gives a ketone:



$$R-C\equiv N: + R'MgX \rightarrow R-\overset{:N:^{-}(MgX)^{+}}{\overset{\|}{C}}-R' \xrightarrow{\text{hydrolysis}} R-\overset{O}{\overset{\|}{C}}-R'$$

Here, a second equivalent of R′MgX does not react because the intermediate imine salt bears a negative charge. Unlike the ester intermediate, where elimination of OR′⁻ leads to ketone, loss of the charge by elimination of R′ merely reverses the reaction.

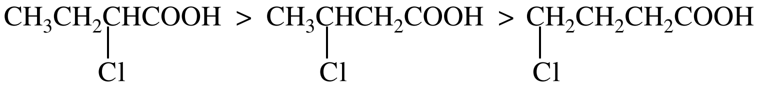
Straight Objective Type

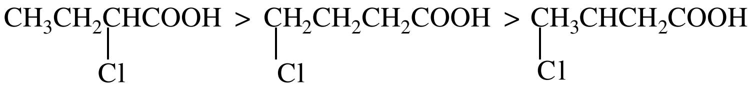
General Characteristics

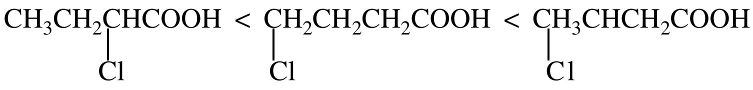
1. Which of the following orders of acid strength is correct?
   (a) RCOOH > ROH > HOH > HC≡CH (b) RCOOH > HOH > ROH > HC≡CH
   (c) RCOOH > HOH > HC≡CH > ROH (d) RCOOH > HC≡CH > HOH > ROH
2. Which of the following orders of base strength is correct?
   (a) $R^- > NH_2^- > HC\equiv\bar{C} > RCOO^-$ (b) $R^- > NH_2^- > RCOO^- > HC\equiv\bar{C}$
   (c) $R^- > RCOO^- > NH_2^- > HC\equiv\bar{C}$ (d) $HC\equiv\bar{C} > NH_2^- > RCOO^- > R^-$

3. Which of the following orders of acid strength is correct?

(a) 
$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCOOH < CH_3\underset{Cl}{\underset{|}{C}}HCH_2COOH < \underset{Cl}{\underset{|}{C}}H_2CH_2CH_2COOH$

(b) 
$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCOOH > CH_3\underset{Cl}{\underset{|}{C}}HCH_2COOH > \underset{Cl}{\underset{|}{C}}H_2CH_2CH_2COOH$

(c) 
$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCOOH > \underset{Cl}{\underset{|}{C}}H_2CH_2CH_2COOH > \underset{Cl}{\underset{|}{C}}H_3CHCH_2COOH$

(d) 
$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCOOH < \underset{Cl}{\underset{|}{C}}H_2CH_2CH_2COOH < \underset{Cl}{\underset{|}{C}}H_3CHCH_2COOH$

4. Which of the following orders of acid strength is correct?
(a) $FCH_2COOH < BrCH_2COOH < ICH_2COOH$
(b) $FCH_2COOH < ICH_2COOH < BrCH_2COOH$
(c) $FCH_2COOH > BrCH_2COOH > ICH_2COOH$
(d) $FCH_2COOH > ICH_2COOH > BrCH_2COOH$

5. Acetic acid differs from formic acid in that
(a) acetic acid is stable to heat
(b) formic acid is stable to heat
(c) acetic acid acts as a reducing agent
(d) acetic acid shows positive test with Tollens reagent

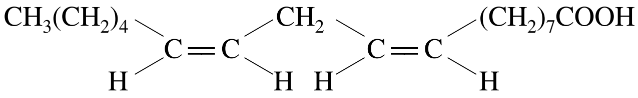
6. Which of the following reagent/solution can be used to distinguish between methanoic acid and ethanoic acid?
(a) Tollens reagent
(b) $FeCl_3$ solution
(c) NaOH solution
(d) Na_2CO_3 solution

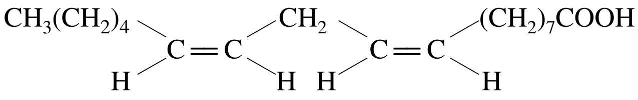
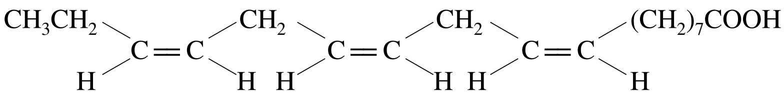
7. Which of the following sequences is correct?
(a) $pK_a^\circ(p\text{-}O_2NC_6H_4COOH) > pK_a^\circ(C_6H_5COOH) > pK_a^\circ(p\text{-}HOC_6H_4COOH)$
(b) $pK_a^\circ(p\text{-}O_2NC_6H_4COOH) < pK_a^\circ(C_6H_5COOH) < pK_a^\circ(p\text{-}HOC_6H_4COOH)$
(c) $pK_a^\circ(p\text{-}O_2NC_6H_4COOH) > pK_a^\circ(C_6H_5COOH) < pK_a^\circ(p\text{-}HOC_6H_4COOH)$
(d) $pK_a^\circ(p\text{-}O_2NC_6H_4COOH) < pK_a^\circ(C_6H_5COOH) > pK_a^\circ(p\text{-}HOC_6H_4COOH)$

8. Palmitic acid is
(a) $CH_3(CH_2)_{14}COOH$
(b) $CH_3(CH_2)_{16}COOH$
(c) $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$
(d) $CH_3(CH_2)_{10}COOH$

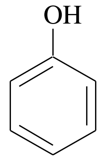
9. Stearic acid is
(a) $CH_3(CH_2)_{14}COOH$
(b) $CH_3(CH_2)_{16}COOH$
(c) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
(d) $CH_3(CH_2)_{10}COOH$

10. Oleic acid is
(a) $CH_3(CH_2)_{14}COOH$
(b) $CH_3(CH_2)_{16}COOH$
(c) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
(d) $CH_3(CH_2)_{10}COOH$

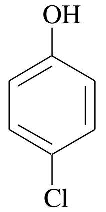
11. Linoleic acid is
(a) $CH_3(CH_2)_{14}COOH$
(b) $CH_3(CH_2)_{16}COOH$
(c) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
(d) 

12. Linolenic acid is
(a) $CH_3(CH_2)_{16}COOH$
(b) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
(c) 
(d) 

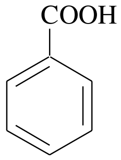
13. The correct acidity order of the compounds



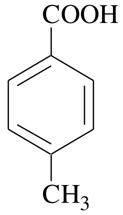
(I)



(II)



(III)



(IV)

is

(a) (III) > (IV) > (II) > (I) (b) (IV) > (IIII) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I) (2009)

14. *p*-Nitrobenzoic acid is a stronger acid than benzoic acid. This is due to
(a) direct resonance interaction between —NO_2 and —COOH groups.
(b) —NO_2 group generates a strong-electron withdrawing inductive effect due to positive charge on carbon bearing —COOH group.
(c) —NO_2 group generates a strong-electron withdrawing inductive effect due to positive charge on *meta* position to —COOH group.
(d) strong inductive effect of —NO_2 group.

15. Which of the following order regarding acid strength is correct?
(a) *p*-$NO_2C_6H_4COOH$ > *m*-$NO_2C_6H_4COOH$ and *p*-ClC_6H_4COOH > *m*-ClC_6H_4COOH
(b) *p*-$NO_2C_6H_4COOH$ < *m*-$NO_2C_6H_4COOH$ and *p*-ClC_6H_4COOH < *m*-ClC_6H_4COOH
(c) *p*-$NO_2C_6H_4COOH$ > *m*-$NO_2C_6H_4COOH$ and *p*-ClC_6H_4COOH < *m*-ClC_6H_4COOH
(d) *p*-$NO_2C_6H_5COOH$ < *m*-$NO_2C_6H_5COOH$ and *p*-ClC_6H_5COOH > *m*-ClC_6H_5COOH

16. *p*-HOC_6H_5COOH is weaker acid than C_6H_5COOH whereas the reverse is true for *m*-OHC_6H_5COOH. This is because
(a) resonance interaction predominates over inductive effect
(b) inductive effect predominates over resonance interaction.
(c) only resonance interaction with no inductive effect in *meta* isomer
(d) only inductive effect with no resonance interaction in *meta* isomer.

17. Which of the following orders regarding acid strength of isomers of nitrobenzoic acid is correct?
(a) *para* > *meta* > *ortho* (b) *para* > *ortho* > *meta*
(c) *ortho* > *para* > *meta* (d) *ortho* > *meta* > *para*

18. Which of the following orders regarding acid strength of isomers of hydroxybenzoic acid is correct?
(a) *para* > *meta* > *ortho* (b) *para* > *ortho* > *meta*
(c) *orhto* > *para* > *meta* (d) *ortho* > *meta* > *para*

Chemical Reactions

19. The relative order of esterification of alcohols is
(a) 1° < 2° < 3° (b) 1° > 2° > 3° (c) 1° > 3° > 2° (d) 1° < 3° < 2°

20. The relative order of esterification of acids is
(a) $RCH_2COOH > R_2CHCOOH > R_3CCOOH$ (b) $RCH_2COOH < R_2CHCOOH < R_3CCOOH$
(c) $RCH_2COOH < R_3CCOOH < R_2CHCOOH$ (d) $R_3CCOOH > RCH_2COOH > R_2CHCOOH$

21. The treatment of CH_3CH_2COOH with chlorine in the presence of phosphorus gives
(a) CH_3CH_2COCl (b) $CH_3CH_2CH_2Cl$ (c) $CH_3CH(Cl)COOH$ (d) $H_2(Cl)CH_2COOH$

22. Which of the following reactants produces benzophenone on heating?
(a) Calcium formate + Calcium benzoate (b) Calcium acetate + Calcium benzoate
(c) Calcium benzoate (d) Calcium acetate + Calcium formate

23. Which of the following reactants produces an aldehyde on heating?
(a) Calcium formate + Calcium benzoate (b) Calcium acetate + Calcium benzoate
(c) Calcium acetate (d) Calcium benzoate

24. The reaction of formic acid with concentrated H_2SO_4 gives
(a) CH_3COOH (b) $CO_2 + H_2O$ (c) $CO + H_2O$ (d) HCHO

25. Which of the following reactants would produce acetophenone on heating?
(a) Calcium acetate + Calcium formate (b) Calcium formate + Calcium benzoate
(c) Calcium acetate + Calcium benzoate (d) Calcium acetate

26. The Hell-Volhard-Zelinsky reaction is used in the synthesis of
(a) aldehydes (b) α-haloacids (c) acid halides (d) ketones

27. 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 (1999)

28. Which of the following reducing agents can be used to reduce RCOOH to RCH_2OH?
(a) $NaBH_4$ (b) Na/EtOH (c) $LiAlH_4$ (d) H_2/catalyst.

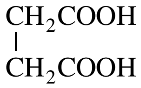
29. Which of the following reducing agents can be used to reduce RCOOH to RCH_2OH?
(a) H_2/catalyst (b) $NaBH_4$
(c) Na/EtOH (d) BF_3/THF followed by H_3O^+

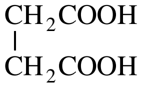
30. Which of the following carboxylic acids is **not** reduced to the corresponding 1° alcohol by BH_3/THF?
(a) $CH_3CH(CH_3)CH_2COOH$ (b) *p*-$CH_3COC_6H_4COOH$
(c) *m*-$O_2NC_6H_4COOH$ (d) (*Z*)-$CH_3CH{=}CHCH_2COOH$

31. Which of the following carboxylic acids is **not** reduced to the corresponding 1° alcohol by $LiAlH_4$?
(a) $CH_3CH(CH_3)COOH$ (b) *p*-$CH_3COC_6H_4COOH$
(c) Cyclohexanecarboxylic acid (d) (*Z*)-$CH_3CH{=}CHCH_2COOH$

32. Which of the following carboxylic acids is **not** reduced to the corresponding 1° alcohol by $LiAlH_4$?
(a) $CH_3CH(CH_3)COOH$ (b) (*Z*)-$CH_3CH{=}CHCH_2COOH$
(c) *p*-$O_2NC_6H_4COOH$ (d) Cyclohexanecarboxylic acid.

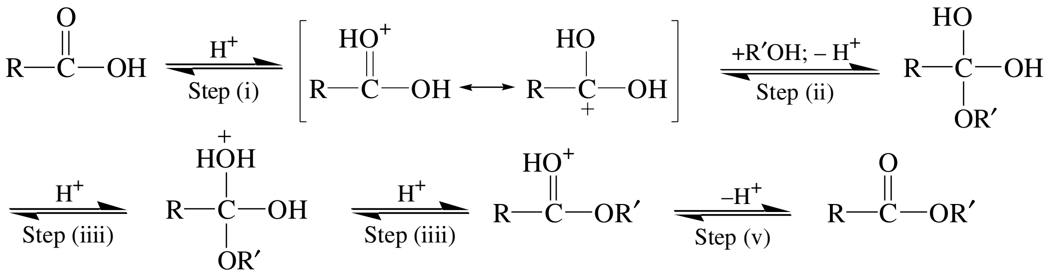
33. Which of the following carboxylic acids is **not** reduced to the corresponding 1° alcohol by $LiAlH_4$?
(a) $BrCH_2CH_2CH_2COOH$ (b) Cyclohexanecarboxylic acid
(c) (*Z*)-$CH_3CH{=}CHCH_2COOH$ (d) $CH_3CH(CH_3)CH_2COOH$

34. Which of the following dicarboxylic acids gives a cyclic anhydride on heating?
(a) $CH_2(COOH)_2$ (b)

$$\begin{array}{l}CH_2COOH\\ \;|\\ CH_2COOH\end{array}$$
(c) $HOOC(CH_2)_4COOH$ (d) $HOOC(CH_2)_5COOH$

35. Which of the following dicarboxylic acids gives cyclic ketone on heating?
(a) $CH_2(COOH)_2$ (b)

$$\begin{array}{l}CH_2COOH\\ \;|\\ CH_2COOH\end{array}$$
(c) $HOOC(CH_2)_3COOH$ (d) $HOOC(CH_2)_4COOH$

36. Which of the following dicarboxylic acids gives a linear polymeric anhydride?
(a) $HOOC(CH_2)_3COOH$ (b) $HOOC(CH_2)_4COOH$
(c) $HOOC(CH_2)_5COOH$ (d) $HOOC(CH_2)_6COOH$

37. 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)

38. Which of the following Carboxylic acid undergoes decarboxylation easily?
(a) $C_6H_5COCH_2COOH$ (b) $C_6H_5COCOOH$ (c) $C_6H_5CH(OH)COOH$ (d) $C_6H_5CH(NH_2)COOH$
(1995)

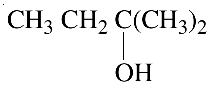
39. Benzoyl chloride is prepared from benzoic acid by
(a) Cl_2, *hv* (b) SO_2Cl_2 (c) $SOCl_2$ (d) Cl_2, H_2O (2000)

40. Which of the following acids has the smallest dissociation constant?
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$ (2002)

41. Identify the correct order of boiling points of the following compounds:
$\underset{1}{CH_3CH_2CH_2CH_2OH}$, $\underset{2}{CH_3CH_2CH_2CHO}$, $\underset{3}{CH_3CH_2CH_2COOH}$ (2002)
(a) 1 > 2 > 3 (b) 3 > 1 > 2 (c) 1 > 3 > 2 (d) 3 > 2 > 1

42. The reagents used in the reduction reactions
$CH_3COC_6H_4COOH \rightarrow CH_3COC_6H_4CH_2OH$
$CH_3CH{=}CHCH_2COOH \rightarrow CH_3CH{=}CHCH_2CH_2OH$
respectively are
(a) BH_3/THF followed by H_3O^+ and $LiAlH_4$ (b) BH_3/THF and BH_3/THF
(c) $LiAlH_4$ and $LiAlH_4$ (d) $LiAlH_4$ and BH_2/THF

43. The reaction of CH_3CH_2COOH with $2CH_3Li$ yields
(a) CH_3CH_2CHO (b) $CH_3CH_2CH_2CHO$ (c) $CH_3CH_2COCH_3$ (d)



$CH_3\,CH_2\,\underset{\underset{OH}{|}}{C}(CH_3)_2$

Carboxylic Acid Derivatives

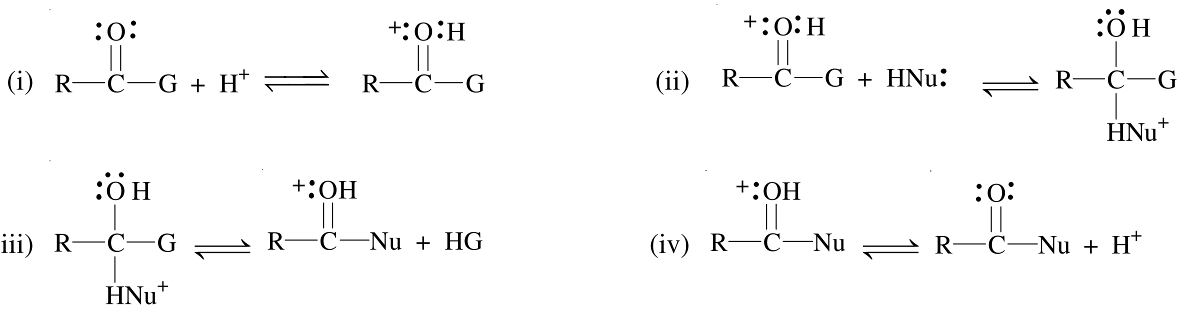
44. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?
(a) acid chloride > anhydride > ester (b) acid chloride < anhydride < ester
(c) acid chloride > ester > anhydride (d) anhydride > acid chloride > ester

45. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?
(a) anhydride > amide > ester (b) anhydride > ester > amide
(c) amide > anhydride > ester (d) amide > ester > anhydride

46. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct?
(a) $Cl^- > RCOO^- > RO^-$ (b) $Cl^- > RO^- > RCOO^-$ (c) $RO^- > RCOO^- > Cl^-$ (d) $RO^- > Cl^- > RCOO^-$

47. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct?
(a) $Cl^- < RO^- < NH_2^-$ (b) $Cl^- > NH_2^- > RO^-$ (c) $RO^- > Cl^- > NH_2^-$ (d) $RO^- > NH_2^- > Cl^-$

48. The mechanism of nucleophilic acyl substitution in the acyl derivative proceeds as follows.



(i) $R{-}\overset{\overset{:O:}{\|}}{C}{-}G + H^+ \rightleftharpoons R{-}\overset{\overset{+:O:H}{\|}}{C}{-}G$

(ii) $R{-}\overset{\overset{+:O:H}{\|}}{C}{-}G + HNu: \rightleftharpoons R{-}\underset{\underset{HNu^+}{|}}{\overset{\overset{:\ddot{O}H}{|}}{C}}{-}G$

(iii) $R{-}\underset{\underset{HNu^+}{|}}{\overset{\overset{:\ddot{O}H}{|}}{C}}{-}G \rightleftharpoons R{-}\overset{\overset{+:OH}{\|}}{C}{-}Nu + HG$

(iv) $R{-}\overset{\overset{+:OH}{\|}}{C}{-}Nu \rightleftharpoons R{-}\overset{\overset{:O:}{\|}}{C}{-}Nu + H^+$

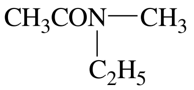
Amongst the above four steps, the slowest step is
(a) Step (i) (b) Step (ii) (c) Step (iii) (d) Step (iv)

49. The correct sequence regarding the activity of the given acid derivative is
(a) $RCOCl > RCON_3 > (RCO)_2O$ (b) $RCOCl > (RCO)_2O > RCON_3$
(c) $RCON_3 > RCOCl > (RCO)_2O$ (d) $RCON_3 > (RCO)_2O > RCOCl$

50. Which of the following statements is correct?
(a) 1° amide liberates N_2 when treated with HNO_2.
(b) 2° amide liberates N_2 when treated with HNO_2.
(c) 3° amide liberates N_2 when treated with HNO_2.
(d) None of 1°, 2° and 3° amides produce N_2 when treated with HNO_2.

51. Which of the following statements is correct?
- (a) 1° amide produces N-nitrosoamide when treated with HNO_2.
- (b) 2° amide produces N-nitrosoamide when treated with HNO_2.
- (c) 3° amide produces N-nitrosoamide when treated with HNO_2.
- (d) None of 1°, 2° and 3° amides produce N-nitrosoamide when treated with HNO_2.

52. Which of the following amides does not react with HNO_2?

(a) CH_3CONH_2 (b) $CH_3CONHCH_3$ (c) 
$CH_3CO\underset{C_2H_5}{N}-CH_3$
(d) $HCONH_2$

53. The correct sequence of decreasing order of reactivity of hydrolysis of acid chlorides is
- (a) $PhCOCl > p\text{-}O_2NC_6H_4COCl > p\text{-}CH_3OC_6H_4COCl$
- (b) $PhCOCl > p\text{-}CH_3OC_6H_4COCl > p\text{-}O_2NC_6H_4COCl$
- (c) $p\text{-}O_2NC_6H_4COCl > PhCOCl > p\text{-}CH_3OC_6H_4COCl$
- (d) $p\text{-}O_2NC_6H_4COCl > p\text{-}CH_3OC_6H_4Cl > PhCOCl$

54. Which of the following statements regarding amides is **not** correct?
- (a) Amides do not form salts when treated with aqueous acids.
- (b) The aqueous solutions of amides are alkaline.
- (c) Amides are very poor nucleophiles.
- (d) Amides are considerably less reactive than acid chlorides.

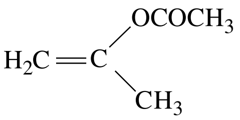
55. Which of the following facts is **not** correct?
- (a) As compared to RNH_2, $RCONH_2$ is stabilised by delocalisation of the nitrogen lone-pair electrons by the carbonyl group.
- (b) As compared to RNH_3^+, $RCONH_3^+$ is destabilised because the electron-withdrawing carbonyl group destablises the positive charge on nitrogen.
- (c) $\Delta G°$ for the conversion of $RNH_2 \xrightarrow{H^+} RNH_3^+$ is more than that of the reaction $RCONH_2 \xrightarrow{H^+} RCONH_3^+$.
- (d) Increased stability of $RCONH_2$ relative to RNH_2 and decreased stability of $RCONH_3^+$ relative to RNH_3^+ make amines more basic than amides.

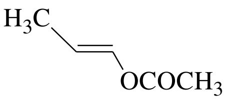
56. In the following groups

—OAc	—OMe	$—OSO_2Me$	$—OSO_2CF_3$
I	II	III	IV

the order of leaving group ability is
- (a) I > II > III > IV
- (b) IV > III > I > II
- (c) III > II > I > IV
- (d) II > III > IV > I (1997)

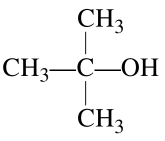
57. Given are the two organic compounds A and B:

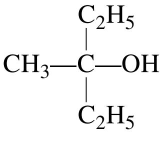

(A)

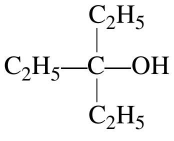

(B)

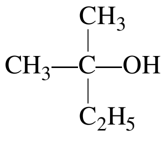
Which of the following reagents can distinguish between the products of acid hydrolysis of the two compounds?
- (a) Lucas reagent
- (b) 2,4-DNP
- (c) Fehling's solution
- (d) $NaHSI_3$ (2003)

58. Methyl acetate on treating with excess of C_2H_5MgBr produces

(a) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

(b) 
$CH_3-\underset{C_2H_5}{\overset{C_2H_5}{C}}-OH$

(c) 
$C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{C}}-OH$

(d) 
$CH_3-\underset{C_2H_5}{\overset{CH_3}{C}}-OH$ (2003)

59. The correct sequence regarding the activity of the given acid derivatives is
- (a) $RCOCl > (RCO)_2O > RCON_3$
- (b) $RCOCl > RCON_3 > (RCO)_2O$
- (c) $RCON_3 > RCOCl > (RCO)_2O$
- (d) $RCON_3 > (RCO)_2O > RCOCl$ (2004)

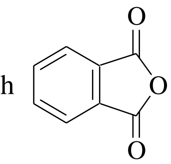
60. The treatment of an ester with $LiAlH_4$ followed by acid hydrolysis produces
(a) two alcohols
(b) two acids
(c) two aldehydes
(d) one molecule of alcohol and another of carboxylic acid

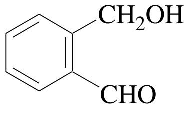
61. Which of the following sequences of relative rates of alkaline hydrolysis of esters is correct?
(a) $CH_3COOCH_3 > CH_3COOC_2H_5 > CH_3COOC_3H_7$
(b) $CH_3COOCH_3 < CH_3COOC_2H_5 < CH_3COOC_3H_7$
(c) $CH_3COOCH_3 < CH_3COOC_2H_5 > CH_3COOC_3H_7$
(d) $CH_3COOCH_3 > CH_3COOC_2H_5 < CH_3COOC_3H_7$

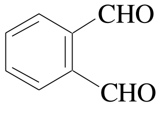
62. Which of the following sequences of relative rates of alkaline hydrolysis of esters is correct?
(a) $CH_3COOC_3H_7 > CH_3COOCH(CH_3)_2 > CH_3COOC(CH_3)_3$
(b) $CH_3COOC_3H_7 < CH_3COOCH(CH_3)_2 < CH_3COOC(CH_3)_3$
(c) $CH_3COOC_3H_7 < CH_3COOCH(CH_3)_2 < CH_3COOC(CH_3)_3$
(d) $CH_3COOC_3H_7 > CH_3COOCH(CH_3)_2 < CH_3COOC(CH_3)_3$

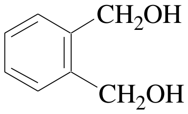
63. Which of the following sequences of relative rates of alkaline hydrolysis of esters is correct?
(a) $HCOOCH_3 < CH_3COOCH_3 < (CH_3)_2CHCOOCH_3$
(b) $HCOOCH_3 > CH_3COOCH_3 < (CH_3)_2CHCOOCH_3$
(c) $HCOOCH_3 < CH_3COOCH_3 < (CH_3)_2CHCOOCH_3$
(d) $HCOOCH_3 > CH_3COOCH_3 > (CH_3)_2CHCOOCH_3$

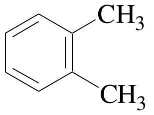
64. Which of the following sequences of rates of alkaline hydrolysis of esters is correct?
(a) $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
(b) $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$
(c) $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
(d) $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$

65. The treatment of $LiAlH_4$ with  leads to

(a) 

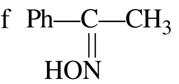
(b) 

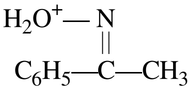
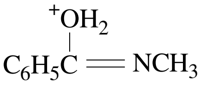
(c) 

(d) 

66. The treatment of $CH_3CH{=}CHCH_2CONHPh$ with $LiAlH_4$ gives
(a) $CH_3CH{=}CHCH_2CH_2NHPh$
(b) $CH_3CH_2CH_2CH_2CH_2NHPh$
(c) $CH_3CH{=}CHCH_2CH(OH)NHPh$
(d) $CH_3CH_2{=}CH_2CH_2CH(OH)NHPh$

67. The correct order of reactivity of PhCOCl(X) p-$O_2NC_6H_4COCl$(Y) and p-$CH_3OC_6H_4COCl$(Z) towards hydrolysis is
(a) X > Y > Z (b) X > Z > Y (c) Y > X > Z (d) Y > Z > X

68. Which of the following compounds in not observed in the mechanism of Beckmann rearrangement of  $\mathrm{Ph{-}\underset{\underset{HON}{\|}}{C}{-}CH_3}$?

(a)  $\mathrm{C_6H_5{-}\overset{\overset{H_2O^+{-}N}{\|}}{C}{-}CH_3}$ (b) $C_6H_5\overset{+}{C}{=}NCH_3$ (c)  $\mathrm{C_6H_5\overset{\overset{^+OH_2}{|}}{C}{=}NCH_3}$ (d) $CH_3CONHC_6H_5$

69. In the reaction $CH_3CO\overset{*}{O}C_2H_5 \xrightarrow{H_3O^+} A + B$ the products A and B, respectively, are
(a) CH_3COOH, $C_2H_5\overset{*}{O}H$
(b) $CH_3CO\overset{*}{O}H$, C_2H_5OH
(c) $CH_3CO\overset{*}{O}H$, $C_2H_5\overset{*}{O}H$
(d) $CH_3CO\overset{*}{O}H$, C_2H_5OH

Multiple Correct Choice Type

1. A useful derivative of a carboxylic acid can be prepared by making it react with
   (a) PCl_5 followed by treating with NH_3.   (b) PCl_5 followed by treating with aniline.
   (c) PCl_5 followed by treating with water.   (d) PCl_5 followed by treating with HI.

2. Aspirin can be described by a/an
   (a) acetyl ester of a phenol   (b) *o*-acetylsalicyclic acid
   (c) methyl salicylate   (d) methyl ether of phenol

3. Methanoic acid can be distinguished from ethanoic acid by using
   (a) ammoniacal silver nitrate solution   (b) alcoholic ferric chloride
   (c) heating with soda lime   (d) $NaHCO_3$ solution

4. Which of the following statements is/are correct?
   (a) Benzaldehyde shows positive Fehling's test.
   (b) One of the examples of Claisen-Schmidt reaction is

$$C_6H_5CHO + C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH{=}CHC_6H_5 + O_2$$

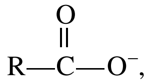
   (c) pK_a°(formic acid) is lesser than pK_a°(acetic acid).
   (d) *o*-Toluidine is more basic than aniline

5. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2. The intermediates involved in this reaction are
   (a) RCONHBr   (b) RNHBr   (c) R—N=C=O   (d) $RCONBr_2$ (1992)

6. Which of the following statements is/are correct?
   (a) RCOCl can be converted into $RCONH_2$ but the reverse is not possible.
   (b) Saponification of an ester is faster and irreversible as compared to acid hydrolysis.
   (c) Urea is a diacidic base.
   (d) Amides are less acidic than NH_3.

7. Which of the following statements are **not** correct?
   (a) Formic acid like acetic acid can be halogenated in the presence of red phosphorus and Cl_2.
   (b) Formic acid is a stronger acid than acetic acid.
   (c) The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molar mass.
   (d) The IUPAC name of $CH_3CH_2CH_2CN$ is propanenitrile.

8. Which of the following statements are correct?
   (a) The reduction of RCOOH with $LiAlH_4$ produces RCH_3.
   (b) The —COOH group attached to benzene ring is *meta* director.



   (c) In $R\text{—}\overset{\overset{O}{\|}}{C}\text{—}O^-$, both the carbon-oxygen bond lengths are identical. It is more than carbon-oxygen double bond length, and less than carbon-oxygen single bond length.
   (d) Electron-withdrawing substituents stabilises the carboxylate anion and hence increase the acidity of carboxylic acid.

9. Which of the following statements are correct?
   (a) The —OH group present at the *meta* position in benzoic acid has an acid-weakening effect.
   (b) The —OH group present at the *para* position in benzoic acid has an acid-strengthening effect.
   (c) The substitutent —Cl present at *meta* or *para* positions in benzoic acid has an acid-strengthening effect.
   (d) At *ortho* position, nearly all electron-withdrawing and electron-releasing substituents have the acid-strengthening effect in substituted benzoic acid.

10. Which of the following statements are correct?
   (a) Thionyl chloride is more convenient and more preferred reagent than phosphorus trichloride (or pentachloride) in order to convert carboxylic acid into acid chloride.
   (b) The ease of esterification of alcohol is 2° > 1° > CH_3OH

(c) The ease of esterification of carboxylic acid is

$$R_3CCOOH > R_2CHCOOH > RCH_2COOH > CH_3COOH > HCOOH$$

(d) Aliphatic carboxylic acid can be halogenated in the presence of phosphorus to give α-halogenated carboxylic acid.

11. Which of the following statements are correct?

(a) Carboxylic acids and their derivatives are collectively known as acyl compounds.

(b) Acyl compounds (RCOW) undergo electrophilic substitution reaction in which W is replaced by some other basic group.

(c) Acyl compounds undergo nucleophilic substitution reactions more readily than the compounds containing no carbonyl group.

(d) The acyl compounds differ from aldehydes or ketones in the respect that the former undergo nucleophilic substitution reactions while the latter undergo nucleophilic addition reactions.

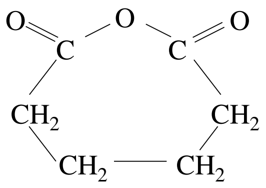
12. Which of the following statements are correct?

(a) The ease with which :W of the acyl compound RCOW is lost depends upon its basicity; the weaker the base, the better the leaving group.

(b) Aldehydes or ketones undergo nucleophilic addition reactions instead of substitution reactions because the leaving group ($:H^-$ or $:R^-$) are the strongest bases of all.

(c) It is more convenient to prepare amides and esters by first converting carboxylic acid into acid chloride followed by its reaction with ammonia or an alcohol.

(d) Adipic acid $HOOC(CH_2)_4COOH$ on heating produces cyclic adipic anhydride having structure.



13. Which of the following statements are **not** correct?

(a) Alkaline hydrolysis of an ester is a reversible reaction.

(b) In the alkaline hydrolysis of an ester, the bond broken is the bond between oxygen and alkyl group.

(c) Alkaline hydrolysis of an ester follows second order kinetics and is thus S_N2.

(d) An electron-withdrawing group G in p-$GC_6H_4COOC_2H_5$ decreases the rate of hydrolysis as compared to $C_6H_5COOC_2H_5$.

14. Which of the following statements are **not** correct?

(a) An electron-releasing group G in p-$GC_6H_4COOC_2H_5$ decreases the rate of hydrolysis as compared to $C_6H_5COOC_2H_5$.

(b) The rate of alkaline hydrolysis of RCOOR′ increases with the increase in the carbon atoms in the alkyl group R′.

(c) The rate of alkaline hydrolysis of RCOOR′ increases with the increase in the carbon atoms in the alkyl group R.

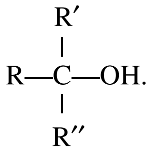
(d) The rate of alkaline hydrolysis of RCOOR′ decreases with the increase in the branching of carbon skeleton of the alkyl group R.

15. Which of the following statements are **not** correct?

(a) The rate of alkaline hydrolysis of RCOOR′ increases with the increase in the branching of carbon skeleton of the alkyl group R′.

(b) Acid hydrolysis of an ester follows second order kinetics.

(c) Acid hydrolysis of an ester is an irreversible reaction.

(d) The reaction between RCOOR′ and R″MgX produces an alcohol  $R—\overset{\overset{\Large R'}{|}}{\underset{\underset{\Large R''}{|}}{C}}—OH$.

16. Which of the following statements are correct?
   (a) Urea on treatment with NaOH produces ammonium ion and CO_2.
   (b) Urea on treating with nitrous acid produces ammonia gas.
   (c) With alkaline hypohalites, urea is converted into nitrogen and carbonate.
   (d) Reduction of an ester produces two alcohols.

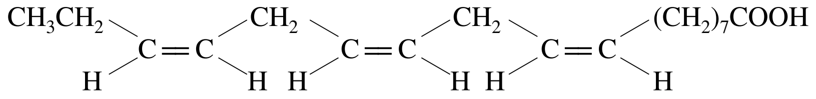
17. Which of the following statements are correct?
   (a) Oxalic acid is a weaker acid as compared to malonic acid.
   (b) Malonic acid is a stronger acid as compared to succinic acid.
   (c) Malonic acid is a stronger acid as compared to acetic acid.
   (d) The correct order of acid strength of the following acids is acetic acid > malonic acid > succinic acid

18. Which of the following statements are **not** correct?
   (a) The correct order of acid strength of the given acids is

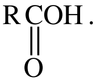
$$H_2SO_4 > CH_3COOH > H_2O > HC{\equiv}CH > C_2H_5OH$$

   (b) The presence of bulky substituents in either the alcohol group or the acid group slows down both esterification and hydrolysis.
   (c) Naturally occurring fatty acids generally contain even number of carbon atoms.
   (d) Unsaturated fatty acids have higher melting points than the corresponding saturated acids.

19. Which of the following statements are correct?
   (a) The melting point of a *trans* fatty acid is higher than its *cis* isomer.
   (b) The IUPAC name of



is *cis*,*cis*,*cis*-3,6,9-octadecatrien-18-oic acid.
   (c) Vinegar is a 5% aqueous solution of acetic acid.
   (d) The C=O bond in RCOOH is longer than in RCHO.

20. Which of the following statements are correct?
   (a) The reactivity of C=O towards nucleophiles in RCOOH is less than that in RCHO.
   (b) Soft soaps are K^+ salts of fatty acids.
   (c) Hard soaps are Na^+ salts of fatty acids.
   (d) Peroxy acids,  $R\underset{\underset{\displaystyle O}{\|}}{C}OOH$, are much stronger acid than  $R\underset{\underset{\displaystyle O}{\|}}{C}OH$.

21. Which of the following statements are correct?
   (a) p-$NO_2C_6H_4COOH$ is more acidic than the *meta* isomer.
   (b) *p*-Chlorobenzoic acid is more acidic than its *meta* isomer.
   (c) *m*-Toluic acid is more acidic than its *para* isomer.
   (d) Me_3CCH_2COOH is less acidic than Me_3SiCH_2COOH.

22. Which of the following statements are correct?
   (a) $H_2C{=}CHCH_2COOH$ is more acidic than CH_3CH_2COOH.
   (b) The acid $(CH_3)_3CCH_2C(CH_3)_2COOH$ is less acidic than $CH_3(CH_2)_7COOH$.
   (c) *Trans*-4-*t*-butylcyclohexanecarboxylic acid is stronger than the *cis*-isomer
   (d) The pK_{a1}° of a dicarboxylic acid is usually greater than the pK_{a}° of the comparable monoalkylcarboxylic acid.

23. Which of the following statements are correct?
   (a) Maleic acid is a weaker acid than fumaric acid.
   (b) Maleate monoanion is a weaker acid than fumarate monoanion.
   (c) Salicyclic acid, o-HOC_6H_4COOH, is a stronger acid than o-$H_3COC_6H_4COOH$.
   (d) A more reactive acid derivative may be used to prepare a less reactive one by reaction with the appropriate nucleophile.

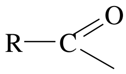
24. Which of the following statements are correct?
   (a) The reactivity of an acid derivative in its reaction with a nucleophile decreases as the base strength of the leaving group increases.
   (b) Acetic anhydride can be prepared by a reaction of CH_3COOH with ketene.
   (c) Heating of adipic acid gives a cyclic anhydride.
   (d) Heating of $HOOC(CH_2)_3COOH$ gives its cyclic anhydride.

25. Which of the following statements are correct?
   (a) Formic anhydride can be prepared by heating formic acid.
   (b) RCOCl can be converted into $RCONH_2$ but the reverse is not possible.
   (c) The rate of esterification of Et_3CCOOH is slower than that of $(i\text{-Pr})_2CHCOOH$.
   (d) It is more efficient to prepare an ester by the sequence: acid → acyl chloride → ester, rather than acid → ester.

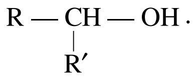
26. Which of the following statements are correct?
   (a) Saponification of an ester is faster and irreversible as compared to acid hydrolysis.
   (b) Amides are less acidic than NH_3.
   (c) Phthalimide is much more acidic than benzamide.
   (d) Urea is a diacidic base.

27. Which of the following statements are **not** correct?
   (a) Bubbling of gaseous carbon dioxide into the ether solution of Grignard reagent, RMgX, followed by acid hydrolysis produces RCOOH.
   (b) Electron-releasing substituents stabilises the carboxylate anion and hence increases the acidity of carboxylic acid.
   (c) Electron-withdrawing substituent destabilised the carboxylate anion and hence decreases the acidity of carboxylic acid.
   (d) The substituent —OH makes benzoic acid a weaker acid.

28. Which of the following statements are **not** correct?
   (a) The substituent —Cl makes benzoic acid a stronger acid.
   (b) Acid-weakening groups are the ones that deactivate the benzene ring towards electrophilic substitution.
   (c) Acid-strengthening groups are the one that activate the benzene ring towards electrophilic substitution.
   (d) Alpha halogenation of aliphatic carboxylic acid is known as Hell-Volhard-Zelinsky reaction.

29. Which of the following statements are correct?
   (a) The group  is known as acyl group.
   (b) The acid amides has quite high boiling point as compared to acid chlorides.
   (c) The acid derivatives are hydrolyzed more readily in either alkaline or acidic solution than in neutral solution.
   (d) Toward nucleophilic attack, acid chlorides are more reactive than alkyl chloride.

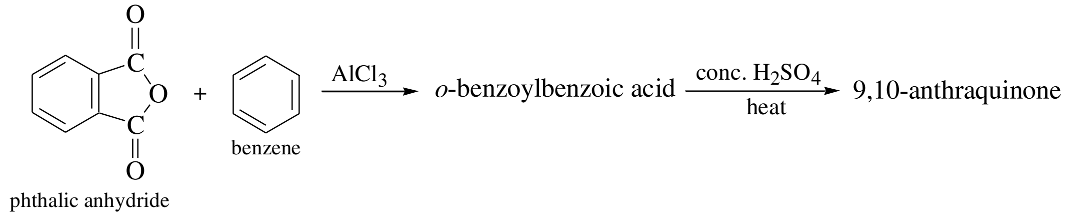
30. Which of the following statements are correct?
   (a) Toward nucleophilic attack, amides are more reactive than amines.
   (b) Toward nucleophilic attack, esters are more reactive than ethers.
   (c) The most reactive derivatives of carboxylic acids are acid chlorides.
   (d) Aromatic acid chlorides are considerably more reactive than the aliphatic acid chlorides.

31. Which of the following statements are **not** correct?
   (a) The molecular structure of ketene is $CH_2{=}C{=}O$.
   (b) Amides undergo Hofmann degradation to give amines.
   (c) The reaction between carboxylic esters and Grignard reagents produces secondary alcohols.
   (d) The reaction between RCOOR′ and R″MgX produces an alcohol  $R-\underset{\displaystyle R'}{\underset{|}{CH}}-OH$.

32. Which of the following statements are correct?
   (a) Calcium salt of a carboxylic acid produces a compound containing CO group on heating.
   (b) Formic acid on heating produces CO_2 and H_2.

(c) Formic acid on treating with concentrated H_2SO_4 produces CO and H_2O.
(d) K_a of *p*-nitrobenzoic acid is smaller than that of *p*-hydroxybenzoic acid.

33. Which of the following statements are
(a) *o*-Hydroxybenzoic acid is more acidic than benzoic acid.
(b)



(c) The rate of alkaline hydrolysis of methyl acetate is larger than that of ethyl acetate. This is due to the steric effect.
(d) The rate of alkaline hydrolysis of methyl formate is smaller than that of methyl acetate.

34. Which of the following order of acid strengths are
(a) $\mathrm{p}K_a^\circ(H_2C{=}CHCH_2COOH) < \mathrm{p}K_a^\circ(CH_3CH_2COOH)$
(b) $\mathrm{p}K_a^\circ(H_2C{=}CHCH_2COOH) > \mathrm{p}K_a^\circ(CH_3CH_2COOH)$
(c) $\mathrm{p}K_a^\circ(CH_3COCH_2COOH) < \mathrm{p}K_a^\circ(CH_3CH_2COOH)$
(d) $\mathrm{p}K_a^\circ(CH_3COCH_2COOH) > \mathrm{p}K_a^\circ(CH_3CH_2COOH)$

35. Which of the following dicarboxylic acids form cyclic ketone on heating?
(a) $HOOC(CH_2)_2COOH$ (b) $HOOC(CH_2)_3COOH$
(c) $HOOC(CH)_4COOH$ (d) $HOOC(CH_2)_5COOH$

Linked Comprehension Type

1. The acid-weakening or acid-strengthening effect of *para* substituent in benzoic acid depends whether it is ring activator or deactivator. Predict the acidity of the compound in the following three questions.

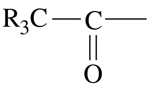
(i) Identify the substituent leading to the maximum increase in $\mathrm{p}K_a^\circ$ value of benzoic acid.
(a) —OH (b) $—OCH_3$ (c) $—CH_3$ (d) —Br

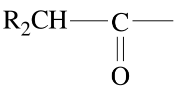
(ii) Identify the substituent leading to the maximum decrease in $\mathrm{p}K_a^\circ$ value of benzoic acid.
(a) —Cl (b) —CHO (c) —CN (d) $—NO_2$

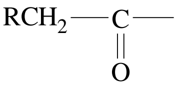
(iii) Identify the substituent leading to the maximum increase in the value of K_a of benzoic acid.
(a) $—OCH_3$ (b) $—NH_2$ (c) —CN (d) $—CH_3$

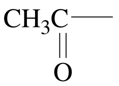
2. The relative stability of carboxylic acid derivatives is largely decided by steric and electronic factors. Identify the correct statements in the following three questions.

(i) Which of the following carbonyl group attached to the same acid derivative is most reactive towards nucleophilic acyl substitution reaction?

(a) 
$R_3C{-}\underset{\underset{O}{\|}}{C}{-}$

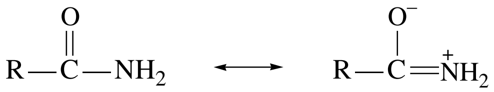
(b) 
$R_2CH{-}\underset{\underset{O}{\|}}{C}{-}$

(c) 
$RCH_2{-}\underset{\underset{O}{\|}}{C}{-}$

(d) 
$CH_3\underset{\underset{O}{\|}}{C}{-}$

(ii) Electronically, the more stronger polar acid derivative is attacked more readily than the less polar acid derivative. Based on this, identify the order of reactivity in the following carboxylic acid derivatives?
(a) $RCONH_2 > RCOOR' > RCOCl$ (b) $RCONH_2 > RCOCl > RCOOR'$
(c) $RCOCl > RCONH_2 > RCOOR'$ (d) $RCOCl > RCOOR' > RCONH_2$

(iii) Which of the following statements regarding the activity of carboxylic acid derivative is **not** correct?
(a) Any factor that raises energy difference between the carboxylic acid derivative and the transition state decreases the reaction rate.
(b) Amide are least reactive because of resonance stabilization of their ground state.


$$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \longleftrightarrow R{-}\overset{\overset{O^-}{|}}{C}{=}\overset{+}{N}H_2$$

The loss of this resonance in the transition state results in the enhancement of energy difference between amide and its transition state
(c) It is possible to transform a more stable acid derivative to a lesser stable acid derivative.
(d) In nature, only ester and amides and not anhydride and acid chlorides occur freely.

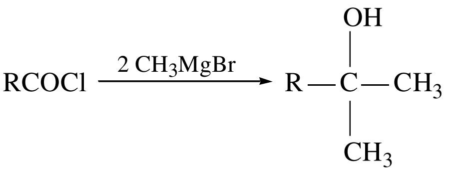
3. In the following reactions, identify the reaction not shown by carboxylic acid derivatives.

(i) Which of the following reactions is **not** correctly depicted?

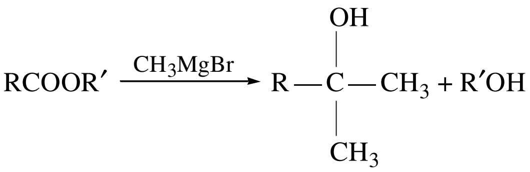
(a) $RCOCl \xrightarrow[2.\ H_3O]{1.\ LiAlH_4,\ ether} RCH_2OH$ (b) $RCOOCOR \xrightarrow{LiAlH_4} 2RCH_2OH$

(c) $RCOOR' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$ (d) $RCONH_2 \xrightarrow[ether]{LiAlH_4} RCH_2OH$

(ii) Which of the following products cannot be isolated when Grignard reagent reacts with carboxylic acid derivatives?

(a) 

$RCOCl \xrightarrow{2\ CH_3MgBr} R-\overset{OH}{\underset{CH_3}{C}}-CH_3$

(b) 

$RCOOR' \xrightarrow{CH_3MgBr} R-\overset{OH}{\underset{CH_3}{C}}-CH_3 + R'OH$

(c) $R-C{\equiv}N \xrightarrow{CH_3MgBr} RCOCH_3 + NH_3$ (d) $RCOCl \xrightarrow{CH_3MgBr} RCOCH_3$

(iii) Which of the following conversions cannot be carried out?

(a) $RCONH_2 \xrightarrow{SOCl_2} RCOCl$ (b) $RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$

(c) $RCONH_2 \xrightarrow{Br_2/KOH} RNH_2$ (d) $RCONH_2 \xrightarrow{H^+} RCHOOH + NH_4^+$

4. The Hofmann rearrangement of amide is shown by carboxylic acid amide. Identify the correct choice in the following.

(i) The reagent used in carrying out Hofmann rearrangement is

(a) Bromine in acidic medium (b) Bromine in alkaline medium

(c) NaBr in aqueous medium (d) NaBr in acidic medium

(ii) Which of the following species is **not** formed in the intermediate steps?

(a) RCONHBr (b) $RCONBr_2$ (c) RCON (d) $R-N{=}C{=}O$

(iii) The end product is

(a) an amine (b) an isocycanate (c) acyl nitrene (d) a nitrile

5. Considering the four dicarboxylic acids, namely, oxalic acid, malonic acid, succinic acid and glutaric acid, identify the correct answer in the following three questions.

(i) Which acid is expected to have the maximum difference in the values of pK°_{a2} and pK°_{a1}?

(a) Oxalic acid (b) Malonic acid (c) Succinic acid (d) Glutaric acid

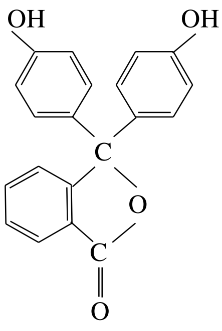
(ii) Which acid is expected to have the minimum difference in the values of pK°_{a2} and pK°_{a1}?

(a) Oxalic acid (b) Malonic acid (c) Succinic acid (d) Glutaric acid

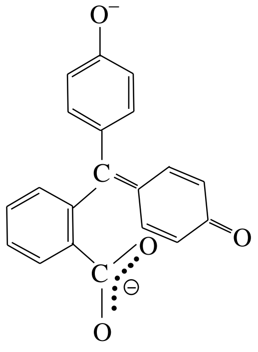
(iii) Which acid is expected to have the largest value of pK°_{a2}?

(a) Oxalic acid (b) Malonic acid (c) Succinic acid (d) Glutaric acid

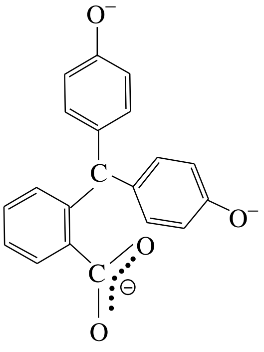
6. Phenolphthalein is obtained by condensing phthalic acid with two equivalents of phenol in anhydrous $ZnCl_2$. It can exist in the following three structures depending upon the pH of the solution.



(colourless)
I



(red)
II



(colourless)
III

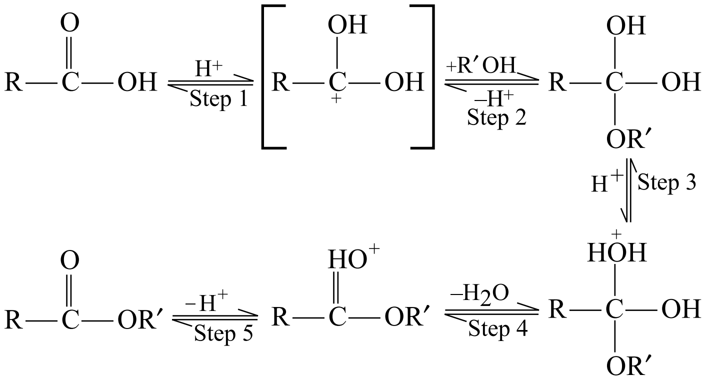
Answer the following questions.

(i) In strongly acidic solution, phenolphthalein predominantly exists as
(a) structure I
(b) structure II
(c) structure III
(d) a mixture of 50% contribution from each of I and II

(ii) In strongly alkaline medium, phenolphthalein predominantly exists as
(a) structure I
(b) structure Ii
(c) structure III
(d) a mixture of 33% contributions from the three structures

(iii) Around pH = 8, phenolphthalein predominantly exists as
(a) structure I
(b) structure II
(c) structure III
(d) a mixture of 50% contributions from structures II and III

7. The mechanism of esterification of a carboxylic acid is as follows.

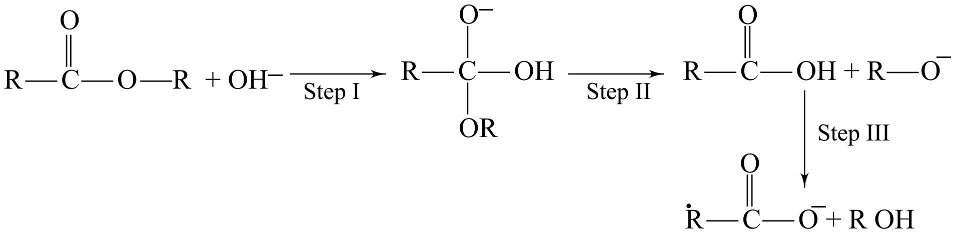


(i) The slow step in the mechanism is
(a) Step 1
(b) Step 2
(c) Step 3
(d) Step 5

(ii) The overall order of the reaction is
(a) 1
(b) 2
(c) 3
(d) zero

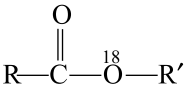
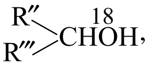
(iii) The rate of esterification with the three different alcohols CH_3OH, C_2H_5OH and $CH_3CH_2CH_2OH$ will follow the order
(a) $CH_3OH > C_2H_5OH > C_3H_7OH$
(b) $CH_3OH < C_2H_5OH < C_3H_7OH$
(c) $CH_3OH > C_3H_7OH > C_2H_5OH$
(d) $C_2H_5OH > C_3H_7OH > CH_3OH$

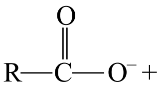
8. A mechanism for base-promoted hydrolysis of an ester is as follows.

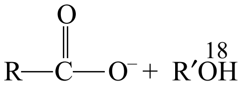


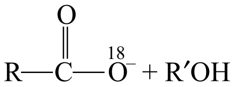
(i) Which of the following steps is/are a slow step?
(a) Step I
(b) Step II
(c) Step III
(d) Steps I and II

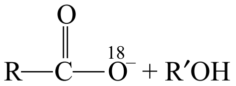
(ii) Which of the following steps is/are not a reversible step?
(a) Step I
(b) Step II
(c) Step III
(d) All the three steps

(iii) If an ester  $R{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{18}{O}{-}R'$ form a chiral alcohol  $\overset{R''}{\underset{R'''}{>}}CH\overset{18}{O}H$, then the products of hydrolysis are

(a)  $R{-}\overset{\overset{\large O}{\|}}{C}{-}O^-$ + $R'\overset{18}{O}H$ with retention of configuration of R′

(b) 
$R-\overset{\overset{O}{\|}}{C}-O^- + R'\overset{18}{O}H$ with inversion of configuration of R′

(c) 
$R-\overset{\overset{O}{\|}}{C}-\overset{18}{O}^- + R'OH$ with retention of configuration of R′

(d) 
$R-\overset{\overset{O}{\|}}{C}-\overset{18}{O}^- + R'OH$ with inversion of configuration of R′

9. The product obtained on treating a haloacid with aq.NaOH depends on the position of halogen with respect to —COOH group. Identify the correct product obtained in the following haloacids.

(i) The major product obtained on treating α-haloacid $CH_3CH_2CHBrCOOH$ with aq. NaOH is

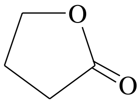
(a) $CH_3CH{=}CHCOOH$
(b) $CH_3CH_2CH(OH)COOH$
(c) $CH_2{=}CHCH_2COOH$
(d) $CH_3CH{=}CH_2$

(ii) The major product obtained on treating β-haloacid $CH_3CHBrCH_2COOH$ with aq. NaOH is

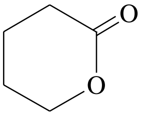
(a) $CH_2{=}CHCH_2COOH$
(b) *trans*-$CH_3CH{=}CHCOOH$
(c) *cis*-$CH_3CH{=}CHCOOH$
(d) $CH_3CHOHCH_2COOH$

(iii) The major product obtained on treating γ-haloacid $BrCH_2CH_2CH_2COOH$ with aq. NaOH is

(a) $CH_2{=}CHCH_2COOH$
(b) $HOCH_2CH_2CH_2COOH$

(c) 

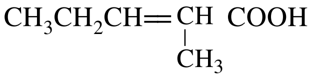
(γ-Butyrolactone)

(d) 

(δ-Valerolactone)

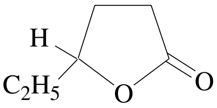
10. The product obtained on heating a hydroxyacid depends on the position of hydroxyl group with respect to —COOH group. Identify the correct product obtained on heating the following hydroxyacid?

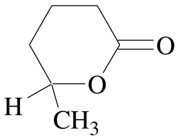
(i) The major product obtained on heating β-hydroxyacid $CH_3(CH_2)CHOHCH_2COOH$ is

(a) *cis*-$CH_3(CH_2)_2CH{=}CHCOOH$
(b) $CH_3CH_2CH{=}CHCH_2COOH$
(c) 
$CH_3CH_2CH{=}\underset{\underset{CH_3}{|}}{C}H\ COOH$
(d) *trans*-$CH_3(CH_2)_2CH{=}CHCOOH$

(ii) The major product obtained on heating γ-hydroxyacid $CH_3CH_2CHOHCH_2CH_2COOH$ is

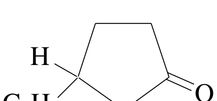
(a) $CH_3CH{=}CHCH_2CH_2COOH$
(b) $CH_3CH_2CH{=}CHCH_2COOH$

(c) 

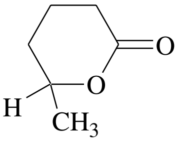
(d) 

(iii) The major product obtained on heating γ-hydroxyacid $CH_3CHOH(CH_2)_3COOH$ is

(a) $CH_2{=}CH(CH_2)_3COOH$
(b) $CH_3CH{=}CH(CH_2)_2COOH$

(c) 

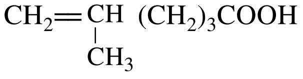
(4-Ethyl-γ-butyrolactone)

(d) 

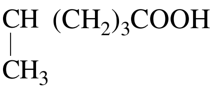
(5-methyl-δ-valerolactone)

(iv) The major product obtained on heating ∈-hydroxyacid $HOCH_2(CH_2)_4COOH$ is

(a) $CH_2{=}CH(CH_2)_3COOH$

(b) 
$CH_2{=}\underset{\underset{CH_3}{|}}{C}H\ (CH_2)_3COOH$

(c) a long chain of polymeric ester

(d) a mixture of $CH_2{=}CH(CH_2)_3COOH$ and 
$CH_2{=}\underset{\underset{CH_3}{|}}{C}H\ (CH_2)_3COOH$

11. The product obtained on heating a straight-chain dicarboxylic acid depends on the length of the chain. Identify the correct choice in each of the three following questions

(i) The maximum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a cyclic anhydride is

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

(ii) The maximum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a cyclic alkanone is

(a) 2 (b) 3 (c) 4 (d) 5

(iii) The manimum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a linear polymeric anhydride is

(a) 2 (b) 4 (c) 5 (d) 6

12. Given are the following reactions.

$$CH_3COCH_3 \xrightarrow{700\ °C} A \xrightarrow{CH_3COOH} B \xrightarrow[\text{distil}]{RCOOH} C$$

Based on these reactions, answer the following three question.

(i) The compound A is

(a) $CH_3CHOHCH_3$ (b) CH_3COCH_3 (c) $H_2C{=}CHCH_3$ (d) $H_2C{=}C{=}O$

(ii) The compound B is

(a) H_3CCOCH_3 (b) H_3CCHO (c) $(CH_3CO)_2O$ (d) $CH_4 + CO_2$

(iii) The compound C is

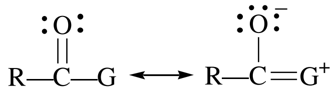
(a) $CH_3COOCOCH_3$ (b) RCOOCOR (c) $CH_3COOCOR$ (d) $RCOCH_2OH$

Assertion and Reason Type

Given below are questions, each containing two statements. Answer each question based on the following key.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is correct and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	Acetate ion is more basic than the methoxide ion.	The acetate ion is resonance stabilized. (1994)
2.	p-$NO_2C_6H_4COOH$ is more acidic than the *meta* isomer.	Through resonance p-NO_2 induces positive charge on the ring C beaing the COO– while m-NO_2 induces positive charge on the ring C *ortho* to the C bearing the COO^-.
3.	p-$ClC_6H_4COO^-$ is more acid than the *meta* isomer.	Only inductive effect is operating, the effect is stronger acid-strengthening effect from the nearer *meta* position.
4.	3-Butynoic acid is stronger than 3-butenoic acid.	$—C{\equiv}C—$ is better electron withdrawing group than $\rangle C{=}CH_2 \langle$.
5.	pK°_{a1} of dicarboxylic acid $HOOCCH_2CH_2COOH$ is smaller than the pK°_a of $CH_3CH_2CH_2COOH$.	HOOC group has electron withdrawing effect on the second HCOOH group in the dicarboxylic acid making its pK°_a less than the pK°_a value of butanoic acid.
6.	It is more efficient to prepare an ester by the route acid → acyl chloride → ester, rather than acid-ester.	The reaction of acid with alcohol is slower.
7.	RCOCl can be converted into $(RCO)_2O$ but the reverse of this is not feasible.	A more reactive acyl derivative can be converted into less reactive derivative and not vice versa.
8.	The relative reactivity of acyl derivative is governed by resonance stabilization	The greater the degree of delocalization, the less reactive is acyl derivative RCOG.



$$R—\overset{:\ddot{O}:}{\overset{\|}{C}}—G \longleftrightarrow R—\overset{:\ddot{O}:^-}{\overset{|}{C}}{=}G^+$$

9.	$RCONH_2$ is most reactive and RCOCl is least reactive.	NH_2 allows maximum resonance stabilization while X has little or no delocaliztion.
10.	Alkyl halides are much more reactive than RCOCl in undergoing nucleophilic reaction.	C in C═O is more positive than C in C—X.
11.	H bonded to N in 1° and 2° amides is weakly acidic.	The amidate anoin formed by extracting H bonded to N is stabilized by delocalization.

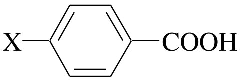
Matrix Match Type

1. Column I lists some of the acids. Their pK_a° values are given in Column II. Match correctly the acids in Column I with their pK_a° values given in Column II.

Column I	**Column II**
(a) HCOOH	(p) 3.44
(b) CH_3COOH	(q) 4.21
(c) PhCOOH	(r) 3.75
(d) $p\text{-}NO_2C_6H_4COOH$	(t) 4.76

2. Column I lists some of the substituted benzoic acid. Their pK_a° values are given in Column II. Match the acids in Column I with their pK_a° values given in Column II.

Column I	**Column II**
(a) *p*-$CH_3C_6H_4COOH$	(p) 4.12
(b) *m*- $CH_3C_6H_4COOH$	(q) 4.28
(c) *p*-HOC_6H_4COOH	(r) 4.35
(d) *m*-HOC_6H_4COOH	(t) 4.54

3. Column I lists substitutent X in  and pK_a° values are given in Column II. Match correct entries in Column I and Column II.

Column I	**Column II**
(a) —OH	(p) 3.55
(b) —CN	(q) 4.55
(c) —Cl	(r) 4.46
(d) —H	(s) 3.96
(e) —OCH_3	(t) 4.19

ANSWERS

Straight Objective Type

1. (b)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (a)	**7.** (b)
8. (a)	**9.** (b)	**10.** (c)	**11.** (d)	**12.** (d)	**13.** (a)	**14.** (b)
15. (c)	**16.** (d)	**17.** (c)	**18.** (d)	**19.** (b)	**20.** (a)	**21.** (c)
22. (c)	**23.** (a)	**24.** (c)	**25.** (c)	**26.** (b)	**27.** (d)	**28.** (c)
29. (d)	**30.** (d)	**31.** (b)	**32.** (c)	**33.** (a)	**34.** (b)	**35.** (d)
36. (d)	**37.** (b)	**38.** (a)	**39.** (c)	**40.** (c)	**41.** (b)	**42.** (a)
43. (c)	**44.** (a)	**45.** (b)	**46.** (c)	**47.** (a)	**48.** (b)	**49.** (a)
50. (a)	**51.** (b)	**52.** (c)	**53.** (c)	**54.** (b)	**55.** (c)	**56.** (b)
57. (c)	**58.** (b)	**59.** (b)	**60.** (a)	**61.** (a)	**62.** (a)	**63.** (d)
64. (b)	**65.** (c)	**66.** (a)	**67.** (c)	**68.** (d)	**69.** (a)	

Multiple Correct Choice Type

1. (a), (b) **2.** (a), (b) **3.** (a), (c) **4.** (c), (d)
5. (a), (c) **6.** (a), (b) **7.** (a), (c), (d) **8.** (b), (c), (d)
9. (c), (d) **10.** (a), (d) **11.** (a), (c), (d) **12.** (a), (b), (c)
13. (a), (b), (d) **14.** (b), (c), (d) **15.** (a), (b), (c), (d) **16.** (c), (d)
17. (b), (c) **18.** (a), (c) **19.** (a), (c), (d) **20.** (a), (b), (c)
21. (a), (c) **22.** (a), (b), (c) **23.** (b), (c), (d) **24.** (a), (b), (d)
25. (b), (d) **26.** (a), (c) **27.** (b), (c) **28.** (b), (c)
29. (a), (b), (c), (d) **30.** (a), (b), (c) **31.** (c), (d) **32.** (a), (b), (c)
33. (a), (b), (c) **34.** (a), (c) **35.** (c), (d)

Linked Comprehension Type

1. **(i)** (a) **(ii)** (d) **(iii)** (c)
2. **(i)** (d) **(ii)** (d) **(iii)** (c)
3. **(i)** (d) **(ii)** (d) **(iii)** (a)
4. **(i)** (b) **(ii)** (b) **(iii)** (a)
5. **(i)** (a) **(ii)** (d) **(iii)** (b)
6. **(i)** (a) **(ii)** (c) **(iii)** (b)
7. **(i)** (b) **(ii)** (c) **(iii)** (a)
8. **(i)** (a) **(ii)** (c) **(iii)** (a)
9. **(i)** (b) **(ii)** (b) **(iii)** (c)
10. **(i)** (d) **(ii)** (c) **(iii)** (d) **(iv)** (c)
11. **(i)** (b) **(ii)** (c) **(iii)** (d)
12. **(i)** (d) **(ii)** (c) **(iii)** (b)

Assertion and Reason Type

1. (d) **2.** (a) **3.** (d) **4.** (b) **5.** (a) **6.** (b) **7.** (b)
8. (a) **9.** (d) **10.** (d) **11.** (a)

Matrix Match Type

1. (a)-(r); (b)-(s); (c)-(q); (d)-(p) **2.** (a)-(r); (b)-(q); (c)-(s); (d)-(p)
3. (a)-(q); (b)-(p); (c)-(s); (d)-(t); (e)-(r)

Hints and Solutions

Straight Objective Type

1. The order of acid strength is RCOOH > HOH > ROH > HC≡CH

Electron-releasing alkyl group R in ROH makes it lesser acidic than H_2O.

2. The base strength follows the reverse order as shown by the corresponding acids. The acids are RH, NH_3, HC≡CH and RCOOH. Its order is RCOOH > HC≡CH > NH_3 > RH. Hence, the correct order of the conjugate bases is $RCOO^- < HC{\equiv}C^- < NH_2^- < R^-$.

3. Nearer the chlorine to the —COOH group, stronger the acidity. Hence, the correct order is

$$CH_3CH_2CHClCOOH > CH_3CHClCH_2COOH > CH_2ClCH_2CH_2COOH$$

4. Larger the electronegativity of halogen, stronger the acidity. Hence, the correct order is

$$FCH_2COOH > BrCH_2COOH > ICH_2COOH$$

5. Acetic acid differs from formic acid in that acetic acid is stable to heat.

6. Tollens reagent gives white precipitate with methanoic acid and not with ethanoic acid.

7. Electron-releasing group makes benzoic acid a weaker acid while electron-attracting group makes it a stronger acid. Stronger the acid, lesser the value of pK_a°. Hence, the correct order is

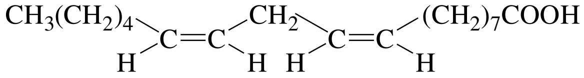
$$pK_a^\circ(p\text{-}O_2NC_6H_4COOH) < pK_a^\circ(C_6H_5COOH) < pK_a^\circ(p\text{-}HOC_6H_4COOH)$$

8. Palmitic acid is $CH_3(CH_2)_{14}COOH$.

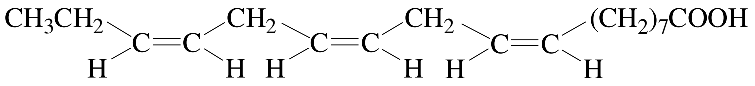
9. Stearic acid is $CH_3(CH_2)_{16}COOH$.

10. Oleic acid is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

11. Linoleic acid is

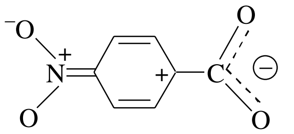


12. Linolenic acid is



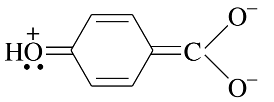
13. Carboxylic acids are stronger acids than phenols.
Methyl group is an electron-releasing group, it weakens the acidity of carboxylic acid.
Chlorine is electron-attracting group, it strengthens the acidity of phenol. Hence, the correct acidity order of the given compounds is (III) > (IV) > (II) > (I)

14. The nitro group interacts with the phenyl ring and thereby induces some positive charge on the ring bearing the COO^- causing a strong electron-withdrawing inductive effects on COO^- group. This effect is base-stabilizing and thus acid strengthening.



15. Due to resonance interaction, *p*-NO_2 generates a positive charge on C bearing —COOH group. *m*-NO_2 generates the positive charge at the *ortho* position to the carbon. Thus, *m*-$NO_2C_6H_4COOH$ is less acidic than its *para* isomer.
Chlorine geneatates a negative charge on C bearing —COOH group. However, chlorine also has strong electron-withdrawing inductive effect on —COOH group which stabilizes the base and thus strengthening the acid. Its effect is stronger from *meta* position (due to more near to the —COOH) as compared to the *para* position. Thus making *p*-ClC_6H_4COOH weaker than its *meta* isomer.

16. At *para* position, —OH places negative charge on the carboxylate group and thus making it



weaker than bezoic acid. This effect predominates over its electron-withdrawing acid strengthening inductive effect. However, at *meta* position, there is no such resonance effect and only inductive effect operates and because of its nearness to the COOH group, *meta* isomer is stronger acid than its *para* isomer.

17. —NO_2 is acid strengthening. Its affect at *para* position is more than at *meta* position (see Q.15). *Ortho*-isomer is most acidic due to the *ortho* effect.

18. *Meta* hydroxy is stronger than *para* isomer (see Q.16). Because of the *ortho effect*, *ortho* isomer is the strongest acid.

19. Increasing crowdiness near the site of esterification decreases the rate of esterification. Hence, the correct order is 1° > 2° > 3°.

20. same as Q.19. The correct order is $RCH_2COOH > R_2CHCOOH > R_3CCOOH$

21. α-Hydrogen is replaced by chlorine. The product is $CH_3CH(Cl)COOH$.

22. Heating calcium benzoate produces benzophenone.

23. Heating calcium formate along with calcium benzoate produces benzaldehyde.

24. The products are CO and H_2O. $HCOOH \xrightarrow{\text{Conc. } H_2SO_4} CO + H_2O$.

25. Heating calcium acetate along with calcium benzoate produces acetophenone.

26. The Hell-Volhard-Zelinsky reaction is used in the synthesis of α-haloacids.

27. CO_2 comes from bicarbonate.

28. $LiAlH_4$ can be used to reduce RCOOH.

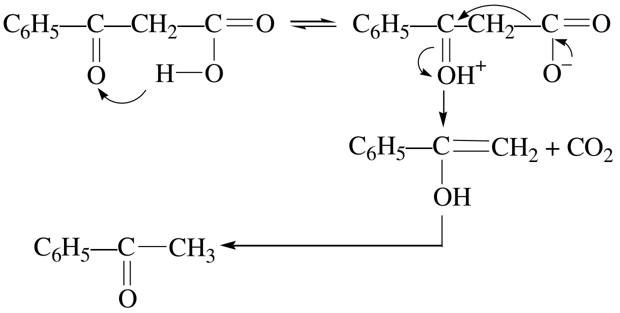
29. BF_3/THF followed by H_3O^+ can be used to reduce RCOOH to RCH_2OH.

30. (Z)–$CH_3CH{=}CHCH_2COOH$ is not reduced to corresponding alcohol as the hydrogenation of double bond also occurs.

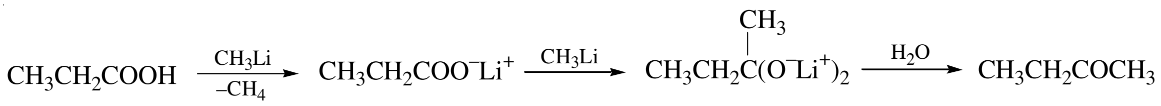
31. In *p*-$CH_3COC_6H_4COOH$, the CO group is also reduced by $LiAlH_4$.

32. *p*-$O_2NC_6H_4COOH$ is not reduced by $LiAlH_4$ to the corresponding 1° alcohol.

33. $BrCH_2CH_2CH_2COOH$ is not reduced by $LiAlH_4$ to the corresponding 1° alcohol.
34. Succinic acid ($HOOCCH_2CH_2COOH$) gives cyclic anhydride on heating.
35. $HOOC(CH_2)_4COOH$ gives cyclopentanone on heating.
36. $HOOC(CH_2)_6COOH$ gives a linear polymeric anhydride.
37. Attachement of R′OH to the protonated alcohol is the slowest step (i.e. choice b is correct)
38. *β*-Ketoacids are unstable acids. These readily undergo decarboxylation through a cyclic transition state.

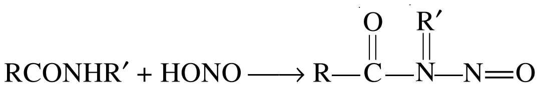


40. Bromine is lesser electronegative than fluorine. Bromine attached to β-carbon will cause least enhancement in the dissociation of halo substituted propanoic acid.
41. Carboxylic acids have relatively high boiling points because of hydrogen bonds. Their boiling points are somewhat higher than those of alcohols of comparable molar masses. Since there exists no hydrogen bondings in aldehydes, their boiling points are lower than those of corresponding alcohols.
42. BH_3/THF followed by H_3O^+ reduces only —COOH group without affecting —CO— group. $LiAlH_4$ reduces only —COOH group without affecting C=C group.
43. The reaction is



$$CH_3CH_2COOH \xrightarrow[-CH_4]{CH_3Li} CH_3CH_2COO^-Li^+ \xrightarrow{CH_3Li} CH_3CH_2\overset{\overset{CH_3}{|}}{C}(O^-Li^+)_2 \xrightarrow{H_2O} CH_3CH_2COCH_3$$

44. The order of reactivity is acid chloride > anhydride > ester.
45. The order of reactivity is anhydride > ester > amide.
46. The correct order is $Cl^- < RCOO^- < RO^-$.
47. The correct order is $Cl^- < RO^- < NH_2^-$.
48. Attachement of HNu: to the protonated acyl derivatives is the slowest step (i.e. choice b is correct).
49. The activity order is $RCOCl > RCON_3 > (RCO)_2O$. The order of reactivity decreases as the base strength of the leaving group increases.
50. 1° amide liberates N_2 when treated with HNO_2. $RCONH_2 + HONO \longrightarrow RCOOH + N_2 + H_2O$
51. 2° amide produces N-nitrosoamide when treated with HNO_2.



$$RCONHR' + HONO \longrightarrow R—\overset{\overset{O}{\|}}{C}—\overset{\overset{R'}{\|}}{N}—N{=}O$$

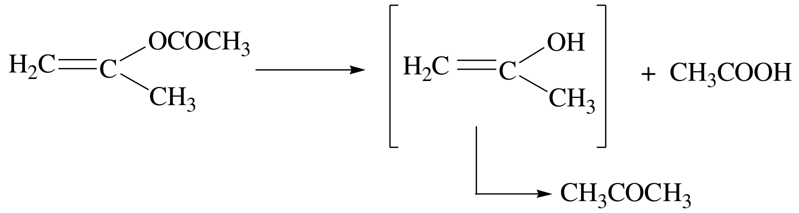
52. $CH_3CON(CH_3)C_2H_5$ does not react with HNO_2.
53. Electron-withdrawal group increasing reactivity of hydrolysis while the electron-releasing group decreases reactivity. The correct order is $p\text{-}O_2NC_6H_4COCl > PhCOCl > p\text{-}CH_3OC_6H_4COCl$.
54. The aqueous solution of amide acts as an acid. $RCONH_2 + H_2O \rightleftharpoons RCONH^- + H_3O^+$
55. $\Delta G°$ for the reaction $RNH_2 \xrightarrow{H^+} RNH_3^+$ is less (more negative) than that of the reaction $RCONH_2 \xrightarrow{H^+} RCONH_3^+$.
56. The weaker the base, the greater its leaving-group ability. Alternatively, the stronger the conjugate acid, the greater the leaving-group ability of the base. The strength of the conjugate acid is

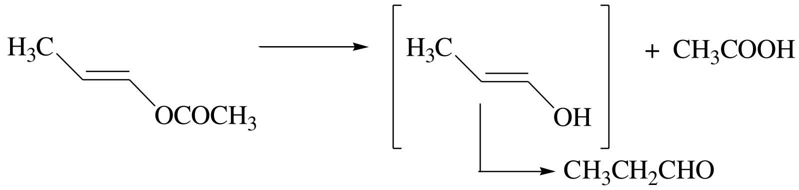
$$HOSO_2CF_3 > HOSO_2Me > HOAc > HOMe$$

The same is the order of leaving-group ability of the base, i.e.,

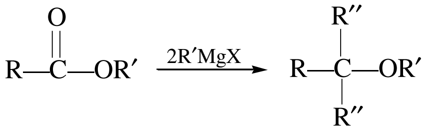
$$—OSO_2CF_3 > —OSO_2Me > —OAc > —OMe$$

57. The products of acid hydrolysis are:





Only Fehling's solution can distinguish between aldehyde and ketone.

58. The reaction may be represented as 

$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'} \xrightarrow{2\mathrm{R'MgX}} \mathrm{R{-}\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R''}{|}}{C}}{-}OR'}$$

59. HN_3 is slightly more acidic than CH_3COOH. N_3^- is slightly less basic than CH_3COO^-, and is a slightly better-leaving group. Thus, $RCON_3$ is less reactive than RCOCl but a little more reactive than the anhydride $(RCO)_2O$.

61. Increasing crowdiness near the site of hydrolysis decreases the rate of alkaline hydrolysis. Hence the correct order is $CH_3COOCH_3 > CH_3COOC_2H_5 > CH_3COOC_3H_7$

62. The correct order of alkaline hydrolysis is $CH_3COOC_3H_7 > CH_3COOCH(CH_3)_2 > CH_3COOC(CH_3)_3$

63. The correct order of alkaline hydrolysis is $HCOOCH_3 > CH_3COOCH_3 > (CH_3)_2CHCOOCH_3$

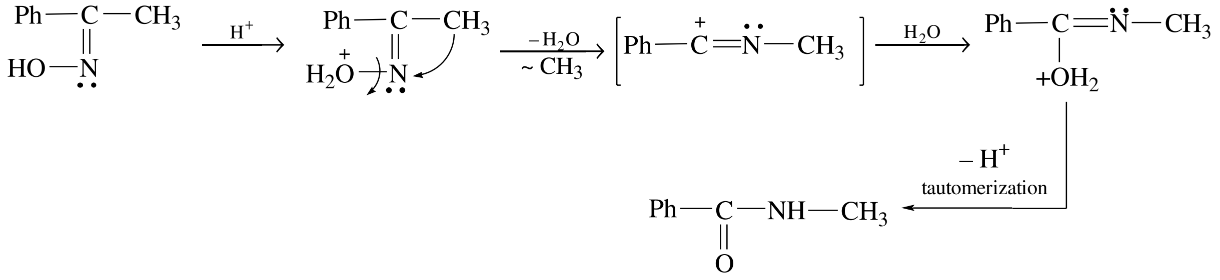
64. The correct order of alkaline hydrolysis is $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$

65. Dialcohol is produced.

66. $LiAlH_4$ does not reduce C=C bond.

67. The correct order is p-$O_2NC_6H_4COCl$ > PhCOCl > p-$CH_3OC_6H_4COCl$.—NO_2 group decreases ΔH^+ while —OCH_3 group increases $\Delta H^\ddagger$ as compared to PhCOCl.

68. The mechanism is



Multiple Correct Choice Type

7. (a) Formic acid does not contain α-hydrogen atom.

(c) The boiling point of carboxylic acid is higher than that of alcohol of comparable molar mass because of more extensive hydrogen bonding.

(d) The —CN group is also counted in the carbon chain. Hence, its name is butanenitrile.

8. (a) The product obtained is RCH_2OH.

(c) This is due to the resonating effect amongst the two CO groups.

(d) The stabilization is due to the dispersal of negative charge of the carboxylate anion.

9. (a) At the *meta* position, the —OH group has an electron-withdrawing acid-strengthening inductive effect.

(b) At the *para* position, the —OH group has an electron-releasing acid-weakening resonance effect.

(c) At both these positions, inductive effect of Cl is more predominant resulting in the acid-strengthening effect.

10. (a) The products formed besides the acid chloride are gases when thionyl chloride is used. This helps in separating acid chloride more readily. Because of its low boiling point, $SOCl_2$ can be removed by distillation.

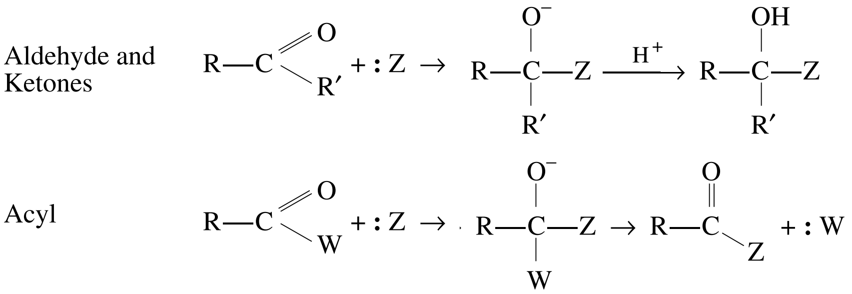
$$RCOOH + SOCl_2 \xrightarrow[\text{reflux}]{} ROCl + SO_2 + HCl; \qquad RCOOH + PCl_5 \xrightarrow[\text{heat}]{} RCOCl + POCl_3 + HCl$$

(b) The presence of bulky groups near the site of reaction slows down esterification. Hence, the ease of esterification is CH_3OH > 1° > 2°.

11. (a) The acyl compounds contain $\overset{|}{\mathrm{RCO}}$ group.

(b) Because of $>C=O$ group, acyl compounds undergo nucleophilic substitution reactions because carbonyl carbon is slightly positively charged.

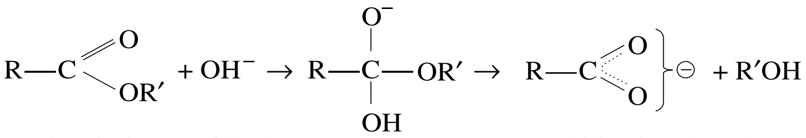
(d)



12. (c) As both the steps are fast and essentially irreversible.

(d) The given structure contains seven membered ring which is not stable as the five and six membered rings. Instead of producing cyclic anhydride, adipic acid loses carbon dioxide and form cyclopentanone.

13. (a) The reaction is



The reaction is irreversible because the resonance-stabilised carboxylate anion shows little tendency to react with an alcohol.

(b) The bond broken is the bond between oxygen and acyl carbon.

(d) An electron-withdrawing group stabilises the intermediate carboxylate anion, hence speeds up the rate of hydrolysis.

14. (a) An electron-releasing group destabilises the intermediate carboxylate anion, hence decreases the rate of hydrolysis.

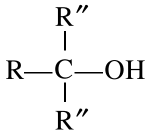
(b) The steric effect and the electron-releasing effect of alkyl group decreases the rate of hydrolysis.

(c) The steric effect will cause the decrease in the rate of hydrolysis.

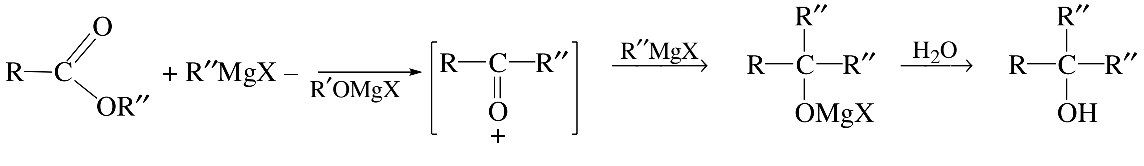
15. (b) It follows first order kinetics and is thus S_N1.

(c) All steps involved in the acid hydrolysis are reversible.

(d) The alcohol produced is



$$R-\underset{R''}{\overset{R''}{C}}-OH$$



16. (a) With NaOH, ammonia gas is released. (b) The gases released are N_2 and CO_2.

17. (a) As the distance between the two —COOH groups is increased, the inductive effect of one on the other weakens. The —COOH group is electron-withdrawing and thus it increases the acid strength. Hence HOOC—COOH is stronger than $HOOCCH_2COOH$.

(b) In malonic acid, the two —COOH group are more near to each other. Thus, the ability of —COOH to withdraw electrons from the second —COOH is more effective.

(c) The —COOH group is better electron-withdrawing as compared to —H.

(d) The correct order is $CH_3COOH < HOOCCH_2CH_2COOH < HOOCCH_2COOH$

18. (a) The correct order is $H_2SO_4 > CH_3COOH > H_2O > C_2H_5OH > HC{\equiv}CH$

(b) Crowding in the tetrahedral intermediates by bulky groups makes them less stable, and the corresponding transition states more difficult to achieve, thus decreasing reaction rates.

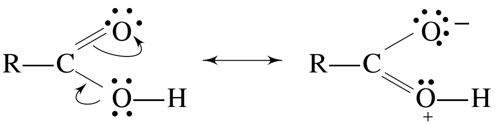
(c) Plants and animals biosynthesise fatty acids by building up CH_3COOH units.

(d) The uniform zig-zag chains of the saturated acids can pack together tightly in the solid. The kink at the *cis* position of the chain diminishes the close packing, thereby lowering the melting point of the *cis* isomer.

19. (a) A *trans* double-bond does not interfere with the uniform zig-zag and close packing is permitted. This makes its melting point higher than its *cis* isomer.

(b) Counting starts with COOH group. The correct name is *cis*, *cis*, *cis*-9,12,15-octadecatrienoic acid.

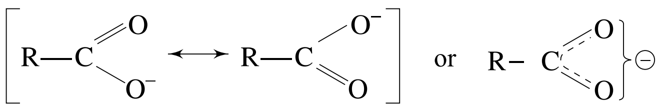
(d) Because of resonating structures



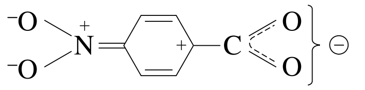
the C=O bond acquires some single-bond character, making its length longer than in RCHO.

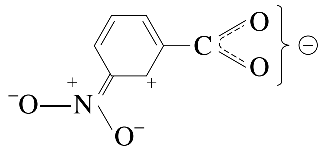
20. (a) In RCOOH there is positive charge on the C=O carbon causing this C to be less electrophilic and less reactive toward nucleophiles.

(d) The conjugate base of RCOOH is stabilised due to the resonance effect while no such stabilisation occurs in the conjugate base of peroxy acid.



21. (a) The resonance structures of *para*- and *meta*-nitrobenzoate anion are as follows.

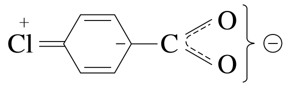


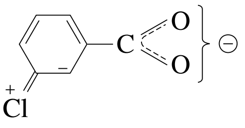


In *para* isomer, the resonance interaction of the NO_2 with the ring induces some positive charge on the ring carbon bearing the COO^-. This induces a strong electron-withdrawing inductive effect which stabilises the base and hence acid-strengthening.

In *meta* isomer, the positive charge is developed at the carbons *ortho* to the carbon bearing COO^-. Its power to withdraw electron from COO^- is less and thus the *meta* isomer is less acidic.

(b) The resonance structures of *para*- and *meta*-chlorobenzoic acid are as follows.





In *para* isomer, there is a negative charge on the ring carbon bearing COO^-. This makes para isomer less acidic than *meta* isomer in which negative charge is on the carbon *ortho* to the carbon bearing COO^-. Also, the electron-withdrawing inductive effect of chlorine is more in the *meta* isomer due to its proximity to COO^-

(c) Methyl group is electron-donating and acid-weakening. The *para* isomer places the negative charges on the ring carbon bearing COO^- while in *meta* isomer, this charge is on the carbon *ortho* to carbon bearing COO^-. This makes the *para* isomer less acidic than the *meta* isomer.

(d) Si is more electropositive and thus it has acid-weakening effect.

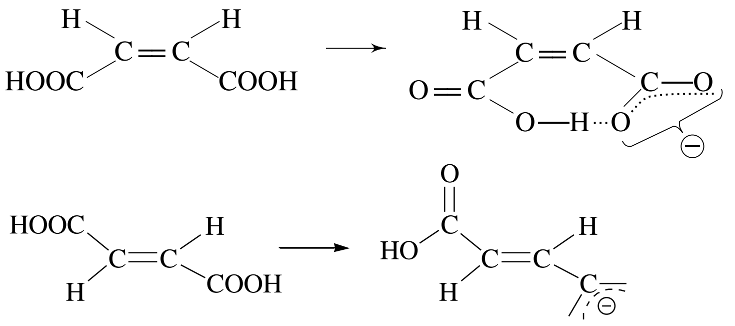
22. (a) The sp^2 hybridised carbon of —C$=$C— attracts the bonded electrons more than the sp^3 hybridised carbon does. Consequently. —C$=$C— is an acid-strengthening electron-withdrawing group.

(b) The $—COO^-$ of the branched acid is shielded from solvent molecules and cannot be stabilised as effectively as can an unhindered anion.

(c) In *trans* isomer, the $—COO^-$ is less shielded and is thus more stabilised by solvent.

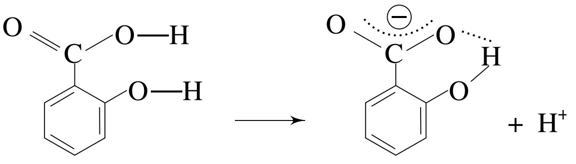
(d) The first ionization of a dicarboxylic acid is larger than that of monoalkylcarboxylic acid because of the electron-withdrawing COOH group of dicarboxylic acid. Hence, pK°_{a1} of dicarboxylic acid is smaller than pK° of monoalkylcarboxylic acid.

23. (a) The maleic acid is a stronger acid because of the stabilisation of its monoanion due to H-bonding between the *cis* COOH and COO^-. This is not present in the *trans* isomer (fumarate anion).



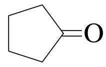
(b) H-bonding in maleate monoanion makes the removal of H more difficult as compared to fumarate monoanion where H-bonding is not present.

(c) H-bonding in salicylate ion makes the salicyclic acid more acidic than o-$H_3COC_6H_4COOH$.



stabilised due to
H-bonding

24. (c) Cyclic anhydride of adipic acid is not formed as there will be a lot of strain in the seven-member ring.

Instead, cyclopentanone is formed. $HOOC(CH_2)_4COOH \xrightarrow[\Delta]{}$  $=O + CO_2 + H_2O$

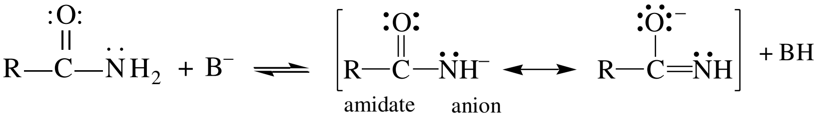
25. (a) Dehydration occurs intramolecularly rather than intermolecularly. $HCOOH \longrightarrow CO + H_2O$.

(b) A more reactive acid derivative can be converted to a less reactive one by reaction with the appropriate nucleophile.

(c) As the size of the substituent on the α-C increases, the tetrahedrally bound intermediate becomes more crowded. The greater the crowding, the large the $\Delta H^\ddagger$ of the transition state and the slower the reaction.

(d) Reaction of acid with alcohol is slower and the equilibrium must be shifted to the right side by removing a product. The acid under non-equilibrium conditions can be converted to acyl chloride (e.g. acid + SO_2Cl_2) which can then be converted to ester by reacting with an alcohol.

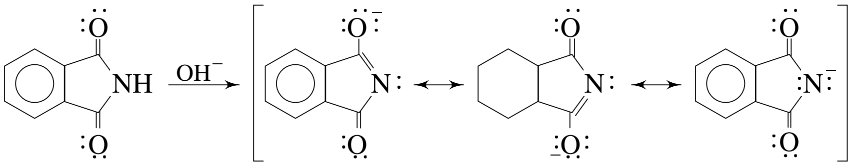
26. (b) Amides are much more acidic than NH_3 due to the stabilisation of amidate by delocalisation.

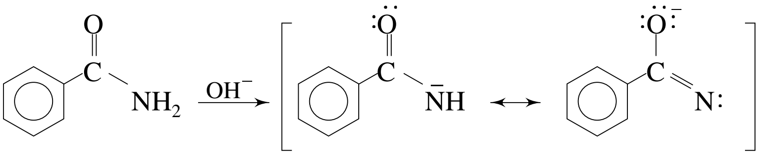


$$R—\overset{\overset{:O:}{||}}{C}—\ddot{N}H_2 + B^- \rightleftharpoons \left[R—\overset{\overset{:O:}{||}}{C}—\ddot{N}H^- \longleftrightarrow R—\overset{\overset{:\ddot{O}:^-}{|}}{C}=\ddot{N}H\right] + BH$$

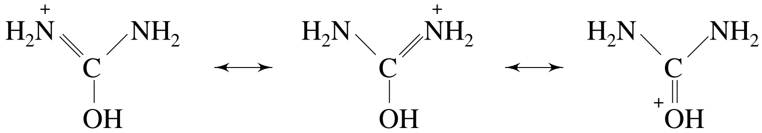
amidate anion

(c) Phthalimide has two carbonyl groups to stabilise the imide while benzamide has only one. There is more destabilisation in phthalimide.





(d) Urea is a monoacidic base and its protonated form exists as a resonance hybride.



27. (b) Electron-releasing substituent distabilised the carboxylate anion and hence decreases the acidity of acid.

(c) Electron-attracting substituent stabilizes the carboxylate anion and hence increases the acidity of acid.

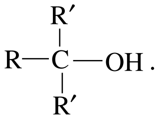
28. (b) Acid-weakening groups activate the benzene ring

(c) Acid-strengthening groups deactive the benzene ring.

29. (c) Alkaline solutions provide hydroxide ion, which acts as a strongly nucleophilic reagent; acid solutions provide hydrogen ion, which attaches to carbonyl oxygen and thus renders the molecule to be more susceptible to nucleophilic attack at carbonyl carbon.

30. (d) Aromatic acid chlorides are less reactive than the aliphatic acid chlorides.

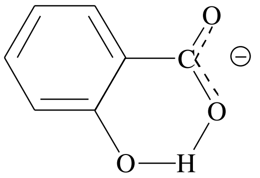
31. (c) A tertiary alcohol is produced. (d) The alcohol produced is



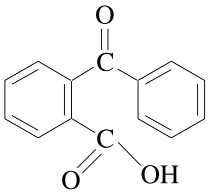
$R-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-OH$.

32. K_a of *p*-nitrobenzoic acid is larger than that of *p*-hydroxybenzoic acid.

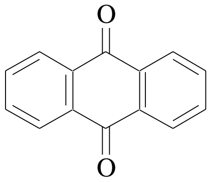
33. (a) This is because of more stabilization of anion due to intramolecular hydrogen bonding.



(b) The structures are



o-benzoylbenzoic acid



9, 10-anthraquinone

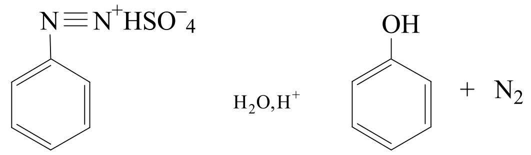
(d) The rate of alkaline hydrolysis of methyl formate is larger than that of methyl acetate. This is due to the more steric factor in methyl acetate.

CHAPTER 29

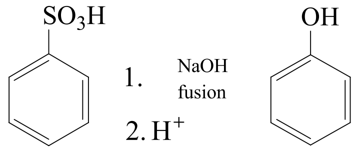
PHENOLS

METHODS OF PREPARATION

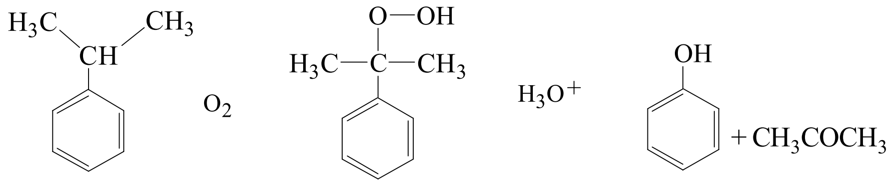
1. Hydrolysis of diazonium salt



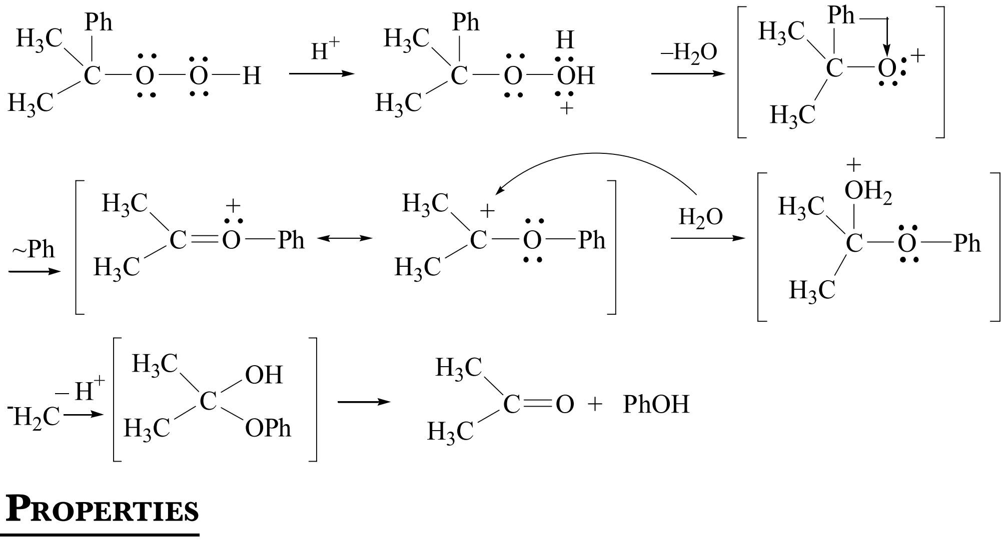
2. Alkali fusion of sulphonates



3. Synthesis from cumene Cumene reacts with air at high temperature by a radical mechanism to form cumene hydroperoxide which on treating with acid gives phenol and acetone.



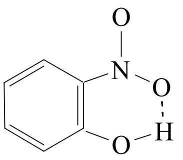
The acid-catalyzed rearrangement of cumene hydroperoxide proceeds as follows.



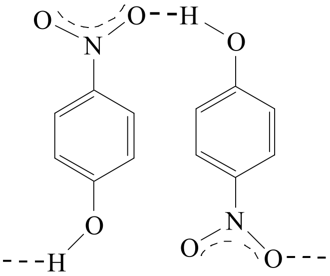
PHYSICAL PROPERTIES

Because of hydrogen bonding, phenols have quite high boiling points. Phenols themselves are colourless but become coloured due to the atmospheric oxidation.

Comparison of physical properties of *o*-nitrophenol with those of *p*-nitrophenol and *m*-nitrophenol revealed wild variations. For example, *o*-nitrophenol has a much lower boiling point, much lower solubility in water than its isomers. It can be steam-distilled while other isomers cannot be. These variations are due to the fact that *o*-nitrophenol involves intramolecular hydrogen bonding whereas the other two isomers involve intermolecular hydrogen bonding:



(monomolecular)



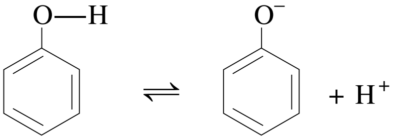
(multimolecular)

The boiling point of *o*-nitrophenol is low because it exists as a monomolecule. The solubility of *m*- and *p*- isomers is due to their ability to form hydrogen bond with water. Steam distillation depends upon the appreciable vapour pressure of the substance at the boiling point of water. *Ortho* isomer being monomolecular has an appreciable vapour pressure whereas *mete* and *para* isomers being multimolecular have low vapour pressures.

CHEMICAL REACTIONS

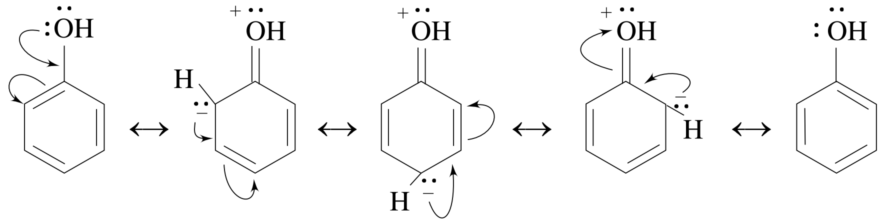
1. Acidic Nature of Phenols Phenols are weak acids. These are soluble in aqueous NaOH and not in aqueous bicarbonates. Phenol are stronger acids than water and alcohols but weaker than carboxylic acids.

Phenols behaves as a weak acid because the resultant phenoxide ion is more stable (because of resonating effect) as compared to phenol.



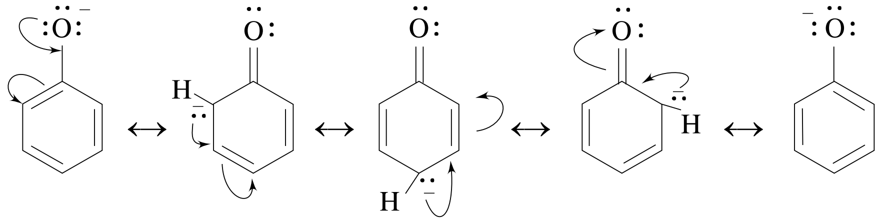
more stable
than phenol

The resonating structures of phenols are as follows.



The structures (II) to (IV) involve separation of charges and thus have much higher energy than those of structures (I) and (V). In other words, the resonance hybrid includes major contribution from (I) and (V).

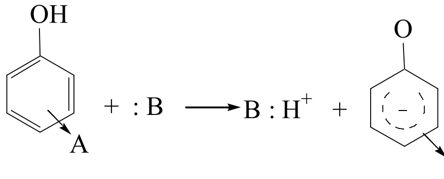
The corresponding structures of phenoxide ion are as follows:



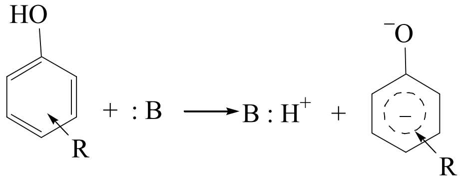
All the five structures have comparable energies, therefore, contribute towards hybrid structure. Consequently, this hybrid structure is more stable than phenol.

Effect of Substituent on the Acidity of Phenol

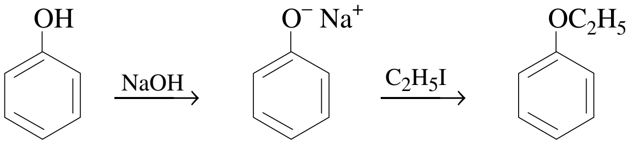
Electron-attracting substituents (—NO_2, —CN, $>$C=O, —COOH) disperse negative charge making PhO^- a weaker base and the phenol a stronger acid.

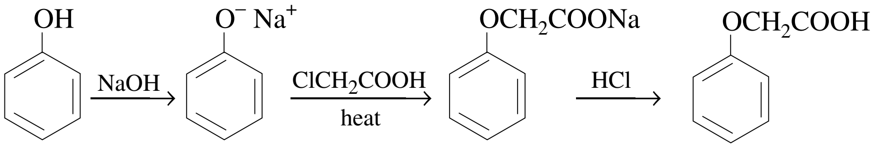

Charge dispersed, less basic; phenol more acidic

Electron-donating substituents (—CH_3, —OR, —NR_2) concentrate negative charge making PhO^- a stronger base and the phenol a weaker acid.

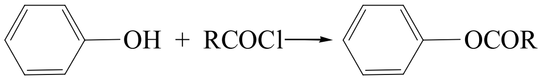

Charge concentrated, more basic; phenol less acidic

2. Formation of Ethers (Williamson Synthesis) In alkaline medium, phenols react with alkyl halides to yield ethers.

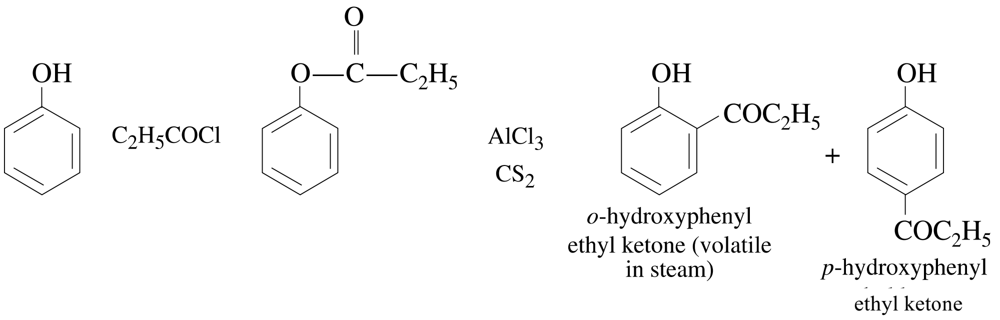

ethyl phenyl ether


phenoxyacetic acid

3. Formation of Esters Phenols are usually converted into their esters by the action of acids, acid chloride or anhydride.



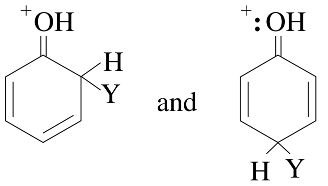
Fries Rearrangement When esters of phenols are heated with $AlCl_3$, the acyl group migrates from the phenolic oxygen to an *ortho* or *para* position of the ring producing a ketone.


o-hydroxyphenyl ethyl ketone (volatile in steam)

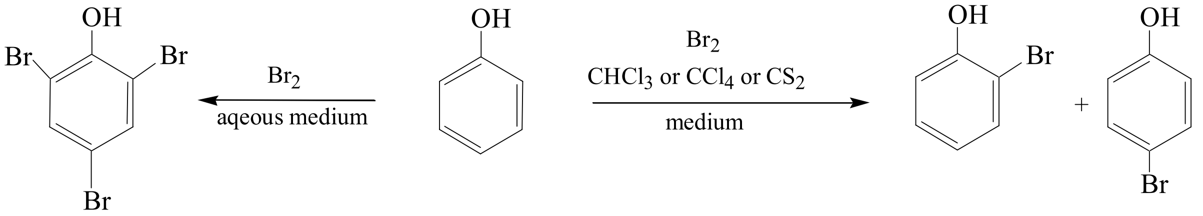
p-hydroxyphenyl ethyl ketone

At 25°C, the rate controlled product (*para*-product) is formed while at higher temperature, more of thermodynamically-controlled product (*ortho*- product) is formed.

4. Ring Substitution The phenolic group is a powerful activating group and is thus *ortho* and *para* directing. The intermediates formed are oxonium ions (instead of carbocations) which are formed faster than the formation of carbocations from benzene, hence, phenols are more reactive towards electrophilic substitution than benzene. The structures of oxonium ions are:

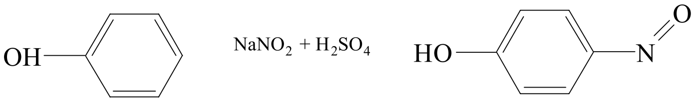


In an aqueous solution, bromination of phenol yields tribromophenol. In lesser polar solvent, such as $CHCl_3$, CCl_4 or CS_2, monobromination products are obtained



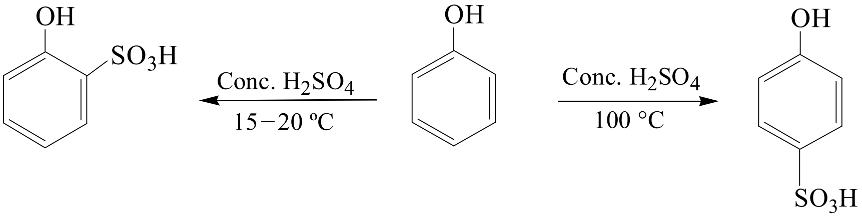
Similarly, concentrated nitric acid gives trinitrophenol (picric acid) with low yield as nitration is accompanied by considerable oxidation. Use of dilute nitric acid gives monosubstituted nitrophenol.

Nitrous acid converts phenol to nitrosophenol.

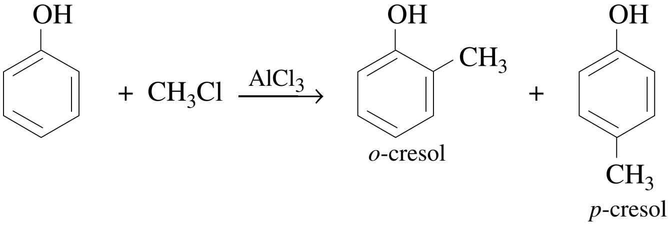


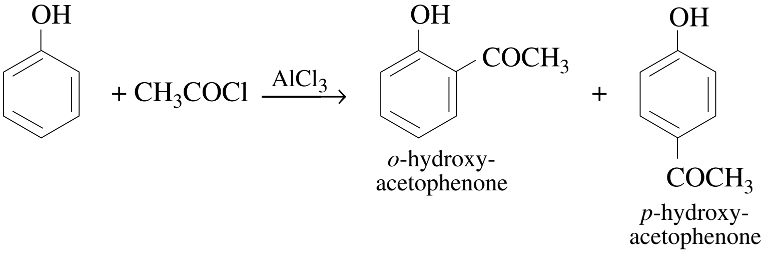
p-nitrosophenol

Phenols can be sulphonated with concentrated H_2SO_4.

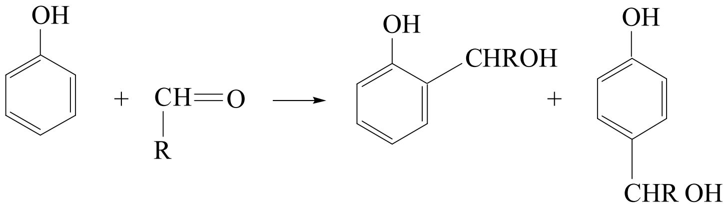


Phenols can undergo Friedel-Crafts alkylation and acylations:



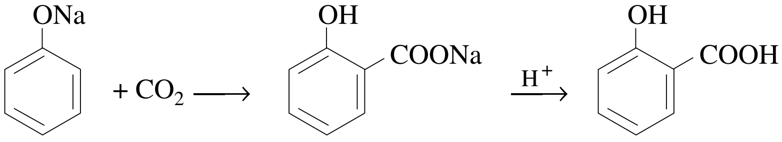


Condensation with Aldehydes Phenol undergoes condensation with aldehydes by electrophilic substitution in *ortho* and *para* positions in presence of acids or alkalis.



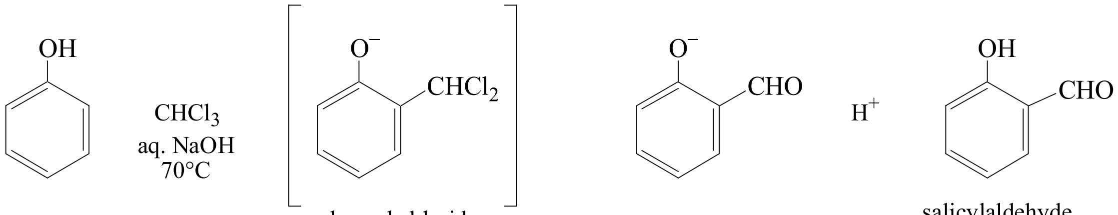
With formaldehyde, phenol forms resin known as bakelite.

5. Kolbe Reaction When the salt of phenol is treated with carbon dioxide, a —COOH group is introduced in the ring:



(main product) salicyclic acid

6. Reimer-Tiemann Reaction When phenol is treated with chloroform and aqueous sodium hydroxide, a —CHO group is introduced in the ring:

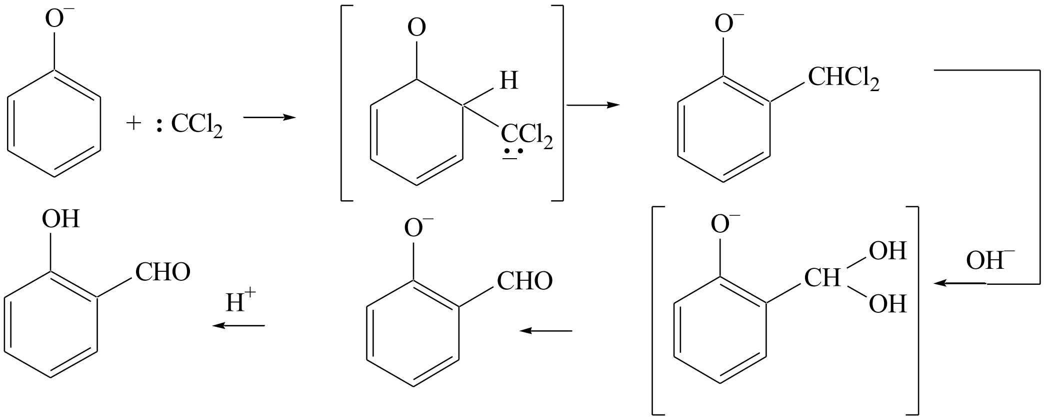


benzal chloride

salicylaldehyde
(main product)

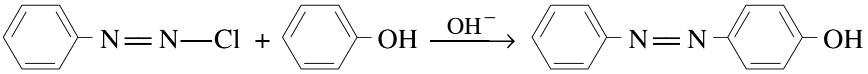
The mechanism of the reaction is

$$OH^- + CHCl_3 \rightleftharpoons H_2O + {}^-:CCl_3 \rightarrow Cl^- + \underset{\text{dichlorocarbene}}{:CCl_2}$$

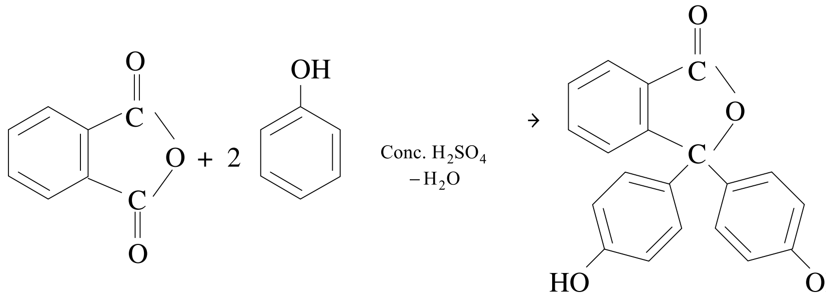


The treatment of phenol with carbon tetrachloride in aqueous NaOH produces salicyclic acid.

7. Coupling Reactions Phenol couples with benzenediazonium chloride in alkaline medium to form *p*-hydroxyazobenzene.

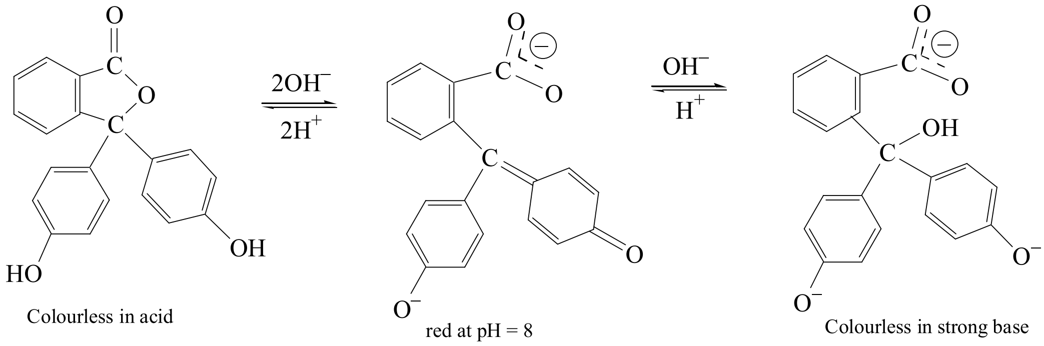


8. Condensation Reactions Phenol on combining with phthalic anhydride in the presence of concentrated sulphuric acid produces phenolphthalein:



phenolphthalein

Phenolphthalein is used as acid-base indicators. Based on the following reversible reactions.

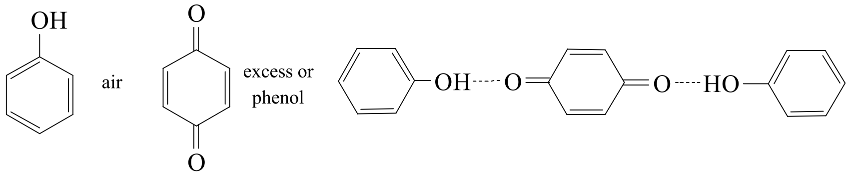


Colourless in acid

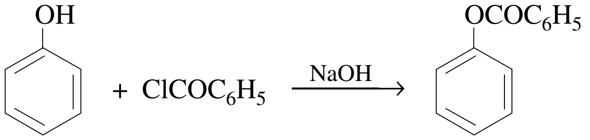
red at pH = 8

Colourless in strong base

9. Oxidation in air Phenol on exposure to air produces a red coloured product called phenoquinone.

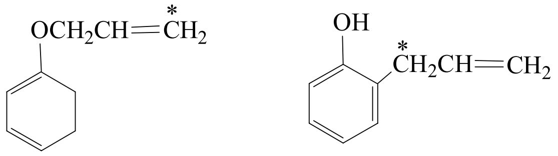


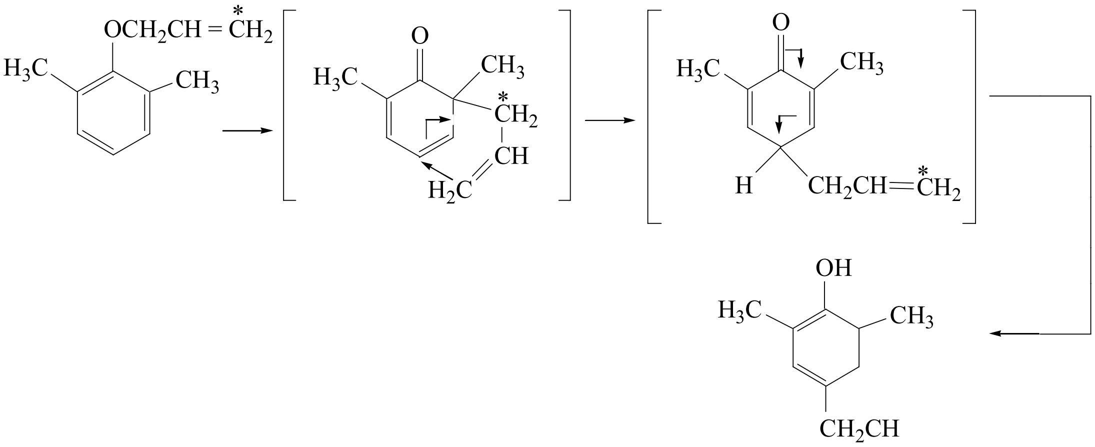
10. Schotten-Baumann Reaction The reaction of phenol with benzoyl chloride is known as Schotten-Baumann reaction.



phenylbenzoate

11. Claisen Rearrangement Allyl phenyl ether undergoes Claisen rearrangement in which allyl group is migrated from O to the *ortho* position of the ring or to the *para* position if *ortho* positions are blocked.





TEST FOR PHENOL

Phenols liberate hydrogen gas when treated with sodium. These are soluble in sodium hydroxide solution and not in sodium bicarbonate solution. Phenols give coloured complexes (usually green, violet, blue) with ferric chloride.

Straight Objective Type

General Characteristics

1. Which of the following statements regarding phenols is **not** correct?
- (a) *o*-Nitrophenol has a much lower boiling point as compared to *p*-nitrophenol.
- (b) *o*-Nitrophenol has much lower solubility in water as compared to *p*-nitrophenol.
- (c) *o*-Nitrophenol is stronger acid than *p*-nitrophenol
- (d) *o*-Nitrophenol can be steam distilled while *p*-nitrophenol cannot be.

2. Which of the following statements regarding phenols is **not** correct?
- (a) Phenols are stronger acids than water and alcohols
- (b) Phenols are weaker acids than carboxylic acids
- (c) Phenols are soluble in both aqueous NaOH and aqueous $NaHCO_3$.
- (d) Phenoxide ions are more stable than the corresponding phenols.

3. Which of the following orders regarding the acid strength of phenols is correct?
- (a) *p*-aminophenol > *p*-chlorophenol > *p*-nitrophenol
- (b) *p*-aminophenol < *p*-chlorophenol < *p*-nitrophenol
- (c) *p*-aminophenol > *p*-nitrophenol > *p*-chlorophenol
- (d) *p*-nitrophenol > *p*-aminophenol > *p*-chlorophenol

4. Which of the following orders regarding acid strengths is correct?
- (a) Benzyl alcohol > phenol > *p*-hydroxybenzoic acid
- (b) Benzyl alcohol < phenol < *p*-hydroxybenzoic acid
- (c) Benzyl alcohol < *p*-hydrobenzoic acid < phenol
- (d) phenol > Benzyl alcohol > *p*-hydroxybenzoic acid

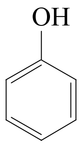
5. Phenol on exposure to air produces a
- (a) red coloured product
- (b) yellow coloured product
- (c) blue coloured produced
- (d) violet coloured product

6. Phenol on exposure to air produces
- (a) *p*-benzoquinone
- (b) *o*-benzoquinone
- (c) *o*-and *p*-benzoquinones
- (d) phenoquinone

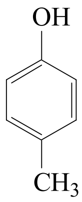
7. Picric acid is
- (a) 2-nitrophenol
- (b) 4-nitrophenol
- (c) 2, 6-dinitrophenol
- (d) 2, 4, 6-trinitrophenol

8. Phenol can be prepared by
- (a) Dow process
- (b) Claisen reaction
- (c) Cannizzaro reaction
- (d) Reimer-Tiemann reaction

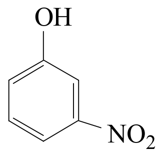
9. In the following compounds



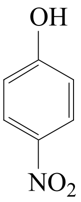
(I)



(II)



(III)

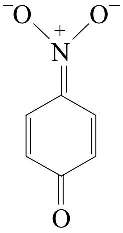


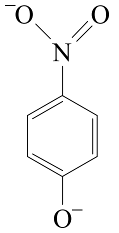
(IV)

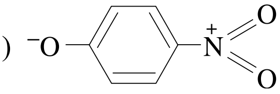
the order of acidity is
- (a) III > IV > I > II
- (b) I > IV > III > II
- (c) II > I > III > IV
- (d) IV > III > I > II

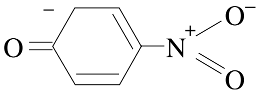
(1996)

10. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(a)


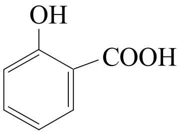
(b)


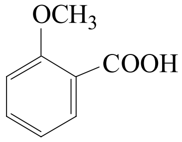
(c)


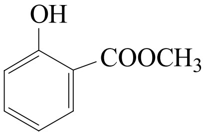
(d)


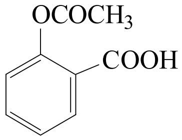
(1999)

11. Which of the following compounds is aspirin?

(a)


(b)


(c)


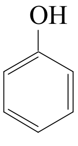
(d)


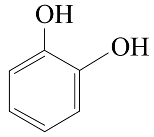
12. Benzene sulphonic acid and 2,4-dinitrophenol on reaction with sodium bicarbonate respectively liberate

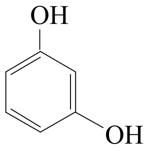
(a) SO_2, NO_2 (b) SO_2, CO_2

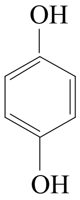
(c) CO_2, NO_2 (d) CO_2, CO_2 (2006)

13. The increasing order of the boiling points of the compounds


(A)


(B)


(C)


(D)

is

(a) A < B < C < D (b) A < B < D < C

(c) D < C < B < A (d) D < A < B < C (2006)

Chemical Reactions

14. When phenol is treated with excess bromine water, it gives

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol

(c) 2,4-dibromophenol (d) 2, 4, 6- tribromophenol (1984)

15. Phenol reacts with bromine in carbon disulphide at low temperature to give

(a) *m*-bromophenol (b) *o*- and *p*-bromophenols

(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol (1988)

16. Salicyclic acid is produced when phenol in alcoholic KOH is treated with

(a) CH_3Cl (b) CH_2Cl_2 (c) $CHCl_3$ (d) CCl_4

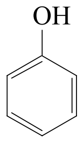
17. Phenol gives salicyldehyde on heating with $CHCl_3$ and NaOH. It is known as

(a) Cannizzaro reaction (b) Claisen reaction

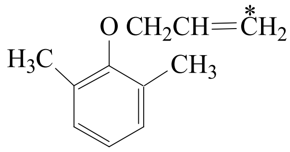
(c) Reimer-Tiemann reaction (d) Hell-Volhard-Zelinsky reaction

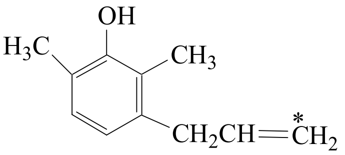
18. The treatment of phenol with phthalic anhydride in the presence of concentrated sulphuric acid produces

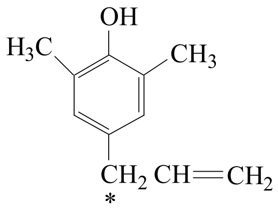
(a) aspirin (b) methyl red (c) methyl orange (d) phenolphthalein

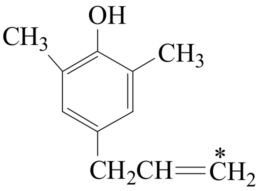
19. In the reaction

+ $C_2H_5\,I$ $\overset{C_2H_5O^-}{\text{(anhydrous } C_2H_5OH)}$ A, the product A is (2003)

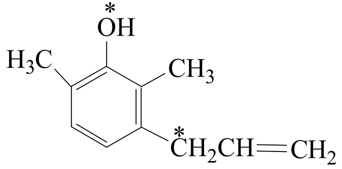
(a) $C_6H_5COC_2H_5$ (b) $C_2H_5OC_2H_5$ (c) $C_6H_5OC_6H_5$ (d) C_6H_5I

20. The Claisen rearrangement of  gives

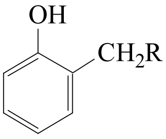
(a) 

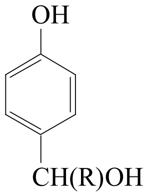
(b) 

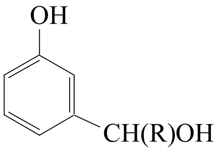
(c) 

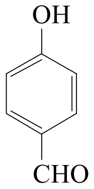
(d) 

21. The reaction of PhOH with an aldehyde RCHO in acidic medium gives

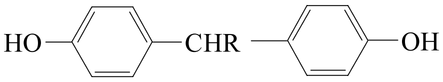
(a) 

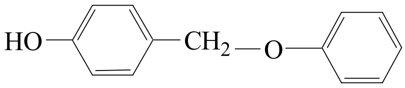
(b) 

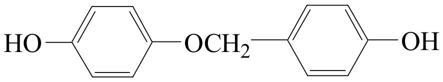
(c) 

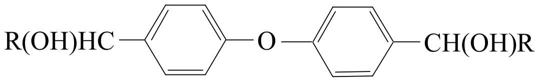
(d) 

22. The reaction of RCHO with 2 eq. of PhOH in acidic medium gives

(a) 

(b) 

(c) 

(d) 

Multiple Correct Choice Type

1. Phenol is less acidic than

(a) acetic acid (b) *p*-methoxyphenol (c) *p*-nitrophenol (d) ethanol (1986)

2. A new carbon-carbon bond formation is possible in

(a) Cannizzaro reaction (b) Friedel-Crafts alkylation

(c) Clemmensen reduction (d) Reimer-Tiemann reaction

3. Which of the following statements are correct?

(a) *o*-Nitrophenol is steam volatile whereas *p*-nitrophenol is not.

(b) Phenol is partially miscible with water. Solubility increases with increase in temperature.

(c) Phenol themselves are colourless.

(d) *o*-Nitrophenol has a higher boiling point than *p*-nitrophenol.

4. Which of the following statements are correct?

(a) *o*-Nitrophenol has lower solubility in water than its *para* isomer.

(b) Phenols and their salts have opposite solubility characteristics in ionic and nonionic solvents.

(c) Phenols are stronger acids than carboxylic acids.

(d) The —O^- group in phenolate ion is more strongly electron-releasing than the —OH group in phenol.

5. Which of the following statements are correct?

(a) The resonance stabilization of phenol is less than that of phenoxide ion.

(b) *p*-Aminophenol is less acidic than phenol.

(c) Heating of an ester of a phenol with aluminium chloride causes rearrangement of acyl group from the phenolic oxygen to an *ortho* or *para* position of the ring.

(d) If halogenation of phenol is carried out in a less polar medium such as $CHCl_3$, CCl_4 or CS_2, only monohalogenated products are obtained.

6. Which of the following statements are correct?
 (a) The relative amounts of *o*-phenolsulphonic acid and *p*-phenolsulphonic acid obtained during sulphonation of phenol depends upon the temperature at which reaction is carried out.
 (b) *o*-Phenolsulphonic acid is converted into the *para* isomer by sulphuric acid at 100 °C.
 (c) Alkaline hydrolysis of $CHCl_3$ is much more rapid than CH_2Cl_2.
 (d) It is not possible to separate the compounds in a mixture containing $ArNO_2$, $ArNH_2$, ArCOOH and ArOH.

7. Which of the following statements are correct?
 (a) Unlike alkyl halide, aryl halides are not readily prepared from the corresponding hydroxyl compounds.
 (b) Most ethers are inert toward bases, but 2,4-dinitroanisole is readily cleaved to methanol and 2,4-dinitrophenol when refluxed with dilute aqueous NaOH.
 (c) The bromination of *p*-methylanisole produces 2-bromo-3-methylanisole as the principal product.
 (d) The nitration of *m*-nitroanisole produces a mixture of 3,4-dinitro-anisole and 2,5-dinitroanisole.

8. Which of the following statements are correct?
 (a) Phenol is a stronger acid than ROH.
 (b) PhO^- is a stronger base than RO^-.
 (c) $NaHCO_3$ does not react with phenol because it is less acidic than phenol.
 (d) Na_2CO_3 reacts with phenol because it is more acidic than phenol.

9. Which of the following statements are correct?
 (a) Decreasing order of acidic character of nitrophenols is

$$p\text{-}O_2NC_6H_4OH > o\text{-}O_2NC_6H_4OH > m\text{-}O_2NC_6H_4OH.$$

 (b) Decreasing order of acidic character of chlorophenols is

$$p\text{-}ClC_6H_4OH > o\text{-}ClC_6H_4OH > m\text{-}ClC_6H_4OH$$

 (c) *meta*-Cresol is a weaker acid than *ortho* or *para*-cresol.
 (d) Sulphonation of phenol is a reversible reaction.

10. Which of the following statements are **not** correct?
 (a) Sulphonation of phenol at low temperature is rate-controlled to give *o*-$HOC_6H_4SO_3H$.
 (b) Sulphonation of phenol at higher temperatures is thermodynamically controlled to give *o*-$HOC_6H_4SO_3H$.
 (c) The —OH is more activating than —O^- towards aromatic electrophilic substitution reactions.
 (d) Bromination of phenol in aqueous medium gives monobrominated phenol while in nonaqueous medium, tribrominated phenol is formed.

11. Which of the following statements are correct?
 (a) The reaction of $CH_3CH_2OCH_2CH_2CH_3$ with one equivalent of HI produces CH_3CH_2I and $CH_3CH_2CH_2OH$.
 (b) The reaction of $PhOCH_2CH_3$ with one equivalent of HI gives PhI and CH_3CH_2OH.
 (c) Fries rearrangement is a reversible reaction. At lower temperature (25 °C), rate-controlled product (*p*-hydroxyacetophenone) is formed while at higher temperatures (165 °C) thermodynamically-controlled product (*o*-hydroxyacetophene) is formed.
 (d) *p*-Hydroxyacetophenone can be converted to *o*-hydroxyacetophenone on increasing the temperature from 25 °C to 165 °C.

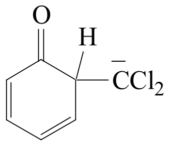
12. Which of the following statements are **not** correct?
 (a) The acidity of phenol is due to the resonance stabilisation of its anion.
 (b) Formation of phenol from chlorobenzene is an example of electrophilic aromatic substitution.
 (c) Phenol is acidic because of resonance stabilization of its conjugate base, namely phenoxide ion.
 (d) Among the three isomers of nitrophenol, the one that is least soluble in water is *p*-nitrophenol.

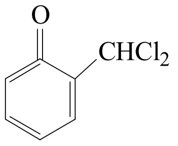
13. Which of the following statements are **not** correct?
 (a) Phenols are weaker acids than carbonic acid.
 (b) Phenols are soluble in sodium bicarbonate solution.
 (c) Nitrophenol is less acidic than phenol.
 (d) Bromination of aqueous solution of phenol results in the formation of 2,4,6-tribromophenol.

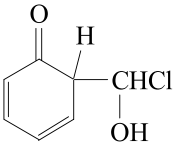
14. Which of the following statements are correct?
 (a) Picric acid is 2,4,6-trinitrophenol.
 (b) Kolbe reaction helps in converting phenol to salicyclic acid.
 (c) Reimer-Tiemann reaction involving phenol and chloroform converts the former into salicyclic acid.
 (d) Phenol gives characteristic colour with $FeCl_3$. This test is due to enol structure.

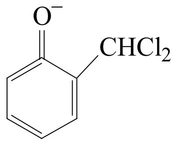
15. Which of the following statements are correct?
(a) Phenol reacts with CCl_4 in the presence of NaOH solution at 70°C to give salicyclic acid.
(b) Phenol reacts with phthalic anhydride in the presence of concentrated H_2SO_4 forming phenolphthalein which is used as acid-base indicator.
(c) Phenol on exposure to air produces a red coloured product known as phenoquinone.
(d) The treatment of concentrated H_2SO_4 at 15–20 °C with phenol produces *p*-phenolsulphonic acid whereas at 100 °C, *o*-phenolsulphonic acid is produced.

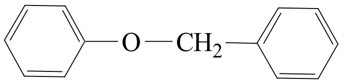
16. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

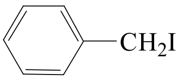
(a) 

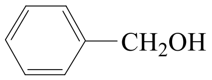
(b) 

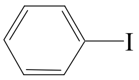
(c) 

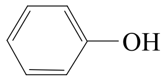
(d) 

17. The ether  when treated with HI produces (1999)

(a) 

(b) 

(c) 

(d) 

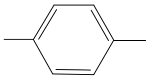
18. Which of the following statements is/are correct?
(a) When vapours of phenol are passed over Zn dust, benzene is formed.
(b) The penolic —OH group is *ortho*- and *para*- directing.
(c) *o*-Nitrophenol has a lower boiling point as compared to that of *p*-nitrophenol.
(d) Phenol is more acidic than *o*-cresol.

Linked Comprehension Type

1. Substituents in phenol affects its acidity. Predict the acidity in the following three questions.
(i) The correct order of acid strength amongst the isomers of nitrophenol is
  (a) *o*-Nitrophenol > *p*-nitrophenol > *m*-nitrophenol
  (b) *o*-Nitrophenol > *m*-nitrophenol > *p*-nitrophenol
  (c) *p*-Nitrophenol > *o*-nitrophenol > *m*-nitrophenol
  (d) *p*-Nitrophenol > *m*-nitrophenol > *o*-nitrophenol
(ii) The correct order of acid strength amongst the isomers of chlorophenol is
  (a) *o*-Chlorophenol > *m*-chlorophenol > *p*-chlorophenol
  (b) *o*-Chlorophenol > *p*-chlorophenol > *m*-chlorophenol
  (c) *p*-Chlorophenol > *o*-chlorophenol > *m*-chlorophenol
  (d) *p*-Chlorophenol > *m*-chlorophenol > *o*-chlorophenol
(iii) The correct order of acid strength amongst the methyl substituted phenol is
  (a) *p*-cresol > *m*-cresol > phenol (b) *p*-cresol > phenol > *m*-cresol
  (c) phenol > *p*-cresol > *m*-cresol (d) phenol > *m*-cresol > *p*-cresol

Assertion and Reason Type

Given below are questions, each containing two statements. Answer correctly each question based on the following key.
(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is incorrect and Statement-2 is correct.

	Statement – 1	**Statement – 2**
1.	*p*-Nitrophenol is a stronger acid than *o*-nitrophenol.	Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer. (1989)
2.	Phenol is more reactive than benzene towards electrophilic substitution reaction.	In the case of phenol, the intermediate carbocation is more resonance stabilized. (2000)
3.	1,3,5-Trihydroxybenzene reacts with H_2NOH to form trioxime while its isomers 1,2,4-and 1,2,3-trihydroxybenzenes do not react with H_2NOH.	The triketo tautomer of 1,3,5-trihydroxy--benzene has considerable stability because of the large resonance energy of its three C = O group.
4.	The compound HOOC——OH is named as *p*-hydroxybenzoic acid and not as *p*-carboxyphenol.	—COOH has priority over —OH in naming an organic compound.
5.	*o*-Nitrophenol and *o*-hydroxybenzaldehyde have lower boiling and decreased water solubility as compared with their *m*- and *p*-isomers.	*o*-Nitrophenol and *o*-hydroxybenzaldehyde involve intermolecular hydrogen bonding while their *m*- and *p*-isomers involve intramolecular hydrogen bonding.
6.	Phenol does not react with $NaHCO_3$.	Phenol is weaker acid than H_2CO_3.
7.	Phenol does not react with Na_2CO_3.	Phenol is a stronger acid than HCO_3^-.
8.	Phenol is more readily oxidized than that of benzene.	The strong-donating effect of OH makes the ring of phenol very electron-rich, enabling it to readily donate electrons to oxidizing agent.

ANSWERS

Straight Objective Type

1. (c) **2.** (c) **3.** (b) **4.** (b) **5.** (a) **6.** (d) **7.** (d)
8. (a) **9.** (d) **10.** (c) **11.** (d) **12.** (d) **13.** (a) **14.** (d)
15. (b) **16.** (d) **17.** (c) **18.** (d) **19.** (b) **20.** (c) **21.** (b)
22. (a)

Multiple Correct Choice Type

1. (a), (c) **2.** (b), (d) **3.** (a), (b), (c)
4. (a), (b), (d) **5.** (a), (b), (c), (d) **6.** (a), (b), (c)
7. (a), (b), (d) **8.** (a), (c), (d) **9.** (a), (d)
10. (b), (c), (d) **11.** (c), (d) **12.** (b), (d)
13. (b), (c) **14.** (a), (b), (d) **15.** (a), (b), (c)
16. (a), (d) **17.** (a), (d) **18.** (a), (b), (c), (d)

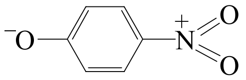
Linked Comprehension Type

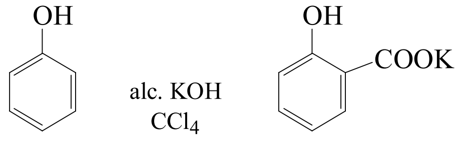
1. (i) (c) **(ii)** (a) **(iii)** (d)

Assertion and Reason Type

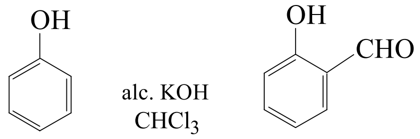
1. (a) **2.** (c) **3.** (b) **4.** (a) **5.** (c) **6.** (a) **7.** (d)
8. (a)

Straight Objective Type

1. *o*-Nitrophenol is less strong acid than *p*-nitrophenol due to intramolecular hydrogen bonding.
2. Phenols are insoluble in aqueous $NaHCO_3$ solution.
3. Electron-releasing group makes phenol less acidic while electron-attracting group makes it more acidic. The correct order of acidity is *p*-aminophenol < *p*-chlorophenol < *p*-nitrophenol.
4. Alcohol is less acidic than phenol, and phenol is less acidic than carboxylic acid. The correct order is
Benzyl alcohol < phenol < *p*-hydroxybenozic acid
5. A red coloured product phenoquinone when phenol is exposed in air.
6. The product is phenoquinone. **7.** 2,4,6-Trinitrophenol is known as picric acid.
8. Phenol can be produced by Dow process.
9. The correct order of acidity *p*-nitrophenol > *m*-nitrophenol > phenol > *p*-methylphenol.
10. The structure  is most unlikely as N containing 5 valence electrons should not carry positive charge.
12. Both benzene sulphonic acid and 2,4-dinitrophenol are stronger acid than carboxylic acid. Both liberate CO_2 on reaction with sodium bicarbonate.
13. Phenol will have the lowest boiling point as it contains a single hydroxyl group. Of the dihydroxyl compounds, the *para* isomer will have maximum boiling point due to the more involved hydrogen bondings. The *ortho* isomer is expected to have lower boiling point than the *meta* isomer as former is expected to have lesser involved hydrogen bondings.
14. The product formed is 2,4,6-tribromophenol.
15. In less polar solvent, phenol reacts with bromine to give a mixture of *o*- and *p*-bromophenol.
16. The reaction is

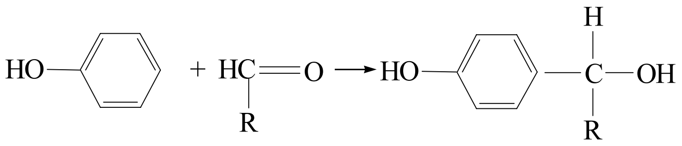


17. The reaction

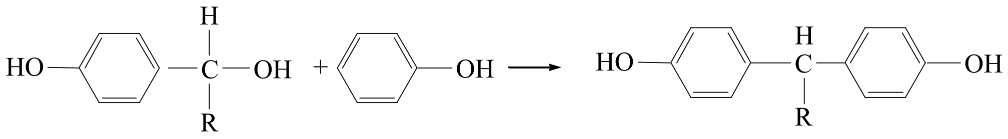


is known as Reimer-Tiemann reaction.

18. Phenolphthalein is produced when phenol is treated with phthalic anhydride in the presence of conc. H_2SO_4.
19. Phenoxide ion is less reactive than alkoxide ion.
20. Since *ortho* positions are occupied, the allyl group migrates to *para* position via two rearrangements of allyl group.
21. The reaction is



22. First reaction is the same as in Q.21. Second C_6H_5OH reacts as



Multiple Correct Choice Type

1. Carboxylic acid is more acidic than phenol. Electron-attracting group also increases the acidity of phenol. thus, phenol is less acidic than acetic acid and *p*-nitrophenol.
3. (a) *o*-Nitrophenol involves intramolecular hydrogen bond whereas *p*-nitrophenol involves intermolecular hydrogen bond. Consequently, the former exists as single molecule whereas the latter exists as multimolecular form.

(d) Because of intramolecular hydrogen bonding in *o*-nitrophenol, the latter has lower boiling point as compared to *p*-nitrophenol (which has intermolecular hydrogen bonding).

4. (b) Phenol is essentially a covalent compound whereas its salt is ionic.

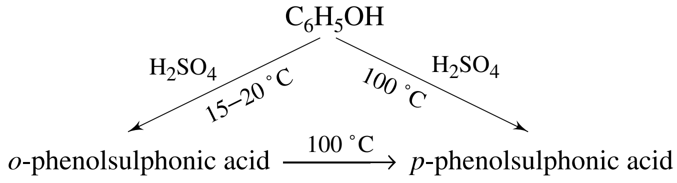
(d) It is because phenolate ion contains full-fledged negative charge on oxygen.

5. (a) The resonating structrues of phenol involves charge separation while those of phenoxide ion do not involve any charge separation. Since energy is needed to separate opposite charges, the structrues of phenol involve more energy and thus are less stable than the structures of phenoxide ion.

(b) Electron-releasing substituent destabilizes the phenoxide ion, hence, makes the such substituted phenol less acidic.

(c) This is known as Fries rearrangement.

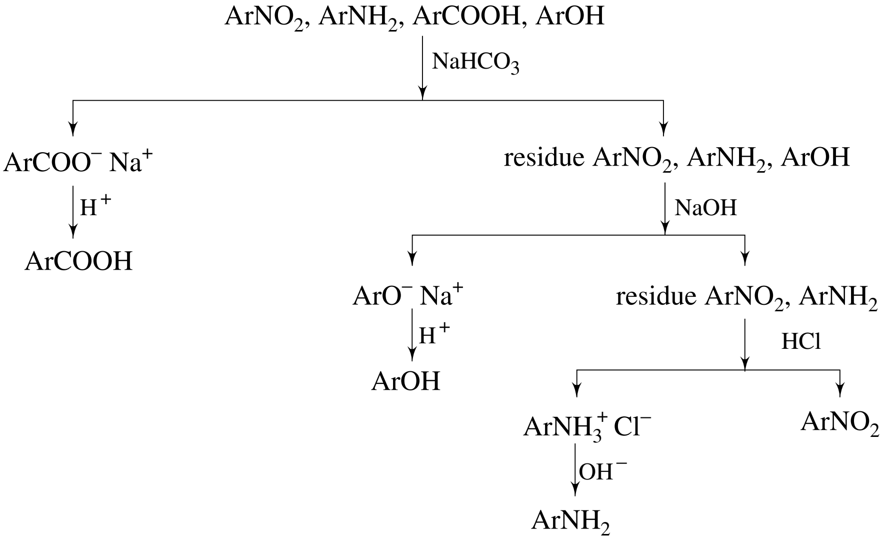
6. (a)



(b) Sulphonation is reversible. The *ortho* isomer is formed more rapidly; the *para* isomer is more stable. At 15—20°C, there is rate control of product composition; at 100°C, there is equilibrium control.

(c) The hydrogen atom in $CHCl_3$ is more acidic than in CH_2Cl_2.

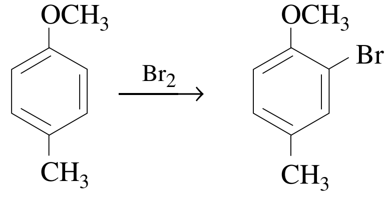
(d) These can be separated as follows.



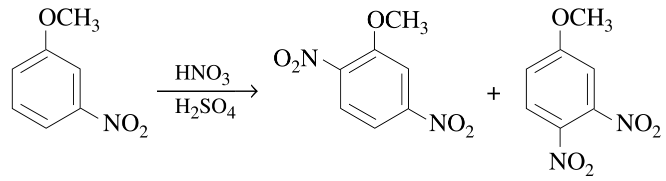
7. (a) The bond Ar—O in phenols is strong, due to partial double-bond character and/or sp^2 hybridization of aromatic carbon.

(b) The reaction is nucleophilic aromatic substitution of —OH for —OCH_3. This is achieved due to the deactivation of two nitro groups in the *ortho* and *para* positions.

(c) The principal directing group is —OCH_3. Therefore, the obtained compound would be 1-bromo-3-methylanisole.



(d) The principal directing group is —OCH_3.



8. (b) The negative charge on the alkoxide anion, RO^-, is completely localised, but the negative charge on PhO^- is delocalised by extended π-bonding to the *ortho* and *para* ring positions. This makes PhO^- weaker base than RO^- and PhOH a stronger acid than ROH.

(c) The reaction of phenol with $NaHCO_3$ would produce the following reaction

$$\begin{array}{ccccccc} \text{PhOH} & + & HCO_3^- & \not\longrightarrow & PhO^- & + & H_2CO_3 \\ pK_a^\circ = 10 & & pK_b^\circ = 7.6 & & pK_b^\circ = 4 & & pK_a^\circ = 6.4 \\ \text{(weaker)} & & \text{(weaker)} & & \text{(stronger)} & & \text{(stronger)} \end{array}$$

Both the reactants are weaker than the corresponding species on the right side. Thus, the reaction would not proceed to the right side.

(d) The reaction would be

$$\begin{array}{ccccccc} \text{PhOH} & + & CO_3^{2-} & \longrightarrow & PhO^- & + & HCO_3^- \\ pK_a^\circ = 10 & & pK_b^\circ = 3.7 & & pK_b^\circ = 4 & & pK_a^\circ = 10.3 \\ \text{(stronger)} & & \text{(stronger)} & & \text{(weaker)} & & \text{(weaker)} \end{array}$$

Both the products are weaker than the corresponding species on the left side. Thus, the reaction proceeds to the right side.

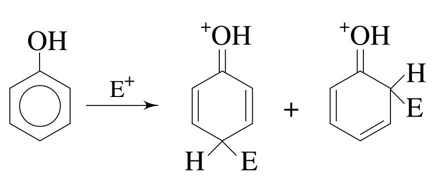
9. (a) The nitro group is electron-withdrawing and acid-strengthening by both induction and resonance. The induction operates from all the three positions. Its effectiveness decreases with increasing separation of NO_2 and OH. The resonance effect is effective from the *ortho* and *para* positions. However, at the *ortho* position, intramolecular hydrogen-bonding weakens the acidic character to a large extent. Hence, the correct order is $p\text{-}O_2NC_6H_4OH > o\text{-}O_2NC_6H_4OH > m\text{-}O_2NC_6H_4OH$

(b) Although Cl is electron-donating by resonance, its electron-withdrawing inductive effect, that decreases with increasing separation of Cl and OH, predominates, making all the chlorophenols more acidic than phenol. The correct sequence of acidic character is *o*-chlorophenol > *m*-chlorophenol > *p*-chlorophenol

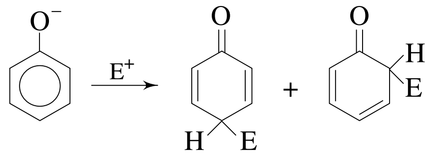
(c) Methyl group is electron-donating inductively from all the three positions and hyperconjugatively only from the *ortho* and *para* positions. Thus, *m*-cresol is a stronger acid than either *o*-cresol or *p*-cresol because hyperconjugation effect does not operate at the *meta* position.

10. (b) The reaction is reversible and thus at higher temperatures, thermodynamically controlled *para* isomer is formed.

(c) PhO^- reacts faster than PhOH with an electrophile because the intermediate formed with PhO^- is a fairly stable uncharged species while in PhOH, a less stable positively-charged intermediate is formed. Thus, $\Delta H^\ddagger$ for the reaction of PhO^- is less than the $\Delta H^\ddagger$ for the reaction of PhOH.



Phenol Oxonium ions



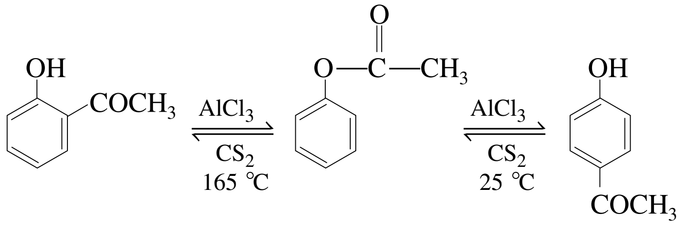
unsaturated ketone
(more stable uncharged species)

(d) In aqueous solution, some phenol is ionised to give more reactive PhO^- species, which, in turn, forms a tribrominated phenol. In nonaqueous medium, the ionisation is not possible and the monobromination of less reactive PhOH occurs.

11. (a) Unsymmetrical dialkyl ether gives a mixture of two sets of products.

$CH_3CH_2OH + CH_3CH_2CH_2I$ and $CH_3CH_2I + CH_3CH_2CH_2OH$

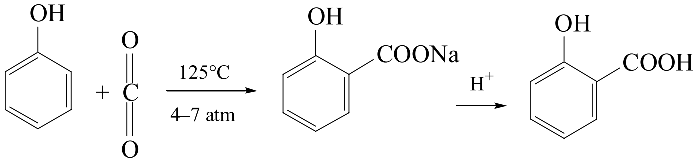
(b) The products are PhOH and CH_3CH_2I. Aryl ethers do not cleave on the Ar side, only on the alkyl side.

(c) 

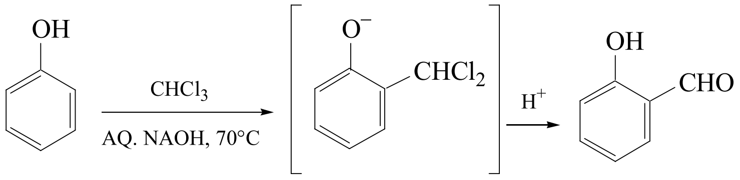
12. (b) This is an example of nucleophic substitution.
(d) The isomer *o*-nitrophenol is least stable due to intramolecular hydrogen bonding.

13. (b) Phenols are insoluble in $NaHCO_3$ solution. (c) Nitrophenol is more acidic than phenol. Electron-attracting substituents tend to disperse the negative charge of phenoxide ion rendering it more stable. Hence, increases the acid strength of phenol.

14. (b) The reactions are

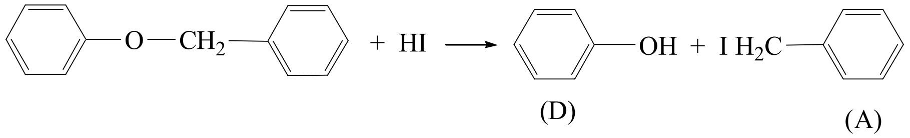


(c) The compound formed is salicylaldehyde.



15. (d) At low temperature, *o*-phenolsulphonic acid is formed which is converted into *p*-phenolsulphonic acid at higher temperature.

17. The aromatic ethers are cleaved to give phenol one of the products.



Linked Comprehension Type

1. (i) —NO_2 is electron-withdrawing and acid-strengthening by both induction and resonance. Its resonance effect is almost equally effective from *ortho* and *para* positions. The resonance effect predominates over inductive effect which operates from all positions with a decrease effectiveness as the distance of —NO_2 from —OH is increased. Thus, *m*-nitrophenol is the weakest amongst the three isomers. The *ortho* isomers is weaker than *para* isomer due to the existence of intramolecular H-bond in the former.

(ii) —Cl is electron-donating by resonance but the electron-withdrawing inductive effect is more dominating in deciding the acid strength. The inductive effect decreases with increasing separation between —Cl and —OH groups.

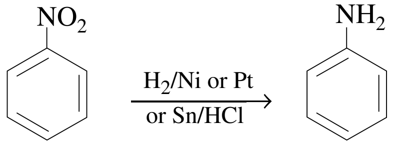
(iii) —CH_3 is electron-donating substituent via hyperconjugation and thus *m*- and *p*-cresole are weaker acid than phenol. The effect of hyperconjugation is more effective from the *ortho* and *para* positions. *m*-Cresol is stronger than p-isomer because hyperconjugative effect is not effective from the *meta* position.

CHAPTER 30

AMINES

METHODS OF PREPARATION

1. Reduction of nitro compounds Reduction can be done by using either molecular hydrogen and a catalyst (Ni or Pt) or a metal (usually granulated tin) and an acid (hydrochloric acid). For example,



2. Reaction of halides with ammonia

$$RX + NH_3 \rightarrow RNH_3^+X^-; \qquad RNH_3^+X^- + OH^- \rightarrow RNH_2 + H_2O + X^-$$

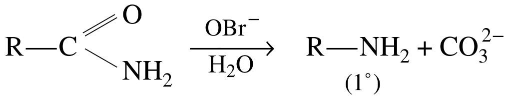
Replacement of X by NH_2 is a nucleophilic substitution reaction. Tertiary alkyl halide generally produces alkene.

Aryl halides show low reactivity. These can be converted into amine if a strong deactivating group, such as $—NO_2$, is also attached to the ring at *ortho* or *para* position to halogen.

During the ammonolysis of halides, ammonia is taken in excess so as to avoid the formation of other amines (2° and 3°)

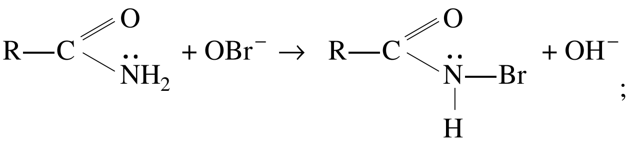
$$RX \xrightarrow{NH_3} \underset{(1°)}{RNH_2} \xrightarrow{RX} \underset{(2°)}{R_2NH} \xrightarrow{RX} \underset{(3°)}{R_3N}$$

3. Hofmann degradation of amides

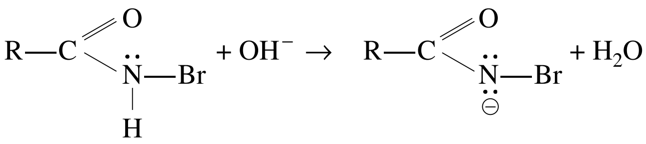


The reaction, known as Hafmann rearrangement, involves migration of a group from carbonyl carbon to the adjacent nitrogen atom. The reaction is believed to proceed by the following steps.

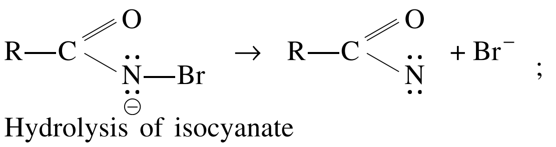
(a) Halogenation of amide



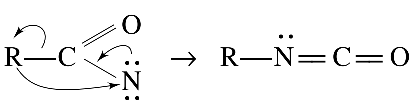
(b) Abstraction of H^+ by OH^-



(c) Separation of halide ion



(d) Rearrangement to produce isocyanate

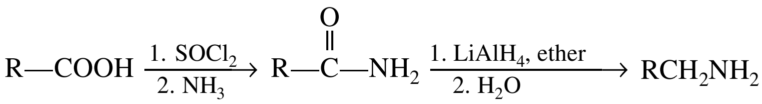


(e) Hydrolysis of isocyanate

$$R—N=C=O + H_2O \longrightarrow R—\ddot{N}H_2 + CO_2$$

4. Reduction of nitriles and amides

$$R—X \xrightarrow{NaCN} R—CN \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ ether} RCH_2NH_2$$



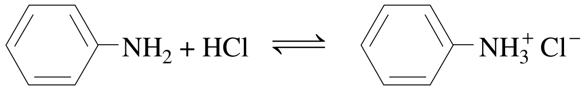
$$R—COOH \xrightarrow[2.\ NH_3]{1.\ SOCl_2} R—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2 \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ ether} RCH_2NH_2$$

PHYSICAL PROPERTIES

Amines are polar compounds. Except tertiary amines, primary and secondary amines form intermolecular hydrogen bonding. Amines have lower boiling points than alcohols and carboxylic acids of comparable molar masses.

CHEMICAL REACTIONS

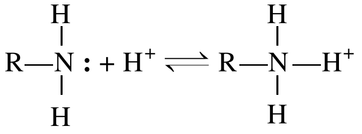
1. Basic Nature of Amines Nitrogen of amines contains lone pair of electrons which can be shared with other species and thus these act as Lewis bases. Amines form salts with acids. For example,



aniline anilinium chloride

Aliphatic amines are somewhat stronger bases than ammonia. This is due to the fact that alkyl group is electron-releasing group which, in turn, increases the availability of lone pair of electrons. On the other hand, aromatic amines are considerably weaker than ammonia. This is due to the electron-withdrawing nature of phenyl group which decreases the availability of lone pair of electrons.

Alternatively, the more stable the ion relative to the amine from which it is formed, the more basic the amines. For example, the ion formed in the reaction



$$R—\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{N}}: + H^+ \rightleftharpoons R—\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{N}}—H^+$$

is stabilized by alkyl group and hence increases basicity of RNH_2 as compared to NH_3.

Two factors operate in deciding the basicity of alkylamines.

(i) *Inductive Effect* The alkyl group being electron releasing increases the charge density on nitrogen. This in turn increases the basicity of amines. The expected order of basicity is

$$R_3N > R_2NH > RNH_2 > NH_3$$

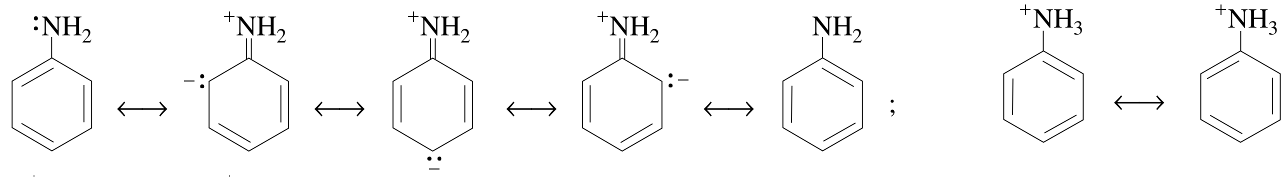
(ii) *Solvation Effect* Because of the positive charge carried by the conjugate acid of an amine, it is stabilized by the hydrogen bonding with the solvent water. The larger the number of hydrogens attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity of the alkylamines will be

$$NH_3 > RNH_2 > R_2NH > R_3N$$

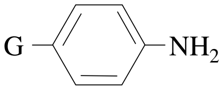
The inductive and solvent effects predict the opposite trend in the basiscity of alkylamines. In going from R_2NH to R_3N, the solvation effect plays a more dominating role as compared to the inductive effect making R_2NH more basic than R_3N.

A simple explanation is that the steric factor in R_3N makes the availability of a lone pair of electrons on nitrogen poor than in the dialkylamine, predicting R_2NH a stronger base than R_3N.

In aromatic amines, the resonance stabilization of $ArNH_2$ is larger than $ArNH_3^+$, because there are more resonating structures of $ArNH_2$ as compared to those of $ArNH_3^+$:



Effect of substituents on basicity of aromatic amines Electron-releasing group pushes electrons toward nitrogen and hence increases the availability of lone pair of electrons and thus increases its basicity. On the other hand, electron-withdrawing group decreases the availability hence makes the amine less basic.

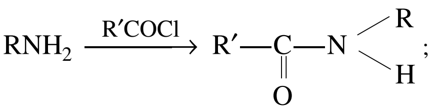
In terms of the stability of ion, electron-releasing group stabilizes cation and hence increases basicity whereas electron-withdrawing group destabilizes cation making the amine less basic. For example  is more basic if G is —NH_2 or —OCH_3 or —CH_3 and is less basic if G is —NH_3^+ or —NO_2 or SO_3^- or —COOH or —X.

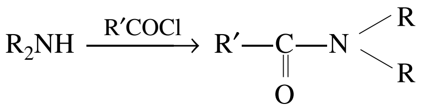
It may be pointed out that the basicity of an amine and acidity of a carboxylic acid are affected by a substituent in the opposite manner. This is to be expected, since basicity depends upon ability to accommodate a positive charge (or ability to share lone pair) and acidity depends upon ability to accommodate a negative charge (or to accept lone pair of electrons).

2. Alkylation

$$\underset{(1°)}{RNH_2} \xrightarrow{RX} \underset{(2°)}{R_2NH} \xrightarrow{RX} \underset{(3°)}{R_3N} \xrightarrow{RX} \underset{\substack{\text{quaternary}\\ \text{ammonium}\\ \text{halide}}}{R_4N^+X^-}$$

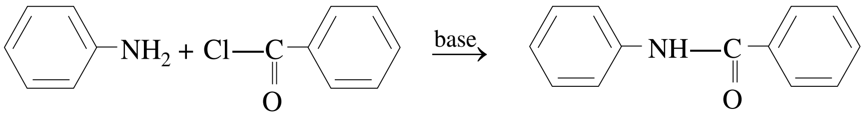
3. Conversion of Amines into Substituted Amides Primary and secondary amines react with acid chloride to give substituted amides.





Tertiary amines do not react this way as they contain no replaceable hydrogen.

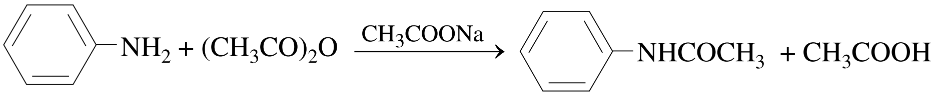
Schotten–Baumann Technique to prepare substituted amides of aromatic carboxylic acid In this method acid chloride is added to the amine in the presence of a base (aqueous NaOH or pyridine).



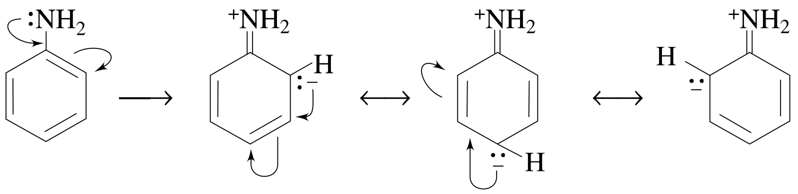
benzanilide

Substituted amides undergo hydrolysis on heating in the presence of acid or base to give amine and carboxylic acid.

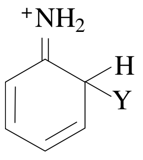
Acetylation of aniline is generally carried out by using acetic anhydride instead of acetyl chloride.



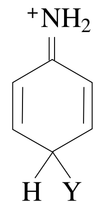
4. Ring Substitution in Aromatic Amines The —NH_2, —NHR and —NR_2 are benzene activating groups through resonance effect of nitrogen where the lone pair of nitrogen is shifted to the benzene ring making *ortho* and *para* positions available for electrophilic attack.



The cation formed as intermediate are

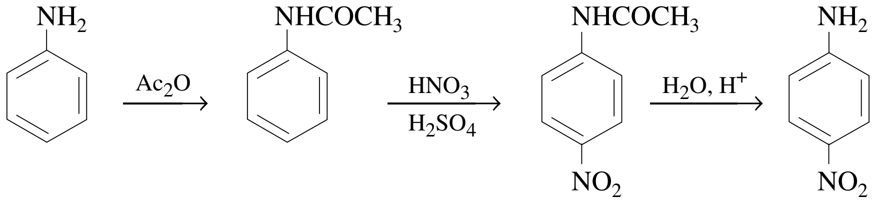


and

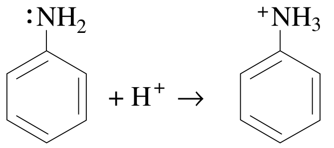


In these structures, nitrogen atom carries a positive charge and is joined to the benzene ring by a double bond. Such structures are quite stable as each atom (except hydrogen) has a complete octet of electrons.

The group —$NHCOCH_3$ is less powerful *ortho* and *para* director because of the electron-withdrawing characteristic of oxygen makes nitrogen a poor source of electrons. This fact is made use in preparing mono substituted aniline. The — NH_2 group is such a powerful activator, that substitution occurs at all available *ortho* and *para* positions of aniline. If, however, —NH_2 group is converted to — $NHCOCH_3$, the molecule becomes less powerful activator. Hence, only mono substitution products are obtained. Finally, —$NHCOCH_3$ is converted back to —NH_2 by hydrolyzing with acid. This technique is especially used while nitrating aniline as strong oxidizing agent destroys the highly reactive ring.



If acetylation is not done, nitration of aniline gives about two-thirds *meta* and one-third *para* products, besides loss of aniline. This is due to the fact that the strong acid converts aniline to anilinium ion:



Now the group —$\overset{+}{N}H_3$ is the *meta* director because of its positive charge.

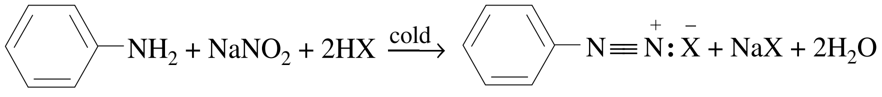
5. Reactions of Amine with Nitrous Acid In the reacting mixture, nitrous acid is generated by the action of mineral acid on sodium nitrite. The products obtained depend on the type of amine:

Aliphatic primary amine It forms unstable diazonium salt which on decomposing liberates nitrogen and mixture of alcohols and alkenes.

$$R—NH_2 + NaNO_2 + HX \rightarrow [R—N^+_2\,X^-] \xrightarrow{H_2O} N_2 + \text{mixture of alcohols and alkenes}$$

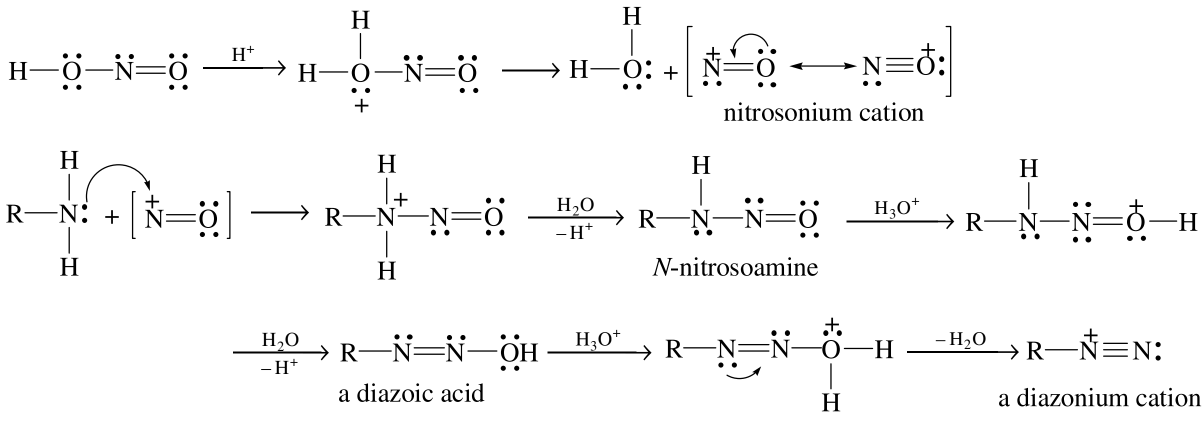
Nitrogen obtained is quantitative and hence can be used to determine the strength of amine.

Aromatic primary amine It forms stable diazonium salt.

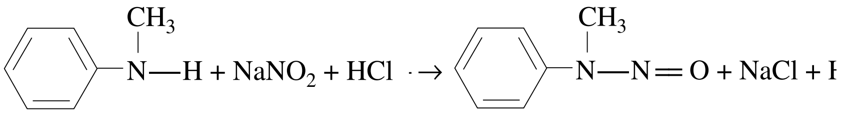


a diazonium salt

The formation of a diazonium cation proceeds as follows .

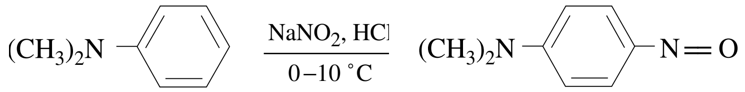


Aliphatic and Aromatic Secondary Amines Both of these produce *N*–nitrosoamines.



N-nitroso-*N*-methylaniline

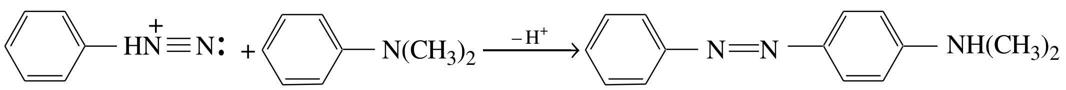
Tertiary Aromatic Amine This undergoes ring substitution, to yield a compound in which a nitroso group, —N═O, is joined to carbon**:**



p-nitroso-*N*, *N*-dimethylanilin

In this reaction, the electrophile —$^+$NO (or H_2O^+—NO) replaces H^+ of benzene.

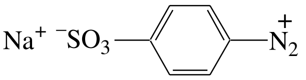
6. Coupling Reaction of Diazonium Salt ArN_2^+ is a weak electrophile that undergoes diazocoupling only with rings activated by —OH, —NH_2, —NHR and —NR_2.

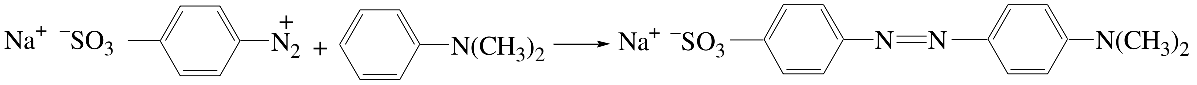


p-N, *N*-Dimethylaminoazobenzene

Electron-withdrawing groups make the diazonium ion less stable and thus more reactive than PhN_2^+.

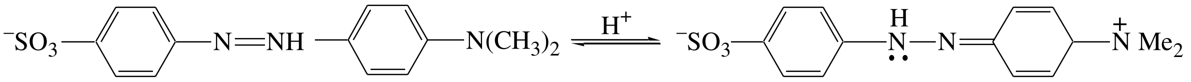
For example PhN_2^+ does not couple with C_6H_5OR but 2,4-$(O_2N)_2C_6H_5N_2^+$ does couple with the comopound C_6H_5OR.

The coupling of  with $PhN(CH_3)_2$ forms the acid-base methyl orange indicator.



Methyl orange

At pH ≥ 4.4, methyl orange is yellow while at pH ≤ 3.1, it is red in colour.



(yellow) (red)

For coupling reactions, solution should neither be strongly basic nor strongly acidic but mild acidic.

In strongly basic or acidic medium, the following reactions prevent coupling.

Strongly basic $\mathrm{Ar}\overset{+}{\mathrm{N}}\equiv\mathrm{N}\colon \xrightleftharpoons{OH^-} \mathrm{Ar}\ddot{\mathrm{N}}{=}\ddot{\mathrm{N}}\text{—}\mathrm{OH} \xrightleftharpoons{-H^+} \mathrm{Ar}\ddot{\mathrm{N}}{=}\ddot{\mathrm{N}}\text{—}\mathrm{O}^-$

a diazoic acid a diazotate anion

Strongly acidic $ArNH_2 \xrightarrow{H^+} Ar\,NH_3^+$

7. Synthetic Use of Diazonium Salt One of the best general ways of introducing F, Cl, Br, I, CN, OH and H into an aromatic ring is via diazonium salt. The freshly prepared diazonium salt (primary aromatic amine in cold aqueous mineral acid + sodium nitrite) is treated with other reagents to get the required product.

(a) The replacement by —Cl or —Br can be carried out by either of the following ways**:**
Sandmeyer Reaction The diazonium salt is treated with cuprous chloride or cuprous bromide

$$Ar\text{—}N_2^+\,X^- \xrightarrow{CuX} Ar\text{—}X + N_2$$

Gattermann Reaction In this, copper powder and hydrogen halide are used in place of cuprous halide.

(b) The replacement by —I is achieved by simply adding KI to diazonium salt

$$\text{Ar—N}_2^+\text{X}^- + \text{I}^- \rightarrow \text{Ar—I} + \text{N}_2 + \text{X}^-$$

(c) The replacement by —F is achieved as follows

$$\text{Ar—N}_2^+\text{X}^- \xrightarrow{\text{HBF}_4} \underset{\substack{\text{stable salt,}\\ \text{filtered and dried}}}{\text{Ar—N}_2^+\text{BF}_4^-} \xrightarrow{\text{heat}} \text{Ar—F} + \text{BF}_3 + \text{N}_2$$

(d) The replacement by —CN is carried out by adding cuprous cyanide to diazonium salt

$$\text{Ar—N}_2^+\text{X}^- \xrightarrow{\text{CuCN}} \text{Ar—CN} + \text{N}_2$$

Hydrolysis of nitrile produces carboxylic acid.

(e) The replacement by —OH is carried out by adding water to diazonium salt.

$$\text{Ar—N}_2^+\text{X}^- + \text{H}_2\text{O} \rightarrow \text{Ar—OH} + \text{N}_2 + \text{H}^+$$

To avoid coupling of Ar—OH with Ar—$\text{N}_2{}^+\text{X}^-$ (which form azo compounds by coupling), the latter is slowly added to large volume of water.

(f) The replacement by —H is achieved by the reducing agent hypophosphorous acid, H_3PO_2

$$\text{Ar—N}_2^+\text{X}^- + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{Ar—H} + \text{N}_2 + \text{H}_3\text{PO}_3 + \text{HX}$$

8. Hofmann Elimination Amines can be made to undergo an elimination reaction under suitable conditions to yield alkenes. The reaction is known as elimination reaction. The amine is methylated with excess of methyl iodide, yielding a quaternary ammonium iodide. The latter produces an alkene when heated with silver oxide. The less substituted alkene in contrast to the more substituted stable alkene predominates in this reaction. For example, 1-butene is formed from butylamine.

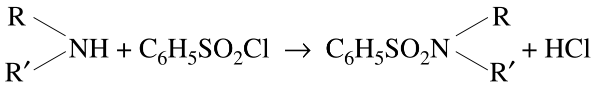
$$\begin{tikzcd}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \arrow[r, "\text{CH}_3\text{ I}", "\text{(excess)}"'] & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{N}}(\text{CH}_3)_3\ \text{I}^- \arrow[d, "\text{Ag}_2\text{O, H}_2\text{O}", "-\text{AgI}"'] \\
\underset{\text{1-butene}}{\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2} & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{N}}(\text{CH}_3)_3\text{OH}^- \arrow[l, "\Delta"']
\end{tikzcd}$$

Hofmann Rule In Hofmann elimination, an alkene is formed as a result of the loss of more acidic βH (which follows the trend 1° > 2° > 3°). Since the amine is relatively poor leaving group, the transition state involves more C–H$^\beta$ bond breaking. Thus, the acidity of the βH becomes the deciding factor in the formation of the double bond.

9. Separation of a Mixture of Amines The mixture of the amine salt and quarternary salt is distilled with KOH solution. The three amines distil over leaving the quarternary salt behind. The three amines can be separated by either of the two methods given below.

(a) Hinsberg Method The mixture of three amines is treated with Hinsberg reagent (benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$). The primary and secondary amines react with Hinsberg reagent while tertiary does not. The reactions are

$$\text{R—NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \underset{\substack{N\text{-alkylbenzene-}\\ \text{sulphonamide}}}{\text{C}_6\text{H}_5\text{SO}_2\text{NHR}} + \text{HCl}\ ;$$



$$\text{RR}'\text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{SO}_2\text{NRR}' + \text{HCl}$$

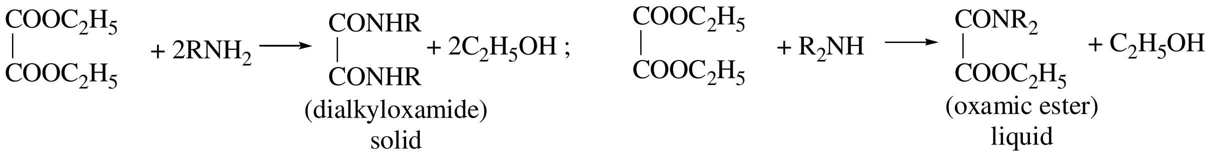
N, *N*-dialkylbenzene-sulphonamide

After the reactions are over, the solution is made alkaline with NaOH. The sulphonamide of primary amine is soluble in NaOH (due to the acidic hydrogen attached with the nitrogen) while that of secondary amine is insoluble (as there is no acidic hydrogen attached to nitrogen).

So after treating with NaOH, two layers are formed; aqueous phase containing soluble salt of primary amine ($\text{C}_6\text{H}_5\text{SO}_2\underset{\substack{|\\ \text{Na}}}{\text{N}}\text{R}$) and second layer containing insoluble salt of secondary amine and tertiary amine as such. The two layers are separated with the help of ether. The aqueous phase is hydrolysed with concentrated HCl when the primary amine is regenerated.

The ether layer is distilled and tertiary amine is distilled over. The residue is hydrolysed with concentrated HCl to recover secondary amine.

(b) Hofmann's Method The mixture of amines is treated with diethyloxalate which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react. The resultant mixture is filtered to separate solid which on treating with KOH liberates primary amine. The filtrate is fractionally distilled when tertiary amine distils over. The remaining liquid is treated with KOH and distilled when the secondary amine is distilled over. The reactions occurring are as follows.



$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + 2RNH_2 \longrightarrow \underset{\substack{\text{(dialkyloxamide)} \\ \text{solid}}}{\begin{array}{l} CONHR \\ | \\ CONHR \end{array}} + 2C_2H_5OH\ ; \quad \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + R_2NH \longrightarrow \underset{\substack{\text{(oxamic ester)} \\ \text{liquid}}}{\begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \end{array}} + C_2H_5OH$$

Test for Primary Amine (Carbylamine reaction) The treatment of a primary amine with chloroform and alcoholic potash produces carbylamine (isocyanide) which has most offensive smell

$$RNH_2 + CHCl_3 + 3KOH \rightarrow R—NC + 3KCl + 3H_2O$$

This reaction is not exhibited by secondary and tertiary amines.

Test for Secondary Amine (Libermann reaction) The secondary amine is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solution is warmed with phenol and concentrated H_2SO_4, a brown or red colour is formed at first. Soon it change to blue and then to green. The colour changes to red on dilution and further changes to greenish-blue or violet on treating with alkali.

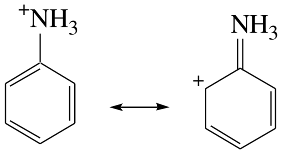
Straight Objective Type

General Characteristics

1. Chlorobenzene can be prepared by reacting aniline with
   (a) hydrochloric acid
   (b) cuprous chloride
   (c) chlorine in the presence of anhydrous aluminium chloride
   (d) nitrous acid followed by heating with cuprous chloride (1984)

2. Amongst the following, the most basic compound is
   (a) benzylamine (b) aniline (c) acetanilide (d) *p*-nitroaniline (1990)

3. Examine the following two structures for the anilinium ion and chose the correct statement from the ones given below.



(I) (II)

   (a) II is not acceptable canonical structure because carbonium ions are less stable than ammonium ions
   (b) II is not an acceptable canonical structure because it is nonaromatic
   (c) II is not an acceptable canonical structure because nitrogen has 10 valence electrons
   (d) II is an acceptable canonical structure (1993)

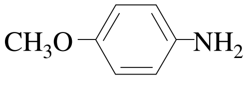
4. Which of the following statements is **not** correct?
   (a) Replacement of halogen by NH_2 in alkyl halide is a nucleophilic substitution reaction
   (b) Aryl halides show more reactivity as compared to alkyl halides in the replacements of halogen by the NH_2 group

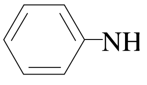
(c) During the replacement of halogen by —NH_2 group, ammonia is taken in large excess so as to avoid the formation of 2° and 3° amines
(d) Tertiary alkyl halide generally produces alkene instead of the replacement of halogen by NH_2 group

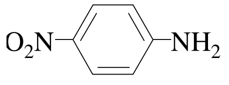
5. Which of the following statements is not correct?
(a) Primary amines show intermolecular hydrogen bonding.
(b) Secondary amines show intermolecular hydrogen bonding.
(c) Tertiary amines show intermolecular hydrogen bonding.
(d) Amines have lower boiling points as compared to those of alcohols and carboxylic acids of comparable molar masses.

6. Which of the following statements is **not** correct?
(a) Aliphatic amines are stronger bases than ammonia.
(b) Aromatic amines are stronger bases than ammonia.
(c) The alkyl group in alkyl ammonium ion more stabilizes the ion relative to the amine.
(d) The aryl group in aryl ammonium ion less stabilizes the ion relative to the amine.

7 Which of the following order is correct regarding the relative basicity of amines?


I


II


III

(a) I > II > III (b) I < II < III (c) I < III < II (d) III < I < II

8. Activation of benzene ring by — NH_2 in aniline can be reduced by treating with
(a) dilute HCl (b) ethyl alcohol (c) acetic acid (d) acetyl chloride

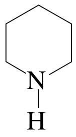
9. Which of the following orders is correct regarding the basic strength of substituted aniline?
(a) *p*–nitroaniline > *p*–aminobenzaldehyde > *p*–bromoaniline
(b) *p*–nitroaniline < *p*–bromoaniline < *p*–aminobenzaldehyde
(c) *p*–nitroaniline < *p*–aminobenzaldehyde < *p*–bromoaniline
(d) *p*–nitroaniline > *p*–aminobenzaldehyde < *p*–bromoaniline

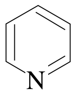
10. Which of the following orders regarding the basic strength of substituted aniline is correct?
(a) *p*–methylaniline > *p*–chloroaniline > *p*– aminoacetophenone
(b) *p*–methylaniline > *p*–aminoacetophenone > *p*–chloroaniline
(c) *p*–aminoacetophenone > *p*–methylaniline > *p*–chloroaniline
(d) *p*–aminoacetophenone > *p*–chloroaniline > *p*–methylaniline

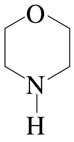
11. The number of resonating structures of arylammonium ion is
(a) 2 (b) 3 (c) 4 (d) 5

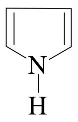
12. The number of resonating structures of aniline is
(a) 2 (b) 3 (c) 4 (d) 5

13. In the following compounds


(I)


(II)


(III)


(IV)

the order of basicity is
(a) IV > I > III > II (b) III > I > IV > II
(c) II > I > III > IV (d) I > III > II > IV (1997)

14. Among the following, the strongest base is
(a) $C_6H_5NH_2$ (b) *p*-$NO_2C_6H_4NH_2$ (c) *m*-$NO_2C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$ (2000)

15. The correct sequence regarding base strength of aliphatic amines in aqueous solution is
(a) $R_3N > R_2NH > RNH_2 > NH_3$ (b) $R_2NH > RNH_2 > R_3N > NH_3$
(c) $R_2NH > R_3N > RNH_2 > NH_3$ (d) $RNH_2 > R_2NH > R_3N > NH_3$

16. The correct sequence regarding base strength of aliphatic amines in gaseous phase is
(a) $R_3N > R_2NH > RNH_2 > NH_3$ (b) $R_3N > RNH_2 > R_2NH > NH_3$
(c) $R_2NH > R_3N > RNH_2 > NH_3$ (d) $R_2NH > RNH_2 > R_3N > NH_3$

17. The correct sequence for the complex formation of aliphatic amines with $B(CH_3)_3$ is
(a) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$
(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(c) $(CH_3)_2NH > NH_3 > CH_3NH_2 > (CH_3)_3N$
(d) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N > NH_3$.

18. Increasing order of basicity of $CH_3CH_2CH_2NH_2$, $H_2C{=}CHCH_2NH_2$ and $HC{\equiv}CCH_2NH_2$ is
(a) $CH_3CH_2CH_2NH_2 < HC{\equiv}CCH_2NH_2 < H_2C{=}CHCH_2NH_2$
(b) $CH_3CH_2CH_2NH_2 < H_2C{=}CHCH_2NH_2 < CH{\equiv}CCH_2NH_2$
(c) $HC{\equiv}CCH_2NH_2 < H_2C{=}CHCH_2NH_2 < CH_3CH_2CH_2NH_2$
(d) $HC{\equiv}CCH_2NH_2 < CH_3CH_2CH_2NH_2 < H_2C{=}CHCH_2NH_2$

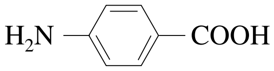
19. Decreasing order of basicity of $C_6H_5CH_2NH_2$, cyclohexyl—CH_2NH_2 and p-$O_2NC_6H_4CH_2NH_2$ is
(a) p-$O_2NC_6H_4CH_2NH_2 > C_6H_5CH_2NH_2 >$ cyclohexyl—CH_2NH_2
(b) p-$O_2NC_6H_4CH_2NH_2 >$ cyclohexyl—$CH_2NH_2 > C_6H_5CH_2NH_2$
(c) cyclohexyl—$CH_2NH_2 > C_6H_5CH_2NH_2 > p$-$O_2NC_6H_4CH_2NH_2$
(d) cyclohexyl—$CH_2NH_2 > p$-$O_2NC_6H_4CH_2NH_2 > C_6H_5CH_2NH_2$

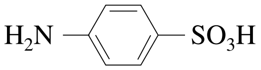
20. Decreasing order of basicity of the three isomers of nitroaniline is
(a) *p*-nitroaniline > *o*-nitroaniline > *m*-nitroaniline (b) *p*-nitroaniline > *m*-nitroaniline > *o*-nitroaniline
(c) *m*-nitroaniline > *p*-nitroaniline > *o*-nitroaniline (d) *m*-nitroaniline > *o*-nitroaniline > *p*-nitroaniline

21. Decreasing order of basicity of the three isomers of methoxyaniline is
(a) p-$CH_3OC_6H_4NH_2 > o$-$CH_3OC_6H_4NH_2 > m$-$CH_3OC_6H_4NH_2$
(b) p-$CH_3OC_6H_4NH_2 > m$-$CH_3OC_6H_4NH_2 > o$-$CH_3OC_6H_4NH_2$
(c) o-$CH_3OC_6H_4NH_2 > p$-$CH_3OC_6H_4NH_2 > m$-$CH_3OC_6H_4NH_2$
(d) o-$CH_3OC_6H_4NH_2 > m$-$CH_3OC_6H_4NH_2 > p$-$CH_3OC_6H_4NH_2$

22. The correct sequence of basicity of $CH_3CH_2NH_2$, CH_3CONH_2 and $PhCONH_2$ is
(a) $CH_3CH_2NH_2 > CH_3CONH_2 > PhCONH_2$ (b) $CH_3CH_2NH_2 > PhCONH_2 > CH_3CONH_2$
(c) $CH_3CONH_2 > PhCONH_2 > CH_3CH_2NH_2$ (d) $PhCONH_2 > CH_3CONH_2 > CH_3CH_2NH_2$

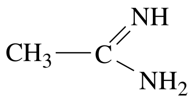
23. Which of the following compounds does not exist as a bipolar ion?
(a) H_2NCH_2COOH

(b)


(c)


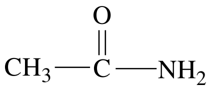
(d) $H_2NCH_2CH_2CH_2OH$

24. The correct order of basicities of the following compounds


$CH_3-C(=NH)-NH_2$
1

$CH_3-CH_2-NH_2$
2

$(CH_3)_2NH$
3

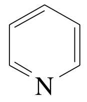

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$
4

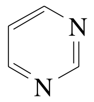
is
(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4 (c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4 (2001)

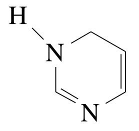
25. The correct order of basicities of $PhNH_2$(A), Ph_2NH(B) and cyclohexyl—NH_2(C) is
(a) A > B > C (b) A > C > B (c) C > A > B (d) C > B > A

26. The correct order of basicities of CH_3CONH_2(A), $PhCONH_2$(B) and $CH_3CH_2NH_2$(C) is
(a) A > B > C (b) A > C > B (c) C > A > B (d) C > B > A

27. The correct order of basicity of


(I)
pyridine


(II)
pyrimidine


(III)
imidazole

is
(a) III > I > II (b) I > III > II (c) III > II > I (d) I > II > III

28. The correct order of basicity of RCN, $RCH{=}NR$ and RNH_2 is
(a) $RNH_2 > R{-}C{\equiv}N > R{-}CH{=}NR$ (b) $RNH_2 > R{-}CH{=}NR > R{-}C{\equiv}N$
(c) $R{-}C{\equiv}N > RNH_2 > R{-}CH{=}NR$ (d) $R{-}C{\equiv}N > R{-}CH{=}NR > RNH_2$

29. The correct order of basicity of $CH_3CH_2NH_2$, $HO(CH_2)_3NH_2$ and $HO(CH_2)_2NH_2$ is
(a) $HO(CH_2)_2NH_2 < HO(CH_2)_3NH_2 < CH_3CH_2NH_2$
(b) $HO(CH_2)_2NH_2 < CH_3CH_2NH_2 < HO(CH_2)_3NH_2$
(c) $HO(CH_2)_3NH_2 < HO(CH_2)_2NH_2 < CH_3CH_2NH_2$
(d) $HO(CH_2)_3NH_2 < CH_3CH_2NH_2 < HO(H_2)_2NH_2$

30. The correct order of base strength of the amines $CH_3(CH_2)_2NH_2$, $CH_2{=}CHCH_2NH_2$ and $HC{\equiv}CCH_2NH_2$ is
(a) $CH_3(CH_2)_2NH_2 < H_2C{=}CHCH_2NH_2 < HC{\equiv}CCH_2NH_2$
(b) $CH_3(CH_2)_2NH_2 < HC{\equiv}CCH_2NH_2 < H_2C{=}CHCH_2NH_2$
(c) $HC{\equiv}CCH_2NH_2 < H_2C{=}CHCH_2NH_2 < CH_3(CH_2)_2NH_2$
(d) $HC{\equiv}CCH_2NH_2 < CH_3(CH_2)_2NH_2 < H_2C{=}CHCH_2NH_2$

31. The correct order of base strength of the three isomers of methoxyaniline is
(a) $p\text{-}CH_3OC_6H_4NH_2 > o\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2$
(b) $p\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2 > o\text{-}CH_3OC_6H_4NH_2$
(c) $o\text{-}CH_3OC_6H_4NH_2 > p\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2$
(d) $o\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2 > p\text{-}CH_3OC_6H_4NH_2$

Chemical Reactions

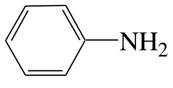
32. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is
(a) methylamine (b) ethylamine (c) diethylamine (d) triethylamine (1981)

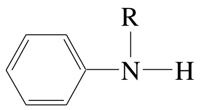
33. Acetamide is treated separately with the following reagents. Which one of these would give methylamine?
(a) PCl_5 (b) sodalime (c) $NaOH + Br_2$ (d) hot concentrated H_2SO_4 (1983)

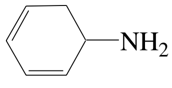
34. Carbylamine test is performed in alcoholic KOH by heating a mixture of
(a) chloroform and silver powder (b) trihalogenated methane and a primary amine
(c) an alkyl halide and a primary amine (d) an alkyl cyanide and a primary amine (1984)

35. Which of the following amines form N–nitroso derivative when treated with $NaNO_2$ and HCl.

(a) CH_3NH_2

(b) 

(c) 

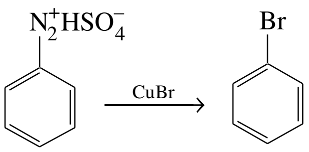
(d) 

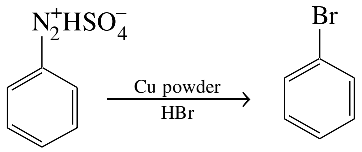
36. On warming an aqueous solution of benzenediazonium chloride, the product obtained is
(a) benzene (b) aniline (c) phenol (d) amide

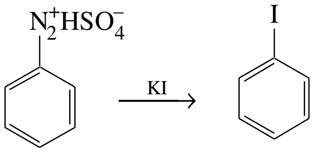
37. Which of the following reagents can convert benzenediazonium chloride into benzene?
(a) Water (b) Acid
(c) Hypophosphorous acid (d) HCl

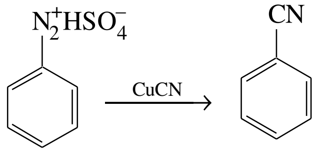
38. The bromination of aniline produces
(a) 2-bromoaniline (b) 4-bromoaniline
(c) 2, 4, 6-tribromoaniline (d) 2, 6-dibromoaniline

39. Which of the following reactions is an example of Sandmeyer reaction?

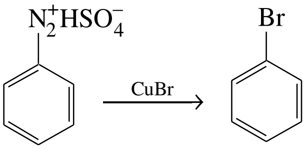
(a) 

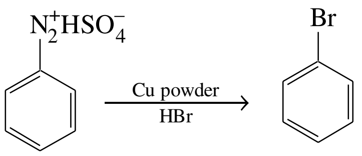
(b) 

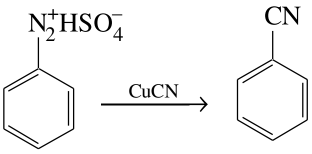
(c) 

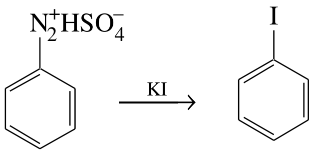
(d) 

40. Which of the following reactions is an example of Gattermann reaction?

(a) 

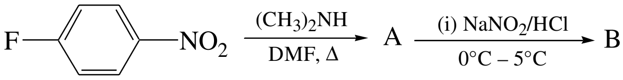
(b) 

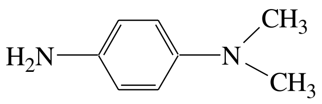
(c) 

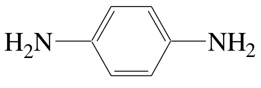
(d) 

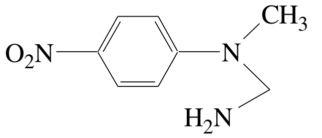
41. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives
(a) diphenyl ether (b) *p*-hydroxyazobenzene (c) chlorobenzene (d) benzene (1998)

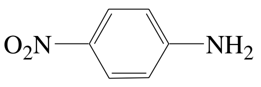
42. The reduction of $PhNO_2$ with $Zn/NH_4Cl(aq)$ gives
(a) PhNHOH (b) $PhNH_2$ (c) PhNHNHPh (d) PhOH

43. In the reaction  the product B is

(a) 

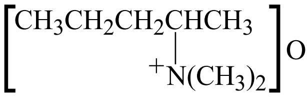
(b) 

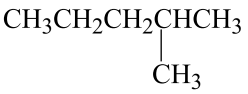
(c) 

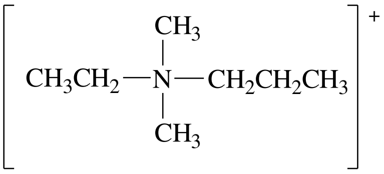
(d) 

44. In the reaction $RNH_2 + CHCl_3 + KOH \longrightarrow A + 3KCl + H_2O$
(a) R—CN (b) $R - \overset{\ominus}{N} \equiv \overset{\oplus}{C}:$ (c) $R - \overset{\oplus}{N} \equiv \overset{\ominus}{C}:$ (d) R—NHCl (2006)

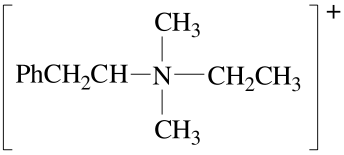
Hofmann Elimination

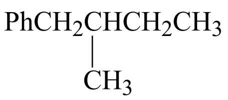
45. The major product obtained on heating  $\left[CH_3CH_2CH_2\underset{^+N(CH_3)_2}{\underset{|}{C}}HCH_3\right]OH^-$ is

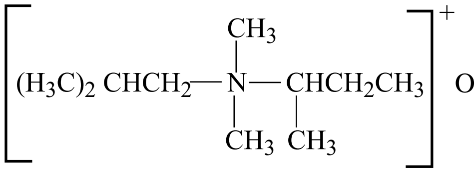
(a) $CH_3CH_2CH=CHCH_3$
(b) $CH_3CH_2CH_2CH=CH_2$
(c) $CH_3CH=CH_2$
(d)  $CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$

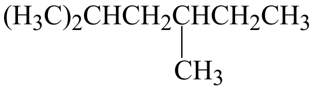
46. The major product obtained on heating of  $\left[CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N}}}}-CH_2CH_2CH_3\right]^+ OH^-$ is

(a) $H_2C=CH_2$ (b) $H_2C=CH-CH_3$ (c) H_3C-CH_3 (d) $CH_3CH_2CH_2CH_2CH_3$

47. The major product obtained on heating of  $\left[PhCH_2CH-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N}}}}-CH_2CH_3\right]^+ OH^-$ is

(a) $H_2C=CH_2$ (b) $PhCH=CH_2$ (c)  $PhCH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$ (d) H_3C-CH_3

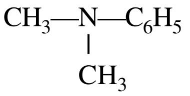
48. The heating of  $\left[(H_3C)_2CHCH_2-\overset{CH_3}{\underset{CH_3}{N}}-\underset{CH_3}{CHCH_2CH_3}\right]^+ OH^-$ gives

(a) $CH_3CH=CHCH_3$
(b) $(CH_3)_2C=CH_2$
(c) $CH_2=CHCH_2CH_3$
(d)  $(H_3C)_2CHCH_2\underset{CH_3}{CH}CH_2CH_3$

Characterization

49. Hinsberg's reagent is
(a) phenylisocyanide
(b) benzenesulphonyl chloride
(c) *p*-toluenesulphonic acid
(d) *o*-dichlorobenzene

50. Hofmann's method to separate amines in a mixture uses the reagent
(a) benzenesulphonyl chloride
(b) diethyl oxalate
(c) benzeneisocyanide
(d) *p*-toluenesulphonic acid

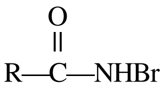
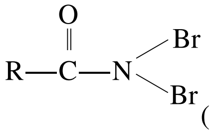
51. Which of the following compounds will dissolve in an alkali solution after it has undergone reaction with Hinsberg reagent?
(a) $(C_2H_5)_2NH$
(b)  $CH_3-\underset{CH_3}{N}-C_6H_5$
(c) CH_3NH_2
(d) $C_6H_5NHC_6H_5$

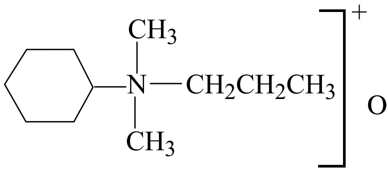
52. A positive carbylamine test is given by
(a) *N*, *N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine (1999)

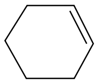
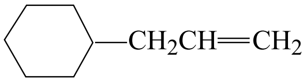
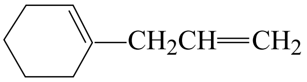
53. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by
(a) Sandmeyer reaction
(b) $NaHCO_3$
(c) $AgNO_3$
(d) Carbylamine test (1998)

Multiple Correct Choice Type

1. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediates involved in the reaction are

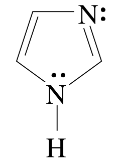
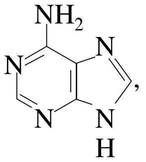
(a)  $R-\overset{O}{\overset{\|}{C}}-NHBr$
(b) R—NHBr
(c) R—N═C═O
(d)  $R-\overset{O}{\overset{\|}{C}}-N\begin{smallmatrix}Br\\Br\end{smallmatrix}$ (1993)

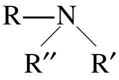
2. The product(s) obtained on heating  OH⁻ is/are

(a) 
(b) $H_2C=CHCH_3$
(c) 
(d) 

3. Aniline
(a) is more basic than ammonia
(b) can be steam distilled
(c) forms phenol when reacted with HNO_2 at 0°C
(d) gives ethane with C_2H_5MgBr

4. Sandmeyer's reaction can be represented by
(a) $C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl$
(b) $C_6H_5N_2Cl \xrightarrow{\text{Copper powder}} C_6H_5Cl$
(c) $C_6H_5N_2Cl \xrightarrow{Cu_2(CN)_2} C_6H_5CN$
(d) $C_6H_5N_2Cl \xrightarrow{Cu_2Br_2} C_6H_5Br$

5. Which of the following statements are **not** correct?
   (a) Guanidine $(H_2N)_2C{=}NH$ is expected to be a strong base.
   (b) Aniline is more basic than pyridine.
   (c) Imidizole,  , has two basic sites.
   (d) Purine, , has five basic sites.

6. Which of the following statements are **not** correct?
   (a) Amines have lower boiling points than nonpolar compounds of the same molar mass.
   (b) Amines have higher boiling points than alcohols or carboxylic acids of comparable molar mass.
   (c) Aliphatic amines are as basic as ammonia but aromatic amines are more basic.
   (d) Although nitrogen in  is chiral and also the mirror image of the molecule is not superimposable on the molecule itself, yet the molecule does not show optical activity.

7. Which of the following statements are correct?
   (a) Quaternary ammonium salts in which nitrogen holds four different groups show optical activity.
   (b) Aliphatic amines can be prepared by ammonolysis of alkyl halides but not aromatic amines.
   (c) Ammonolysis of alkyl halides gives highest yield with tertiary halides and is worthless for primary halides.
   (d) The more stable the substituted ammonium ion relative to the amine from where it is formed, the more basic is the amine.

8. Which of the following statements are correct?
   (a) Aniline is less basic than ammonia because resonance stabilization of aniline is larger than the resonance stabilization of anilinium ion.
   (b) Electron-releasing substituent decreases the basicity of aniline.
   (c) Electron-withdrawing substituent increases the basicity of aniline.
   (d) Base-strengthening substituents are the one that activate an aromatic ring toward electrophilic substitution.

9. Which of the following statements are **not** correct?
   (a) Base-weakening substituents are the one that activate an aromatic ring toward electrophilic substitution.
   (b) Aliphatic amine forms stable diazonium salt with nitrous acid.
   (c) All amino compounds can be distinguished by using the reagents chloroform and potassium hydroxide.
   (d) The sulphonamide formed from secondary amine does not form sodium salt and is also insoluble in water.

10. Which of the following statements are correct?
   (a) Only one NO_2 group is reduced in *m*-dinitrobenzene if treated with NH_4SH.
   (b) $C_6H_5N(CH_3)(C_2H_5)$ can be resolved into enantiomers.
   (c) Bromination of aniline produces *ortho-* and *para*-bromoaniline.
   (d) Nitration of aniline is carried out by first converting aniline to acetanilide.

11. Which of the following statements are **not** correct?
   (a) The order of acid strength in the given compounds is $NH_3 > CH_3CONH_2 > (CH_3CO)_2NH$.
   (b) *p*-Aminobenzoic acid is a dipolar ion.
   (c) Sulphanilic acid can exist as a dipolar ion.
   (d) In Hoffmann elimination, a more substituted alkene is produced.

12. Which of the following statements are correct?
   (a) In aqueous solution, R_2NH is a stronger base than RNH_2.
   (b) In aqueous solution, R_3N is a stronger base than R_2NH.
   (c) In aqueous solution, R_3N is a stronger base then RNH_2.
   (d) In gaseous phase, R_3N is a stronger base than R_2NH, which, in turn, is greater than RNH_2.

13. Which of the following statements are correct?
(a) The ability of complex formation of $(CH_3)_3N$ with $B(CH_3)_3$ is greater than that of $(CH_3)_2NH$.
(b) The ability of complex formation of $(CH_3)_2NH$ with $B(CH_3)_3$ is greater than that of CH_3NH_2.
(c) The increasing order of basicity of RCN, RCH═NR and RNH_2 is

$$R—C\equiv N: < R—CH═NR < RNH_2$$

(d) The increasing order of basicity of $CH_3CH_2NH_2$, $HO(CH_2)_3NH_2$ and $HO(CH_2)_2NH_2$ is

$$HO(CH_2)_2NH_2 > HO(CH_2)_3NH_2 > CH_3CH_2NH_2$$

14. Which of the following statements are correct?
(a) NF_3 is less basic than NH_3.
(b) Guanidine, $HN═C(NH_2)_2$, is a weak base.
(c) The bond angle in NH_3 is greater than in NF_3.
(d) The decreasing base strength of the amines $CH_3(CH_2)_2NH_2$, $CH_2═CHCH_2NH_2$ and $HC\equiv CCH_2NH_2$ is

$$CH_3(CH_2)_2NH_2 > H_2C═CHCH_2NH_2 > HC\equiv CCH_2NH_2.$$

15. Which of the following statements are correct?
(a) The decreasing base strength of the three isomers of nitroaniline is

o-nitroaniline > *p*-nitroaniline > *m*-nitroaniline

(b) All *ortho*-substituted anilines are less basic than *para*-substituted amilines regardless of the electronic effect of the substituent.
(c) The decreasing base strength of aniline and three isomers of methoxyaniline is

$$p\text{-}CH_3OC_6H_4NH_2 > C_6H_5NH_2 > o\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2$$

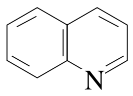
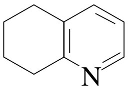
(d) The decreasing base strength of aniline and three toluidines is

$$p\text{-}CH_3C_6H_4NH_2 > C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2 > m\text{-}CH_3C_6H_4NH_2$$

16. Which of the following statements are correct?
(a) Amides are much weaker bases than amines.
(b) $PhCONH_2$ is a stronger base than CH_3CONH_2.
(c) N, N-Dimethylaniline is only slightly more basic than aniline whereas 2,6-dimethyl-N,N-dimehylanline is much more basic than 2,6-dimethylaniline.
(d) *p*-Nitroaniline is a weaker base than *p*-cyanoaniline.

17. Which of the following statements are **not** correct?
(a) 3,4,5-Trinitroaniline is less basic than 4-cyano-3,5-dinitroaniline.
(b) The increasing order of basicities of pyrrole, pyridine and piperidine is

Pyrrole < Pyridine < Piperidine.

(c) Pyrrole is soluble in dilute HCl.
(d) The catalytic reduction of quinoline  involving two equivalents of H_2 produces 

18. Which of the following statements are correct?
(a) The main product obtained in the reaction of chloroform with aniline in the presence of excess of alkali is benzeneisonitrile.
(b) Amines are more basic than alcohols, ethers and esters.
(c) Nitrogen involves sp^2 orbitals in bonding with other atoms or groups in amines.
(d) Amines are less basic than water and also less basic than hydroxide ion.

19. Which of the following statements are **not** correct?
(a) pK_b°(aniline) is less than pK_b°(*p*-nitroaniline).
(b) pK_b°(aniline) is more than pK_b°(*p*-aminoaniline).
(c) Aliphatic amines are more basic than ammonia.
(d) The $—NH_2$ group is more powerful activator of aromatic ring than $—NHCOCH_3$.

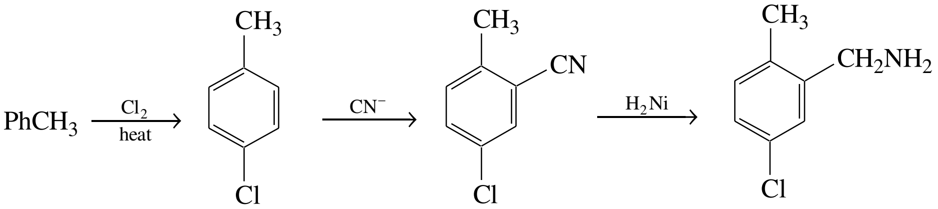
20. Which of the following statements are **not** correct?
(a) Secondary amines, both aliphatic and aromatic, react with nitrous acid to yield N-nitrosoamines.
(b) Tertiary aromatic amines react with nitrous acid to yield *p*-nitroso derivatives.

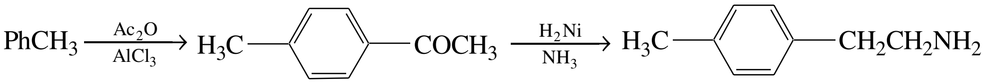
(c) In Sandmeyer reaction, the reagent KCl is added to aromatic diazonium salt to yield Ar—Cl.
(d) In Gattermann reaction, the reagent CuCl is added to aromatic diazonium salt to yield Ar—Cl.

21. Which of the following statements are **not** correct?
(a) Iodobenzene can be obtained from benzenediazonium salt by adding the reagent KI.
(b) Flurobenzene can be obtained from benzenediazonium salt by adding the reagent KF followed by heating.
(c) Benzenediazonium salt reacts with water to yield phenol.
(d) Benzenediazonium salt reacts with water to yield benzene.

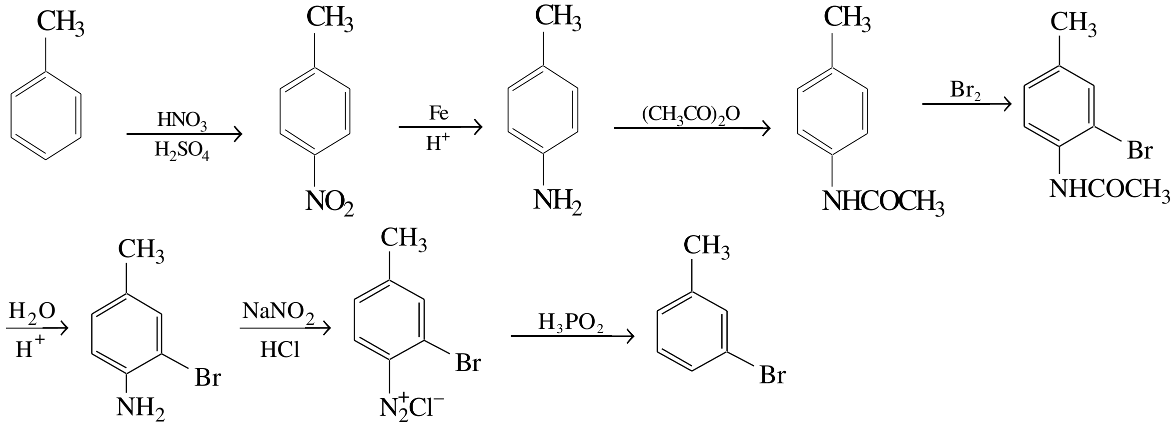
22. Which of the following statements are **not** correct?
(a) Hinsgberg test involves the reagent benzenesulphonyl chloride, in the presence of aqueous potassium hydroxide to distinguish primary, secondary and tertiary amines.
(b) Libermann reaction is shown only by primary amines.
(c) Primary amine gives liquid oxamide when treated with diethyloxalate.
(d) Secondary amine gives solid oxamide when treated with diethyloxalate.

23. Which of the following reactions are **not** correctly formulated?

(a) 

(b) 

(c) $PhCH_3 \xrightarrow{KMnO_4} PhCOOH \xrightarrow{PCl_5} \xrightarrow{NH_3} PhCONH_2 \xrightarrow{OBr^-} PhNH_2$

(d) 

24. Among the following compounds, which will react with acetone to give a product containing $>C{=}N-$?
(a) $C_6H_5NH_2$
(b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$
(d) $C_6H_5NHNH_2$

Linked Comprehension Type

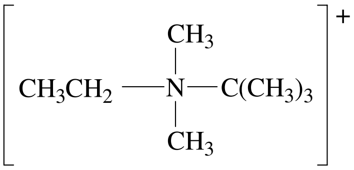
1. Consider the aliphatic amines NH_3, RNH_2, R_2NH and R_3N. These are basic in nature. Identify the correct choice is the following.

(i) The most basic amine in aqueous solution is
(a) NH_3
(b) RNH_2
(c) R_2NH
(d) R_3N

(ii) The most basic amine in gaseous phase is
(a) NH_3
(b) RNH_2
(c) R_2NH
(d) R_3N

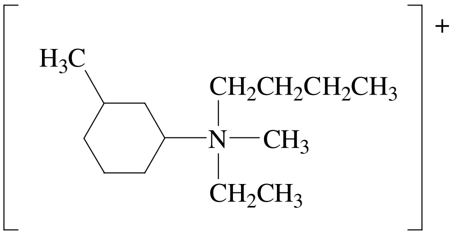
(iii) The least basic amine both in aqueous solution and gaseous phase is
(a) NH_3 (b) RNH_2 (c) R_2NH (d) R_3N

2. Amines can be made to undergo an elimination reaction under suitable conditions to yield alkenes. The amine is methylated with excess of methyl iodide yielding a quaternary ammonium chloride followed by heating with silver oxide. The less substituted alkene in contrast to more substituted stable alkene is formed in predominate amount. The acidity of the βH decides the nature of product formed. The more acidic βH is eliminated to give the product. Based on this information, answer the following three questions.

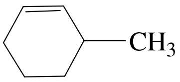
(i) The major product formed on heating 

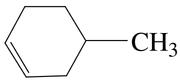
$\left[\mathrm{CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-C(CH_3)_3}\right]^+$ OH^- is

(a) $CH_2{=}CH_2$ (b) $(CH_3)_2C{=}CH_2$ (c) $CH_3CH{=}CHCH_3$ (d) $(CH_3)_2C{=}C(CH_3)_2$

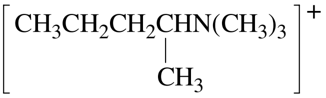
(ii) The major product formed on heating 

OH^- is

(a) 

(b) 

(c) $H_2C{=}CH_2$ (d) $CH_2CHCH_2CH_3$

(iii) The major product on heating of 

$\left[\mathrm{CH_3CH_2CH_2\underset{\displaystyle CH_3}{C}HN(CH_3)_3}\right]^+$ OH^- is

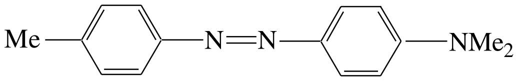
(a) $CH_3CH_2CH_2CH{=}CH_2$ (b) $H_2C{=}CH{-}CH_3$ (c) $(CH_3)_2C{=}CH_2$ (d) $(CH_3)_2C{=}CHCH_3$

Assertion and Reason Type

Given below are questions, each containing two statements. Based on the following key, answer correctly each question.

(a) Both statements are correct and the Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and the Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is incorrect and Statement-2 is correct.

	Statement – 1	**Statement – 2**
1.	In strongly acidic conditions, aniline becomes more reactive towards electrophilic reagents.	The amino group being completely protonated in strongly acid solution, the lone pair of electrons on the nitrogen is no longer available for resonance. (2001)
2.	*p*-Nitroaniline is more basic than *p*-cyanoaniline.	The nitro group is more effective than cyano group in weakening the basic nature of aniline.
3.	Primary amines, RNH_2, add to aldehydes and ketones to yield imines. The yield is maximum at pH about 4.5.	The yield is maximum at pH about 4.5 because at low pH protonation of amine occurs and at high pH protonation of intermediate carbinolamine cannot occur.
4.	Aniline on reaction with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.	The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with *β*-naphthol is due to the extended conjugation.

5. Aryl diazonium ions are more stable than alkyl diazonium ions.	Electron-release from the *ortho* and *para* positions of the ring stabilizes the aryl diazonium ion.
6. PhN_2^+ couples with $PhNMe_2$ and not with $PhCH_3$.	PhN_2^+ couples only with the rings activated by strong activating groups.
7. *p*-Me–C_6H_4–N_2^+ couples with $C_6H_4NMe_2$ to give  This is not formed from MeC_6H_5 and p-N_2^+ –C_6H_4 –NMe_2.	MeC_6H_5 is not active enough to couple with *p*-N_2^+–C_6H_4–NMe_2.
8. Sulphanic acid has a very low melting point.	Sulphanic acid exists as dipolar ion *p*-$^-O_3SC_6H_4NH_3^+$.

ANSWERS

Straight Objective Type

1. (d) **2.** (a) **3.** (c) **4.** (b) **5.** (c) **6.** (b) **7.** (a)
8. (d) **9.** (c) **10.** (a) **11.** (a) **12.** (d) **13.** (d) **14.** (d)
15. (b) **16.** (a) **17.** (a) **18.** (c) **19.** (d) **20.** (c) **21.** (a)
22. (b) **23.** (b) **24.** (b) **25.** (c) **26.** (d) **27.** (a) **28.** (b)
29. (a) **30.** (c) **31.** (a) **32.** (c) **33.** (c) **34.** (b) **35.** (c)
36. (c) **37.** (c) **38.** (c) **39.** (a) **40.** (b) **41.** (b) **42.** (a)
43. (a) **44.** (c) **45.** (b) **46.** (a) **47.** (b) **48.** (c) **49.** (b)
50. (b) **51.** (c) **52.** (d) **53.** (c)

Multiple Correct Choice Type

1. (a), (c) **2.** (a), (b) **3.** (b), (d) **4.** (a), (d)
5. (b), (c), (d) **6.** (a), (b), (c) **7.** (a), (b), (d) **8.** (a), (d)
9. (a), (b), (c) **10.** (a), (d) **11.** (a), (b), (d) **12.** (a), (d)
13. (b), (c) **14.** (a), (c), (d) **15.** (b), (c) **16.** (a), (b), (c), (d)
17. (a), (c), (d) **18.** (a), (b), (c) **19.** (a), (b) **20.** (c), (d)
21. (b), (d) **22.** (b), (c), (d) **23.** (a), (b) **24.** (a), (d)

Linked Comprehension Type

1. **(i)** (c) **(ii)** (d) **(iii)** (a)
2. **(i)** (b) **(ii)** (c) **(iii)** (a)

Assertion and Reason Type

1. (d) **2.** (d) **3.** (a) **4.** (d) **5.** (a) **6.** (a) **7.** (a)
8. (d)

Hints and Solutions

Straight Objective Type

1. Chlorobenzene can be prepared by reacting aniline with nitrous acid followed by heating with curous chloride.

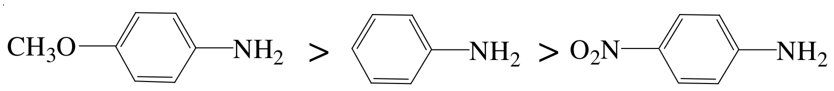
2. Alkyl amine (benzyl amine, $C_6H_5CH_2NH_2$) is the most basic compound.

4. The choice b is incorrect because aryl halides show less reactivity as compared to alkyl halides in the replacement of halogens by the NH_2 group.

5. The choice c is incorrect as tertiary amines do not possess hydrogen atom attached to nitrogen.

6. The choice b is incorrect as aromatic amines are less basic than ammonia.

7. Electron-relesing group makes aniline more basic and electron attracting group makes it less basic. The correct order of basicity is

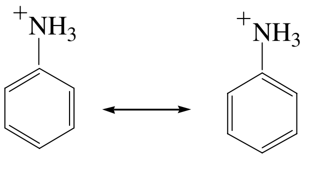


8. Acetyl chloride converts $C_6H_5NH_2$ into $C_6H_5NHCOCl$. The group —NHCOCl is less benzene activator than —NH_2 group.

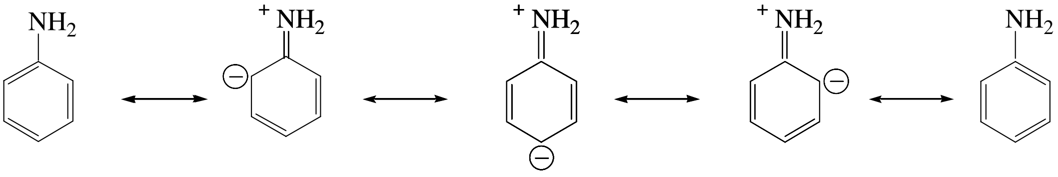
9. Electron-releasing group increases basicity of aniline while electron-withdrawing group decreases the basicity. Thus, the correct order of basicity is *p*-nitroaniline < *p*-aminobenzaldehyde < *p*-bromoaniline

10. Same as Q.9. The correct order of basicity is *p*-methylaniline > *p*-chloraniline > *p*-aminoacetophenone

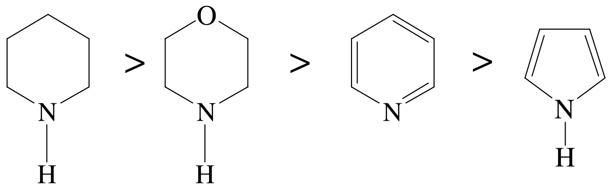
11. Arylammonium ion has two resonating structure



12. There are five resonating structures of aniline.



13. The order of basicity is



14. Aliphate amine ($C_6H_5CH_2NH_2$) is the strongest base.

15. In aqueous medium, the order of basicity is $R_2NH > RNH_2 > R_3N > NH_3$

16. In gaseous phase, the order of basicity is $R_3N > R_2NH > RNH_2 > NH_3$.

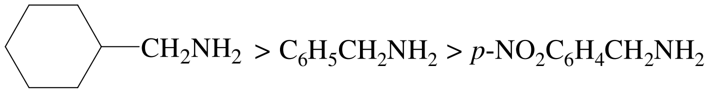
17. The correct sequence for the formation of complex of aliphatic amines with $B(CH_3)_3$ is

$(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3\,N$

18. The larger the s-character of a hybrid orbital of carbon, the larger electron-withdrawing (by induction) effect it has, consequently, the larger is its base-weakening effect. Thus, the correct order of basicity is

$HC \equiv CCH_2NH_2 < H_2C{=}CHCH_2NH_2 < CH_3CH_2CH_2NH_2$

19. The C^β in cyclohexyl —CH_2NH_2 uses sp^3 hybrid orbitals while C^β in the benzalamines uses sp^2 hybrid orbitals. The electron-withdrawing *p*-NO_2 makes the phenyl ring even more electron-withdrawing and base weakening. Hence, the correct order is



20. Nitro group is electron-withdrawing, by induction from all positions but mainly by extended bonding from the *ortho* and *para* positions. Hence, *para* isomer is less basic than *meta* isomer. Hence, the correct order is

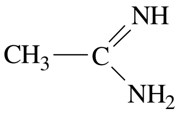
$C_6H_5NH_2 > m\text{-}NO_2C_6H_4NH_2 > p\text{-}NO_2C_6H_4NH_2$

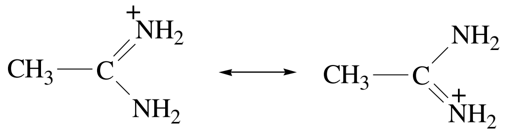
21. CH_3O is electron-releasing group. At *ortho* and *para* positions, the extended π bonding completely submerges the electron-withdrawing inductive effect. Only at *meta* position, the inductive effect predominates. Which makes *meta* isomer less basic than *para* and *ortho* isomers. At *ortho* position, due to steric hindrance, the substituents, irrespective of electron-releasing and electron-withdrawing effects, make the aniline less basic than the *p*-substituted aniline. Hence, the correct order is

$$p\text{-}CH_3OC_6H_4NH_2 > o\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2$$

22. The adjacent C═O weakens the basicity due to the delocalization of electron density from N to O. In $PhCONH_2$, this effect is weakened due to the formation of cross-conjugation.
Hence, the correct order of basicity is $CH_3CH_2NH_2 > PhCONH_2 > CH_3CONH_2$

23. *p*-Aminobenzoic acid is a much weaker acid. This is due to the electron-releasing —NH_2 group. Hence, this compound does not exist as a bipolar ion.

24. 
$CH_3—C(=NH)NH_2$ is most basic as its protonation leads to resonating cation with a large delocalization energy.



2° amine is more basic than 1° amine.

25. Cyclohexylamine is most basic as it is an aliphatic amine. Due to the delocalization of lone pair of electrons on N to the benzene ring, $PhNH_2$ and Ph_2NH are less basic than cyclohexylamine. The larger the number of Ph groups, more the delocalization and lesser basic is the compound.

26. Amide is a weaker base than an aliphatic amine owing to delocalization of lone pair of electrons of N to O. In $PhCONH_2$, the phenyl group increases the extent of delocalizing, hence, is a poor base than CH_3CONH_2.

27. Imidazole is stronger base than pyridine and pyrimidine.

28. The more s-character in the hybrid orbital of N with the lone pair of electrons, the less basic the molecule.

29. The larger the distance of O (which has electron-withdrawing inductive effct) from N, the stronger the base.

30. The larger the s-character of a hybrid orbital of carbon, the larger-electron withdrawing (by induction) effect and thus weaker the base.

31. The methoxy group is electron-donating by resonance from the *ortho* and *para* positions and thus increases the availability of electrons on N making them more basic. The resonance effect predominates over inductive effect which has electron-withdrawing effect. *Ortho* isomer is weaker than *para* isomer because of the *ortho* effect in which the solvation of cation is sterically hindered. *Meta* isomer is weakest because only inductive effect operates here.

32. Secondary amines produce nitrosoamines with aqueous nitrous acid at low temperature.

33. $CH_3CONH_2 \xrightarrow{\text{Na OH} + Br_2} CH_3NH_2$

34. Carbylamine test is performed in alcoholic KOH by heating a mixture of trihalogenated methane (say, $CHCl_3$) and a primary amine.

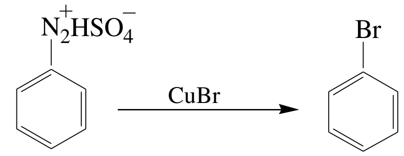
35. Secondary amines form N–nitroso derivatives with nitrous acid.

36. On warming an aqueous solution of benzenediazonium chloride, phenol is formed.

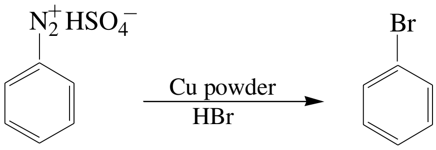
37. Hypophosphorous acid is used to convert benzenediazonium chloride into benzene.

38. The bromination of aniline produces 2,4,6-tribromoaniline.

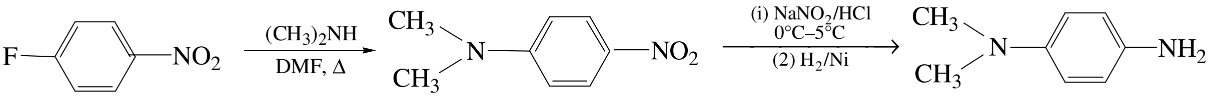
39. The Sandmeyer reaction is



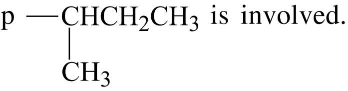
40. The Gattermann reaction is



41. Benzenediazonium chloride on reacting with phenol produces *p*-hydroxyazobenzene.
42. The product is PhNHOH.
43. The reactions are



44. The compound A is alkyl isonitrile $(R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:})$.
45. Since 1° H is most acidic, the double bond is formed by the elimination of H from the terminal —CH_3 group.
46. The removal of β 1° H from the terminal methyl of $^{\beta}CH_3CH_2$— group leads to the formation of $H_2C{=}CH_2$.
47. Due to the phenyl group, benzylic βH (Ph $CH_2\overset{\beta}{C}H$—) becomes the most acidic and also due to the stability of conjugated alkene, the compound $PhCH{=}CH_2$ rather than $H_2C{=}CH_2$ is formed.
48. Elimination of β 1° H from the group



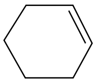
$$-\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$$

is involved.
49. Hinsberg reagent is benzenesulphonyl chloride.
50. Diethyl oxalate is used in Hofmann's method to separate amines.
51. Primary amine is soluble in alkali solution after it has undergone reaction with Hinsberg reagent.
52. *p*-Methylbenzylamine (a primary amine) shows carbylamine test.
53. Anilinium hydrochloride will give white precipitates of AgCl with $AgNO_3$.

Multiple Correct Choice Type

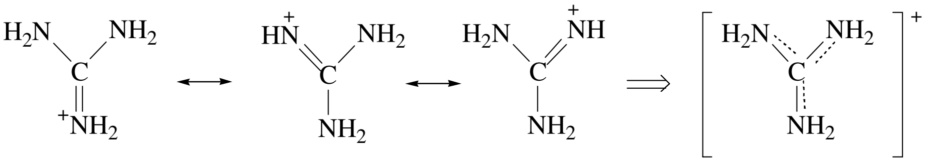
1. The intermediates involved in the reaction are RCONHBr and R—N=C=O.

2. Here there are two β 2° H. Hence, two products



and $H_2C{=}CHCH_3$ are formed.

5. Guanidine is a strong base as there is a greater resonance stabilization of the cation $[C(NH_2)_3]^+$. This is due to the contribution from three equivalent structures with the accommodation of positive charge by three nitrogens.

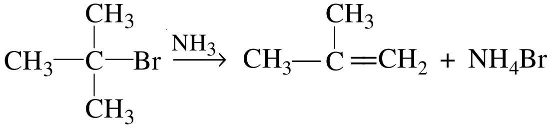


(a) The lone pair on nitrogen in aniline is considerably delocalised to the benzene ring, making the molecule quite stable. This stability is destroyed when H^+ adds to the nitrogen, thereby decreasing the basicity of aniline.
(b) The electron pair of H—N: is delocalised over the ring to provide the aromatic sextet. and thus is not a basic site. The nitrogen of :N=C retains electron density and is a basic site.
(c) Purine has three basic sites. These are the three double-bonded nitrogen. The lone pair of NH_2 and NH are involved in delocalisation.

6. (a) Being more polar than nonpolar compounds, amines have higher boiling point. There also exist hydrogen bonds amongst amines.
(b) Amines are less polar than alcohols and carboxylic acids.
(c) Aromatic amines are less basic than ammonia and aliphatic amines. Phenyl ring being electron attractor makes lone pair on nitrogen less readily available to an acid. Aliphatic amines are more basic than ammonia.
(d) The molecule and its mirror image is rapidly interconvertible. The energy barrier between the two is very less.

7. (b) Aryl halides have low reactivity toward nucleophilic substitution.
(c) Ammonolysis gives good yield with primary amines as nucleophilic substitution predominates but is worthless for tertiary amines as elimination reaction predominates to give alkenes.

$CH_3CH_2CH_2Br \xrightarrow{NH_3} CH_3CH_2CH_2NH_3^+Br^-$;



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow{NH_3} CH_3-\overset{CH_3}{C}=CH_2 + NH_4Br$$

8. (a) Aniline involves five resonating structures whereas anilinium ion involves only two. Hence, the former gets more stabilization than the latter. This fact makes aniline less basic. Alternatively, electron-attracting phenyl group makes lone pair less readily available to an acid as compared to ammonia.

(b) Electron-releasing substituent tends to disperse the positive charge of anilinium ion and thus stabilizes the ion relative to the amine making substituted aniline more basic than aniline.

(c) Electron-withdrawing substituent tends to increase the positive charge of anilinium ion and thus destabilized the ion relative to amine. This makes substituted aniline less basic than aniline.

9. (a) Electron-releasing groups are aromatic ring activators and they also push electrons toward nitrogen making lone pair of electrons more readily available for an acid. Hence, they are base-strengthening groups. Electron-withdrawing groups act in the opposite direction, hence, they are base-weakening group.

(b) Aliphatic amines form unstable diazonium salt which decompose to give nitrogen and aliphatic alcohols.

(c) Only primary amine can be distinguished as it produces carbylamine having most offensive smell

$$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$$

10. (b) Low energy barrier of inversion of configaration prevents resolution of the enantiomers of the given compound.

(c) 2, 4, 6-tribromoaniline is produced.

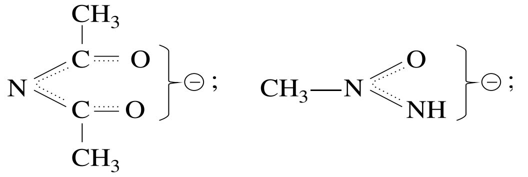
(d) This is done to avoid oxidation of aniline by nitric acid.

11. (a) The correct order is $NH_3 < CH_3CONH_2 < (CH_3CO)_2NH$

In the anion from ammonia, the negative charge is localized on nitrogen.

In the anion from acetamide, the negative charge is shared by nitrogen and one oxygen. In the anion from diacetamide, the negative charge is shared by nitrogen and two oxygens.

most stable



$^-NH_2$ least stable

(b) *p*-Aminobenzoic acid does not exist as dipolar ion. An aromatic —NH_2 group is a weak base and it cannot neutralize the —COOH group. It can, however, neutralize the stronger acidic —SO_3H group. Thus, sulphanilic acid can exist as dipolar ion.

(d) In Hofmann elimination, a less substituted alkene is produced.

12. (a) The base strength of aliphatic amines is decided by the following two factors:

(i) *Induction factor* Increasing replacement of H by R (electron-releasing group) increases electron density on N, thus making it more basic. $^-NH_2$ least stable

(ii) *Solvation factor* Stabilisation of conjugate acid through H-bonding with water. More the number of H atoms, more the stability and thus more basic is the amine.

Thus, induction and solvation operate in opposite directions. Induction dominates to make all three alkylamines stronger bases than NH_3 and to make dimethylamine stronger than methylamine. However, adding a third R as in R_3N does not further enhance the basicity because now the opposing solvation effect assumes more importance.

(d) Only induction factor operates in deciding the base strength.

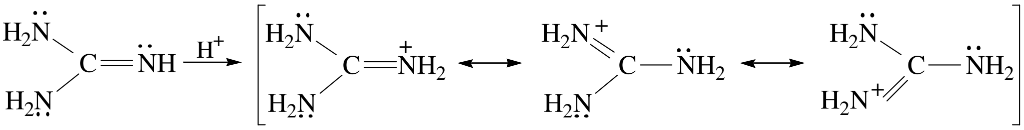
13. (a) The three methyl groups on N sterically interfere with the methyl groups on B, hindering close approach of the two molecules. Hence, the ability of R_3N to form a complex with $B(CH_3)_3$ is less than that of R_2NH.

(c) The more s-character in the hybrid orbital of N with the unshared pair of electrons, the less basic the molecule. Nitrile involves sp hybrid orbital, imine involves sp^2 hybrid orbital and amine involves sp^3 hybrid orbital of nitrogen to accommodate the unpaired electron.

(d) The electron-withdrawing inductive effect of oxygen decreases the electron density on nitrogen causing decrease in the basicity of amine. This effect diminishes with the distance from the amino group. Hence, the correct sequence is $CH_3CH_2NH_2 > HO(CH_2)_3NH_2 > HO(CH_2)_2NH_2$

14. (a) In NF_3, nitrogen acquires δ^+ charge because it is less electronegative than fluorine. With positive charge on nitrogen, the lone pair of electrons are more tightly held in NF_3.

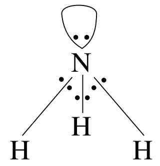
(b) In guanidine, the imino (=NH) nitrogen is sp^2 hybridised while amino (—NH_2) is sp^3 hybridised. The proton is likely to be attached to —NH_2 as its nitrogen has less s-character. Actually the imino nitrogen is protonated because this leads to the stable symmetrical resonating cation with very high delocalisation energy as there are three contributing structures.



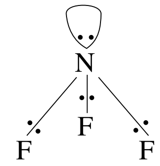
Because of the large delocalisation energy, the cation is very much stabilised leading the guanidine to act as a strong base.

(c) Ammonia involves more bonding pair-bonding pair electronic repulsion as the pairs are located near the nitrogen atom due to its more electronegative character. In NF_3, F is more electronegative and thus bonding pair lies more near F leading to less electronic repulsion.

(d) The larger the s-character of a hybrid orbital of carbon, the larger electron-withdrawing (by induction) effect it has, consequently, the larger is its base-weakening effect.



more electronic repulsion, more bond angle



less electronic repulsion, less bond angle

15. (a) Nitro group is electron-withdrawing, both by inductance and by extended π-bonding. The inductive effect operates from all positions with the sequence *ortho*-> *meta*-> *para*-. The electron-withdrawing through extended π-bonding operates only at *ortho* and *para* positions. Hence the electron-withdrawing effect will be maximum at *ortho* position and is least at *meta* position. Hence, the *meta* isomer is most basic and *ortho* isomer is least basic. Thus, the correct order is

$$m\text{-}O_2NC_6H_4NH_2 > p\text{-}O_2NC_6H_4NH_2 > o\text{-}O_2NC_6H_4NH_2$$

(b) This effect is attributed to steric hindrance to solvation of the cation by the *ortho* substitutent. This steric effect destabilises the cation making the amine a weaker base.

(c) The methoxy group is strong in electron-donating from the *ortho* and *para* positions by extended π-bonding. This effect is much larger than the electron-withdrawing inductive effect of oxygen. The *ortho* isomer is less basic than *para* isomer and aniline because of *ortho* effect in which the solvation of cation is sterically hindered, causing destabilisation of cation and thus making *ortho* isomer a weaker base. In *meta* isomer, only inductive effect operates making the base weakest one.

(d) An alkyl group is inductively electron-donating and base-strengthening from all the three positions —*ortho, para* and *meta*. Besides this, methyl group in *ortho* and *para* positions is electron-donating by hyperconjugation. Thus, in the three positions, the following effects operate.

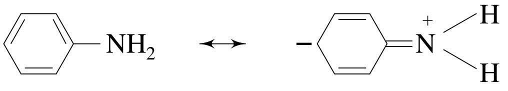
para isomer—Both hyperconjugation and induction effects
meta isomer—Only induction effect
ortho isomer—Both hyperconjugation and induction, but *ortho* effect (steric hinderanc) predominates.

Thus, the correct order of basicity is $p\text{-}CH_3C_6H_4NH_2 > m\text{-}CH_3C_6H_4NH_2 > C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2$

16. (a) The adjacent C=O weakens the basicity by delocalisation of electron density from N to O.

(b) The ability of C=O to cause base-weakening is attenuated by the phenyl group, making benzamide a stronger base than acetamide.

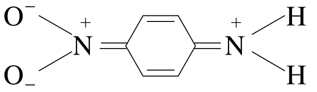
(c) Phenyl group has a base-weakening effect because of its ability to form extended p-bonding between the amino N and the phenyl ring.

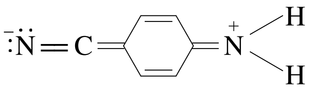


(I) (II)

In the structure II, N—H bonds are in the plane of benzene ring. In 2,6-dimethyl-N,N-dimethylaniline, the formation of extended π-bonding is sterically hindered and thus interfere with the base-weakening extended π-bonding making this compound much more basic than 2, 6-dimethylaniline.

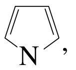
(d) The nitro group is more effective than cyano group in weakening the basic nature of aniline.



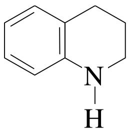


In nitroaniline, electron delocalisation ends up with the negative charge on the more electronegative oxygen atom whereas in cyanoaniline, the negative charge ends up in the nitrogen atom (which is less electronegative fhan oxygen).

17. (a) The base-weakening via electron delocalisation is achieved when N—O bonds of nitro group in nitroaniline are in the same plane of benzene ring. In 3,4,5-trimethylaniline, the attainment of coplanarity is sterically hindered and is thus not effective in base-weakening compared to 4-cyano-3-5-dinitroaniline. Cyano group, being linear, does not encounter this hinderance.

(b) In pyrrole , the lone pair on nitrogen is involved in the delocalisation over the ring and thus there is insufficient electron density on nitrogen to serve as a basic site. Piperidine is much more basic because it has sp^3 hybrid orbital (less s-character) while the N of pyridine has sp^2 hybrid orbital (more s-character).

(c) Pyrrole nitrogen has insufficient electron density to act as a basic site. It is not soluble in HCl.

(d) It is the pyridine ring which is reduced because this ring is more electron-deficient due to the electron-withdrawing N. Thus, the product is 

18. (d) Amines are more basic than water.

19. (a) *p*-Nitroaniline is less basic than aniline, i.e.

K_b(nitroaniline) < K_b(aniline) or pK_b°(*p*-nitroaniline) > pK_b°(aniline)

(b) *p*-aminoaniline is more basic than aniline, i.e.

K_b(aminoaniline) > K_b(aniline) or pK_b°(aminoaniline) < pK_b°(aniline)

20. (c) In Sandmeyer reaction, CuCl is added.

(d) In Gattermann reaction, the reagents Cu powder and hydrogen chloride are added.

21. (b) The reagent HBF_4 is added.

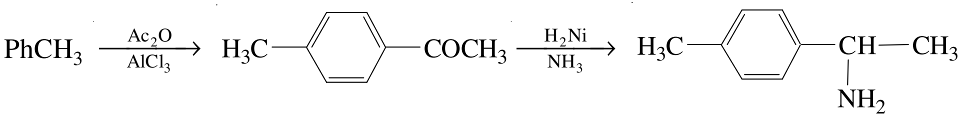
(d) The reagent H_3PO_2 is added.

22. (b) Secondary amines show Libermann reaction.

(c) Solid oxamide is obtained.

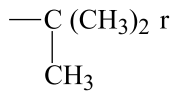
(d) Liquid oxamide is obtained.

23. (a) $PhCH_3 \xrightarrow[\text{heat}]{Cl_2} PHCH_2Cl \xrightarrow{CN^-} PhCH_2CN \xrightarrow{H_2/N:} PhCH_2CH_2NH_2$

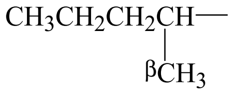
(b) 

Linked Comprehension Type

2.

(i) The removal of β 1° H from the  $—\underset{\displaystyle CH_3}{\underset{|}{C}}(CH_3)_2$ results in the formation of $(CH_3)_2C{=}CH_2$. The $H_2C{=}CH_2$ is also formed but to a lesser amount.

(ii) Here, the elimination of β 1° H of $—CH_2CH_3$ results into the formation of $H_2C{=}CH_2$.

(iii) The removal of β 1°H from the terminal methyl of  $CH_3CH_2CH_2\underset{\displaystyle {}^{\beta}CH_3}{\underset{|}{CH}}—$ leads to the formation of $CH_3CH_2CH_2CH{=}CH_2$.

CHAPTER 31

CARBOHYDRATES

As the name implies, carbohydrates means "hydrates of carbon". These are, infact, polyhydroxylated aldehydes and ketones.

Carbohydrates are classified as follows.

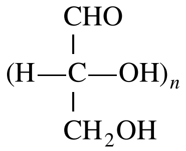
Monosaccharides These cannot be broken into smaller carbohydrates by hydrolysis. The general formula is $C_nH_{2n}O_n$ with n varying from 3 to 7. These are also known as simple sugars.

Oligosaccharides These include two to ten monosaccharides linked together.

Polysaccharides These include more than ten monosaccharides linked together.

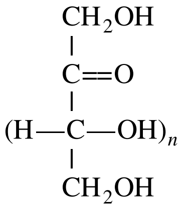
MONOSACCHARIDES

Monosaccharides may be represented as follows.



$$\begin{array}{c} \mathrm{CHO} \\ | \\ (\mathrm{H{-}C{-}OH})_n \\ | \\ \mathrm{CH_2OH} \end{array}$$

A polyhydroxy aldehyde



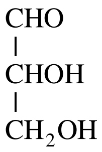
$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{C{=}O} \\ | \\ (\mathrm{H{-}C{-}OH})_n \\ | \\ \mathrm{CH_2OH} \end{array}$$

A polyhydroxy ketone

Monosaccharides are named as follows.

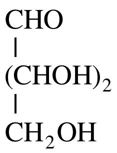
1. The class name of monosaccharide begins with the prefix 'aldo' for polyhydroxy aldehydes and 'keto' for polyhydroxy ketones.
2. The class name ends with suffix "ose".
3. In between prefix and suffix, the number of carbon atoms (i.e. di, tri, tetr, pent, hex, etc.) is inserted.

Examples



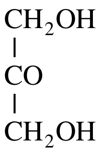
$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Aldotriose



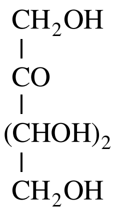
$$\begin{array}{c} \mathrm{CHO} \\ | \\ (\mathrm{CHOH})_2 \\ | \\ \mathrm{CH_2OH} \end{array}$$

Aldotetrose



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Ketotriose

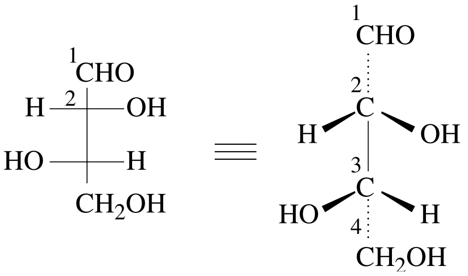


$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CO} \\ | \\ (\mathrm{CHOH})_2 \\ | \\ \mathrm{CH_2OH} \end{array}$$

Ketopentose

Fischer Projection Formula

In Fischer projection formula, the carbon chains is positioned vertically with the substituents drawn to the right and left on the chain. The horizontal lines represent bond coming towards the reader and the vertical lines represent bonds projected away from the reader. The aldehydic or ketonic group is placed at the top of vertical line. For example,



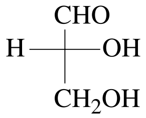
Note The numbering of carbon atoms is done from the top to bottom of the vertical line containing carbon atoms.

Stereoisomers

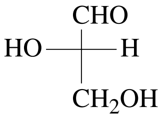
Carbohydrates contain asymmetric carbon atom(s). Thus, they can have stereoisomers, the number of which is equal to 2^n, where n is the number of asymmetric carbon atoms in the molecule of carbohydrate.

If the hydroxyl group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right, the molecule is said to have D absolute configuration and if it lies on left, the molecule is said to have L configuration.

The dextrorotatory (rotating the left to right) and levorotatory (rotating the light to left) are indicated by plus and minus signs written within the paranthesis and inserted immediate after the symbols D and L as shown in the following structures.

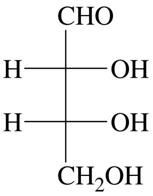


D (+)-Glyceraldehyde

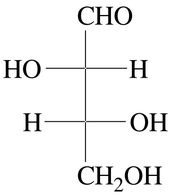


L (−)-Glyceraldehyde

Diastereoisomers with more than one stereocenter that differ in the configuration about one stereocentre are called *epimers*. For example, D-threose and D-erythrose are epimers.



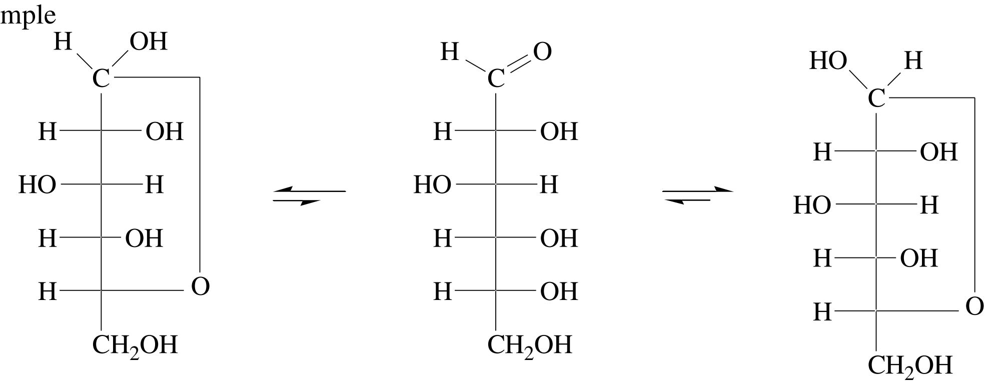
D–Erythrose



D–Threose

Cyclic Structures

Each carbohydrate molecule contains both a carbonyl group and a hydroxy group. If these two functional groups are properly positioned in the same molecule, there can occur an intramolecular rearrangement forming a cyclic hemiacetal structure. For example



α-D-Glucose Open-chain Glucose β-D-Glucose

The hemiacetal formation is preferred with the ^{5}C hydroxyl group due to the geometric constraints and the stability of the product.

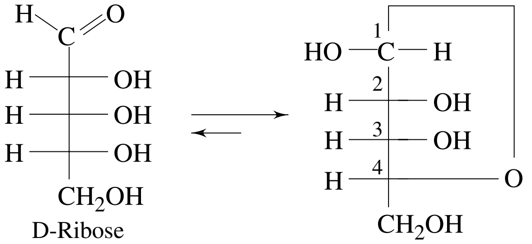
When CH $=$ O is converted into a cyclic hemiacetal its ^{1}C becomes a chiral centre. One diastereomer has the OH on the right side and the other on the left side. These are called *anomers*.

Haworth Projection

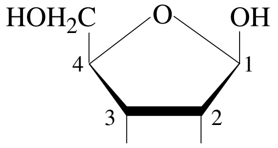
The cyclic structure of a monosaccharide can be more conveniently shown by a Haworth projection. In this structure, a ring is shown as a plane perpendicular to the plane of the paper. The edge of the plane that would project out of the paper toward the reader is darkened to emphasize its orientation. The hydroxyl groups are then positioned above or below the plane. The hydrogen atoms are usually not shown. A Hawroth projection is drawn as follows.

1. Draw the ring structure so that the hemiacetal (also known as anomeric) carbon is on the far right. Remembering it is the carbonyl carbon in the open-chain structure.
2. Continue the ring by adding the other carbon in a clockwise direction.
3. The hydroxyl group positioned on the right of Fischer projection is shown below the plane of the ring and those lying on the left are shown above the plane of the ring.
4. The terminal CH_2OH group is shown above the ring for D configuration and below the ring for L configuration.

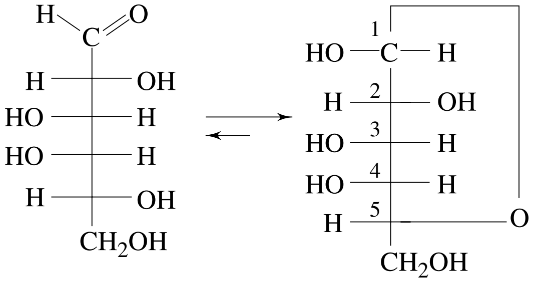
Examples

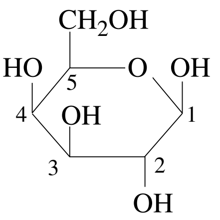


D-Ribose



D-Ribose
(Furanose—five
membered ring)





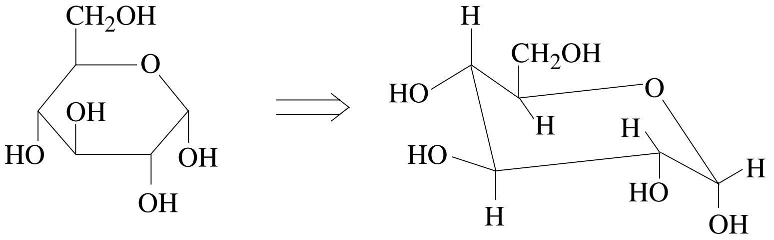
D-Galactose
(Pyranose—six membered ring)

Chair Conformational Formula

The chair conformational formula gives the accurate three-dimensional picture of pyranose rings. Haworth projections can be converted into chair representations by following the steps given below.

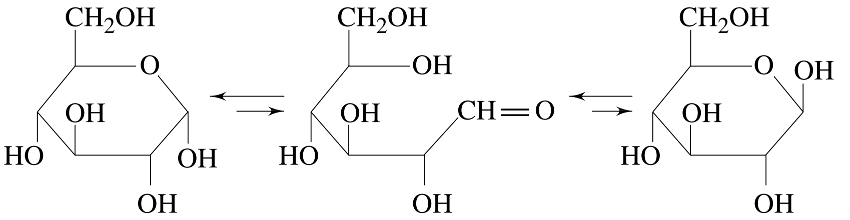
1. Draw the Haworth projection with the ring oxygen atom at the upper right.
2. Raise the left most carbon atom (C4) above the ring plane.
3. Lower the anomeric carbon atom (C1) below the ring plane.

Example



Mutarotation

When an open-chain monosaccharide cyclizes to a furanose or pyranose form, a new chiral centre at the carbonyl carbon (known as anomeric carbon) is created. The two diastereomers produced are called *anomers*.


α-D-Glucophranose (36%)
m.p. 146 °C
Specific rotation: 112.2°

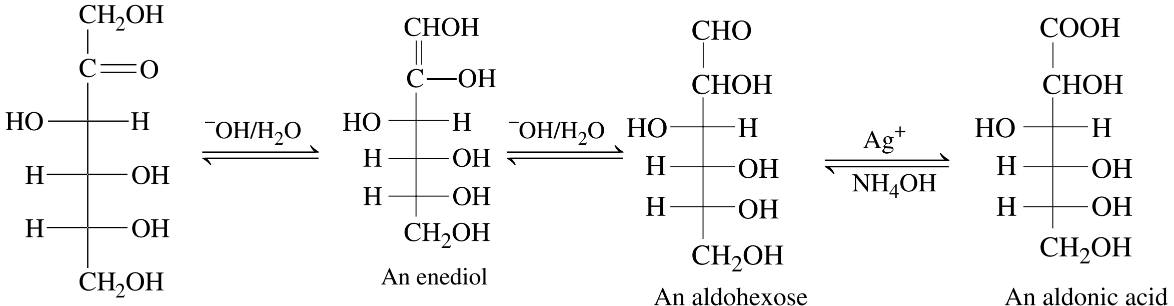
β-D-Glucopyranose (64%)
m.p. 148-155 °C
Specific rotation: 18.7°

When either α-form or β-form of glucose is dissolved in water, optical rotation changes and eventually a value of + 52.6° is obtained. Thus α-form changes to β-form (or vice versa) and eventually a solution containing 36% of α-form and 64% of β-form is obtained. This phenomenon is known as *mutarotation*.

Reducing and Nonreducing Sugars

Reducing sugars are easily oxidized to give carboxylic acid. They reduce (i) Tollens reagent (an ammonical solution of silver nitrate) to shiny silver mirror, (ii) Fehling's solution (an aqueous solution of cupric ion and tartrate salts) to red precipitate of cuprous oxide, and (iii) Benedict's reagent (an alkaline solution containing a cupric citrate complex) to red precipitate of cuprous oxide.

All aldoses are reducing sugars, but some ketoses are reducing sugars as well. For example, fructose reduces Tollens reagent even it contains no aldehydic group. This occurs because fructose is readily isomerized to an aldose in basic solution:


D-Fructose

An enediol

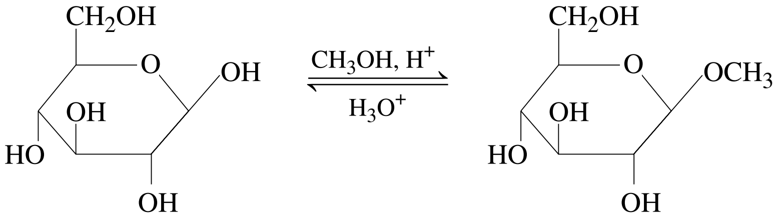
An aldohexose

An aldonic acid

However, aqueous bromine solution oxidizes only aldoses to aldonic acids. More powerful oxidizing agent such as dilute nitric acid oxidizes both the adehydic group at C1 and the terminol—CH_2OH group to —COOH groups giving aldaric acid.

Other Characteristic Reaction

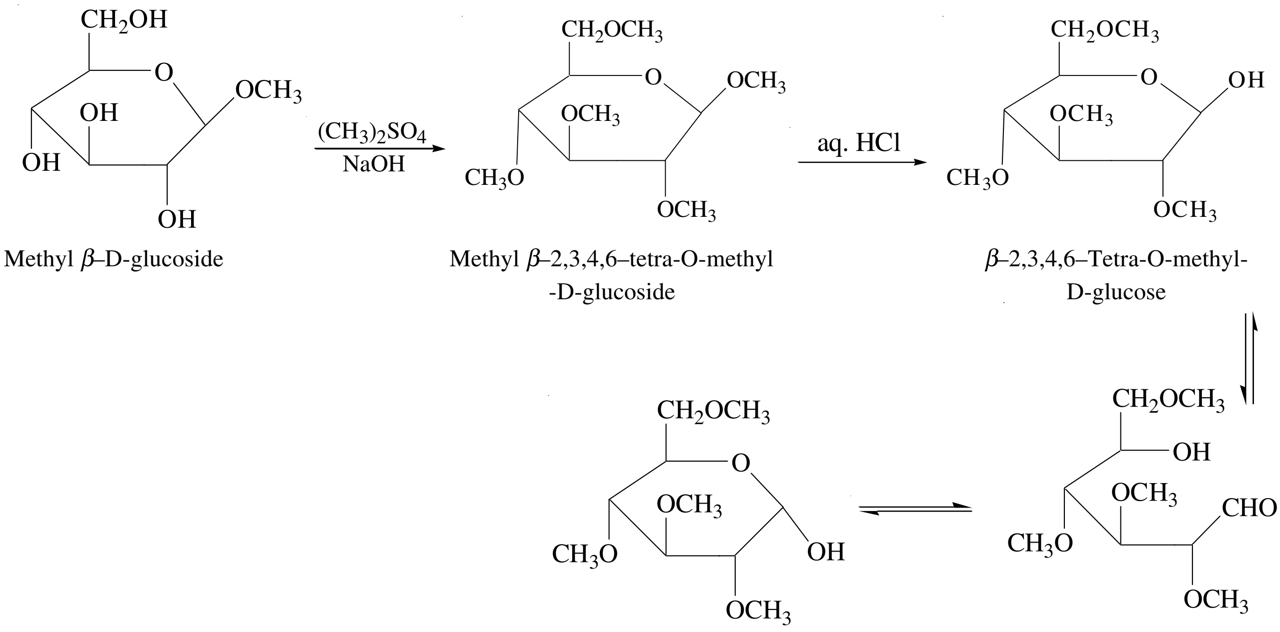
Aldehydic or keto group in sugars can be reduced to alcohol by using sodium borohydride. The hydroxyl groups in carbohydrates can be converted into esters and ethers. Treatment of a monosaccharide hemiacetal with methyl alcohol and dry hydrogen chloride catalyst gives an acetal in which the anomeric hydroxide is converted into an alkoxy group, known as glycosides.


β-D-Glucopyranose

Methyl β-D-Glucopyranoside

Note If anomeric —OH is above the plane of ring, it is said to form β-glycoside. If it is below the plane it gives α-glycoside.

Treatment of a methyl-D-glucoside with methyl sulphate and sodium hydroxide brings about methylation of the four remaining —OH groups, and yields a methyl tetra-o-methyl-D-glucoside.
If the latter is treated with dilute hydrochloric acid, removes $–OCH_3$ at ^1C giving tetra-o-methyl-D-glucose. Only the reactive acetal linkage is hydrolyzed under the mild condition.


Methyl β–D-glucoside

Methyl β–2,3,4,6–tetra-O-methyl -D-glucoside

β–2,3,4,6–Tetra-O-methyl- D-glucose

Degradation with HIO_4

Sugar is completely degraded with HIO_4 yielding the following products.

—CHO and CHOH are converted into HCOOH
—CH_2OH is converted into HCHO
—CO— is converted into CO_2

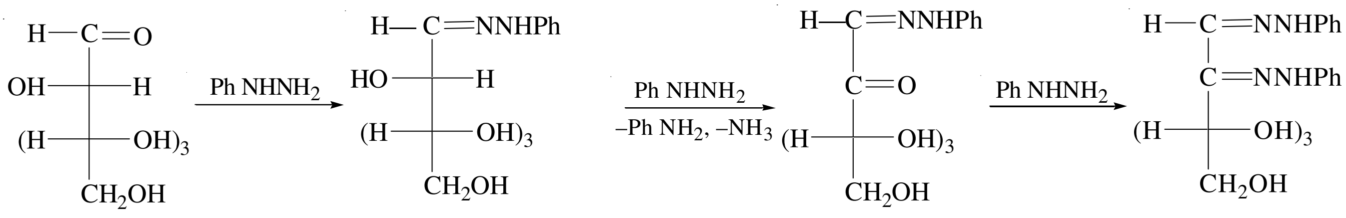
For example,

$$HOCH_2(CHOH)_4CHO \xrightarrow{HIO_4} 5HCOOH + HCHO$$

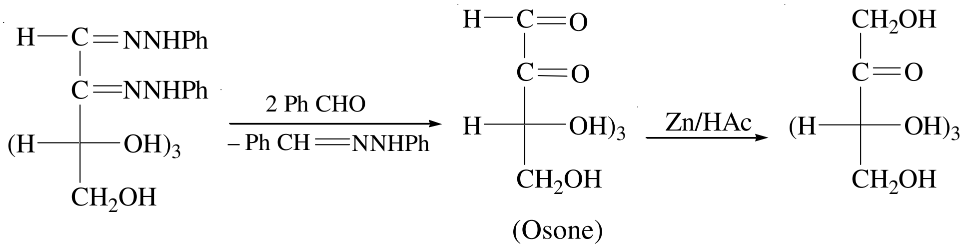
$$HOCH_2(CHOH)_3COCH_2OH \xrightarrow{HIO_4} 2HCHO + 3HCOOH + CO_2$$

Reaction with Phenylhydrazine

Sugars form characteristic osazones with phenylhydrazine.


an osazone

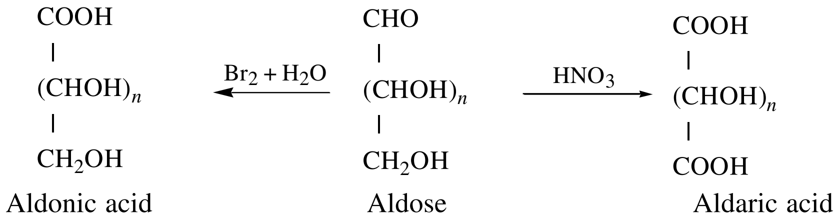
Via osazone, an aldose may be converted into ketose.


(Osone)

The more reactive aldehyde group of the osone is reduced, not the less reactive keto group.

Oxidation Reactions

Bromine water oxidizes aldoses, but not ketoses. Only —CHO group is oxidized to —COOH giving aldonic acid. With more vigorous oxidizing agent nitric acid brings about the oxidation of both —CHO and —CH_2OH giving aldaric acid.

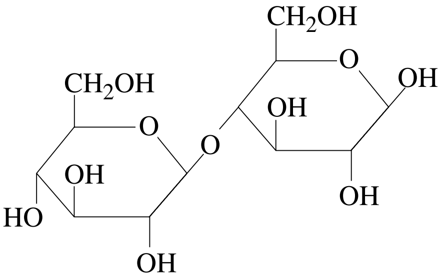


$$\underset{\text{Aldonic acid}}{\begin{array}{c}COOH\\|\\(CHOH)_n\\|\\CH_2OH\end{array}} \xleftarrow{Br_2 + H_2O} \underset{\text{Aldose}}{\begin{array}{c}CHO\\|\\(CHOH)_n\\|\\CH_2OH\end{array}} \xrightarrow{HNO_3} \underset{\text{Aldaric acid}}{\begin{array}{c}COOH\\|\\(CHOH)_n\\|\\COOH\end{array}}$$

DISACCHARIDES

Disaccharides contain a glycosidic acetal bond between C1 of one sugar and a hydroxyl group at any position on the other sugar. Common disaccharides contain C1 – C4′ linkage. The glycosidic bond can be either alpha or beta. The end monosaccharide on the right is known as a glycone. Some of the common disaccharides are as follows..

Cellobiose (1, 4′-β-glycoside)

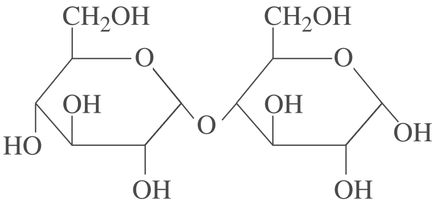


4–O-(β-D-Glucopyranosyl)-D-glucopyranos

Cellobiose is a reducing sugar, forms an osazone, exists in alpha and beta forms that undergo mutarotation. It is hydrolyzed into two molecules of D-(+)-glucose.

(+)-Cellobiose is hydrolyzed by the enzyme *emulsin* which hydrolyze only β-glucoside linkages.

Maltose (1, 4′-β-glycoside)



4–O-(α-D-Glucopyranosyl)-D-glucopyranos

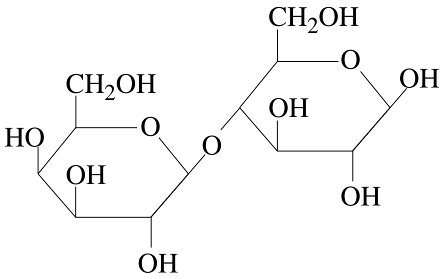
Maltose reduces Tollens and Fehling's reagents and hence is a reducing sugar. It forms osazone with phenylhydrazine and is oxidized by bromine water to a monocarboxylic acid known as maltobionic acid.

Maltose also exhibits mutarotation. The specific rotations are:

$$[\ \alpha\ ]_{\text{alpha}} = +168°;\ [\ \alpha\ ]_{\text{beta}} = +112° \text{ and } [\ \alpha\ ]_{\text{eq}} = +136°$$

When hydrolyzed in aqueous acid or when treated with the enzyme *maltase*, maltose is converted into D-(+)-glucose. The enzyme maltase breaks only alpha glucosidic linkage.

Lactose (1, 4′-β-glycoside)

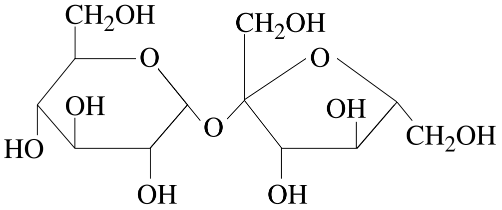


4-O-(β-D-Galactopyranosyl)-D glucopyranose

Lactose is found in human milk and of cow's milk. It is a reducing sugar, forms an osazone, and exists in alpha and beta forms and undergo mutarotation. It is cleaved by the enzyme emulsin indicating β-glucosidic linkage. The products are D-(+)-glucose and D+(+)-galactose.

Hydrolysis of lactosazone yields D-(+)-galactose and D-glucosazone. Similarly, hydrolysis of lactobionic acid yields D-gluconic acid and D-(+)-galactose. These indicate that lactose is a galactoside and not a glucoside.

Sucrose (1, 2′-glycoside)



2-O-(α-D-Glucopyranosyl)-*β*-D-fructofuranoside

or 2-O-(β-D-Fructofuranosyl)-*α*-D-Glucopyranoside

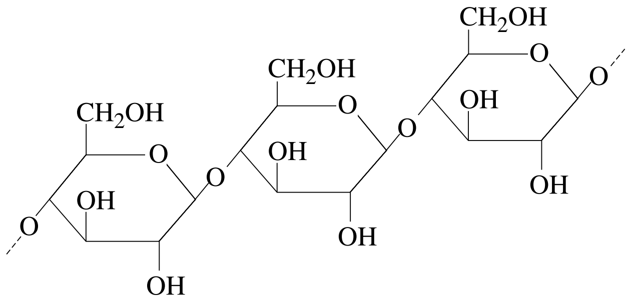
Sucrose is known as invert sugar, sign of optical rotation changes (invert) on going from sucrose to a glucose and fructose mixture. The specific rotations are as follows: $[\alpha]_{\text{sucrose}}$ = +66.5°; $[\alpha]_{\text{glucose}}$ = +52.7°; $[\alpha]_{\text{fructose}}$ = –92.4° $[\alpha]_{\text{eq}}$ = –22.0°. Enzyme invertase cleaved the glucosidic linkage in sucrose. Sucrose is not a reducing sugar because glucose and fructose are linked via 1,2′ glycosidic bond. It does not form an osazone, does not exist in anomeric forms and does not show mutarotation in solution. All these facts indicate that (+)-sucrose does not contain a free aldehyde or ketone group.

(+)-Sucrose is made up of a D-glucose unit and a D-fructose unit. Since there is no free carbonyl group, it is both a D-glucoside as well as well a D-fructoside. The two hexose units are joined by a glucosidic linkage between C – 1 of glucose and C – 2 of fructose because only this way the carbonyl groups of both units are blocked. Thus, sucrose contains 1,2′-glycosidic linkage.

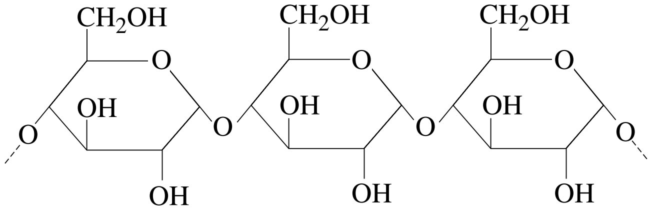
POLYSACCHARIDES

Polysaccharides contain more than ten simple sugars linked together through glycosidic bonds. These are nonreducing sugars and do not exhibit mutarotation. Cellulose and starch are the two common polysaccharides.

Cellulose Formed from D-glucose via 1, 4′-β-glycoside bonds.



Starch Formed from D-glucose via 1, 4′-α-glycoside bonds.



Starch can be separated into a cold-water-soluble fraction (80%) called amylopectin and a cold-water-insoluble fraction (20%) called amylose.

Amylose is a straight-chain polymer while amylopectin contains branches occurring approximately every 25 glucose units via 1, 6′-α-glycoside bonds.

All monosaccharides and some disaccharides have sweet taste. These are commonly referred to as sugars. The relative sweetness of some sugars are as follows.

Sucrose (100), glucose (74), fructose (173), galactose (32), maltose (32) and lactose (16).

Straight Objective Type

General Characteristics

1. The value of n in $C_nH_{2n}O_n$ for monosaccharides varies from
(a) 2 to 8 (b) 3 to 7 (c) 3 to 8 (d) 3 to 10

2. The number of monosaccharides in oligosaccharides varies from
(a) 2 to 10 (b) 2 to 12 (c) 2 to 8 (d) 3 to 12

3. The prefix L in L-glyceraldehyde implies
(a) levorotatory
(b) the absolute configuration of asymmetric carbon
(c) the —OH group attached to the right of asymmetric carbon in the Fischer projection.
(d) the rotation of plane polarized light to left.

4. The number of optical isomers in an aldose containing n asymmetric carbon atoms is
(a) $2n + 1$ (b) $2n + 2$ (c) 2^n (d) 2^{2n}

5. The pair of compounds showing positive Tollens reagent test is
(a) glucose and sucrose (b) fructose and sucrose
(c) glucose and fructose (d) acetophenone and pentanal (2004)

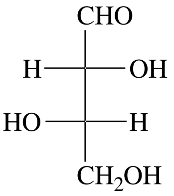
6. Which of the following substances does not fall in the category of carbohydrates?
(a) Sugars (b) Starch (c) Glycerol (d) Cellulose

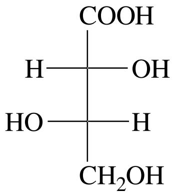
7. Which of the following substance falls in the category of carbohydrates?
(a) Glycogen (b) Insulin (c) Cytosine (d) Glycerol

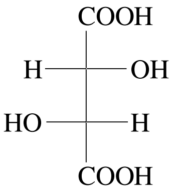
8. Which of the following statements regarding carbohydrates is **not** correct?
(a) The general formula of most of the carbohydrates can be written as $C_nH_{2n}O_n$.
(b) The main functions of carbohydrates is to support the structure of plants and to store chemical energy as sugars and starch
(c) Monosaccharides possess free carbonyl groups
(d) Carbohydrates may be defined as polyhydroxy acetals or ketals which on hydrolysis produce hydroxy carbonyl compounds

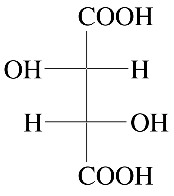
9. The relative sweetness of sugars is measured with respect to the sugar
(a) glucose (b) fructose (c) galactose (d) sucrose

10. Which of the following structures represents L-tartaric acid?

(a)


(b)


(c)


(d)


Monosaccharides

11. The specific rotation of α-D-glucose is
(a) 49° (b) 98° (c) 112° (d) 134°

12. The specific rotation of β-D-glucose is
(a) 19° (b) 98° (c) 112° (d) 134°

13. The specific rotation of sucrose solution eventually attains a value of
(a) 49° (b) 52.7° (c) 65° (c) 112°

14. D-Glucose contains
(a) 50% each of α-D-glucose and β-D-glucose
(b) 64% of α-D-glucose and 36% of β-D-glucose
(c) 36% of α-D-glucose and 64% of β-D-glucose
(d) 33% of each of α-D-glucose, β-D-glucose and open structure

15. In Haworth projection, the α anomer of glucose contains the —OH group
(a) above the plane of ring (b) below the plane of ring
(c) in the plane of ring pointing outwardly (d) in side the plane of ring pointing inwardly

16. In Haworth projection, the β anomer of glucose contains the —OH group
(a) above the plane of ring (b) below the plane of ring
(c) in the plane of ring pointing outwardly (d) inside the plane of ring pointing inwardly

17. D-Ribose contains
(a) 4 carbon atoms (b) 5 carbon atoms (d) 6 carbon atoms (d) 8 carbon atoms

18. D-Galactose contains
(a) 4 carbon atoms (b) 5 carbon atoms (c) 6 carbon atoms (c) 8 carbon atoms

19. In alkaline medium, fructose is
(a) a reducing sugar (b) a nonreducing sugar (c) an aldose (d) a furanose

20. Which of the following sugars is most sweet?
(a) Glucose (b) Fructose (c) Maltose (d) Sucrose

21. Which of the following sugars is least sweet?
(a) Glucose (b) Fructose (c) Maltose (d) Sucrose

22. Two forms of D-glucopyranose are frequently called
(a) enantiomers (b) anomers (c) diastereomers (d) stereoisomers

23. Which of the following does not belong to the category of hexoses?
(a) Glucose (b) Fructose (c) Galactose (d) Ribose

24. Which of the following represents a pentose?
(a) Maltose (b) Lactose (c) Deoxyribose (d) Fructose

25. Which of the following statements regarding monosaccharides is **not** correct?
(a) The general formula of monosaccharides is $(CH_2O)_n$
(b) Carbohydrates are monosaccharides if the number of carbon atoms is between three to seven
(c) Dextrose is an example of disaccharide
(d) Monosaccharides are optical active compounds

26. Which of the following statements is **not** correct?
(a) Symbols D-and L-before the name of monosaccharides refer to the direction of rotation of the light
(b) Pyranose has a six-membered ring structure
(c) Furanose has a five-membered sing structure
(d) Pyranose and furanose are the examples of hemiketal

27. Which of the following statements is **not** correct?
(a) Cyclization of glucose results into two structures of pyranose, known as anomers.
(b) The two anomers of pyranose have different specific rotation of polarized light
(c) Specific rotation of α-D-glucose is +11.2°
(d) Specific rotation of β-D-glucose is +52.7°

28. Glucose and fructose, respectively, are
(a) aldohexose and 2-ketohexose (b) 2-ketohexose and aldohexose
(c) monosaccharide and disaccharide (d) disaccharide and monosaccharide

29. Bromine water oxidizes
(a) both aldoses and ketoses (b) aldoses and not ketoses
(c) ketoses and not aldoses (d) neither aldoses nor ketoses

30. Aldoes can be converted into aldonic acids by treating with
(a) Fehling's reagent (b) Tollens reagent (c) bromine water (d) nitric acid

31. Glucose can be converted into glutaric acid by treating with
(a) Fehling's reagent (b) Tollens reagent (c) bromine water (d) nitric acid

32. The formation of osazone of an aldose consumes
(a) 1 molecule of phenylhydrazine (b) 2 molecules of phenylhydrazine
(c) 3 molecules of phenylhydrazine (d) 4 molecules of phynylhydrazine

33. Glucose and fructose separately treated with 1. NaCN/HCN, 2. H_2O^+ and 3. HI/P. The final products respectively are
(a) Straight-chain and branched carboxylic acids
(b) branched and straight-chain carboxylic acids
(c) Straight-chain and straight chair carboxylic acids
(d) branched and branched carboxylic acids

34. Acetylation of aldohexose with excess Ac_2O/NaOAc produces
(a) a mixture of equal amounts of pentaacetates of hemiacetal and aldehyde
(b) a mixture of unequal amounts of pentaacetates of hemiacetal and aldehyde.
(c) a mixture of α- and β-pentaacetate of hemiacetal
(d) pentaacetate of aldehyde only

35. Furanose and pyranose respectively contain
(a) five-membered and six-membered rings (b) six-membered and five-membered rings
(c) five-membered and seven-membered rings (d) six-membered and seven-membered rings

36. The specific rotation of α- and β-anomers of glucose are +112° and +19°, respectively. If the specific rotation of the equilibrium mixture is +52.7°, then the mole fractions of α-and β-anomers in mixture respectively are
(a) 0.25 and 0.75 (b) 0.75 and 0.25 (c) 0.36 and 0.64 (d) 0.64 and 0.36

37. The specific rotations of α-maltose, β-maltose and equilibrium mixture of α-and β-maltoses are +168°, +112° and +136°, respectively. The mole fractions of α-and β-maltoeses in the equilibrium mixture respectively are
(a) 0.57, 0.43 (b) 0.43, 0.57 (c) 0.67, 0.23 (d) 0.23, 0.67

38. Treatment of glucitol ($HOCH_2(CHOH)_4CH_2OH$) with periodic acid produces
(a) 4 HCOOH + OHCCOOH (b) 4 HCOOH + 2 HCHO
(c) $HOOC(CH_4OH)_4COOH$ (d) 6 HCOOH

39. Treatment of glucaric acid ($HOOC(CHOH)_4COOH$) with HIO_4 produces
(a) 4 HCOOH + 2 CHO (b) 3HCOOH + HCHO + OHC – COOH
(c) 2 HCOOH + 2 OHC – COOH (d) 6 HCOOH

40. Treatment of glucaric acid consumes
(a) 2 mol of HIO_4 (b) 3 mol of HIO_4 (c) 4 mol of HIO_4 (d) 5 mol of HIO_4

Disaccharides

41. Cellobiose is a
(a) 1, 4′-α-glycoside (b) 1, 4′-β-glycoside (c) 1, 2′-α-glycoside (d) 1, 2′-β-glycoside

42. Cellobiose is a
(a) monosaccharide (b) Disaccharide (c) polymer (d) trisaccharide

43. Maltose is a
(a) 1, 4′-α-glycoside (b) 1, 4′-β-glycoside (c) 1, 2′-α-glycoside (d) 1, 2′-β-glycoside

44. Sucrose is a
(a) 1, 4′-β-glycoside (b) 1, 4′-α-glycoside (c) 1, 2′-β-glycoside (d) 1, 2′-glycoside

45. Invert sugar is
(a) cellobiose (b) maltose (c) sucrose (d) lactose

46. Sucrose is a
(a) reducing sugar (b) nonreducing sugar
(c) mixture of glucose and fructose (d) monosaccharide

47. Which of the following statements regarding α-D-cellobiose is correct?
(a) The molecule does not exhibit mutarotation.
(b) It is a nonreducing sugar
(c) The human digestive system can break cellobiose in two glucose units
(d) It does not contain potential aldehyde group.

48. Which of the following statements regarding sucrose is **not** correct?
(a) Sucrose is a dextrorotatory
(b) In acid solution, sucrose solution becomes less dextrorotatory
(c) Sucrose is sweetest of all sugars
(d) In acid solution, sucrose solution eventually becomes levorotatory.

49. Sucrose involves
(a) Head to tail linkage
(b) Head to head linkage
(c) Tail to tail linkage
(d) 50% each of head to tail and head to head linkages.

50. Which of the following reagents can be used to convert aldoses to aldaric acid?
(a) Tollens reagent (b) Bromine solution (c) Fehling's solution (d) dilute nitric acid

51. Which of the following does not represent a disaccharide?
(a) Sucrose (b) Maltose (c) Lactose (d) Dextrose

52. Maltose is formed by the union of
(a) one molecule of glucose and one molecule of fructose
(b) one molecule of glucose and one molecule of galactose
(c) two molecules of glucose
(d) two molecules of galactose

53. Sucrose is formed by the union of
(a) one molecule of glucose and one molecule of fructose
(b) one molecule of glucose and one molecule of galactose
(c) two molecules of glucose
(d) two molecules of galactose

54. Lactose is formed by the union of
(a) one molecule of glucose and one molecule of fructose
(b) one molecule of glucose and one molecule of galactose
(c) two molecules of glucose
(d) two molecules of galactose

55. Which of the following sugars has the largest relative sweetness with respect to sucrose?
(a) Glucose (b) Fructose (c) Galactose (d) Maltose

56. Invert sugar is a mixture of
(a) glucose and sucrose (b) glucose and fructose (c) glucose and maltose (d) lactose and maltose

Polysaccharides

57. Starch is a polymer of
(a) glucose (b) fructose (c) galactose (d) lactose

58. Starch contains
(a) 20% of amylose and 80% of amylopectin (b) 30% of amylose and 70% of amylopectin
(c) 80% of amylose and 20% of amylopectin (d) 70% of amylose and 30% of amylopectin

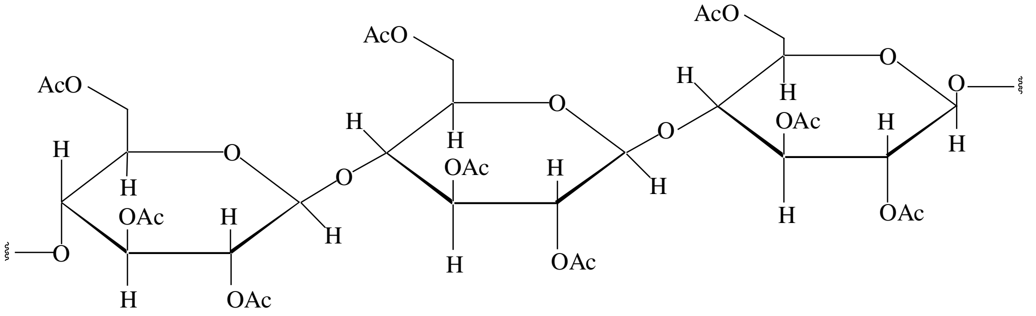
59. Glycogen
(a) is a linear polymer with no branching (b) contains more branching than amylopectin
(c) contains less branching than amylopectin (d) cannot be digested by human beings.

60. Which of the following is a linear polymer?
(a) Amylopectin (b) Glycogen (c) Starch (d) Amylose

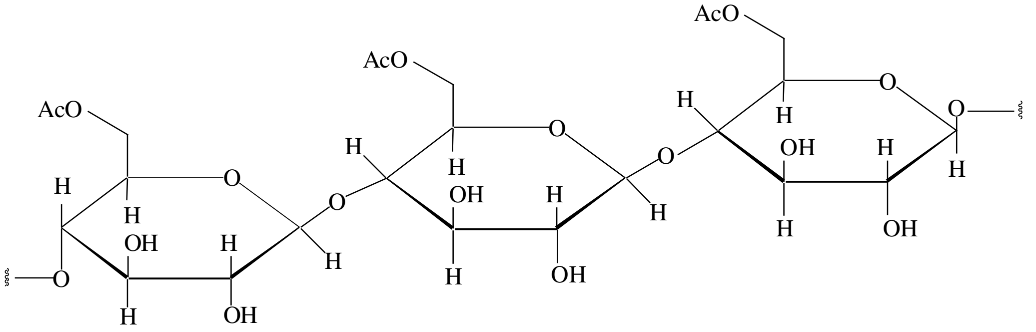
61. Cellulose is formed from
(a) D-glucose units (b) L-glucose units
(c) 50% each of D- and L- glucose units (d) D-galactose units

62. Cellulose upon acetylation with excess acetic anhydride / H_2SO_4 (catalytic) gives cellulose triacetate whose structure is

(a)



(b)



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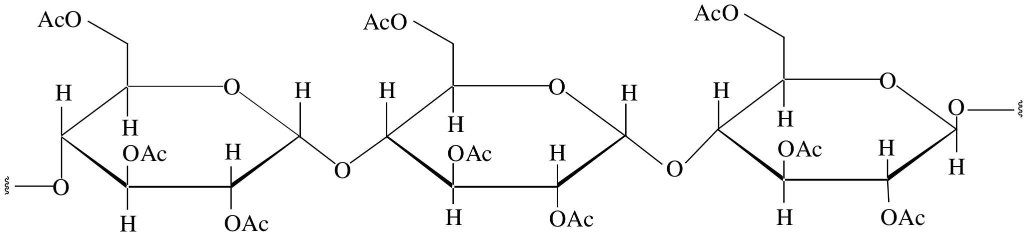

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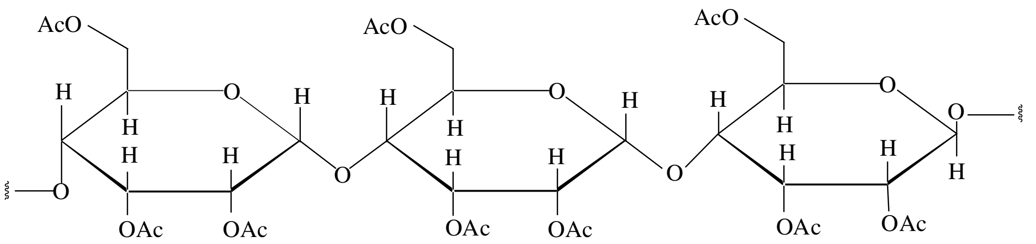


(2008)

63. Which of the following statements is correct?
(a) A polymer of α-Glucose is readily digested by human beings and not that of β-glucose
(b) A polymer of β-Glucose is readily digested by human beings and not that of α-glucose
(c) Polymers of both α-and β-glucoses are readily digested by human beings
(d) Polymers of both α-and β-glucose are not readily digested by human beings

64. Which of the following is a linear polymer?
(a) Amylopectin (b) Glycogen (c) Starch (d) Amylose

65. Monomer of cellulose is
(a) lactose (b) maltose (c) fructose (d) glucose

66. Which of the following statements is **not** correct?
(a) Polysaccharides are also known as glycans
(b) Glycogen, starch and cellulose are the examples of homopolysaccharids
(c) Amylose is a branched polymer of α-glucose
(d) Starch exists in two polymorphic forms-α-amylose and amylopectin

67. Which of the following statements is **not** correct?
- (a) Amylopectin is water insoluble compound
- (b) Amylopectin is a linear polymer of glucose
- (c) Cellulose is not digested by man
- (d) Grazing animals can digest cellulose

68. Which of the following statements is **not** correct?
- (a) Cellulose is a linear polymer of β-glucose
- (b) Gums and pectins are polysaccharides
- (c) Cellulose acetate is used in nail polish
- (d) Glycogen is the food reserve of plants

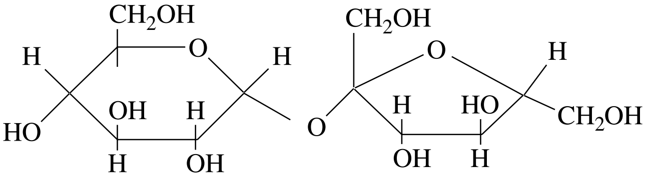
Multiple Correct Choice Type

1. Which of the following statements are **not** correct?
- (a) The phenomenon of mutarotation refers to the change in specific rotation of either of the two anomers in solution with time and attains a constant equilibrium value
- (b) Specific rotation of β-D-glucose is +52.6°
- (c) Ring structures of sugars can be broken by periodic acid
- (d) α-D-Glucose in water attains a constant specific rotation of 112.2°

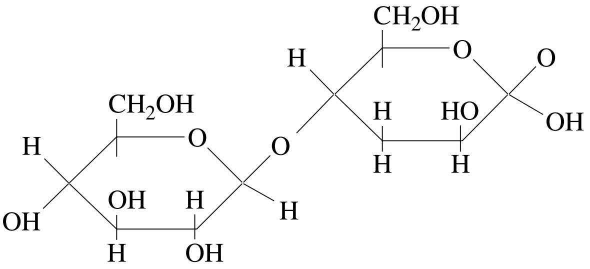
2. Which of the following statements are **not** correct?
- (a) The free hydroxyl groups of sugars can be completely acetylated or methylated
- (b) Uronic acids are produced when the hydroxyl groups of sugars are also oxidized
- (c) Saccharic acid is the oxidation product of fructose
- (d) Only one methyl glucoside is obtained when glucose is methylated with methyl alcohol

3. The correct statements(s) about the sugars

(X)



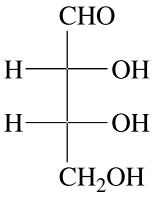
; (Y)



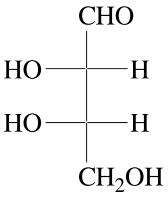
is/are (2009)
- (a) X is a reducing suger and Y is a nonreducing sugar
- (b) X is a nonreducing suger and Y is a reducing sugar
- (c) The glucosidic linkages in X and Y are α and β, respectively.
- (d) The glucosidic linkages in X and Y are β and α, respectively.

4. Which of the following compounds on reduction give *meso*-1, 2, 3, 4-butanetetrol

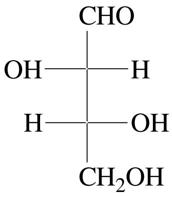
(a)



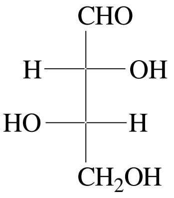
(b)



(c)



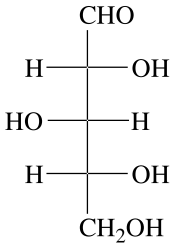
(d)

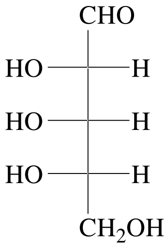


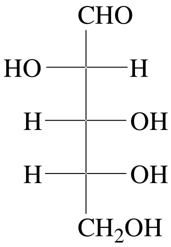
5. 2-Ketohexose reacts with
- (a) Tollens reagent
- (b) Fehling's solution
- (c) Benedict's reagent
- (d) Br_2/H_2O

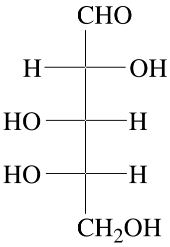
6. Which of the following statements are **not** correct?
- (a) Glucose is the only aldose that shows mutarotation
- (b) Ketoses also show mutarotation
- (c) Glycosides also show mutarotation
- (d) A sugar which shows mutarotation also reduces Fehling's reagent

7. Which of the following gives optically inactive aldaric acid on oxidation with dilute nitric acid?

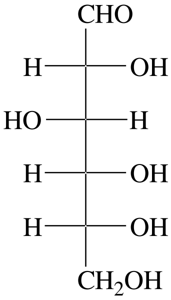
(a)


(b)


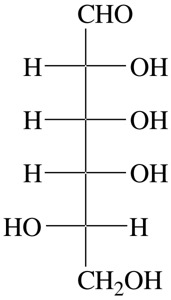
(c)


(d)


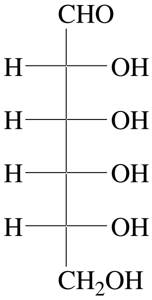
8. From the compounds



(I)



(II)

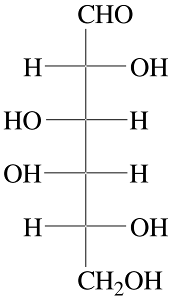


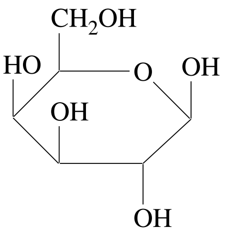
(III)

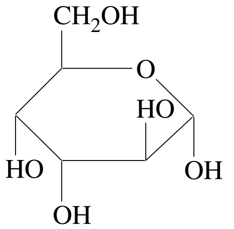
the pairs of epimers are

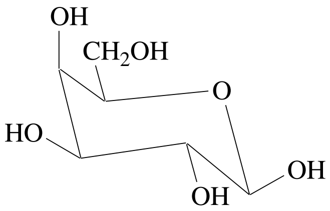
(a) (I) and (II) (b) (I) and (III) (c) (II) and (III) (d) none

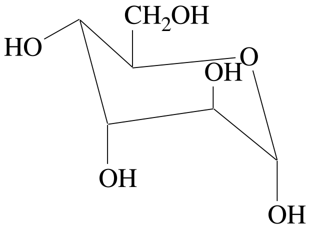
9. Which of the following structures represent



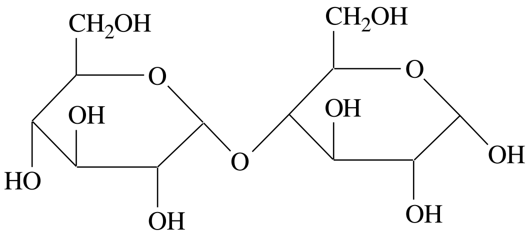
(a)


(b)


(c)


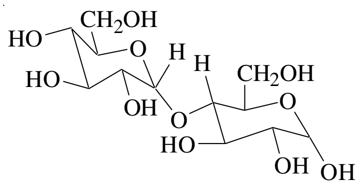
(d)


10. The structure of maltose is



Which of the following structures also represent maltose?

(a)



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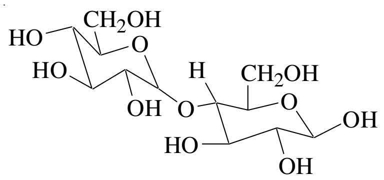
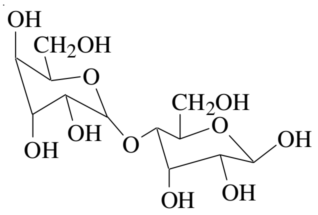
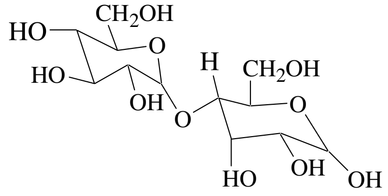


(c)



(d)

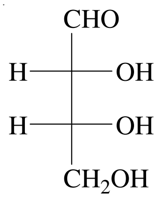


Linked Comprehension Type

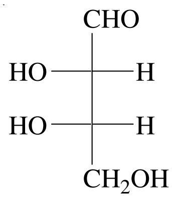
1. Erythrose and threose are aldotetrose. Based on these sugars, answer the following three questions.

(i) Which of the following structures represents D-threose?

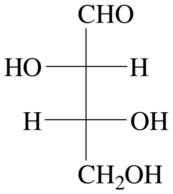
(a)



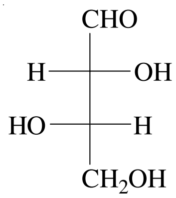
(b)



(c)



(d)



(ii) The mild oxidation of the compound $OHCCH(OH)CH(OH)CH_2OH$ gives

(a) $HOOCCH(OH)CH(OH)CH_2OH$ (b) $OHCCH(OH)CH(OH)CHO$

(c) $OHCCH(OH)CH(OH)COOH$ (d) $HOOCCH(OH)CH(OH)COOH$

(iii) The mild oxidation of D-erythrose and D-threose, respectively, give

(a) optically active enantiomer and *meso*-isomer (b) optically active enantiomers

(c) *meso*-isomer (d) *meso*-isomer and optically active enantiomer

2. The specific rotations of sucrose, glucose and fructose are as follows

$$[\alpha]_{\text{sugar}} = 66.5°; \quad [\alpha]_{\text{glucose}} = 52.7°; \quad [\alpha]_{\text{fructose}} = -92.4°$$

Based on this information, answer the following three questions

(i) The hydrolysis of sucrose in the presence of dilute acid produces

(a) glucose only

(b) fructose only

(c) a mixture of glucose and fructose

(d) mutarotation where α-sucrose is converted into β-sucrose and vice versa.

(ii) If $[\alpha]_{\text{soln}}$ is the specific rotation of the solution, then the fraction of sucrose undergone hydrolysis is given by

(a) $\dfrac{[\alpha]_{\text{soln}} - [\alpha]_{\text{sugar}}}{[\alpha]_{\text{glucose}} + [\alpha]_{\text{fructose}}}$ (b) $\dfrac{[\alpha]_{\text{soln}} - [\alpha]_{\text{sugar}}}{[\alpha]_{\text{glucose}} + [\alpha]_{\text{fructose}} + [\alpha]_{\text{soln}}}$

(c) $\dfrac{[\alpha]_{\text{soln}} - [\alpha]_{\text{sugar}}}{[\alpha]_{\text{glucose}} + [\alpha]_{\text{fructose}} - [\alpha]_{\text{soln}}}$ (d) $\dfrac{[\alpha]_{\text{soln}} - [\alpha]_{\text{sugar}}}{[\alpha]_{\text{glucose}} + [\alpha]_{\text{fructose}} - \{[\alpha]_{\text{soln}} + [\alpha]_{\text{sugar}}\}}$

(iii) The specific rotation of the solution, when sucrose solution has undergone complete hydrolysis is

(a) – 19.85° (b) – 39.70° (c) – 25.15° (d) – 9.95°

3. An organic compound containing two or more —OH and ═O groups on adjacent carbon atoms undergoes oxidative cleavage by periodic acid (HIO_4). Predict the products in the following three questions.

(i) Oxidative cleavage of gluconic acid ($HOOCCHOHCHOHCHOHCHOHCH_2OH$) with HIO_4 produces

(a) 4 HCOOH + OHC—COOH
(b) 3 HCOOH + HCHO + OHC—COOH
(c) $HOOC(CHOH)_4COOH$
(d) 5 HCOOH + HCHO

(ii) Oxidative cleavage of gluconic acid consumes

(a) 2 mol of HIO_4 (b) 3 mol of HIO_4 (c) 4 mol of HIO_4 (d) 5 mol of HIO_4

(iii) Glucuronic acid ($HOOC(CHOH)_4CHO$) on treating with HIO_4 produces

(a) 4 HCOOH + OHC—COOH
(b) 3 HCOOH + HCHO + OHC—CHO
(c) 3 HCOOH + HCHO + HOOC—COOH
(d) 5 HCOOH + HCHO

Assertion Reason Type

Given below are questions with two statements in each. Answer correctly each question based on the following key.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement-1	**Statement-2**
1.	Aldosugar may be distinguished from ketosugar by treating them with HIO_4.	On treating with HIO_4, —CHO and —CHOH groups are converted into HCOOH —CH_2OH is converted into HCHO and —CO— group is converted into CO_2.
2.	Anomers are epimers.	Anomers differ only about the ^{1}C.
3.	Glycosides do not show Fehling's or Tollens reagent test.	Acetals are stable in the basic solutions. There is no —CHO present to react with Fehling's or Tollens reagent.
4.	The OH's of sugars are more acidic than typical alcohols.	The OH′s in sugars exert mutual electron-withdrawing inductive effect making them more acidic than alcohols.

Matrix Match Type

1. Match the enzymes given in Column I with its working given in Column II.

Column I	**Column II**
(a) Maltase	(p) Partial hydrolysis of starch in aqueous acid
(b) Emulsin	(q) Catalyzes the hydrolysis of α-glycosidic linkage
(c) Diastase	(r) Catalyzes the hydrolysis of β-glycosidic linkage
(d) Invertase	(s) hydrolysis of sucrose

2. Match the carbohydrates given in Column I with their reaction with reagents given in Column II.

Column I	**Column II**
(a) Glucose	(p) Tollens reagent
(b) Fructose	(q) Fehling reagent
(c) Methyl-D-glucoside	(r) Br_2 water
(d) Sucrose	(s) Nitric acid

ANSWER

Straight Objective Type

1. (b)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (a)
8. (c)	**9.** (d)	**10.** (c)	**11.** (c)	**12.** (a)	**13.** (b)	**14.** (c)
15. (b)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (a)	**20.** (b)	**21.** (c)
22. (b)	**23.** (d)	**24.** (c)	**25.** (c)	**26.** (a)	**27.** (d)	**28.** (a)
29. (b)	**30.** (c)	**31.** (d)	**32.** (c)	**33.** (a)	**34.** (c)	**35.** (a)

36. (c) **37.** (b) **38.** (b) **39.** (c) **40.** (b) **41.** (b) **42.** (b)
43. (a) **44.** (d) **45.** (c) **46.** (b) **47.** (c) **48.** (c) **49.** (b)
50. (d) **51.** (d) **52.** (c) **53.** (a) **54.** (b) **55.** (b) **56.** (b)
57. (a) **58.** (a) **59.** (b) **60.** (d) **61.** (a) **62.** (a) **63.** (a)
64. (d) **65.** (d) **66.** (c)
67. (b) **68.** (d)

Multiple Correct Choice Type

1. (b), (d) **2.** (c), (d) **3.** (b), (c) **4.** (a), (b)
5. (a), (b), (c), (d) **6.** (a), (c) **7.** (a), (b) **8.** (b), (c)
9. (a), (c) **10.** (a), (b)

Linked Comprehension Type

1. **(i)** (a) **(ii)** (d) **(iii)** (a)
2. **(i)** (c) **(ii)** (d) **(iii)** (a)
3. **(i)** (b) **(ii)** (c) **(iii)** (a)

Assertion and Reason Type

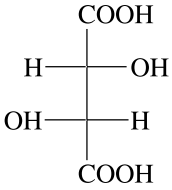
1. (a) **2.** (b) **3.** (a) **4.** (a)

Matrix Match Type

1. (a) – (q); (b) – (r); (c) – (p); (d) – (s)
2. (a) – (p), (q), (r), (s); (b) – (p), (q), (s); (c) – (s); (d) – (r), (s)

Hints and Solutions

Straight Objective Type

1. For monosaccharides, the value of n in $C_nH_{2n}O_n$ varies from 3 to 7.
2. The number of monosaccharides in oligosaccharides varies from 2 to 10.
3. The prefix L in L-glyceraldehyde implies the absolute configuration of asymmetric carbon.
4. The number of optical isomers in an aldose containing n asymmetric carbon atoms is 2^n.
5. Both glucose and fructose are reducing sugars. Sucrose is a non-reducing sugar.
Pentanal contains —CHO group. it shows the test. Acetophenone does not contain —CHO group. it does not show the test.
6. The general formula of most of the carbohydrates can be written as $C_nH_{2n}O_n$. The formula of glycerol is $C_3H_8O_6$.
8. Monsaccharides do not have free carbonyl groups and are involved in acetal or ketal formation. The hydrolysis of the latter produces hydroxy carbonyl compounds.
9. The relative sweetness of sugars is measured with respect to sucrose which is assigned a value of 100.
10. L-Tartaric acid is  . The L isomer has —OH on the left of the last asymmetric carbon placed at the bottom of the molecule.

11. The specific rotation of α-D-glucose is 112.2°. **12.** The specific rotation of β-D-glucose is 19°.
13. The specific rotation of sucrose solution eventually attains a value of 52.7°.
14. D-Glucose contains 36-α-D-glucose and 64% of β-D-glucose.
15. In Haworth projection, the α anomer of glucose contain the —OH group below the plane of ring.

16. In Haworth projection, the β anomes of glucose contains the —OH group above the plane of ring.

17. D-Ribose contains 5 carbon atoms. **18.** D-Galactose contains 6 carbon atoms.

19. In alkaline medium, fructose is a reducing sugar. **20.** Fructose is the most sweet sugar.

21. Maltose is the least sweet amongst the given sugars.

22. The anomers are the cyclic hemiacetal structures in which carbon at C_1 is asymmetric. The anomers with the hydroxyl group projected above the ring is called β-anomer and the other as *α*-anomer.

23. Ribose is pentose. **24.** Deoxyribose is a pentose

25. Dextrose (i.e. glucose) is an example of monosaccharide.

26. Symbols D- and L-refer to the configurations and not to the direction of rotation. When hydroxyl group, attached to the last asymmetric carbon farthest from the aldehydic or carbonic group, is on the right, the configuration is D-; and when the hydroxyl group is on the left, the configuration is L-.

27. Specific rotation of β-D-glucose is +18.7°

28. Glucose is aldohexose and fructose is 2- ketohexose.

29. Bromine water is mild oxidizing agent. It oxidizes —CHO to —COOH.

30. Same as Q.29

31. HNO_3 is a stronger oxidizing agent. It converts both —CHO and —CH_2OH groups to —COOH group.

32. Three molecule of $PhNHNH_2$ is used. Two molecules combine with aldose while the third is converted to $PhNH_2$ and NH_3.

33. HCN adds across —CHO and —CO— groups of glucose and fructose, respectively, producing straight-chain and branched carboxylic acids, respectively.

34. Pentaacetate of both anomers of aldohexose are obtained.

35. Furanose is a five-membered ring while pyranose is a six-membered ring.

36. If x is the mole fraction of α-anomer, then $x(112°) + (1 - x)(19°) = 52.7°$
This gives $x = (52.7° - 19°)/(112° - 19°) = 0.36$

37. If x is the mole fraction of α-maltose, then $x(168°) + (1 - x)(112°) = 136°$
This gives $x = (136° - 112°)/(168° - 112°) = 0.43$

38. $HOCH_2 \mid CHOH \mid CHOH \mid CHOH \mid CHOH \mid CH_2OH \xrightarrow{5HIO_4} HCHO + 4\,HCOOH + HCHO$

39. $HOOC\ CHOH \mid CHOH \mid CHOH \mid CHOH\ COOH \xrightarrow{3HIO_4} HOOC—CHO + 2HCOOH + OHC—COOH$

40. See Q.39

41. Cellobiose is a 1,4′-β-glycoside. **42.** Cellobiose is a disaccharide.

43. Maltose is a 1,4′-a-glycoside. **44.** Sucrose is a 1,2′-glycoside.

45. Invert sugar is sucrose. **46.** Sucrose is a nonreducing sugar.

47. The human digestive system can break cellobiose in two glucose units.

48. The statement sucrose is sweetest of all sugars is incorrect.

49. Sucrose involves head to head linkages.

50. Dilute nitric acid can be used to oxidise aldose to aldaric acid.

51. Dextrose is monosaccharide.

52. Maltose is formed by the union of two molecules of glucose and fructose.

53. Sucrose is formed by the union of one molecule of each of glucose and fructose.

54. Lactose is formes by the union of one molecule of each of glucose and galactose.

55. Fructose relative sweetness is 173 when that of sucrose is take to be 100.

56. Invert sugar is a mixture of glucose and fructose. **57.** Starch is a polymer of glucose.

58. Starch contains 20% amylose and 80% amylopectin.

59. Glycogen contains more branching than amylopectin.

60. Amylose is a linear polymer. **61.** Cellulose is formed from D-glucose units.

62. Cellulose is formed from D-glucose via 1, 4′–β–glycoside bond and in each glucose unit there are three hydroxyl groups in the uncombined state which undergo acetylation.

63. α-Glucose (starch) is readily digested by human beings but a polymer of β-(cellulose) is not digestable.

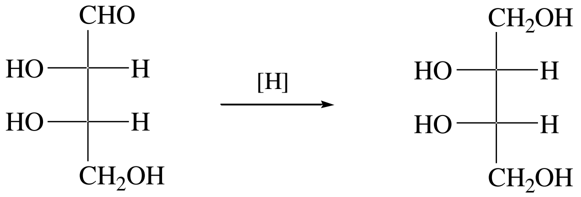
64. Amylose is a linear polymer **65.** Glucose is the monomer of cellulose

66. See Q.64 **67.** Amylopectin is a branched polomer of glucose

68. Glycogen is mainly present in liver and muscels of the animal and serves as a reserve carbohydrate.

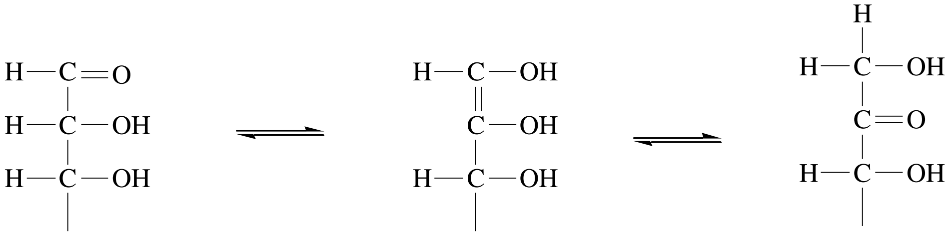
Multiple Correct Choice Type

1. The constant specific rotation in water which either α-D-glucose or β-D-glucose attains is +52.7°.
2. Glucose gives rise to two glycosides with methyl alcohol –α-methyl glycoside and β-methyl glycoside.
3. The structure Y is an aldose, hence it is a reducing sugar.
   The glycoside linkage in X is below the plane, hence it is an α-glycoside.
   The glycoside linkage in Y above the plane, hence it is a β-glycoside.
4. —CHO is reduced to —CH_2OH. D-Erythrose or L-therose give *meso*-1,2,3,4- butanetetrol. For example



meso-isomer

5. 2-Keto sugar rearranges to an aldosugar under the basic conditions.



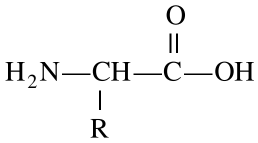
(aldose) (enediol) (ketose)

Thus, 2-keto sugar reacts with all the four reagents. Br_2/H_2O gives $HOCH_2(CHOH)_4COOH$.

CHAPTER 32

AMINO ACIDS AND PEPTIDES

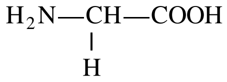
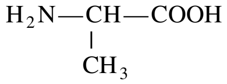
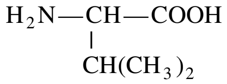
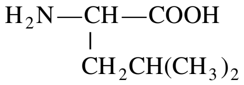
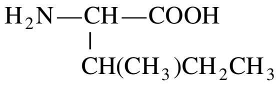
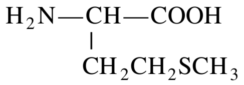
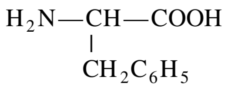
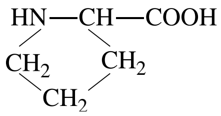
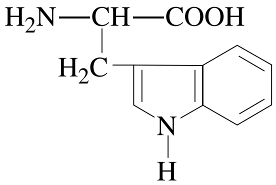
Amino acids contain an amino group attached to α-carbon of a carboxylic acid. These are formulated as



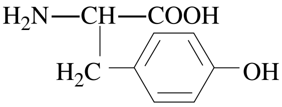
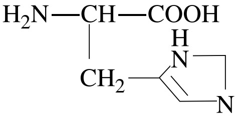
$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Amino acids are the basic units of proteins. There are twenty amino acids commonly found in proteins (Table 32.1). Based on the nature of R group, they have been classified into the three categories.

Table 32.1 Twenty amino acids

*Name**	*Abbreviation*	*Structure*	*Isoelectric point*
Amino Acids with Nonpolar R Group			
Glycine	G or Gly	 $H_2N-\underset{H}{\underset{\mid}{CH}}-COOH$	6.0
Alanine	A or Ala	 $H_2N-\underset{CH_3}{\underset{\mid}{CH}}-COOH$	6.0
Valine	V or Val	 $H_2N-\underset{CH(CH_3)_2}{\underset{\mid}{CH}}-COOH$	6.0
Leucine	L or Leu	 $H_2N-\underset{CH_2CH(CH_3)_2}{\underset{\mid}{CH}}-COOH$	6.0
Isoleucine	I or Ile	 $H_2N-\underset{CH(CH_3)CH_2CH_3}{\underset{\mid}{CH}}-COOH$	6.0
Methioine	M or Met	 $H_2N-\underset{CH_2CH_2SCH_3}{\underset{\mid}{CH}}-COOH$	5.7
Phenylalanine	F or Phe	 $H_2N-\underset{CH_2C_6H_5}{\underset{\mid}{CH}}-COOH$	5.5
Proline	P or Pro		6.3
Troptophan	W or Trp		5.9

Contd.

Amino Acids with Polar R Group			
Serine	S or Ser	$H_2N-\underset{CH_2OH}{CH}-COOH$	5.7
Threonine	T or Thr	$H_2N-\underset{CH(CH_3)OH}{CH}-COOH$	5.6
Tyrosine	Y or Tyr		5.7
Cysteine	C or Cys	$H_2N-\underset{CH_2SH}{CH}-COOH$	5.0
Glutamine	Q or Gln	$H_2N-\underset{CH_2CH_2CONH_2}{CH}-COOH$	5.7
Asparagine	N or Asn	$H_2N-\underset{CH_2CONH_2}{CH}-COOH$	5.4
Amino Acids with Charged R Groups			
Aspartic acid	D or Asp	$H_2N-\underset{CH_2COO^-}{CH}-COOH$	3.0
Lysine	K or Lys	$H_2N-\underset{CH_2(CH_2)_3NH_3^+}{CH}-COOH$	9.7
Histidine	H or His		7.6
Glutramic acid	E or Glu	$H_2N-\underset{CH_2CH_2COO^-}{CH}-COOH$	3.2
Arginine	R or Arg	$H_2N-\underset{CH_2(CH_2)_2NH-\overset{NH_2}{C}=\overset{+}{N}H_2}{CH}-COOH$	10.8

Essential Amino Acids The human body can synthesize only 10 of the 20 amino acids. The remaining amino acids which are shown in italics in Table 32.1 are known as essential amino acids. These must be supplied in the human diet.

Chiral Nature of Amino Acids Except glycine all other amino acids contain asymmetric carbon next to the carboxylic acid. Consequently, each amino acid exists in two different stereoisomeric forms, with either a D or L absolute configuration. Proteins contain almost exclusively L isomer.

Acid-Base Behaviour of Amino Acids In highly acidic conditions (pH ≃ 1), both the carboxylic group and the amino group are protonated.

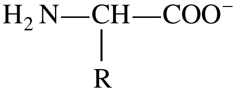
$$H_3\overset{+}{N}-\underset{R}{CH}-CO_2H$$

On increasing pH of the solution, the carboxyl group ionizes to produce a dipolar ion:

$$H_3\overset{+}{N}-\underset{R}{CH}-COO^-$$

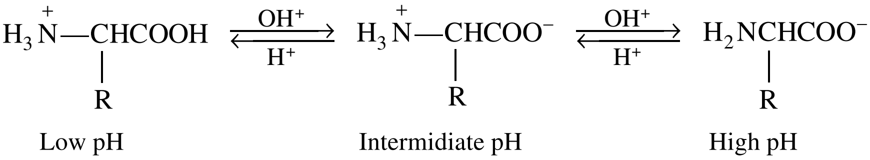
The doubly-charged ion is known as zwitterion (from German meaning double ion). The pH of the solution at which the species becomes zwitterion is known as isoelectric point.

If the pH of the solution is further increased, the amino group is deprotonated to give



$$H_2N\text{—}\underset{\substack{|\\ R}}{CH}\text{—}COO^-$$

At a given pH, the above three species exist in equilibrium.



$$\underset{\text{Low pH}}{H_3\overset{+}{N}\text{—}\underset{\substack{|\\ R}}{C}HCOOH} \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} \underset{\text{Intermidiate pH}}{H_3\overset{+}{N}\text{—}\underset{\substack{|\\ R}}{C}HCOO^-} \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} \underset{\text{High pH}}{H_2N\underset{\substack{|\\ R}}{C}HCOO^-}$$

with $$K_{a1} = \frac{[H_3\overset{+}{N}CH(R)COO^-][H^+]}{[H_3\overset{+}{N}CH(R)COOH]}; \quad K_{a2} = \frac{[H_2NCH(R)COO^-][H^+]}{[H_3\overset{+}{N}CH(R)COO^-]}$$

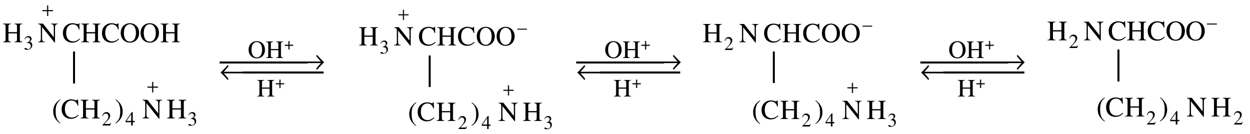
Thus $$K_{a1}K_{a2} = \frac{[H_2NCH(R)COO^-][H^+]^2}{[H_3\overset{+}{N}CH(R)COOH]}$$

At the isoelectric point, $[H_2NCH(R)COO^-] = [H_3\overset{+}{N}CH(R)COOH]$

Thus $K_{a1}K_{a2} = [H^+]^2$ or $pH = (pK^\circ_{a1} + pK^\circ_{a2})/2$

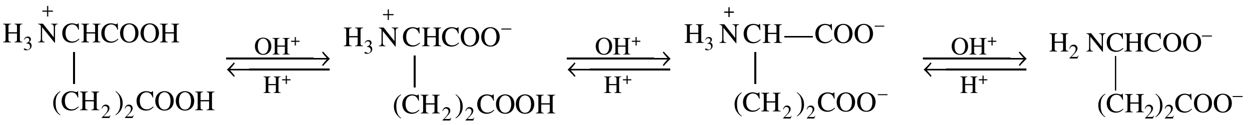
For most of amino acids whose side chain is neither acidic nor basic, $pK^\circ_a \simeq 2.5$ and $pK^\circ_{a2} = 9.5$. Thus, at isoelectric point, $pH \simeq 6.0$.

The following equilibria exists for amino acids containing basic amino group in the side chain:



$$H_3\overset{+}{N}\underset{\substack{|\\ (CH_2)_4\overset{+}{N}H_3}}{C}HCOOH \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_3\overset{+}{N}\underset{\substack{|\\ (CH_2)_4\overset{+}{N}H_3}}{C}HCOO^- \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_2N\underset{\substack{|\\ (CH_2)_4\overset{+}{N}H_3}}{C}HCOO^- \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_2N\underset{\substack{|\\ (CH_2)_4NH_2}}{C}HCOO^-$$

If the side chain contains acidic group, then



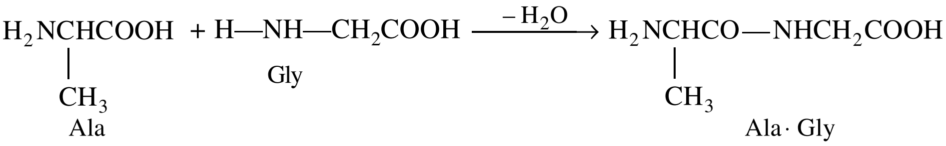
$$H_3\overset{+}{N}\underset{\substack{|\\ (CH_2)_2COOH}}{C}HCOOH \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_3\overset{+}{N}\underset{\substack{|\\ (CH_2)_2COOH}}{C}HCOO^- \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_3\overset{+}{N}\underset{\substack{|\\ (CH_2)_2COO^-}}{CH}\text{—}COO^- \underset{H^+}{\overset{OH^+}{\rightleftharpoons}} H_2N\underset{\substack{|\\ (CH_2)_2COO^-}}{C}HCOO^-$$

In general, the pH of the solution at which amino acids exist as zwitterion follows the order:

Acidic side chain < neutral chain < basic side chain

PEPTIDE LINKAGE

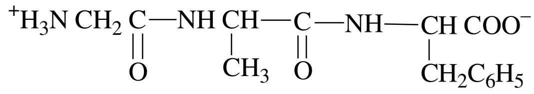
The condensation of two amino acids with the elimination of H_2O produces CO—NH linkage, which in protein chemistry, is known as a peptide linkage. For example,



$$\underset{\text{Ala}}{H_2N\underset{\substack{|\\ CH_3}}{C}HCOOH} + \underset{\text{Gly}}{H\text{—}NH\text{—}CH_2COOH} \xrightarrow{-H_2O} \underset{\text{Ala}\cdot\text{Gly}}{H_2N\underset{\substack{|\\ CH_3}}{C}HCO\text{—}NHCH_2COOH}$$

The species Ala·Gly is known as a dipeptide. The left-end amino acid residue carries an amino group while that at right-end carries a carboxyl group.

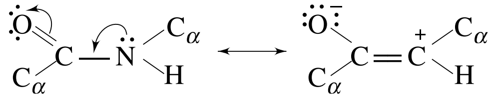
The combination of three amino acids gives tripeptide. For example Gly • Ala • Phe is



$$^+H_3N\,CH_2\,\underset{\substack{\|\\ O}}{C}\text{—}NH\,\underset{\substack{|\\ CH_3}}{CH}\text{—}\underset{\substack{\|\\ O}}{C}\text{—}NH\text{—}\underset{\substack{|\\ CH_2C_6H_5}}{CH}\,COO^-$$

Oligopeptide contains any where between two to ten amino acids. Structures with more than ten amino acids are known as polypeptides.

Geometry of a Peptide Linkage Due to the resonance



all the atoms shown in the above structure lies in a plane.

Proteins A protein is a polypeptide containing a large number of amino acid residues. The relative molecular masses of proteins range from about 1000 to several millions.

Straight Objective Type

1. An amino acid contains an amino group attached to
(a) α-carbon atom (b) β-carbon atom (c) γ-carbon atom (d) δ-carbon atom

2. The amino acids are basic units of
(a) lipids (b) oligosaccharides (c) hormones (d) proteins

3. The number of amino acids commonly found in proteins is
(a) 10 (b) 15 (c) 20 (d) 25

4. The number of essential amino acids is
(a) 10 (b) 15 (c) 20 (d) 25

5. Simplest amino acid is
(a) alanine (b) glycine (c) Leucine (d) valine

6. Which of the following amino acids ($NH_2CHRCOOH$) contains nonpolar R group?
(a) Serine (b) Arginine (c) Isoleucine (d) Cystein

7. Which of the following amino acids ($NH_2CHRCOOH$) contains polar R group?
(a) Methioine (b) Proline (c) Glycine (d) Glutamine

8. Zwitterion is a
(a) neutral species (b) singly-charged species (c) doubly-charged species (d) multifunctional species

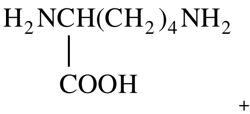
9. At low pH, an amino acid exists as
(a) $H_3\overset{+}{N}CHRCOOH$ (b) $H_3\overset{+}{N}CHRCOO^-$ (c) $H_2NCHRCOO^-$ (d) $H_2NCHRCOOH$

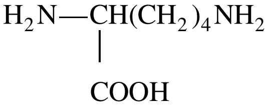
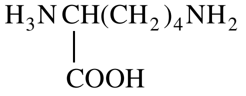
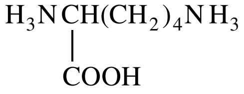
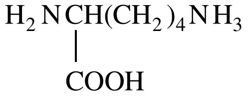
10. At high pH, an amino acid exists as
(a) $H_3\overset{+}{N}CHRCOOH$ (b) $H_3\overset{+}{N}CHRCOO^-$ (c) $H_2NCHRCOO^-$ (d) $H_2NCHRCOOH$

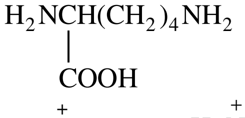
11. If K_{a1} and K_{a2} are the ionization constants of $H_3\overset{+}{N}CHRCOOH$ and $H_3\overset{+}{N}CHRCOO^-$, respectively, the pH of the solution at the isoelectric point is
(a) $pH = pK^\circ_{a1} + pK^\circ_{a2}$ (b) $pH = (pK^\circ_{a1}\ pK^\circ_{a2})^{1/2}$ (c) $pH = (pK^\circ_{a1} + pK^\circ_{a2})^{1/2}$ (d) $pH = (pK^\circ_{a1} + pK^\circ_{a2})/2$

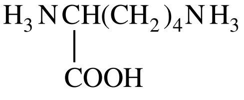
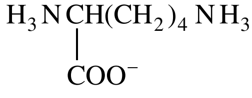
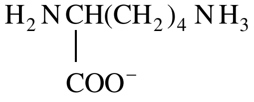
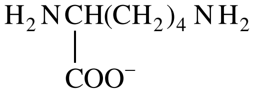
12. Which of the following amino acid is **not** optical active?
(a) Glycine (b) Alanine (c) Valine (d) Glutramic acid

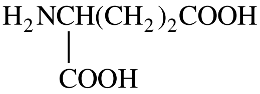
13. Proteins contains
(a) exclusively D isomers of amino acids
(b) exclusively L isomers of amino acids
(c) 50% of each of D- and L-amino acids
(d) 33% of D-form and 67% of L-form of amino acids

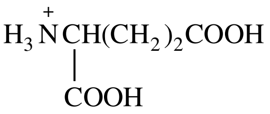
14. The amino acid  $H_2N\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4NH_2$ at low pH exists as

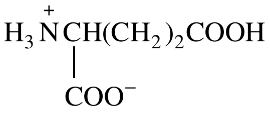
(a)  $H_2N—\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4NH_2$ (b)  $H_3\overset{+}{N}\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4NH_2$ (c)  $H_3\overset{+}{N}\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\overset{+}{N}H_3$ (d)  $H_2N\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\overset{+}{N}H_3$

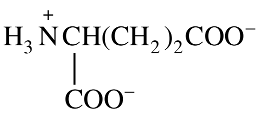
15. The amino acid  $H_2N\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4NH_2$ at high pH exists as

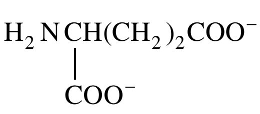
(a)  $H_3\overset{+}{N}\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\overset{+}{N}H_3$ (b)  $H_3\overset{+}{N}\underset{\displaystyle COO^-}{\underset{|}{C}}H(CH_2)_4\overset{+}{N}H_3$ (c)  $H_2N\underset{\displaystyle COO^-}{\underset{|}{C}}H(CH_2)_4\overset{+}{N}H_3$ (d)  $H_2N\underset{\displaystyle COO^-}{\underset{|}{C}}H(CH_2)_4NH_2$

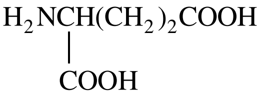
16. The amino acid  $\mathrm{H_2N\underset{\substack{|\\ COOH}}{CH}(CH_2)_2COOH}$ at low pH exists as

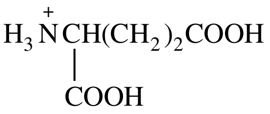
(a)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COOH}}{CH}(CH_2)_2COOH}$

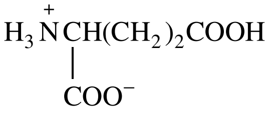
(b)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COOH}$

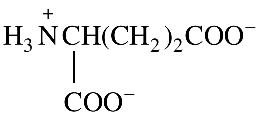
(c)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COO^-}$

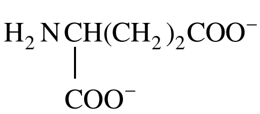
(d)  $\mathrm{H_2N\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COO^-}$

17. The amino acid  $\mathrm{H_2N\underset{\substack{|\\ COOH}}{CH}(CH_2)_2COOH}$ at high pH exists as

(a)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COOH}}{CH}(CH_2)_2COOH}$

(b)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COOH}$

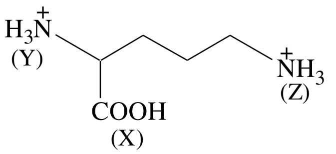
(c)  $\mathrm{H_3\overset{+}{N}\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COO^-}$

(d)  $\mathrm{H_2N\underset{\substack{|\\ COO^-}}{CH}(CH_2)_2COO^-}$

18. The order of pH of the solution at which amino acid with side chain R exists as zwitterion is
(a) Acidic side chain > neutral side chain > basic side chain
(b) Acidic side chain < neutral side chain < basic side chain
(c) Acidic side chain > neutral side chain < basic side chain
(d) Acidic side chain < neutral side chain > basic side chain

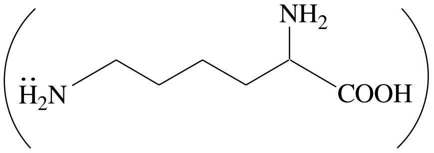
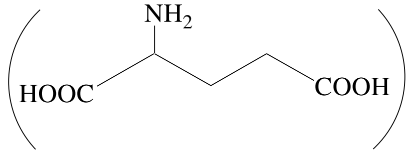
19. In the representation of a dipeptide,
(a) amino group is present at the left end
(b) amino group is present at the right end
(c) carboxylic group is present at the left end
(d) carboxylate ion is present at the left end

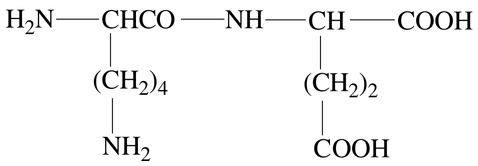
20. An oligopeptide may contain
(a) 2 to 6 amino acids (b) 2 to 8 amino acids (c) 2 to 10 amino acids (d) 2 to 12 amino acids

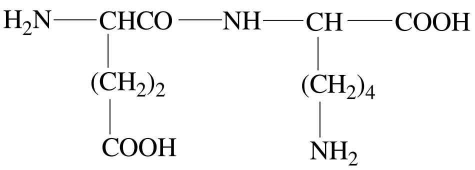
21. In the compound  the order of acidity of positions X, Y and Z is

(a) X > Y > Z (b) X > Z > Y (c) Z > X > Y (d) Y > Z > Z

The structure of alanine at pH = 2 and pH = 10, respectively, are
(a) $\mathrm{CH_3CH(\overset{+}{N}H_3)COOH}$; $\mathrm{CH_3CH(\overset{+}{N}H_2)COO^-}$
(b) $\mathrm{CH_3CH(NH_2)COO^-}$; $\mathrm{CH_3CH(\overset{+}{N}H_3)COOH}$
(c) $\mathrm{CH_3CH(\overset{+}{N}H_3)COO^-}$; $\mathrm{CH_3CH(NH_2)COO^-}$
(d) $\mathrm{CH_3CH(NH_2)COO^-}$; $\mathrm{CH_3CH(\overset{+}{N}H_3)COO^-}$

22. The liosine  and glutamine  may be combined to give two depeptides. Which of the following combinations represent dipeptides?

(I)  $\mathrm{H_2N{-}\underset{\substack{|\\ (CH_2)_4\\ |\\ NH_2}}{CHCO}{-}NH{-}\underset{\substack{|\\ (CH_2)_2\\ |\\ COOH}}{CH}{-}COOH}$

(II)  $\mathrm{H_2N{-}\underset{\substack{|\\ (CH_2)_2\\ |\\ COOH}}{CHCO}{-}NH{-}\underset{\substack{|\\ (CH_2)_4\\ |\\ NH_2}}{CH}{-}COOH}$

(III) 

$H_2N\,\underset{\displaystyle COOH}{\underset{|}{CH}}\,(CH_2)_4\,NH\,CO\,(CH_2)_2\,\underset{\displaystyle NH_2}{\underset{|}{CH}}—COOH$

(IV) 

$H_2N\,\underset{\displaystyle COOH}{\underset{|}{CH}}\,(CH_2)_4\,NH\,CO\,\underset{\displaystyle NH_2}{\underset{|}{CH}}\,(CH_2)_2\,COOH$

(a) (I) and (II)　(b) (I) and (III)　(c) (I) and (IV)　(d) (II) and (III)

Linked Comprehension Type

1. Nucleic acids are biologically significant polymers which store genetic information and transfer it between cells and from generation to generation and also control and direct the biosynthesis of all proteins. There are two kinds of nucleic acids; deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

(i) Which of the following bases is not present in DNA?

(a) Adenine　(b) Guanine　(c) Uracil　(d) Cytosine

(ii) Which of the following bases is not present in RNA?

(a) Adenine　(b) Guanine　(c) Cytosine　(d) Thymine

(iii) The number of bases present respectively in DNA and RNA are

(a) 3, 3　(b) 3, 4　(c) 4, 4　(d) 4, 3

2. Hydrogen bonding between nucleic-acid bases plays important role in the secondary structure of DNA and RNA. Identify the base pairs.

(i) Which of the following base pairs is present in DNA?

(a) Adenine-Guanine　(b) Adenine-Cytosine　(c) Adenine-Thymine　(d) Adenine-Uracil

(ii) Which of the following base pairs is present in RNA?

(a) Adenine-Guanine　(b) Adenine-Cytosine　(c) Adenine-Thymine　(d) Adenine-Uracil

(iii) Which of the following base pairs is present in both DNA and RNA?

(a) Adenine-Guanine　(b) Guanine-Cytosine　(c) Thymine-Uracil　(d) Guanine-Thymine

ANSWERS

Straight Objective Type

1. (a)　**2.** (d)　**3.** (c)　**4.** (a)　**5.** (b)　**6.** (c)　**7.** (d)
8. (c)　**9.** (a)　**10.** (c)　**11.** (d)　**12.** (a)　**13.** (b)　**14.** (c)
15. (d)　**16.** (a)　**17.** (d)　**18.** (b)　**19.** (a)　**20.** (c)　**21.** (a)
22. (a)

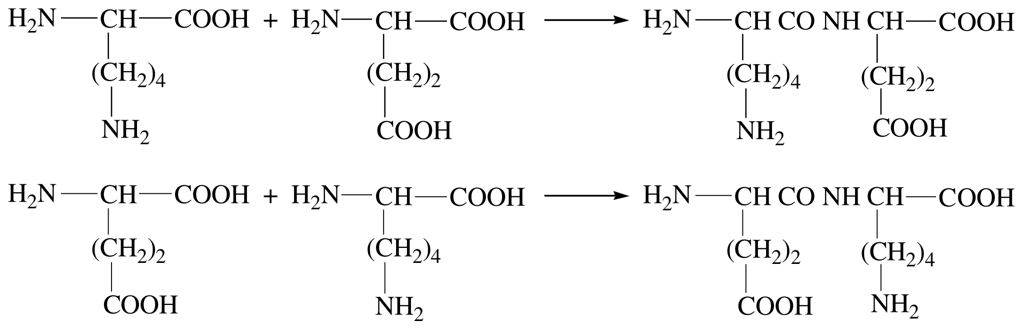
Linked Comprehension Type

1. **(i)** (c)　**(ii)** (d)　**(iii)** (c)
2. **(i)** (c)　**(ii)** (d)　**(iii)** (b)

Hints and Solutions

1. An amino acid contains an amino group attached to α-carbon atom.
2. The amino acids are basic units of proteins.
3. The number of amino acids commonly found in proteins is 20.
4. The number of essential amino acids is 10.
5. Simplest amino acids is glycine.
6. Isoleucine contains nonpolar —$CH(CH_3)CH_2CH_3$ group.
7. Glutamine contains polar —$CH_2CH_2CONH_2$ group.
8. Zwitterion is a doubly-charged species.
9. At low pH, an amino acid exists as $H_3\overset{+}{N}CHRCOOH$.
10. At high pH, an amino acid exists as $H_2NCHRCOO^-$.

11. The pH of the solution at the isoelectric point is pH = $(\mathrm{p}K^\circ_{a1} + \mathrm{p}K^\circ_{a2})$.
12. Glycine does not contain chiral carbon atom. Hence, it is not optically active.
13. Proteins contains exclusively L isomers of amino acids.
14. The amino acid $H_2N\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\,NH_2$ at low pH exists as $H_3\overset{+}{N}\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\,NH_3$.
15. The amino acid $H_2N\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_4\,NH_2$ at high pH exists as $H_2N\,\underset{\displaystyle COO^-}{\underset{|}{C}}H(CH_2)_4\,NH_2$.
16. The amino acid $H_2N\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_2\,COOH$ at low pH exists as $H_3\overset{+}{N}\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_2\,COOH$.
17. The amino acid $H_2N\,\underset{\displaystyle COOH}{\underset{|}{C}}H(CH_2)_2\,COOH$ at high pH exists as $H_2N\,\underset{\displaystyle COO^-}{\underset{|}{C}}H(CH_2)_2\,COO^-$.
18. The pH of the solution at which amino acids exist as Zwetterion follows the order
acidic side chain < neutral chain < basic side chain.
19. In the representation of a dipeptide, amino group is present at the left end.
20. An oligopeptide may contain 2 to 10 amino acids.
21. At pH = 2, alanine is protonated to NH_2 and at pH = 10, —COOH group ionizes to —COO^-
22. Two possible depeptide are



$$H_2N-\underset{\underset{\displaystyle NH_2}{\underset{|}{\underset{\displaystyle (CH_2)_4}{|}}}}{CH}-COOH + H_2N-\underset{\underset{\displaystyle COOH}{\underset{|}{\underset{\displaystyle (CH_2)_2}{|}}}}{CH}-COOH \longrightarrow H_2N-\underset{\underset{\displaystyle NH_2}{\underset{|}{\underset{\displaystyle (CH_2)_4}{|}}}}{CH}\,CO\,NH\,\underset{\underset{\displaystyle COOH}{\underset{|}{\underset{\displaystyle (CH_2)_2}{|}}}}{CH}-COOH$$

$$H_2N-\underset{\underset{\displaystyle COOH}{\underset{|}{\underset{\displaystyle (CH_2)_2}{|}}}}{CH}-COOH + H_2N-\underset{\underset{\displaystyle NH_2}{\underset{|}{\underset{\displaystyle (CH_2)_4}{|}}}}{CH}-COOH \longrightarrow H_2N-\underset{\underset{\displaystyle COOH}{\underset{|}{\underset{\displaystyle (CH_2)_2}{|}}}}{CH}\,CO\,NH\,\underset{\underset{\displaystyle NH_2}{\underset{|}{\underset{\displaystyle (CH_2)_4}{|}}}}{CH}-COOH$$

CHAPTER 33

POLYMERS

A polymer is simply a large molecule (i.e. macromolecule) built up by repetitive binding together of many smaller units called monomers. Some of the natural polymers are polysaccharides (from glucose units), proteins (from amino acids) and nucleic acids (from nucleotide units)

Homopolymer and Copolymer Synthetic polymers derived from a single repeating monomer are known as homopolymers while those derived from two or more type of repeating monomer units is known as copolymer.

Average Molecular Mass of Polymer A polymer sample contains chains of varying lengths and thus its molecular mass is expressed as an average as defined in the following.

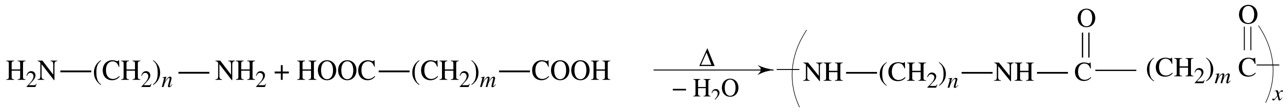
Number Average Molecular Mass, $M_n = \dfrac{\sum_i N_i M_i}{\sum_i N_i}$; *Mass Average Molecular Mass*, $M_m = \dfrac{\sum_i N_i M_i^2}{\sum_i N_i\, M_i}$,

Classification of Synthetic Polymers Based on the method of preparation, the following two types of polymers may be distinguished.

Chain-Growth Polymers Chain-growth polymers (or addition polymers) are produced by chain-reaction polymerization in which an initiator adds to a carbon-carbon double bond to yield a reactive intermediate. The polymer is built as more monomers add successively to the reactive end of the growing chain

$$\mathrm{In}^{\bullet} + \mathrm{CH_2{=}CH_2} \rightarrow [\mathrm{In{-}CHCH_2^{\bullet}}] \xrightarrow{\mathrm{H_2C{=}CH_2}} \underset{\substack{\downarrow \\ \text{Repeated many times to give a polymer}}}{[\mathrm{In{-}CH_2CH_2CH_2CH_2^{\bullet}}]}$$

Step-Growth Polymers Step-growth polymers (or condensation polymers) are prepared by reaction between two functional groups and thereby eliminating small molecules during polymerization.



$$\mathrm{H_2N{-}(CH_2)_n{-}NH_2 + HOOC{-}(CH_2)_m{-}COOH} \xrightarrow[-\mathrm{H_2O}]{\Delta} \left(\mathrm{NH{-}(CH_2)_n{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_m\overset{\overset{\displaystyle O}{\|}}{C}}\right)_x$$

Classification Based on Physical Properties

Based on physical properties, polymers may be classified as follows.

Elastomers Polymers which have ability to return to their original shape after the removal of force which causes stretching in them are known as elastomers. Natural rubber is one of the examples of an elastomer.

Fibre Certain polymers in molten state when passed through a small hole in a die or spinneret can be made in thin thread which on cooling form fibres. Such polymers are known as fibres. Examples are nylon, dacron and polyethylene.

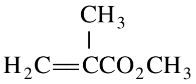
Thermoplastics A polymer which is hard at room temperature but becomes soft and viscous when heated is known as thermoplastic. Examples are polyethylene, poly(viny chloride), polystyrene, etc.

Thermosetting A polymer which becomes highly cross-linked and solidify into a hard, insoluble mass when heated is known as thermosetting polymer (or resin). One of the examples is bakelite. It is widely used for moulded parts, for adhesives and for coatings.

Polymers Formed from Ethylene and Substituted Ethylenes

Table 33.1 describes some of the polymers formed from ethylene and substituted ethylenes.

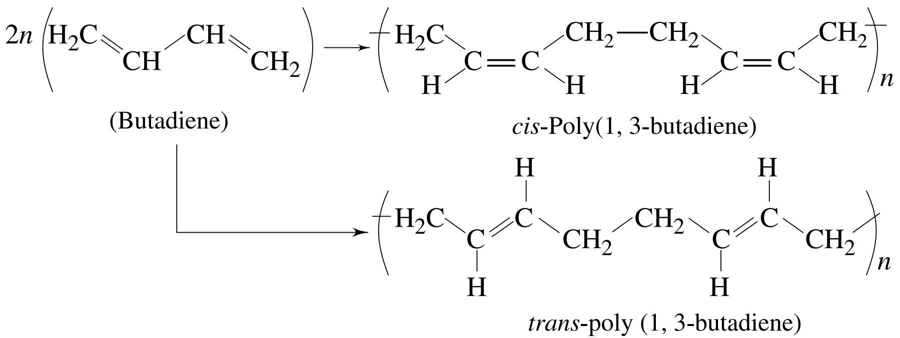
Table 33.1 Polymers formed from ethylene and substituted ethylens

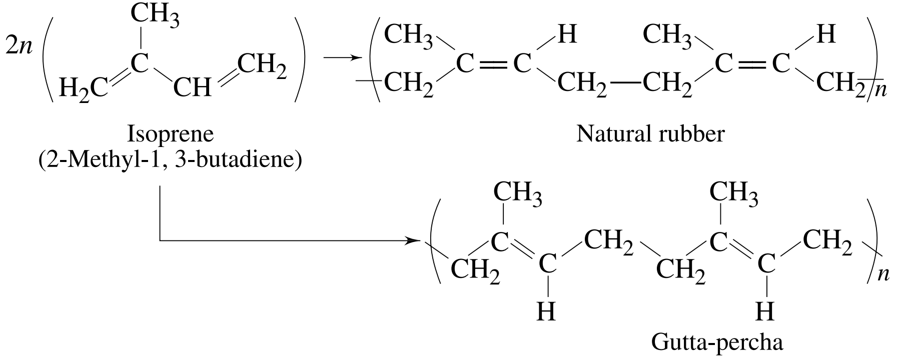
Monomer	*Polymer*	*Uses*
$H_2C{=}CH_2$ (Ethylene)	Polyethylene	Packaging, bottles, cable insulation, films and sheets
$H_2C{=}CHCH_2$ (Propylene)	Polypropylene	Automotive molding, carpet, rope
$H_2C{=}CHCl$ (Vinyl chloride)	Poly(vinyl chloride)	Insulation, films, pipes, Rain coats, hand bags, plastic toys, vinyl flooring
$H_2C{=}CHC_6H_5$ (Styrene)	Polystyrene (styron)	Foam and molded articles (toys), brush handles, combs, television coil, cups, bottle caps, false roofing
$H_2C{=}CHCN$ (Acrylonitrile)	Orlon, Acrilan	Fibers for clothes, carpets, blankets, etc.
$H_2C{=}CHOH$ (Vinyl alcohol)	Poly(vinyl alcohol)	Fibres, adhesives
$H_2C{=}CHOCOCH_3$ (Vinyl Acetate)	Poly(vinyl acetate)	Paints, adhesives
 $H_2C{=}\overset{\overset{\displaystyle CH_3}{\vert}}{C}CO_2CH_3$ (Methyl methacrylate)	Plexiglas, Lucite	Aircraft windows, dentures, molded articles, paints, optical lenses, transparent domes
$F_2C{=}CF_2$ (Tetrafluoroethylene)	Teflon	Values and gaskets, coatings

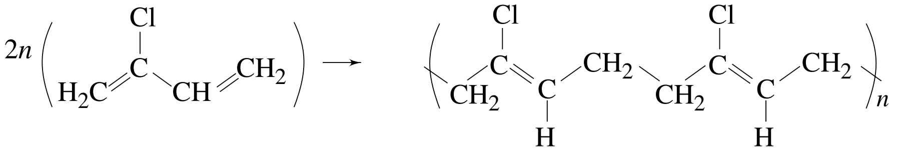
Polymer Formed From Butadiene and Substituted Butadiene

The polymerization reaction corresponds to 1,4 addition of growing chains to each conjugate diene monomer. The resultant polymer has a double bond after every four carbon atoms along the chain. These double bonds may be either *cis* or *trans* and the proper choice of Zeigler-Natta catalyst (an organometallic transition-metal complexes prepared by treating a trialkyl aluminium with a titanium compound) allows the preparation of either of these two choices.

Examples







Chloroprene   Neoprene (a synthetic rubber)

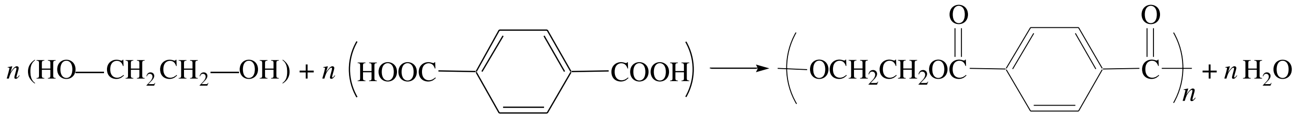
Vulcanization of Rubber Both natural and synthetic rubbers are soft. They can be hardened by the process of vulcanization discovered by Charles Goodyear (1834). In this process, rubber is heated with a per cent by mass of sulphur. This results into the formation of sulphur bridges between polymer chains.

Examples of Copolymers

1. $H_2C{=}CHCl + H_2C{=}CCl_2 \rightarrow$ Saran
   Vinyl chloride   Vinylidene chloride
2. $H_2C{=}CHC_6H_5 + H_2C{=}CHCH{=}CH_2 \rightarrow$ Buna-S
   Styrene (25%)   Butadiene (75%)   (a rubber)
3. $H_2C{=}CHCN + H_2C{=}CHCH{=}CH_2 \rightarrow$ Nitrile rubber
   Acrylonitrile   Butadiene
4. $H_2C{=}C(CH_3)_2 + H_2C{=}C(CH_3)CH{=}CH_2 \rightarrow$ Butyl rubber
   Isobutylene   Isoprene

SOME EXAMPLES OF STEP-GROWTH POLYMERS

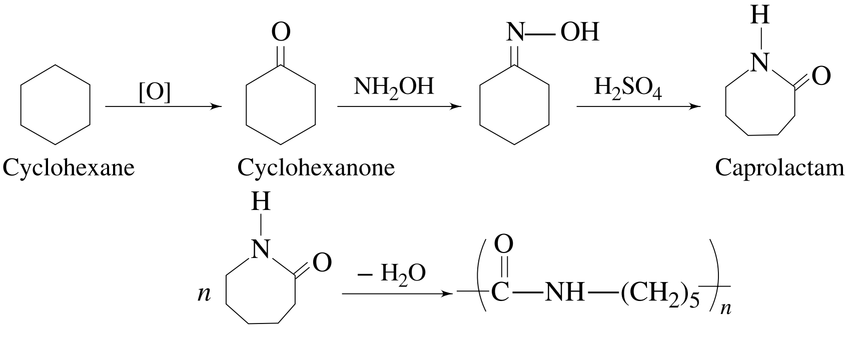
Terylene or Dacron



Ethylene glycol   Terephthalic acid   Terylene

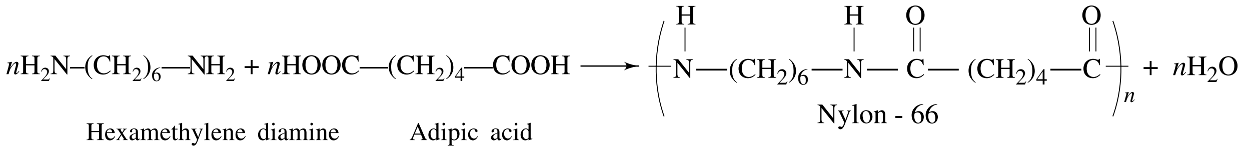
Terylene forms strong fibres. It has dry dip qualities. It is used for blending with cotton in clothing, and also in making seat belts, sails, packing for food, etc.

Nylon-6



Because of six carbon atoms in the monomer, the present polymer is called nylon-6. It is used for the manufacture of tyre cords and ropes.

Nylon-66

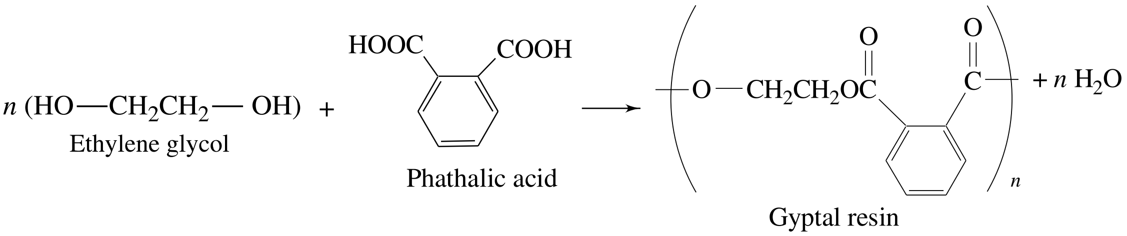


$$nH_2N{-}(CH_2)_6{-}NH_2 + nHOOC{-}(CH_2)_4{-}COOH \longrightarrow \left(\overset{H}{\underset{|}{N}}{-}(CH_2)_6{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}} \right)_n + nH_2O$$

Hexamethylene diamine   Adipic acid   Nylon - 66

Both the monomers have six carbon atoms, hence the name of the polymer is nylon-66. It is used as sheets, bristles for brushes and in textiles.

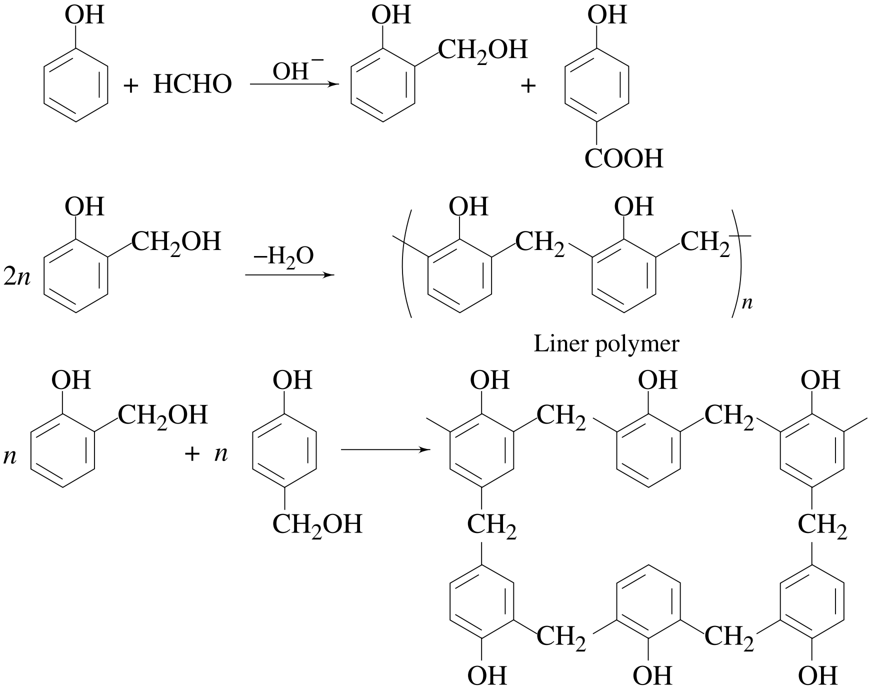
Glyptal or Alkyd Resin



Glyptal resin is used in the manufacture of paints, lacquers, etc.

Bakelite

The starting materials are formaldehyde and phenol. In the presence of a basic catalyst, these two substances combine to give *ortho* and *para* hydroxymethylphenol. These materials undergo condensation to produce cross-linked polymer bakelite involving methylene bridges in *ortho*, *para* or both *ortho* and *para* positions.



Cross-linked polymer bakelite

Straight Objective Type

1. Which of the following is natural polymer?
   (a) Terylene (b) Orlon (c) Starch (d) Dacron
2. Starch is a polymer of
   (a) glucose (b) fructose (c) sucrose (d) ribose
3. Which of the following is a chain-growth polymer?
   (a) Orlon (b) Terylene (c) Nylon-6 (d) Glyptal
4. Which of the following is a step-growth polymer?
   (a) Orlon (b) Terylene (c) Teflon (d) Styron
5. The monomer of natural rubber is
   (a) butadiene (b) chloroprene
   (c) 2-methyl-1, 2-butadiene (d) 2-methyl-1, 3-butadiene

6. The monomer of synthetic rubber is
(a) butadiene (b) chloroprene
(c) 2-methyl-1, 2-butadiene (d) 2-methyl-1, 3-butadiene

7. Which of the following is a copolymer?
(a) Natural rubber (b) Synthetic rubber (c) Gutta-percha (d) Saran

8. The monomer of teflon is
(a) $FClC{=}CClF$ (b) $Cl_2C{=}CCl_2$ (c) $F_2C{=}CF_2$ (d) $FClC{=}CF_2$

9. Starch contains
(a) 1, 6′-β-glycoside bond (b) 1, 4′-α-glycoside bond
(c) 1, 6′-α-glycoside bond (d) 1, 4′-β-glycoside bond

10. Which of the following polymer is hard?
(a) Linear (b) Cross-linked (c) Branched-chain (d) Thermoplastic

11. Which of the following polymers has ester linkages?
(a) Nylon (b) Bakelite (c) Terylene (d) PVC

12. Which of the following polymers has amide linkages?
(a) Nylon (b) Bakelite (c) Terylene (d) PVC

13. Polymerization of caprolactam yields
(a) terylene (b) nylon-6 (c) nylon-66 (d) bakelite

14. Which of the following is a thermosetting plastic?
(a) Nylon-6 (b) Terylene (c) Bakelite (d) Polyethene

15. Cellulose contains
(a) 1, 6′-β-glycosidic bond (b) 1, 6′-α-glycosidic bond
(c) 1, 4′-β-glycosidic bond (d) 1, 4′-α-glycosidic bond

16. Which of the following is an elastomer?
(a) Bakelite (b) Polyethylene (c) Nylon-6 (d) Natural rubber

17. Which of the following is a thermosetting?
(a) Bakelite (b) Polyethylene (c) Nylon-6 (d) Natural rubber

18. Which of the following is a fibre?
(a) Bakelite (b) Polyethylene (c) Nylon-6 (d) Natural rubber

19. Which of the following is a thermoplastic?
(a) Bakelite (b) Polyethene (c) Nylon-6 (d) Natural rubber

20. The monomers of Buna-S polymers are
(a) Vinyl chloride and vinylidene (b) Styrene and butadiene
(c) Acrylonitrile and butadiene (d)Isobutylene and isoprene

21. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is (2009)
(a) Nylon (b) Poly (vinyl chloride)
(c) Cellulose (d) Natural rubber

22. Which of the following is **not** a chain-growth polymer?
(a) Polyethene (b) Terylene (c) Orlon (d) Teflon

23. Which of the following is **not** a step-growth polymer?
(a) Acrilan (b) Terylene (c) Glyptal (d) Nylon-6, 6

24. Polymer obtained by using Ziegler-Natta catalyst is
(a) short-chain branching polymer (b) long-chain branching polymer
(c) linear polymer (d) hard polymer

25. Polymer obtained by using Ziegler-Natta catalyst is
(a) high crystalline polymer
(b) low density polymer
(c) lesser heat resistant as compared to radical-induced polymer
(d) lesser strength than the radical-induced polymer

26. Saran is
(a) simple polymer (b) a copolymer (c) an oligomer (d) a natural rubber

27. Neoprene is a polymer of
(a) vinyl chloride (b) chloroprene (c) butadiene (d) propene

Multiple Correct Choice Type

1. Which of the following polymers involve(s) cross linkages?
(a) Bakelite (b) Melamine (c) Polythene (d) Vulcanised rubber

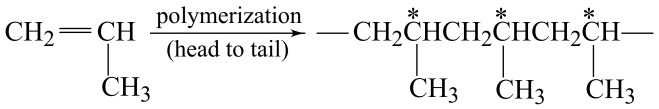
2. Which of the following polymers are examples of thermoplastic polymers?
(a) urea-formaldehyde resin (b) Polystyrene
(c) Nylon-6, 6 (d) Bakelite.

3. Which of the following polymers are examples of synthetic polymers?
(a) Neoprene rubber (b) Cellulose (c) Bunna rubber (d) Glycogen

4. The examples of condensation polymers are
(a) Nylon-6, 6 (b) Teflon (c) Orlon (d) Nylon-6

Linked Comprehension Type

1. Head-to-tail polymerization of propylene produces a polymer in which every other atom is a stereocentre. Many of the physical properties of the polypropylene produced in this way depend on the stereochemistry of these stereocentres.



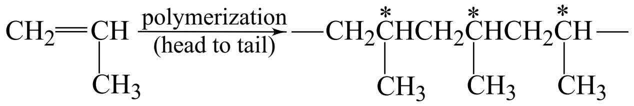
$$CH_2{=}\underset{CH_3}{\underset{|}{CH}} \xrightarrow[\text{(head to tail)}]{\text{polymerization}} -CH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}HCH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}HCH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}H-$$

(i) In which of the following polypropylene, the methyl groups are randomly disposed on either side of the stretched carbon chain?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

(ii) In which of the following polypropylene, all the methyl groups are on the same side of the stretched carbon chain?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

(iii) In which of the following polypropylene, the methyl group alternate regularly from one side of the stretched carbon chain to the other?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

2. Head-to-tail polymerisation of propylene produces a polymer in which every other atom is a stereocentre. Many of the physical properties of the polypropylene produced in this way depend on the stereochemistry of these stereocentres.



$$CH_2{=}\underset{CH_3}{\underset{|}{CH}} \xrightarrow[\text{(head to tail)}]{\text{polymerization}} -CH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}HCH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}HCH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}H-$$

(i) Which of the following polypropylene is/are produced by using Ziegler–Natta catalysts?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

(ii) Which of the following polypropylene is/are noncrystalline?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

(iii) Which of the following polypropylene is/are produced at lower pressures and have comparatively high melting point?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

Matrix Match Type

1. Match the chemical substances in Column I with type of polymers/type of bond in Column II.

Column I	**Column II**
(a) Cellulose	(p) natural polymer
(b) nylon-66	(q) synthetic polymer
(c) protein	(r) amide linkage
(d) sucrose	(s) glucoside linkage

ANSWERS

Straight Objective Type

1. (c) **2.** (a) **3.** (a) **4.** (b) **5.** (d) **6.** (b) **7.** (d)
8. (c) **9.** (b) **10.** (b) **11.** (c) **12.** (a) **13.** (b) **14.** (c)
15. (c) **16.** (d) **17.** (a) **18.** (c) **19.** (b) **20.** (b) **21.** (d)
22. (b) **23.** (a) **24.** (c) **25.** (a) **26.** (b) **27.** (b)

Multiple Correct Choice Type

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

Linked Comprehension Type

1. **(i)** (a) **(ii)** (c) **(iii)** (b)
2. **(i)** (d) **(ii)** (a) **(iii)** (d)

Matrix Match Type

1. (a)-(p),(s); (b)-(q),(r); (c)-(p),(r); (d)-(s)

Hints and Solutions

Straight Objective Type

1. Starch is a natural polymer.
2. Starch is a polymer of glucose.
3. Orlon is a chain-growth polymer.
4. Terylene is a step-growth polymer.
5. Isoprene (2-methyl-1, 3-butadiene) is the monomer of natural rubber.
6. Chloroprene is the monomer of synthetic rubber.
7. Saran is a copolymer.
8. $F_2C{=}CF_2$ is monomer of teflon.
9. Starch contains $1,4'$-α-glycoside bond.
10. Cross-linked polymer is hard.
11. Terylene has ester linkages.
12. Nylon has amide linkages.
13. Polymerization of caprolactam yields nylon-6.
14. Bakelite is an example of thermosetting plastic.
15. Cellulose contains $1,4'$-β-glycosidic bond.
16. Natural rubber is an example of elastomer.
17. Same answer as of Q. 14.
18. Nylon-6 is a fibre.
19. Polyethylene is an example of thermoplastic.
20. Styrene and butadiene are the monomers of Buna-S polymer.
21. Natural rubber is an elastomer. The irregular geometry of the molecules involves weak van der Waals force of attraction.

CHAPTER 34

EXERCISES IN ORGANIC CHEMISTRY

This section deals with the exercises in organic chemistry. These include organic problems on identification of a compound based on its characteristic chemical reactions, increasing/decreasing characteristics, organic reactions with rearrangement and matching items.

Identification of Organic Compounds

Quite often, one has to determine the molecular formula of a compound from the quantitative data on its elements. A brief review of this is described in the following.

1. Carbon is estimated in terms of carbon dioxide

$$\text{Per cent of carbon in the compound} = \frac{M_\text{C}}{M_{\text{CO}_2}} \cdot \frac{m_{\text{CO}_2}}{m_\text{compound}} \times 100 = \left(\frac{12}{44}\right)\left(\frac{m_{\text{CO}_2}}{m_\text{compound}}\right) \times 100$$

2. Hydrogen is estimated in terms of water

$$\text{Per cent of hydrogen in the compound} = \frac{2M_\text{H}}{M_{\text{H}_2\text{O}}} \cdot \frac{m_{\text{H}_2\text{O}}}{m_\text{compound}} \times 100 = \left(\frac{2}{18}\right)\left(\frac{m_{\text{H}_2\text{O}}}{m_\text{compound}}\right) \times 100$$

3. Nitrogen in the compound is estimated using either Dumas' method or Kjeldahl's method.
   In Dumas method, nitrogen is converted into nitrogen gas. From the volume of gas collected, we get

$$\text{Per cent of nitrogen in the compound} = \frac{m_\text{nitrogen}}{m_\text{compound}} \times 100 = \frac{(pV/RT)(M_{\text{N}_2})}{m_\text{compound}} \times 100$$

   If the volume of gas is measured at STP, then we can use the following expression.

$$\text{Per cent of nitrogen in the compound} = \frac{\{(V_{\text{N}_2})_\text{STP}/(22\,400\ \text{cm}^3\text{mol}^{-1})\}\{M_{\text{N}_2}\}}{m_\text{compound}} \times 100$$

   In Kjeldahl's method, nitrogen is converted into ammonia which is absorbed in sulphuric acid. The remaining sulphuric acid is determined by titrating against a standard alkali solution.
   If V_acid and N_acid are the volume and normality of acid solution taken to start with and V_alkali and N_alkali are the volume and normality of alkali solution used in the back titration, then we have

$$\text{Mass per cent of nitrogen in the compound} = \frac{M_\text{N}}{M_{\text{NH}_3}} \cdot \frac{m_{\text{NH}_3}}{m_\text{compound}} \times 100$$

$$\text{where} \quad \frac{m_{\text{NH}_3}}{M_{\text{NH}_3}} = n_{\text{NH}_3} = V_\text{acid}\,N_\text{acid} - V_\text{alkali}\,N_\text{alkali}$$

4. Halogen is estimated in terms of AgX

$$\text{Per cent of X in the compound} = \frac{M_\text{X}}{M_\text{AgX}} \cdot \frac{m_\text{AgX}}{m_\text{compound}} \times 100$$

5. Sulphur is estimated in terms of $BaSO_4$

$$\text{Per cent of S in the compound} = \frac{M_S}{M_{BaSO_4}} \cdot \frac{m_{BaSO_4}}{m_{compound}} \times 100$$

6. Phosphorus is estimated in terms of $Mg_2P_2O_7$ (magnesium pyrophosphate)

$$\text{Mass per cent of P in the compound} = \frac{2M_P}{M_{Mg_2P_2O_7}} \cdot \frac{m_{Mg_2P_2O_7}}{m_{compound}} \times 100$$

From the given percentages of elements, one can determine the empirical formula of the compound as described in the following.

Divide each per cent by the respective relative molar mass. The resultant numbers give the relative ratio of atoms present in the molecule. If fractions appear in the ratio, then one can multiply by the smallest number so as to get integral ratio of atoms.

After determining empirical formula, one has to determine molecular formula, which is an integral multiple of empirical formula. The integral multiple is given as

$$n = \frac{\text{Molar mass of the compound}}{\text{Empirical molar mass of the compound}}$$

Molar mass of the compound is determined by a suitable physico-chemical method, e.g. Victor-Meyer method, volumetrical method, and colligative properties.

A few expressions to compute molar mass of a compound are as follows.

1. *From relative lowering of vapour pressure* $M_2 = \dfrac{m_2}{(m_1/M_1)(-\Delta p_1/p_1^*)}$

2. *From elevation of boiling point* $M_2 = \dfrac{K_b}{\Delta T_b}\dfrac{m_2}{m_1}$

3. *From depression of freezing point* $M_2 = \dfrac{K_f}{(-\Delta T_f)}\dfrac{m_2}{m_1}$

4. *From osmotic pressure* $M_2 = \left(\dfrac{m_2}{V}\right)\dfrac{RT}{\Pi}$

   In all the above expressions, the subscripts 1 and 2 stand for solvent and solute, respectively.

5. *From vapour density*

   By definition, vapour density is the ratio of density of a gas and density of hydrogen gas. Since molar mass of hydrogen is 2 g mol^{-1}, the molar mass of the gas will be

   $$\text{Molar mass of gas} = (2 \text{ g mol}^{-1}) \text{ (vapour density)}$$

6. *From the silver salt method for caboxylic acids*

   The carboxylic acid is converted into silver salt which on strongly heating produces silver. From the masses of silver salt and silver, the molar mass of acid can be determined as follows.

   $$\text{Equivalent mass of silver salt, } (M_{salt})_{eq} = \left(\frac{\text{mass of silver salt}}{\text{mass of silver}} \times 108\right) \text{ g eq}^{-1}$$

   $$\text{Equivalent mass of acid, } (M_{acid})_{eq} = (M_{salt})_{eq} - 107 \text{ g eq}^{-1}$$

   $$\text{Molar mass of acid, } M_{acid} = \text{(basicity)} (M_{acid})_{eq}$$

7. From the platinichloride method for organic bases

   Organic bases form solid platinichlorides (or chloroplatinates) with chloroplatinic acid (H_2PtCl_6). These, on heating, leave behind platinum. Now, each chloroplatinic acid H_2PtCl_6 ($\equiv PtCl_4 \cdot 2HCl$) contains 2 molecules of HCl. Hence,

   $$1 \text{ equivalent of salt} \equiv 1 \text{ equivalent of } H_2PtCl_6 \equiv 1 \text{ equivalent of base} \equiv \frac{1}{2}(\text{molar mass of Pt}) \equiv \frac{195}{2} \text{ g eq}^{-1}$$

   Equivalent mass of platinum salt

$$(M_{\text{salt}})_{\text{eq}} = \frac{\text{mass of platinum salt}}{\text{mass of platinum}} \times \frac{195}{2}\ \text{g eq}^{-1}$$

Equivalent mass of base

$$(M_{\text{base}})_{\text{eq}} = (M_{\text{salt}})_{\text{eq}} - (M_{\text{H}_2\text{PtCl}_6})_{\text{eq}} = \left[(M_{\text{salt}})_{\text{eq}} - \frac{410}{2}\ \text{g eq}^{-1}\right]$$

$$M_{\text{base}} = (\text{acidity})\ (M_{\text{base}})_{\text{eq}}$$

DETECTION OF ELEMENTS (N, S AND HALOGENS)

Nitrogen, sulphur and halogens in an organic compound can be detected by Lassaigne test. In this test, firstly sodium extract of the given organic compound is prepared as described in the following.

A pea sized dry piece of freshly cut sodium metal is taken in an ignition tube. This piece is melted to shining globule by heating the ignition tube, and then a pinch of the organic compound is introduced in the tube. The tube is first heated gently and then strongly till the lower end of the tube becomes red hot. The tube is then plunged and broken in about 20 mL of distilled water taken in porcelain dish. The solution is boiled for about 5 minutes and filtered. The filtrate obtained is known as sodium extract.

Test for Nitrogen To a little sodium extract (say, 2 mL), add a little solid ferrous sulphate. Boil the solution and add a little dilute sulphuric acid. Appearance of prussian blue or green coloration indicates the presence of nitrogen in the compound.

$$\text{Na} + \underbrace{\text{C} + \text{N}}_{\left(\substack{\text{from organic}\\ \text{compound}}\right)} \xrightarrow{\text{Fuse}} \text{Na}^+ + \text{CN}^- \qquad \text{Fe}^{2+} + 6\ \text{CN}^- \rightarrow [\text{Fe(CN)}_6]^{4-}$$

$$3\ [\text{Fe(CN)}_6]^{4-} + 4\text{Fe}^{3+} \rightarrow \underset{\text{(prussian blue)}}{\text{Fe}_4[\text{F}_3(\text{CN})_6]_3}$$

Test for Sulphur To a little sodium extract (say, 2 mL), add a few drops of acetic acid and lead acetate. Appearance of black precipitate indicates the presence of sulphur in the organic compound.

$$\text{Na} + \underset{\text{(from organic compound)}}{\text{S}} \rightarrow \text{Na}^{2+} + \text{S}^{2-} \qquad \text{S}^{2-} + \text{Pb}^{2+} \rightarrow \underset{\text{(black ppt)}}{\text{PbS}}$$

Alternatively, a few drops of freshly prepared sodium nitroprusside is added to 2 mL sodium extract. Appearance of purple coloration indicates the presence of sulphur.

$$\text{S}^{2-} + [\text{Fe (CN)}_5\text{NO}]^{2-} \rightarrow \underset{\text{(purple colour)}}{[\text{Fe(CN)}_5\text{NOS}]^{4-}}$$

Test for Nitrogen and Sulphur Present Together To a little sodium extract (say, 2 mL), add a little dilute sulphuric acid and ferric chloride solution. Appearance of red coloration indicates the presence of both nitrogen and sulphur in the organic compound.

$$\text{Na} + \underbrace{\text{C} + \text{N} + \text{S}}_{\left(\substack{\text{from organic}\\ \text{compound}}\right)} \rightarrow \text{Na}^+ + \text{CNS}^- \qquad \text{Fe}^{3+} + 3\ \text{CNS}^- \rightarrow \underset{\text{red colour}}{\text{Fe(CNS)}_3}$$

Tests for Halogens To about 5 mL of sodium extract, add equivalent volume of concentrated nitric acid. Boil the solution till volume is reduced to half. This ensure the evaporation of CN^-, S^{2-} or CNS^- if present in the solution, since otherwise these ions also show the test carried out for halogens. Cool the solution. To a portion of this solution, add silver nitrate solution. Appearance of

(a) white precipitates soluble in NH_4OH indicates the presence of chlorine.
(b) light yellow precipitates soluble in excess of NH_4OH indicates the presence of bromine.
(c) yellow precipitates insoluble in NH_4OH indicates the presence of iodine.

Bromine and iodine may also be detected by carrying out the carbon tetrachloride (or carbon disulphide) test. To a little solution obtained after treating with concentrated nitric acid, add about 1 mL of CCl_4 (or CS_2). Add a little of chlorine water or concentrated nitric acid. Shake the solution vigorously. Appearance of red (or violet) coloration in CCl_4 layer indicates the presence of bromine (or iodine) in the organic compound.

DETECTION OF FUNCTIONAL GROUP

Test for Alcoholic Hydroxyl Group

1. *Sodium Test* To a little (say, 1 mL) of the organic compound in a dry test tube add a small piece of dry sodium. A brisk effervescence due to evolution of hydrogen indicates the presence of —OH group.
2. *Ceric Ammonium Nitrate Test* To a little (say, 1 mL) of the organic compound in a test tube add a few drops of ceric ammonium nitrate. Appearance of red coloration indicates the presence of —OH group.
3. *Molybdate Test* Heat a little of the organic compound with 2 pellets of KOH. Cool and add 1 mL of ether and 2-3 drops of CS_2. A yellow solution or precipitate will be obtained. Filter the solution and to the filtrate add 1 mL of ammonium molybdate solution and excess of dilute HCl. A red or blue coloration indicates the presence of —OH group.

Test for Phenolic Hydroxyl Group

1. *Ferric Chloride Test* To 1 mL of aqueous (or alcoholic) solution of the compound add a few drops of ferric chloride solution. A violet, red, blue or green coloration indicates the presence of phenolic group.
2. *Ceric Ammonium Nitrate* To 1 mL of aqueous hot solution of the compound, add a few drops of ceric ammonium nitrate. A green or brown precipitates indicates the presence of phenolic group.
3. *Phthalein Test* Heat about 0.1 g of the compound with 0.1 g phthalic anhydride and a few drops of concentrated H_2SO_4. Cool, pour the solution in dilute NaOH solution. A red, blue or fluorescent green coloration indicates the presence of phenolic group.

Tests for Aldehydic and Ketonic Groups

1. *2, 4-Dinitrophenylhydrazine Test* Shake 2-3 drops of alcoholic solution of organic compound with 1 mL of 2, 4-dinitrophenylhydrazine reagent. A yellow or orange precipitate indicates the presence of carbonyl group.
2. *Sodium Bisulphite Test* Shake a little organic compound (say, 0.2 g or 4-5 drops) with 1 mL of a saturated solution of sodium bisulphite. A crystalline precipitates indicates the presence of carbonyl group.

Tests for Aldehydic Group

1. *Tollens reagent test* To a little of the organic compound in a test tube add a 1 mL of Tollens reagent (ammoniacal solution of silver nitrate). Warm and allow to stand. The appearance of silver mirror at the sides of test tube indicates the presence of aldehydic group.
2. *Fehling's Solution Test* Warm a little of organic compound with 1 mL of Fehling's solution. Appearance of red precipitates indicates the presence of aldehydic group.
3. *Schiff's Reagent Test* To a little of organic compound add a few drops of Schiff's reagent. Appearance of pink or violet coloration indicates the presence of aldehydic group.

Test for Ketonic Group

If a carbonyl group is present, the absence of aldehydic group tests indicates the presence of ketonic group.

Tests for Carboxylic Group

1. *Bicarbonate Test* To a little of organic compound add 2-3 mL of 5% $NaHCO_3$ solution. Brisk appearance of CO_2 indicates the presence of —COOH group.
2. *Ester Test* Warm a little organic compound add 2-3 drops of concentrated H_2SO_4 and 2 mL of alcohol. A fragrant smell indicates the presence of —COOH group.

Tests for Primary Amine Group

1. *Isocyanide Test* Warm a little of organic compound with 2-3 drops of chloroform and 1 mL of alcoholic KOH. A very unpleasant odour of isocyanide indicates the presence of $—NH_2$ group.
   After performing the test, add 2-3 mL of concentrated HCl to destroy isocyanide.
2. *Dye Test for aromatic primary amines* Cool in ice 0.2 g (or 4-5 drops) of the organic compound with 1 mL concentrated HCl. Add 2 mL of iced-cold dilute $NaNO_2$ solution. Shake and add 2-3 mL of alkaline β-naphthol solution. A red or orange dye indicates the presence of aromatic $—NH_2$ group.

Test for Secondary Amino Group

Liebermann's Nitroso Reactions Cool in ice 0.2 g (or 4-5 drops) of the organic compound with 10 mL of dilute HCl. Add 2 mL of iced-cold dilute $NaNO_2$ solution. A white or yellow oily emulsion is obtained. Take 2-3 drops of this emulsion and add 3-4 drops of phenol and 3-4 drops of concentrated H_2SO_4. Warm the solution. A blue coloration which changes to red on adding 1-2 mL of water. The colour changes to blue on adding a few drops of NaOH solution.

Test for Nitro Group

1. *Dye Test* To a little of organic compound add 1 mL of concentrated HCl and 3-4 small pieces of granulated tin. Heat the mixture for 5 minutes in a boiling water bath. Filter the solution and cool the filtrate in ice-cold water. Add 1-2 mL of $NaNO_2$ solution followed by 2 mL of alkaline β-naphthol solution. The appearance of red or orange coloured dye indicates the presence of $—NO_2$ group.
2. *Mulliken and Baker's Test* Dissolve a little of organic compound in about 1 mL alcohol. Add about 1 mL of NH_4Cl solution and a pinch of Zn dust. Warm the mixture and filter directly in 2 mL of Tollens reagent. Appearance of grey or black precipitates indicates the presence of $—NO_2$ group.

Straight Objective Type

1. An aromatic compound contains 69.4%C and 5.8%H. A sample of 0.3 g of this compound give ammonia which neutralizes 25 mL of 0.05 M H_2SO_4. The empirical formula of the compound is
(a) $C_5H_5N_2O$ (b) C_7H_7NO (c) $C_6H_5NO_2$ (d) C_6H_8NO

2. An organic compound A contains 49.32%C, 9.59%H and 19.18%N and rest oxygen. The compound A on boiling with NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67%Ag. The compound A is
(a) CH_3CONH_2 (b) $C_2H_5CONH_2$ (c) $C_3H_7CONH_2$ (d) $C_3H_5CONH_2$

3. A compound contains 88.89%C and 11.1%H. It gives white precipitate with ammoniacal silver nitrate. The compound is
(a) $C_5H_7C{\equiv}CH$ (b) $C_8H_9C{\equiv}CH$ (c) $C_6H_{11}C{\equiv}CH$ (d) $C_4H_7C{\equiv}CH$

4. Which of the following compouond does not show the test of N?
(a) NH_2OH (b) $CH_2CH_2NH_2$ (c) $C_6H_5NH_2$ (d) $C_6H_5CONH_2$

5. Liebig method is used for the estimation of
(a) carbon only (b) hydrogen only (c) carbon and hydrogen (d) nitrogen

6. Per cent of carbon in an organic compound is given as

(a) $\frac{M_C}{M_{CO_2}} \cdot \frac{m_{CO_2}}{m_{\text{compound}}} \times 100$ (b) $\frac{M_C}{M_{CO_2}} \frac{m_{\text{compound}}}{m_{CO_2}} \times 100$

(c) $\frac{M_{CO_2}}{M_C} \frac{m_{CO_2}}{m_{\text{compound}}} \times 100$ (d) $\frac{M_{CO_2}}{M_C} \frac{m_{\text{compound}}}{m_{CO_2}} \times 100$

where m is the mass of the substance of M stands for its molar mass.

7. Per cent of hydrogen in an organic compound is given as

(a) $\frac{M_H}{M_{H_2O}} \frac{m_{H_2O}}{m_{\text{compound}}} \times 100$ (b) $\frac{2M_H}{M_{H_2O}} \frac{m_{H_2O}}{m_{\text{compound}}} \times 100$

(c) $\frac{M_{H_2O}}{M_H} \frac{m_{\text{compound}}}{m_{H_2O}} \times 100$ (d) $\frac{M_{H_2O}}{2M_H} \frac{m_{\text{compound}}}{m_{H_2O}} \times 100$

8. Dumas method is used for the estimation of
(a) carbon (b) hydrogen (c) sulphur (d) nitrogen

9. The expression to compute per cent of nitrogen in an organic compound by the Dumas method is

(a) $\frac{(V_{N_2})_{STP} M_{N_2}}{(22414\,\text{cm}^3\,\text{mol}^{-1}) m_{\text{compound}}} \times 100$ (b) $\frac{(V_{N_2})_{STP} m_{\text{compound}}}{(22414\,\text{cm}^3\,\text{mol}^{-1}) M_{N_2}} \times 100$

(c) $\dfrac{\left(22414\,\text{cm}^3\,\text{mol}^{-1}\right)M_{\text{N}_2}}{(V_{\text{N}_2})_{\text{STP}}\,m_{\text{compound}}} \times 100$ (d) $\dfrac{22414\,\text{cm}^3\,\text{mol}^{-1}}{(V_{\text{N}_2})_{\text{STP}}}\,\dfrac{m_{\text{compound}}}{M_{\text{N}_2}} \times 100$

10. Kjeldahl's method is used to estimate the element
(a) carbon (b) hydrogen (c) sulphur (d) nitrogen

11. The expression to compute per cent of nitrogen in an organic compound by the Kjeldahl's method is

(a) $\left(\dfrac{M_{\text{N}}}{M_{\text{compound}}}\right)(V_{\text{acid}}\,N_{\text{acid}} - V_{\text{alkali}}\,N_{\text{alkali}}) \times 100$ (b) $\left(\dfrac{M_{\text{compound}}}{M_{\text{N}}}\right)(V_{\text{acid}}\,N_{\text{acid}} - V_{\text{alkali}}\,N_{\text{alkali}}) \times 100$

(c) $\left(\dfrac{M_{\text{N}}}{M_{\text{compound}}}\right)(V_{\text{acid}} - V_{\text{alkali}}) \times 100$ (d) $\left(\dfrac{M_{\text{compound}}}{M_{\text{N}}}\right)(V_{\text{acid}} - V_{\text{alkali}}) \times 100$

12. The Carius method is used for the estimation of
(a) carbon (b) hydrogen (c) halogens (d) nitrogen

13. The expression to compute the per cent of halogen X in an organic compound by the Carius method is

(a) $\left(\dfrac{M_{\text{AgX}}}{M_{\text{AgX}}}\right)\dfrac{M_{\text{Ag}}}{m_{\text{compound}}} \times 100$ (b) $\dfrac{M_{\text{X}}}{M_{\text{AgX}}}\,\dfrac{M_{\text{AgX}}}{m_{\text{compound}}} \times 100$

(c) $\dfrac{M_{\text{AgX}}}{M_{\text{X}}}\,\dfrac{m_{\text{compound}}}{M_{\text{AgX}}} \times 100$ (d) $\dfrac{M_{\text{X}}}{M_{\text{AgX}}}\,\dfrac{m_{\text{compound}}}{M_{\text{AgX}}} \times 100$

14. Molar mass of volatile compounds can be determined by
(a) volumetric method (b) Victor Meyer's method
(c) depression in freezing point (d) elevation in boiling point

15. Molar mass and vapour density are related to each other through the expression

(a) $M_{\text{substance}} = (2\ \text{g mol}^{-1})$ (Vapour density) (b) $M_{\text{substance}} = \left(\dfrac{1}{2\,\text{g}\,\text{mol}^{-1}}\right)$ (Vapour density)

(c) $M_{\text{substance}} = \left(\dfrac{1\,\text{g}\,\text{mol}^{-1}}{2}\right)$ (Vapour density) (d) $M_{\text{substance}}$ = Vapour density

16. 0.1890 g of an organic compound gives 0.287 g of silver chloride determined by Carius method. The per cent of Cl in the compound is
(a) 18.7 (b) 37.5 (c) 56.2 (d) 75.0

17. An organic compound contains 90% C and 10% H by mass. Its empirical formula is
(a) C_2H_6 (b) C_2H_4 (c) C_3H_8 (d) C_3H_4

18. 0.246 g of the organic compound gave 22.4 cm^3 of nitrogen gas at STP as determined by Dumas method. The per cent of nitrogen in the compound is
(a) 11.38 (b) 17.07 (c) 22.76 (d) 34.14

19. An organic compound contains 58.53% C, 4.06% H and 11.38% N by mass. The empirical formula of the compound is
(a) $C_6H_5N_2O$ (b) $C_6H_5NO_2$ (c) $C_5H_6N_2O$ (d) $C_5H_7NO_2$

20. A monoacid organic base (0.0915 g) requires 15 cm^3 of N/20 HCl for complete neutralization. The molar mass of the base is
(a) 61 g mol^{-1} (b) 122 g mol^{-1} (c) 244 g mol^{-1} (d) 183 g mol^{-1}

21. An organic compound (0.156 g) on Kjeldahl's method for nitrogen estimation requires 16.5 cm^3 of 0.1 M NaOH for the remaining unneutralized acid in 60.25 cm^3 of 0.1 N H_2SO_4 taken to start with. The per cent of nitrogen in the compound is
(a) 39.26 (b) 78.52 (c) 49.26 (d) 59.26

22. A volatile liquid (0.146 g) displaced 30.5 cm^3 of air at 305 K and 760 mmHg pressure. The molar mass of the liquid is
(a) 117.8 g mol^{-1} (b) 118.8 g mol^{-1} (c) 119.8 g mol^{-1} (d) 120.8 g mol^{-1}

23. A compound (0.244 g) containing sulphur yielded 0.9336 g of $BaSO_4$. The per cent of sulphur in the compound is
(a) 25.46 (b) 52.46 (c) 64.25 (d) 46.52

24. An organic compound (0.45 g) on combustion yielded 1.1 g of CO_2 and 0.3 g water. Besides C and H, nitrogen is also present in the compound. The empirical formula of the compound would be
(a) CH_2N (b) C_2H_3N (c) C_3H_4N (d) C_2H_5N

25. 0.1 g of an organic monobasic acid on complete combustion gave 0.2545 g of CO_2 and 0.04428 g of H_2O. For complete neutralization 0.122 g of the acid required 10 cm^3 of 0.1 M NaOH solution. The molecular formula of the acid would be
(a) $C_7H_6O_2$ (b) $C_6H_7O_2$ (c) $C_7H_7O_2$ (d) $C_6H_6O_2$

26. The purification of naphthalene can be done by
(a) filtration (b) sublimation (c) crystallization (d) evaporation

27. A compound which decomposes before its boiling point can be purified by the method of
(a) simple distillation (b) fractional distillation
(c) distillation under reduce pressure (d) steam distillation

28. Phenol can be purified by the method of
(a) distillation (b) steam distillation (c) crystallization (d) fractional distillation

29. Chromatorgraphy is based on the phenomenon of
(a) adsorption (b) absorption (c) solubility (d) chemisorption

30. Essential oils can be isolated by
(a) crystallization (b) steam distillation (c) sublimation (d) distillation

31. Sugar is decolourized by
(a) coal (b) carbon black (c) charcoal (d) coke

32. Two substances having slightly different solubility can be separated by
(a) distillation (b) factional distillation (c) crystallization (d) fractional crystallization

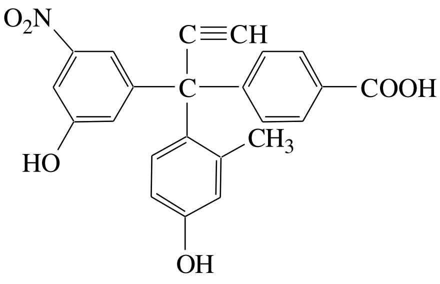
33. Which of the following statements is true regarding the fractional distillation of a mixture of two liquids?
(a) The distillate collected is the liquid of lower boiling point
(b) The distillate collected is the liquid of higher boiling point
(c) The liquid left behind the flask is that of lower boiling point
(d) The composition of distillate and the liquid left behind the flask do not depend upon the length of fractionating column

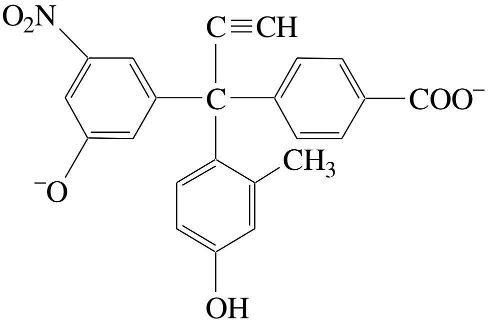
34. For which of the following compounds, Kjeldahl's method can be used to estimate nitrogen?
(a) Aniline (b) Methyl amine (c) Urea (d) Toluidine

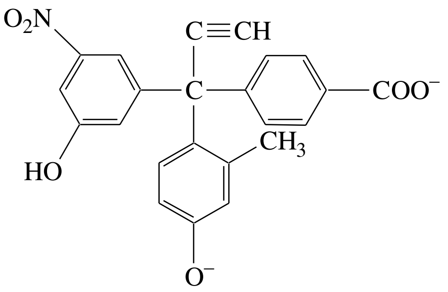
35. Which of the following compounds is not expected to exhibit Lassaigne's test of nitrogen?
(a) CH_3CN (b) CH_3NH_2 (c) CH_3NO_2 (d) NH_2OH

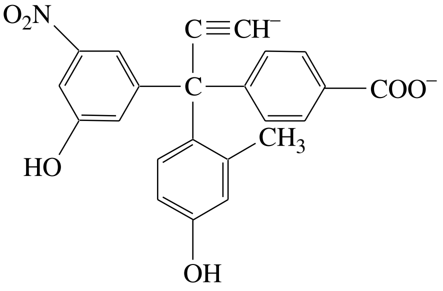
36. Which of the following compounds is expected to give red colouration while performing Lassaigne's test of nitrogen?
(a) Urea (b) Thiourea (c) Aniline (d) Nitrobenzene

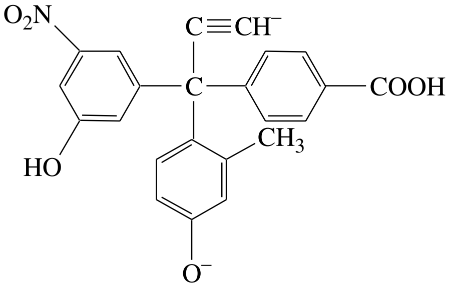
37. Which of the following is an organometallic compound?
(a) Lithium methoxide (b) Lithium acetate (c) Lithium dimethylamide (d) Methyl lithium. [1997]

38. The compound  is treated with 2 mol of $NaNH_2$. The product obtained is

(a) 

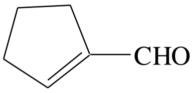
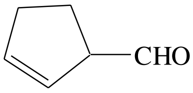
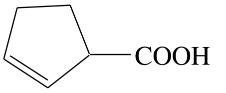
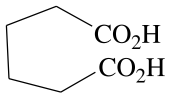
(b) 

(c) 

(d) 

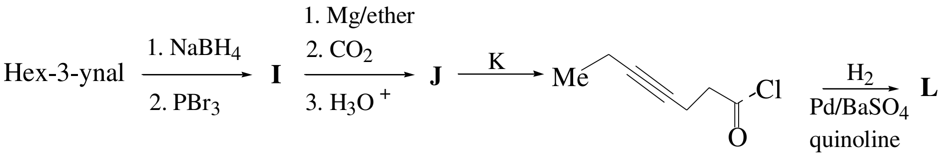
[2003]

39. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound **F** is

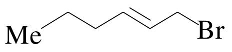
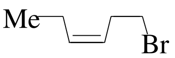
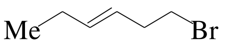
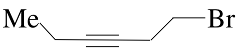
(a) 
(b) 
(c) 
(d) 
[2007]

Linked Comprehension Type

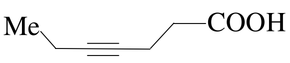
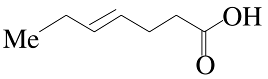
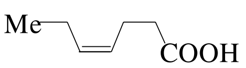
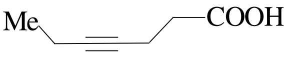
(1) In the following reaction sequence, products **I**, **J** and **L** are formed. **K** represents a reagent.



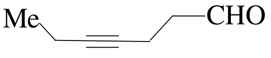
(i) The structure of the product **I** is

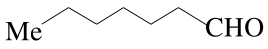
(a) 
(b) 
(c) 
(d) 

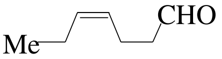
(ii) The structures of compounds **J** and **K**, respectively, are

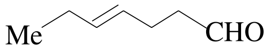
(a)  and $SOCl_2$
(b)  and SO_2Cl_2
(c)  and $SOCl_2$
(d)  and CH_3SO_2Cl

(iii) The structure of product **L** is

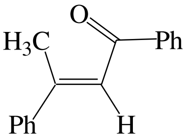
(a) 

(b) 

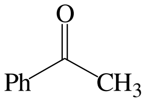
(c) 

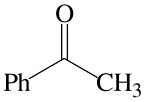
(d)  [2008]

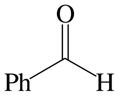
(2) A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

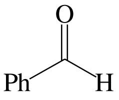
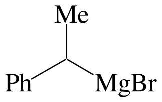
M = 

(i) Compound **H** is formed by the reaction of

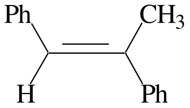
(a)  + PhMgBr

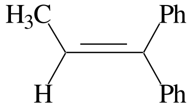
(b)  + $PhCH_2MgBr$

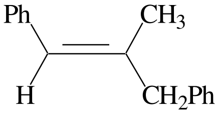
(c)  + $PhCH_2MgBr$

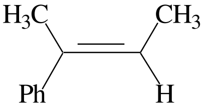
(d)  + 

(ii) The structure of compound **I** is

(a) 

(b) 

(c) 

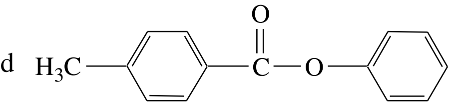
(d) 

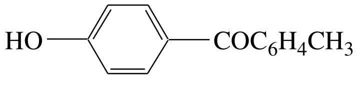
(iii) The structures of compounds **J**, **K** and **L**, respectively, are

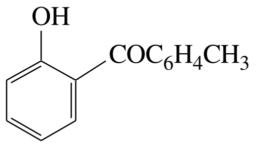
(a) $PhCOCH_3$,$PhCH_2COCH_3$ and $PhCH_2COO^-K^+$ (b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

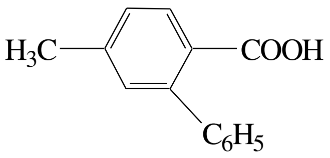
(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$ (d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$ [2008]

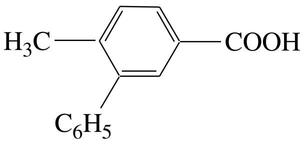
3. The compounds of the type phenyl acetate undergo Fries rearrangement when treated with $AlCl_3$ in an inert solvent to give two phenolic isomers. The product obtained is either kinetic-controlled or thermodynamic controlled depending upon the temperature at which rearrangement is carried out. Based on this, answer the following three questions.

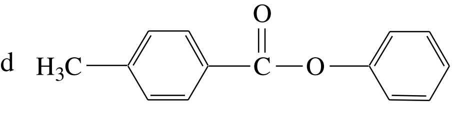
(i) The compound  is treated with $AlCl_3$ in an inert solution. The predominant product obtained at 25° C is

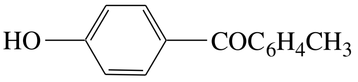
(a) 

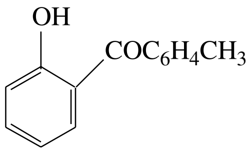
(b) 

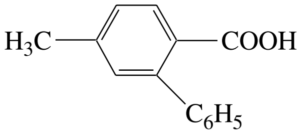
(c) 

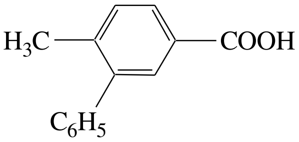
(d) 

(ii) The compound  is treated with $AlCl_3$ in an inert solvent. The predominant product obtained at 165 °C is

(a) 

(b) 

(c) 

(d) 

(iii) *o*-Hydroxyacetophenone may be conveniently separated from *p*-hydroxyacetophenone by the method of

(a) fractional distillation (b) fraction crystallization

(c) steam distillation (d) solvent extraction

Matching Type

1. Match the entries given on the left with those given on the right.

(a) Cyclopropane, chlorine and light	(p) Electrophilic substitution
(b) Propanone and sodium bisulphite	(q) Homologous pair
(c) Ethanal and Methanal	(r) Homolytic addition
(d) Benzene, nitric acid and sulphuric acid	(s) Free radical substitution
(e) Propene, hydrogen bromide and a peroxide catalyst	(t) nucleophilic addition

[1981]

2. Match the entries given on the left with those given on the right.

(a) Pyrolysis of alkanes	(p) Elimination reaction
(b) Benzene + Chloroethane (+ anhydrous $AlCl_3$)	(q) Saponification
(c) $CH_3COOC_2H_5$ + NaOH	(r) Wurtz reaction
(d) Preparation of alkanes	(s) Friedel-craft reaction
(e) Phenol + $CHCl_3$ (NaOH)	(t) Reimer-Tiemann reaction
(f) C_2H_5Br + alcKOH	(u) Cracking

[1982]

3. Match the entries given on the left with those given on the right.

(a) Decarboxylation	(p) Addition reaction
(b) Ozonolysis	(q) Sodalime
(c) Williamson's synthesis	(r) Structure of alkene
(d) Dichloroethylene	(s) Ether

[1983]

4. Match the entries given on the left with those given on the right.

(a) Lucas test	(p) Phenol
(b) Neutral $FeCl_3$	(q) Glucose
(c) Dye test	(r) Tertiary alcohol
(d) Tollens test	(s) Aniline

[1983]

5. Match the entries given on the left with those given on the right.

Friedel-Crafts	oil	alkenes
Fermentation	Lewis acid	soap
Dehydrohalogenation	cuprous chloride	anhydrous $AlCl_3$
Sandmeyer	yeast	chlorobenzene
Saponification	alcoholic alkali	ethanol

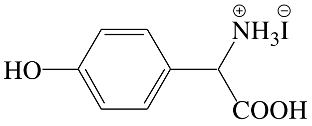
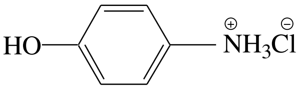
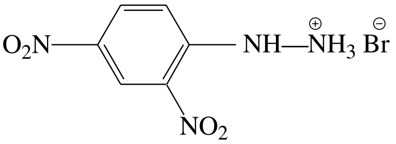
[1988]

6. Match the compounds/ions in Column I with their properties/reactions in Column II.

Column I	**Column II**
(a) C_6H_5CHO	(p) gives precipitate with 2,4-dinitrophenylhydrazine
(b) $CH_3C\equiv CH$	(q) gives precipitate with $AgNO_3$
(c) CN^-	(r) is a nucleophile
(d) I^-	(s) is involved in cyanohydrin formation

[2007]

7. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II.**

Column I	**Column II**
(a) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	(p) sodium fusion extract of the compound gives prussian blue colour with $FeSO_4$
(b) 	(q) gives positive $FeCl_3$ test
(c) 	(r) gives white precipitate with $AgNO_3$
(d) 	(s) reacts with aldehydes to form the corresponding hydrazone derivative

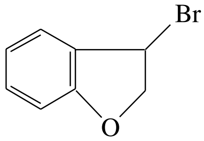
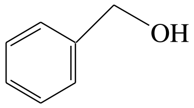
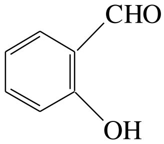
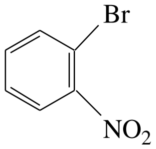
[2008]

8. Match each of the compounds in **Column I** with its characteristic reaction(s) in **Column II**.

Column I	**Column II**
(a) $CH_3CH_2CH_2CN$	(p) Reduction with Pd-C/H_2
(b) $CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2$/HCl
(c) $CH_3-CH=CH-CH_2OH$	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(d) $CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutyl aluminium hydride (DIBAL-H)
	(t) Alkaline hydrolysis

(2009)

9. Match each of the compounds given in **Column I** with the reaction(s) that they can undergo given in **Column II**

Column I	**Column II**
(a) 	(p) Nucleophilic substitution
(b) 	(q) Elimination
(c) 	(r) Nucleophilic addition
(d) 	(s) Esterification with acetic anhydride
	(t) Dehydrogenation

[2009]

Straight Objective Type

1. (b)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (b)
8. (d)	**9.** (a)	**10.** (d)	**11.** (a)	**12.** (c)	**13.** (b)	**14.** (b)
15. (a)	**16.** (b)	**17.** (d)	**18.** (a)	**19.** (b)	**20.** (b)	**21.** (a)
22. (d)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (b)	**27.** (c)	**28.** (b)
29. (a)	**30.** (b)	**31.** (c)	**32.** (d)	**33.** (a)	**34.** (c)	**35.** (d)
36. (b)	**37.** (d)	**38.** (a)	**39.** (a)			

Linked Comprehension Type

1. **(i)** (d)	**(ii)** (a)	**(iii)** (c)
2. **(i)** (b)	**(ii)** (a)	**(iii)** (d)
3. **(i)** (a)	**(ii)** (b)	**(iii)** (c)

Matrix Matching Type

1. (a) – (s);	(b) – (t);	(c) – (q);	(d) – (p);	(e) – (r)
2. (a) – (u); (f) – (p)	(b) – (s);	(c) – (q);	(d) – (r);	(e) – (t);
3. (a) – (q);	(b) – (r);	(c) – (s);	(d) – (p)	
4. (a) – (r);	(b) – (p);	(c) – (s);	(d) – (q)	
5. Friedel-Crafts;	Lewis acid;	anhydrous $AlCl_3$		
Fermentation;	yeast;	ethanol		
Dehydrohalogenation;	alcoholic alkali;	alkenes		
Sandmeyer;	cuprous chloride;	chlorobenzene		
Saponification;	oil;	soap		
6. (a) – (p), (q), (s);	(b) – (q);	(c) – (q), (r), (s);	(d) – (q)	
7. (a) – (r), (s);	(b) – (p), (q);	(c) – (p), (q), (r);	(d) – (p), (s)	
8. (a) – (p), (q), (t);	(b) – (s), (t);	(c) – (p);	(d) – (r)	
9. (a) – (p), (q), (t);	(b) – (p), (s);	(c) – (r), (s);	(d) – (p)	

Hints and Solutions

Straight Objective Type

1. Amount of H_2SO_4 neutralized = $(25 \times 10^{-3}\text{ L})(0.05\text{ M}) = 1.25 \times 10^{-3}$ mol

The neutralization reaction is $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$.

Amount of NH_3 evolved $= 2 \times 1.25 \times 10^{-3}\text{ mol} = 2.5 \times 10^{-3}$ mol

Mass of N in the compound = $(2.5 \times 10^{-3}\text{ mol})(14\text{ g mol}^{-1}) = 0.035$ g

Per cent of N in the compound = $\dfrac{0.035}{0.3} \times 100 = 11.67$

Per cent of O in the compound = $100 - (69.4 + 5.8 + 11.67) = 13.13$

Ratio of atoms in the compound is

$$C : H : N : O :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.67}{14} : \frac{13.13}{16} :: 5.78 : 5.8 : 0.83 : 0.82 :: 7 : 7 : 1 : 1$$

Hence, empirical formula: C_7H_7NO

Alternatively, calculate per cent of C in the given choices which comes out to be (a) 0.55, (b) 0.69, (c) 0.58 and (d) 0.65 only for choice (b), the answer tallies.

2. Empirical formula contains

$$C : H : N : O :: \frac{49.32}{12} : \frac{9.59}{1} : \frac{19.18}{14} : \frac{21.91}{16} : : 4.1 : 9.59 : 1.37 : 1.37 :: 3 : 7 : 1 : 1$$

The given reaction are

$$RCONH_2 \xrightarrow{\text{NaoH}} RCOOH \xrightarrow{\text{Ag}} RCOOAg.$$

Hence $\dfrac{108}{M_{\mathrm{R}} + 44 + 108} = 0.5967.$ This gives $M = 29$ i.e. $\mathrm{R} \equiv \mathrm{C_2H_5}$.

Hence, the compound is $\mathrm{C_2H_5CONH_2}$.

3. Empirical formula contains $\mathrm{C : H} :: \dfrac{88.89}{12} : \dfrac{11.1}{1} :: 7.4 : 11.11 :: 2 : 3$

Only the compound $\mathrm{C_6H_{11}C{\equiv}CH}$ has composition 4 times the composition of empirical formula.

4. The compound $\mathrm{NH_2OH}$ does not contain carbon. Hence, this compound does not show the test of N.

16. Per cent of chlorine $= \left(\dfrac{M_{\mathrm{Cl}}}{M_{\mathrm{AgCl}}}\right)(m_{\mathrm{AgCl}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{35.5}{143.5}\right)(0.287)\left(\dfrac{100}{0.189}\right) = 37.57$

17. $\mathrm{C : H} :: \dfrac{90}{12} : \dfrac{10}{1} :: 7.5 : 10 :: 3.4$ Empirical formula $\mathrm{C_3H_4}$

18. Per cent of nitrogen $= \left(\dfrac{V_{\mathrm{N_2}}}{22400\,\mathrm{cm^3\ mol^{-1}}}\right)(M_{\mathrm{N_2}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{22.4}{22400}\right)(28)\left(\dfrac{100}{0.246}\right) = 11.38$

19. $\mathrm{C : H : N : O} :: \dfrac{58.53}{12} : \dfrac{4.08}{1} : \dfrac{11.38}{14} : \dfrac{26.01}{16} :: 4.88 : 4.08 : 0.81 : 1.63 :: 6 : 5 : 1 : 2.$

Empirical formula $= \mathrm{C_6H_5NO_2}$

21. Initial amount of $\mathrm{H^+} = VM = (0.06025\ \mathrm{dm^3})\ (0.1\ \mathrm{mol\ dm^{-3}}) = 0.006025$ mol

Remaining amount of $\mathrm{H^+} = (0.01625\ \mathrm{dm^3})\ (0.1\ \mathrm{mol\ dm^{-3}}) = 0.00125$ mol

Amount of $\mathrm{H^+}$ reacted $= (0.006025 - 0.001625)$ mol $= 0.0044$ mol

Mass of $\mathrm{NH_3}$ produced = (Amount of $\mathrm{H^+}$) $(M_{\mathrm{NH_3}}) = (0.0044\ \mathrm{mol})\ (17\ \mathrm{g\ mol^{-1}}) = 0.0748$ g

Per cent of nitrogen $= \left(\dfrac{M_{\mathrm{N}}}{M_{\mathrm{NH_3}}}\right)(m_{\mathrm{NH_3}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{14}{17}\right)(0.0748)\left(\dfrac{100}{0.156}\right) = 39.5$

22. $n = \dfrac{pV}{RT} = \dfrac{(1\,\mathrm{atm})(30.5 \times 10^{-3}\,\mathrm{L})}{(0.0825\,\mathrm{L\ atm\ K^{-1}mol^{-1}})(305\,\mathrm{K})} = 0.00121$ mol; $M = \dfrac{m}{n} = \dfrac{0.146\,g}{0.00121\,\mathrm{mol}} = 120.7\ \mathrm{g\ mol^{-1}}$

23. Per cent of sulphur $= \left(\dfrac{M_{\mathrm{S}}}{M_{\mathrm{BaSO_4}}}\right)(m_{\mathrm{BaSO_4}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{32}{233}\right)(0.9336)\left(\dfrac{100}{0.244}\right) = 52.5$

24. Per cent of C $= \left(\dfrac{M_{\mathrm{C}}}{M_{\mathrm{CO_2}}}\right)(m_{\mathrm{CO_2}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{12}{44}\right)(1.1)\left(\dfrac{100}{0.45}\right) = 66.67$

Per cent of H $= \left(\dfrac{2M_{\mathrm{H}}}{M_{\mathrm{H_2O}}}\right)(m_{\mathrm{H_2O}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{2}{18}\right)(0.3)\left(\dfrac{100}{0.45}\right) = 7.4$

$\mathrm{C : H : N} :: \dfrac{66.67}{12} : \dfrac{7.4}{1} : \dfrac{25.93}{14} = 5.56 : 7.4 : 1.85 = 3 : 4 : 1$; Empirical formula $= \mathrm{C_3H_4N}$

25. Per cent of C $= \left(\dfrac{M_{\mathrm{C}}}{M_{\mathrm{CO_2}}}\right)(m_{\mathrm{CO_2}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{12}{44}\right)(0.2545)\left(\dfrac{100}{0.1}\right) = 69.4$

Per cent of H $= \left(\dfrac{2M_{\mathrm{H}}}{M_{\mathrm{H_2O}}}\right)(m_{\mathrm{H_2O}})\left(\dfrac{100}{m_{\text{compound}}}\right) = \left(\dfrac{2}{18}\right)(0.4428)\left(\dfrac{100}{0.1}\right) = 4.9$

$\mathrm{C : H : O} :: \dfrac{69.4}{12} : \dfrac{4.9}{1} : \dfrac{25.7}{16} :: 5.78 : 4.9 : 1.61 :: 3.6 : 3 : 1 :: 7 : 6 : 2$

Empirical formula $= \mathrm{C_7H_6O_2}$; Empirical molar mass $= 122\ \mathrm{g\ mol^{-1}}$

Amount of acid $= VM = (10 \times 10^{-3}\ \mathrm{dm^3})\ (0.1\ \mathrm{mol\ dm^{-3}}) = 10^{-3}$ mol

Molar mass of compound $= \dfrac{m}{n} = \dfrac{0.122\,\mathrm{g}}{10^{-3}\,\mathrm{mol}} = 122\ \mathrm{g\ mol^{-1}}$; Molecular formula $= \mathrm{C_7H_6O_2}$.

ANNEXURE

(I) INCREASING/DECREASING CHARACTERISTICS

1. Increasing reactivity of halogens towards alkanes.

2. Increasing enthalpy of reaction.

$F^{\bullet} + CH_4 \rightarrow HF + CH_3^{\bullet}$ ΔH_1 $Br^{\bullet} + CH_4 \rightarrow HBr + CH_3^{\bullet}$ ΔH_3

$Cl^{\bullet} + CH_4 \rightarrow HCl + CH_3^{\bullet}$ ΔH_2 $I^{\bullet} + CH_4 \rightarrow HI + CH_3^{\bullet}$ ΔH_4

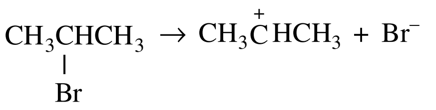
3. Increasing stability of free radicals: $^{\bullet}CH_3$, 1°, 2°, 3°, allyl, vinyl

4. Increasing stability of carbocation: CH_3^+, 1°, 2°, 3°

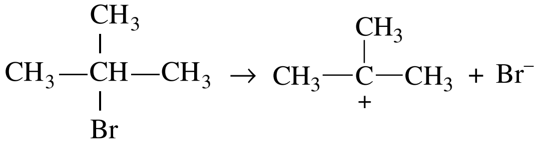
5. Increasing enthalpy of reaction:

$CH_3Br \rightarrow CH_3^+ + Br^-$ ΔH_1

$CH_3CH_2Br \rightarrow CH_3CH_2^+ + Br^-$ ΔH_2



$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} \rightarrow CH_3\overset{+}{C}HCH_3 + Br^-$$ ΔH_3



$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{CH}}—CH_3 \rightarrow CH_3—\overset{\displaystyle CH_3}{\underset{+}{C}}—CH_3 + Br^-$$ ΔH_4

6. Increasing order of reactivity towards S_N2 displacement:
1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

7. Decreasing order of reactivity towards S_N2 displacement:
n-Butyl bromide, isobutyl bromide, *sec*-butyl bromide, *tert*-butyl bromide

8. Increasing order of reactivity towards S_N1 displacement:
1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

9. Increasing reactivity sequence of S_N1 displacement of halogen: CH_3X, 1° X, 2° X, 3° X,

10. Inceasing reactivity sequence of S_N2 displacement of halogen: CH_3X, 1° X, 2° X, 3° X.

11. Increasing reactivity of alcohols towards gaseous HBr:
2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol

12. Increasing order or reactivity towards E2 dehydrohalogenation of the bromides:
ethyl bromide, *n*-proyl bromide, isobutyl bromide, neopentyl bromide

13. Increasing stability of alkenes: $R_2C{=}CR_2$, $R_2C{=}CHR$, $R_2C{=}CH_2$, $RCH{=}CH_2$, $CH_2{=}CH_2$

14. Increasing dehydration of alcohol in the presence of H_2SO_4:
ethyl alcohol, isopropyl alcohol, *tert*-butyl alcohol

15. Decreasing order of reactivity towards E2 dehydrohalogenation:
2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane

16. Increasing order of dehydrohalogenation
1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane

17. Decreasing reactivity towards S_N1 substitution: 1-chloropropene 3-chloropropene, *n*-propylchloride

18. Decreasing acidity: H_2O, $HC{\equiv}CH$, NH_3, RH, ROH

19. Decreasing basicity: R^-, $HC{\equiv}C^-$, NH_2^-, OH^-, OR^-

20. Decreasing order of reactivity towards the addition of HCl:
styrene, *p*-chlorostyrene, *p*-methylstyrene, *p*-nitrostyrene

21. Decreasing order of reactivity towards dehydration:
α-phenyl ethyl alcohol, α-(*p*-nitrophenyl) ethyl alcohol, α-(*p*-aminophenyl) ethyl alcohol

22. Increasing reactivity towards S_N1 solvolysis:
benzyl chloride, *p*-chlorobenzyl chloride, *p*-methoxybenzyl chloride, *p*-methylbenzyl chloride, *p*-nitrobenzyl chloride

23. Increasing order of reactivity towards elimination by alcoholic KOH:
1-phenyl-2-bromopropane, 1-phenyl-3-bromopropane

24. Decreasing order of reactivity towards aqueous HBr: Isomeric pentyl alcohols

25. Increasing order of reactivity towards aqueous HBr:
1-phenyl-1-propanol, 3-phenyl-1-propanol, 1-phenyl-2-propanol

26. Decreasing order of reactivity towards aqueous HBr:
benzyl alcohol, *p*-cyanobenzyl alcohol, *p*-hydroxybenzyl alcohol

27. Increasing order of reactivity towards aqueous HBr:
benzyl alcohol, diphenylmethanol, methanol and triphenylmethanol

28. Decreasing order of reactivity towards bromination:
anisole, benzene, toluene, chlorobenzene, nitrobenzene, phenol

29. Increasing order of reactivity towards bromination:
hydroquinone, *p*-methoxyphenol, *p*-methylphenol, *p*-chlorophenol, *p*-nitrophenol, *sym*-trihydroxybenzene

30. Decreasing order of acidity of carboxylic acids:
butanoic acid, 2-bromobutanoic acid, 3-bromobutanoic acid, 4-bromobutanoic acid

31. Decreasing order of acidity of substituted benzoic acids:
p-chlorobenzoic acid, 2, 4-dichlorobenzoic acid, 2,4,6-trichlorobenzoic acid.

32. Decreasing order of acidity of carboxylic acids:
α-chlorophenylacetic acid, *p*-chlorophenylacetic acid, phenylacetic acid, α-phenylpropionic acid

33. Decreasing order of acidity of carboxylic acids:
p-nitrobenzoic acid, *p*-nitrophenylacetic acid, β-(*p*-nitrophenyl) propionic acid

34. Increasing order of basicity : ammonia, aniline, cyclohexylamine

35. Decreasing order of basicity: ethylamine, 2-aminoethanol, 3-amino-1-propanol

36. Decreasing order of basicity : aniline, *p*-methoxyaniline, *p*-nitroaniline

37. Increasing order of acidity: benzene sulphonic acid, benzoic acid, benzyl alcohol, phenol

38. Decreasing order of acidity: *m*-bromophenol, *m*-cresol, *m*-nitrophenol, phenol

39. Decreasing order of acidity of substituted phenol:
p-chlorophenol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol

40. Decreasing order of reactivity towards KCN: benzyl chloride, chlorobenzene, ethyl chloride

41. Increasing order of nitration: benzene, chlorobenzene, nitrobenzene, toluene

42. Increasing order of reactivity towards alcoholic silver nitrate:
1-bromo-1-butene, 3-bromo-1-butene, 4-bromo-1-butene

43. Decreasing order of reactivity towards alcoholic silver nitrate:
2-bromo-1-phenylethene, α-phenylethyl bromide, β-phenylethyl bromide

44. Increasing order of reactivity towards aqueous NaOH:
chlorobenzene, *m*-chloronitrobenzene, *o*-chloronitrobenzene, 2,4-dinitrochlorobenzene, 2,4,6-trinitrochlorobenzene

45. Increasing reactivity towards HCN: CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$ [1985]

46. Increasing basicity: *p*-toluidine, *N*, *N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline. [1986]

47. Increasing ease of hydrolysis: $CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$, CH_3CONH_2 [1986]

48. Increasing order of acid strength: [1990]
$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

49. Increasing reactivity in nucleophilic substitution reactions: CH_3F, CH_3I, CH_3Br, CH_3Cl [1992]

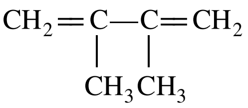
50. Increasing order of expected enol content: CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$ [1992]

51. Decreasing inductive effect: F, NO_2, CH_3, Cl, C_2H_5, OCH_3, $(CH_3)_2CH$, $(CH_3)_3C$, C_6H_5

52. Increasing reactivity of the carbonyl group: HCHO, CH_3COCH_3, CH_3CHO, $CH_3COC_2H_5$, $C_2H_5COC_2H_5$

53. Increasing reactivity towards HX: $CH_2{=}CH_2$, $(CH_3)_2C{=}CH_2$, $CH_3CH{=}CHCH_3$

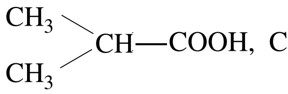
54. Increasing reactivity towards HBr:

$CH_2{=}CHC_2H_5$, $CH_3CH{=}CHCH_3$, $CH_2{=}CHCH{=}CH_2$, $CH_3CH{=}CHCH{=}CH_2$, 
$CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$

55. Increasing order of *m*-orientation: $C_6H_5CH_3$, $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$, $C_6H_5CCl_3$

56. Increasing order of acidity: CH_3OH, *n*-butanol, *sec*-butanol, *tert*-butanol

57. Increasing order of acidity:

CH_3CH_2COOH, 
$(CH_3)_2CH{-}COOH$, CH_3COOH, HCOOH C_6H_5COOH, $ClCH_2COOH$

58. Decreasing order of acidity: CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH

59. Decreasing order of acidity: FCH_2COOH, $ClCH_2COOH$, $BrCH_2COOH$, ICH_2COOH

60. Increasing order of acidity: CH_3COOH, $ClCH_2COOH$, $ClCH_2CH_2COOH$

61. Increasing order of acidity: benzoic acid, *p*-bromobenzoic acid, *p*-chlorobenzoic acid, *p*-nitrobenzoic acid, *p*-toluic acid, *p*-hydroxybenzoic acid

62. Increasing order of acidity: HCl, HCOOH, C_6H_5COOH, C_2H_5OH, H_2O

63. Increasing order of acidity: H_2CO_3, phenol, *p*-nitrophenol, benzoic acid.

64. Increasing order of basicity: NH_3, CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5NHCH_3$ [1988]

65. Increasing order of basicity: CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

66. Increasing reactivity towards Lucas reagent: 1-butanol, 2-butanol, 2-methyl-2-propanol

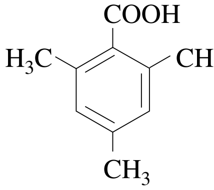
67. Increasing reactivity towards sodium: 1-butanol, 2-butanol, 2-methyl-2-propanol

68. Increasing boiling point: *n*-pentane, isopentane, neopentane

69. Increasing solubility in water: *n*-butanol, isobutyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol

70. Increasing ease in esterification: HCOOH, CH_3COOH, CH_3CH_2COOH, $(CH_3)_2CHCOOH$, $(CH_3)_3CCOOH$

71. Increasing order of esterification: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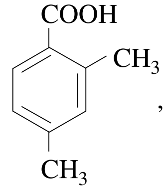
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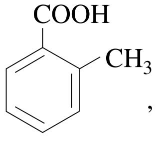
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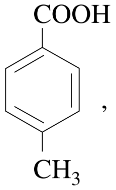
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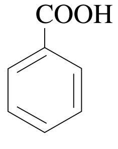
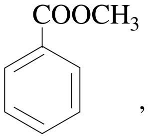


72. Increasing alkaline hydrolysis: $HCOOCH_3$, CH_3COOCH_3, $(CH_3)_2CHCOOCH_3$, $(CH_3)_3CCOOCH_3$

73. Increasing alkaline hydrolysis: CH_3COOCH_3, $CH_3COOC_2H_5$, $CH_3COOCH(CH_3)_2$, $CH_3COOC(CH_3)_3$

74. Increasing alkaline hydrolysis: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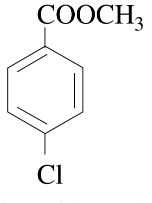
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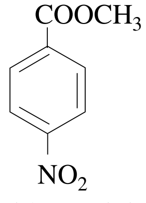
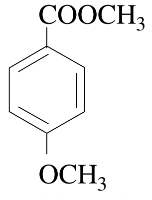

,


75. Increasing acidity: oxalic acid, malonic acid, succinic acid, adipic acid

76. Increasing order of boiling point: *n*-butane, *n*-butanol, *n*-butyl chloride, isobutane [1998]

77. Increasing order of reactivity towards sulphonation with fuming sulphuric acid:
benzene, toluene, methoxybenzene, chlorobenzene [1998]

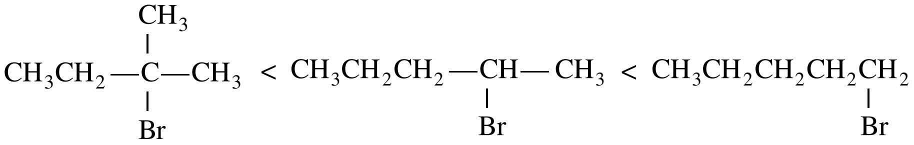
ANSWERS

1. $Br_2 < Cl_2 < F_2$ **2.** $\Delta H_1 < \Delta H_2 < \Delta H_3 < \Delta H_4$

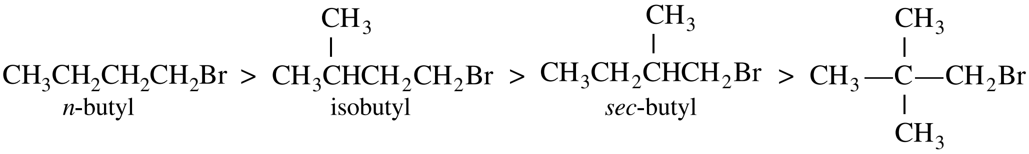
3. Vinyl $< CH_3 < 1^\circ < 2^\circ < 3^\circ <$ allyl

4. $H_3C^+ < 1^{\circ +} < 2^{\circ +} < 3^{\circ +}$. The dispersal of charge stabilizes the carbocation. The greater the number of alkyl groups, the more stable the carbocation.

5. $\Delta H_4 < \Delta H_3 < \Delta H_2 < \Delta H_1$. The more stable the carbocation being formed, lesser the enthalpy of reaction.

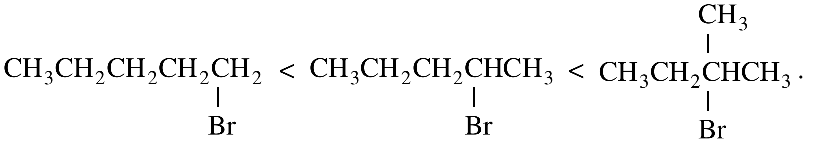
6. 
$CH_3CH_2-\underset{Br}{\overset{CH_3}{C}}-CH_3 < CH_3CH_2CH_2-\underset{Br}{CH}-CH_3 < CH_3CH_2CH_2CH_2\underset{Br}{CH_2}$

The usual S_N2 order is $3^\circ < 2^\circ < 1^\circ$.

7. 
$CH_3CH_2CH_2CH_2Br > CH_3\overset{CH_3}{CH}CH_2CH_2Br > CH_3CH_2\overset{CH_3}{CH}CH_2Br > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br$

n-butyl isobutyl *sec*-butyl *tert*-butyl

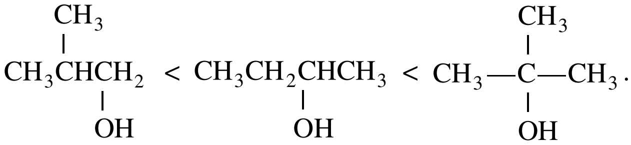
S_N2 is slow for large G in G–CH_2X.

8. 
$CH_3CH_2CH_2CH_2\underset{Br}{CH_2} < CH_3CH_2CH_2\underset{Br}{CH}CH_3 < CH_3CH_2\underset{Br}{\overset{CH_3}{C}}HCH_3$.

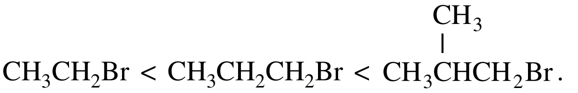
In S_N1, polar factors are controlling factors. The more stable the cation being formed in the first step of ionization, the faster the reaction. The stability of carbocations is $1^\circ < 2^\circ < 3^\circ$.

9. $CH_3X < 1^\circ < 2^\circ < 3^\circ$ Stability of carbocation governs the reactivity.

10. $3^\circ < 2^\circ < 1^\circ < CH_3X$. Steric factor governs the reactivity.

11. 
$CH_3\overset{CH_3}{CH}\underset{OH}{CH_2} < CH_3CH_2\underset{OH}{CH}CH_3 < CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$.

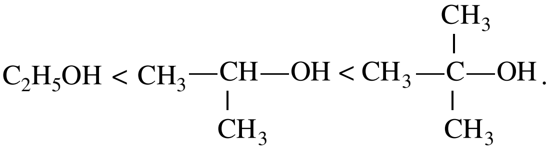
The order of reactivity is $3^\circ > 2^\circ > 1^\circ > CH_3OH$. Electronic factors are important except for 1° alcohols for which steric factors are controlling. Electronic factors are the stability of carbocations.

12. 
$CH_3CH_2Br < CH_3CH_2CH_2Br < CH_3\overset{CH_3}{CH}CH_2Br$.

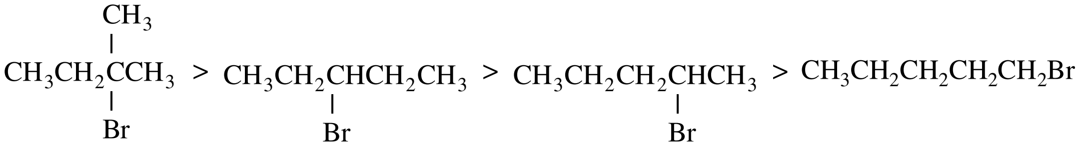
Reactivity in E2 dehydrohalogenation depends mainly on the stability of the alkenes being formed which is governed by Saytzeff's rule.

Neopentyl bromide does not undergo dehydrohalogenation as carbon bearing bromine does not contain hydrogen.

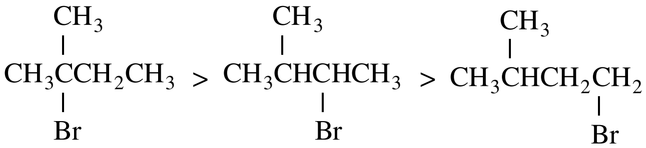
13. $CH_2{=}CH_2 < RCH{=}CH_2 < R_2C{=}CH_2 < R_2C{=}CHR < R_2C{=}CR_2$. The alkene with larger number of alkyl group (i.e. the more substituted alkene) attached to carbon-carbon double bond is more stable.

14. 
$C_2H_5OH < CH_3-\underset{CH_3}{CH}-OH < CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$.

The dehydration proceeds via the formation of carbocation. Hence, the greater the stability of carbocation being formed from alcohol, more easily the latter dehydrated.

15. 
$CH_3CH_2\underset{Br}{\overset{CH_3}{C}}CH_3 > CH_3CH_2\underset{Br}{CH}CH_2CH_3 > CH_3CH_2CH_2\underset{Br}{CH}CH_3 > CH_3CH_2CH_2CH_2CH_2Br$

The stability of alkenes being formed decides the rate of dehydrohalogenation.

16. 

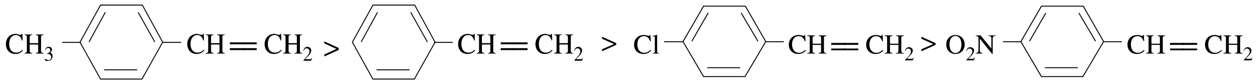
$$CH_3\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3 > CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{Br}{|}}{C}HCH_3 > CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{Br}{|}}{CH_2}$$

The E2 dehydrohalogenation of isomers follows the reactivity order 3° > 2° > 1°.

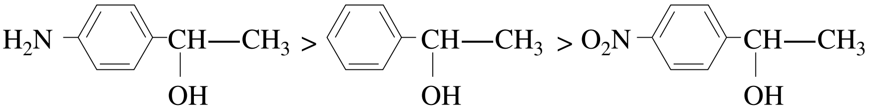
17. $ClCH_2CH{=}CH_2 > CH_3CH_2CH_2Cl > CH_3CH{=}CHCl$. The reactivity is S_N1 substitution depends on the stability of carbocation being formed. In the present case, we will have allylic cation > 1° cation > vinylic cation

18. $H_2O > ROH > HC{\equiv}CH > NH_3 > RH$

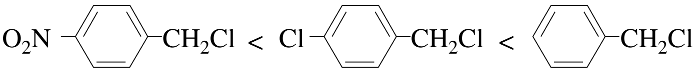
19. $R^- > NH_2^- > HC^-{\equiv}C > OR^- > OH^-$. Strong acid produces weak conjugate base and vice versa. The relative order of acids is $H_2O > ROH > HC{\equiv}CH > NH_3 > RH$. Hence, the conjugate bases follow the reverse order.

20. 

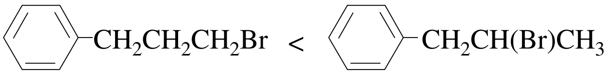
The reactivity of addition across a carbon-carbon double bond mainly depends upon the stability of carbocation. Electron-releasing group causes more electron density on carbon-carbon double bond thereby increases the reactivity. Electron-withdrawing group withdraws electron density causing decrease in the reactivity.

21. 

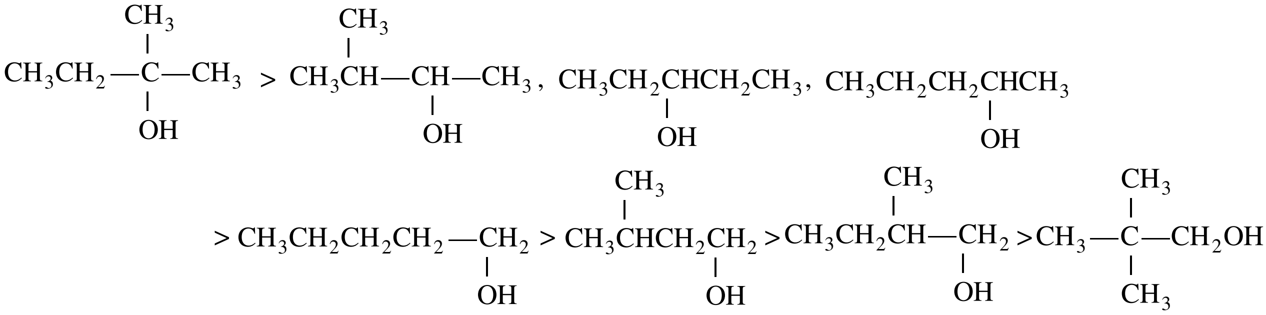
. Same principle as give in Q. 20.

22. 

Solvolysis means replacement of Cl by solvent anion. In S_N1 mechanism, a carbocation is formed as the intermediate. The stability of carbocation decides the reactivity. Electron-releasing group increases stability (and hence reactivity) while electron-withdrawing group decreases the stability (and hence reactivity).

23. 

The more stable conjugated alkene is formed faster than the alkene containing isolated double bond.

24. 

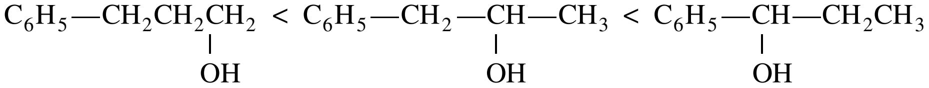
$$CH_3CH_2{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 > CH_3CH{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}H}{-}CH_3,\ CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3,\ CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3$$

$$> CH_3CH_2CH_2CH_2{-}\underset{\underset{OH}{|}}{CH_2} > CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{OH}{|}}{CH_2} > CH_3CH_2\overset{\overset{CH_3}{|}}{C}H{-}\underset{\underset{OH}{|}}{CH_2} > CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2OH$$

In general, the reactivity of an alcohol toward aqueous HBr follows the order.

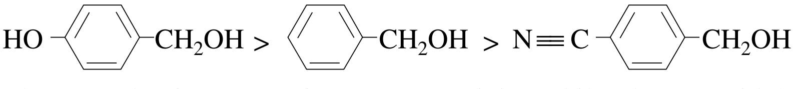
allylic, benzylic > 3° > 2° > 1° < CH_3OH.

For primary alcohols, steric factors dominate the substitution reaction. The substituted primary alcohol has lesser reactivity. For alcohols, other than primary, electronic factors are dominating.

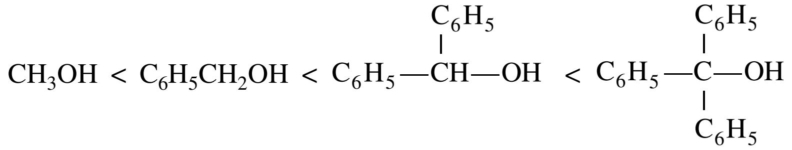
25. 

$$C_6H_5{-}CH_2CH_2\underset{\underset{OH}{|}}{CH_2} < C_6H_5{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 < C_6H_5{-}\underset{\underset{OH}{|}}{CH}{-}CH_2CH_3$$

The reactivity follows the order 1° < 2° < benzylic alcohol

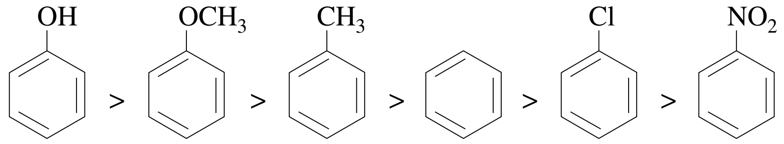
26. 

Electron-releasing group increases reactivity while electron-withdrawing group decreases reactivity

27. 

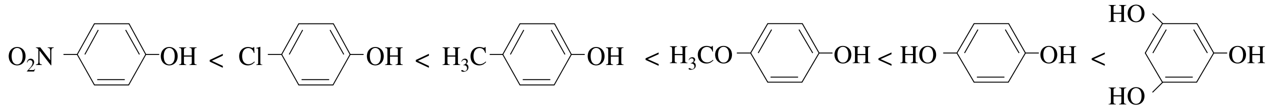
$$CH_3OH < C_6H_5CH_2OH < C_6H_5—\overset{\overset{C_6H_5}{|}}{C}H—OH < C_6H_5—\overset{\overset{C_6H_5}{|}}{\underset{\underset{C_6H_5}{|}}{C}}—OH$$

The reactivity follows the order. CH_3OH < 1° benzylic < 2° benzylic < 3° benzylic alcohol.

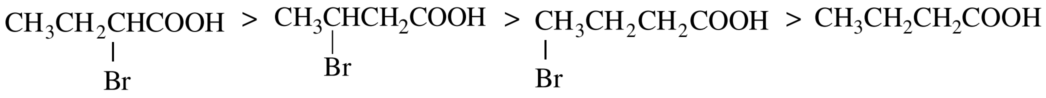
28. 

The decreasing order of activating effect of substituent is

$$—OH > —OCH_3 > —CH_3 > —H > \underbrace{—Cl > —NO_2}_{\text{deactivator}}.$$

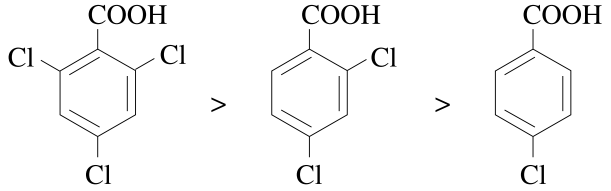
29. 

Ring activator increases the rate of bromination while ring deactivator decreases the rate of bromination.

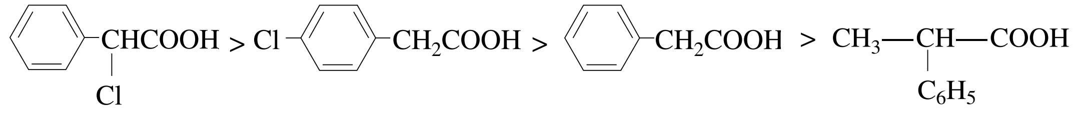
30. 

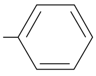
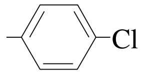
$$CH_3CH_2\underset{\underset{Br}{|}}{C}HCOOH > CH_3\underset{\underset{Br}{|}}{C}HCH_2COOH > \underset{\underset{Br}{|}}{C}H_3CH_2CH_2COOH > CH_3CH_2CH_2COOH$$

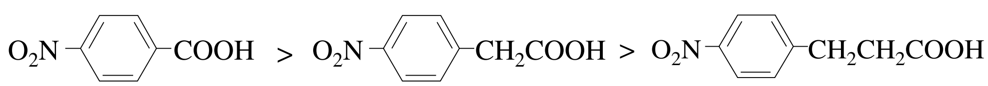
Electron-withdrawing substituent increases acidity. The closer the substituent to —COOH, the greater its effect.

31. 

Chlorine is a deactivator of benzene ring. More chlorine atoms attached to ring, the greater the deactivating effect. The ring deactivator increases the acidity of benzoic acid.

32. 

—Cl,  and  are the electron-withdrawing groups. They increase the acidity of carboxylic acid. α-chlorophenylacetic acid contains two withdrawing groups. The chlorophenyl group is more deactivator than the phenyl group. The weakest acid is phenylacetic acid as it is a little farther away from the —COOH group.

33. 

Nitrophenyl is electron-withdrawing group and it increases the acidity of carboxylic acid. The more near the deactivator to —COOH, the greater the effect.

34. $C_6H_5NH_2 < NH_3 <$ cyclohexylamine. Aliphatic amines are more basic than NH_3 and aromatic amines.

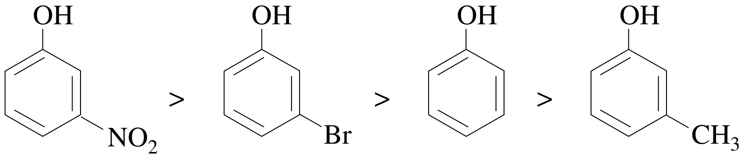
35. $CH_3CH_2NH_2 > HOCH_2CH_2CH_2NH_2 > HOCH_2CH_2NH_2$

Electron-withdrawing group lowers the basicity. The more near the substituent, the greater its effect.

36. $p\text{-}CH_3OC_6H_4NH_2 > C_6H_5NH_2 > p\text{-}O_2NC_6H_4NH_2$.

Electron-releasing group increases the basicity while electron-attracting group decreases the basicity.

37. 

38. 

Electron-releasing group decreases acidity of phenol while electron-withdrawing group increases the acidity.

39. 2, 4, 6-trichloro- > 2, 4-dichloro- > *p*-chlorophenol. Chlorine is ring-deactivator which causes increase in acidity. The larger the number of chlorine in the ring, the greater its effect.

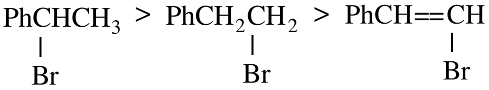
40. benzyl chloride > ethyl chloride > chlorobenzene. The order of reactivity is benzylic > 1° alkyl > aryl

41. $PhNO_2 > PhCl < PhH < PhCH_3$. Ring activator increases the rate while ring deactivator decreases the rate.

42. 

$CH_3CH_2CH{=}\underset{\underset{Br}{|}}{C}H < \underset{\underset{Br}{|}}{C}H_2CH_2CH{=}CH_2 < CH_3\underset{\underset{Br}{|}}{C}HCH{=}CH_2$

The order of reactivity toward generating double bond is allylic > 1° alkyl > vinylic.

43. 

$Ph\underset{\underset{Br}{|}}{C}HCH_3 > PhCH_2\underset{\underset{Br}{|}}{C}H_2 > PhCH{=}\underset{\underset{Br}{|}}{C}H$

The order of reactivity toward generating double bond is benzylic > 1° alkyl > vinylic

44. Chlorobenzene < *m*-nitrochlorobenzene < *o*-chloronitrobenzene < 2, 4- dinitrochlorobenzene < 2, 4, 6- trinitrochlorobenzene.

45. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The nucleophilic addition of HCN across carbonyl group is mainly governed by steric factors. Aldehydes generally undergo nucleophilic addition more readily than ketones because alkyl or aryl group causes more crowding in the transition state. Also, an alkyl group releases electrons causing destabilization of the transition state.

46. *p*-nitroaniline < aniline < *p*-toluidine < *N*, *N*-dimethyl-*p*-toluidine. Electron-releasing group enhances the availability of a pair of electrons on nitrogen while electron-withdrawing group lowers the availability.

47. $CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

48. $(CH_3)_2CHCOOH < CH_3CH_2COOH < ClCH_2CH_2COOH < CH_3COOH < ClCH_2COOH$

49. $CH_3F < CH_3Cl < CH_3Br < CH_3I$

50. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

51. $NO_2 > F > Cl > OCH_3 > C_6H_5 > CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$.

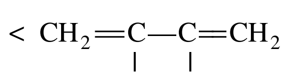
52. $C_2H_5COC_2H_5 < C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The smaller the alkyl group, the more reactive the carboynl group.

53. $CH_2{=}CH_2 < CH_3CH{=}CHCH_3 < (CH_3)_2C{=}CH_2$

The more stable the intermediate carbocation, the greater the reactivity.

54. $CH_2{=}CHC_2H_5 < CH_3CH{=}CHCH_3 < CH_2{=}CH{-}CH{=}CH_2 < CH_3{-}CH{=}CH{-}CH{=}CH_2$



$< CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2$

Conjugated dienes form the more stable allyl carbocations and are thus more reactive than alkenes. Alkyl groups on the unsaturated carbon atoms increase reactivity.

55. $C_6H_5CH_3 < C_6H_5CH_2Cl < C_6H_5CHCl_2 < C_6H_5CCl_3$

56. *tert*-butanol < *sec*-butanol < *n*-butanol < CH_3OH. Alkyl group makes an alcohol less acidic. Bigger the alkyl group, the less acidic the alcohol. Methanol is the strongest and teritary alcohols are the weakest.

57. $(CH_3)_2CHCOOH < C_2H_5COOH < CH_3COOH < C_6H_5COOH < HCOOH < ClCH_2COOH$

58. $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

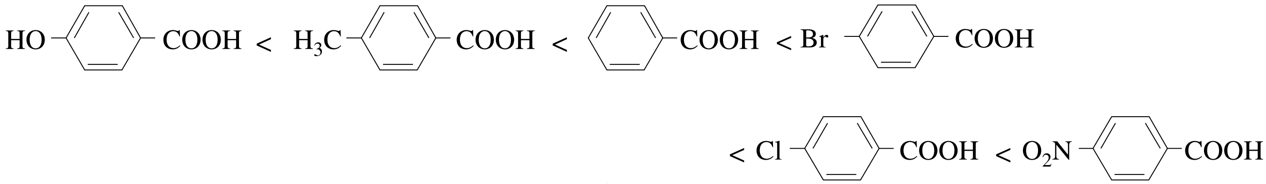
The more the number of electron-withdrawing group, the stronger the acid.

59. $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

The more the electronegativity of halogen, the stronger the acid.

60. $CH_3COOH < ClCH_2CH_2COOH < ClCH_2COOH$

61.



62. $H_2O < C_2H_5OH < C_6H_5COOH < HCOOH < HCl$

63. phenol < *p*-nitrophenol < $H_2CO_3 < C_6H_5COOH$

64. $C_6H_5NH_2 < C_6H_5NHCH_3 < NH_3 < CH_3NH_2 < (CH_3)_2NH$

65. $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$. $(CH_3)_3N$ is the weakest because of steric factors.

66. 1-butanol < 2-butanol < 2-methyl-2-propanol. A tertiary alcohol reacts immediately, a secondary alcohol reacts within five minutes and a primary alcohol does not.

67. 2-methyl-2-propanol < 2-butanol < 1-butanol. Reactivity of ROH is CH_3OH > 1° > 2° > 3°.

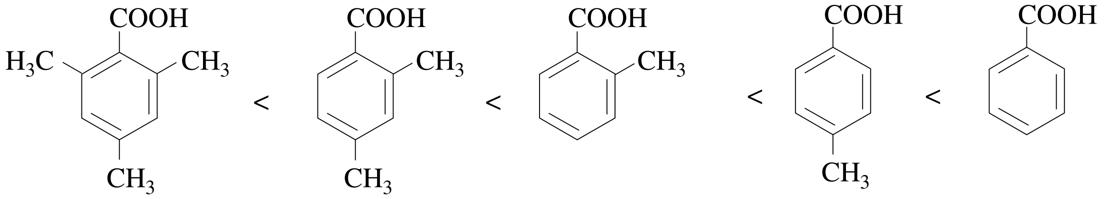
68. neopentane < isopentane < *n*-pentane. A branched chain isomer has a lower boiling point than a straight chain isomer. The more numerous the branches, the lower the boiling point. The branching lowers the boiling point for all families of organic compounds. Branching causes the shape of molecule to approach towards a sphere and thus surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

69. *n*-butyl alcohol < isobutyl alcohol < *sec*-butyl alcohol < *tert*-butyl alcohol. Polarity of O—H bond increases in the same order.

70. $(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH < HCOOH$

The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification as well as de-esterification (hydrolysis).

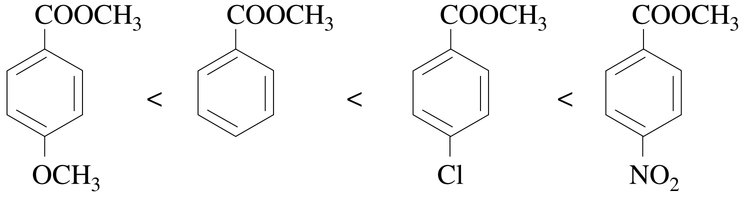
71.



72. $(CH_3)_3CCOOCH_3 < (CH_3)_2CHCOOCH_3 < CH_3COOCH_3 < HCOOCH_3$

73. $CH_3COOC(CH_3)_3 < CH_3COOCH(CH_3)_2 < CH_3COOC_2H_5 < CH_3COOCH_3$

74.



75. adipic acid < succinic acid < malonic acid < oxalic acid
Acidity decreases with increase in the intervening CH_2 groups.

76. isobutane < *n*-butane < *n*-buty1 chloride < *n*-butanol

77. chlorobenzene < benzene < toluene < methoxybenzene

II. ORGANIC CONVERSIONS

Quite often, there is necessity of converting one organic compound into another. This conversion may involve the lengthening or shortening of the carbon chain in a particular homologous series, may involve the conversion of straight chain to branch chain, may involve the conversion of one functional group into another, and so on. In this section, we describe a few methods which are available with us to achieve the desired goal of converting one molecule into another.

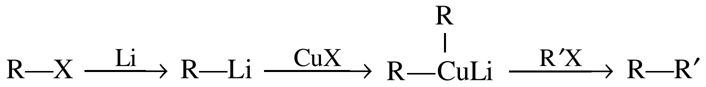
1. To Increase the Number of Carbon Atoms

The following methods may be used.

(a) *Wurtz Synthesis* $RX + 2Na + XR \xrightarrow{ether} R{-}R + 2NaX$

Useful only for the preparation of symmetrical alkanes.

(b) *Corey-House Synthesis*



$$R{-}X \xrightarrow{Li} R{-}Li \xrightarrow{CuX} R{-}\overset{\overset{R}{|}}{Cu}Li \xrightarrow{R'X} R{-}R'$$

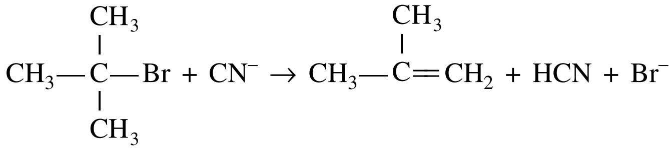
Useful for the preparation of unsymmetrical alkanes.

(c) *Smaller alkyne to bigger alkyne* $RC{\equiv}CH \xrightarrow{LiNH_2} RC{\equiv}C:^- \,Li^+ \xrightarrow{R'X} RC{\equiv}CR' + LiX$

Useful only when R′ is a primary alkyl group. For secondary or tertiary alkyl group, elimination is the predominant reaction.

(d) *Alkyl halide and* KCN $RX + KCN \rightarrow RCN + KX$

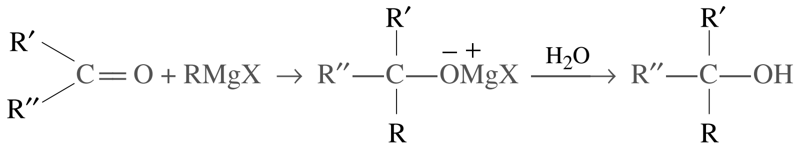
Alkyl nitrile may be hydrolysed to give RCOOH or reduced to RCH_2NH_2. Useful only when R is the primary alkyl group. Tertiary halides undergo elimination reaction.



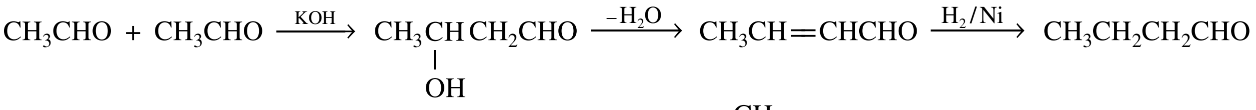
$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}Br + CN^- \rightarrow CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + HCN + Br^-$$

Secondary halide mainly undergoes elimination with a little substitution.

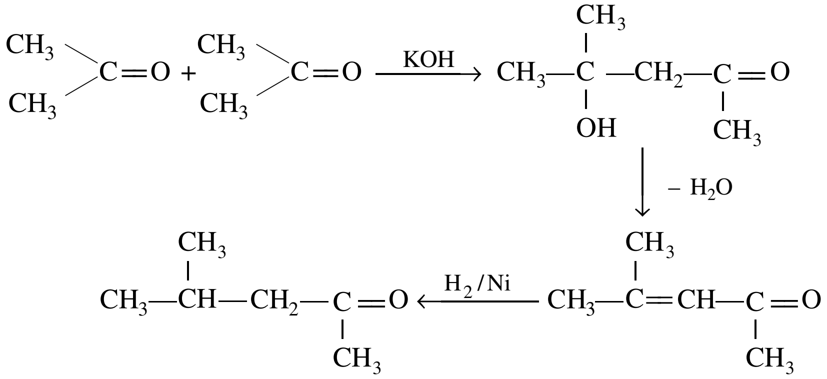
(e) *Use of Grignard reagent*



(f) *Aldol condensation* Lower aldehydes (or ketones) containing α-hydrogen atom may be converted to higher ones with the help of aldol condensation:



$$CH_3CHO + CH_3CHO \xrightarrow{KOH} CH_3\underset{\underset{OH}{|}}{CH}CH_2CHO \xrightarrow{-H_2O} CH_3CH{=}CHCHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2CHO$$



2. To Decrease the Number of Carbon Atoms

(a) *Decarboxylation of sodium salt of fatty acids* $RCOONa \xrightarrow{\text{soda lime}} RH$

(b) *Hofmann degradation of amide* $RCONH_2 \xrightarrow{OBr^-} RNH_2 + CO_3^{2-}$

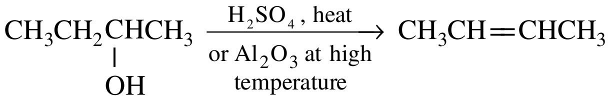
3. Conversion of Functional Groups and Ascending and Descending a Homologoues Series

A few methods to bring about the change in the functional group are as follows.

Alkyl bromide to alkene $CH_3CH_2CHBrCH_3 \xrightarrow{alc.\ KOH} CH_3CH{=}CHCH_3$

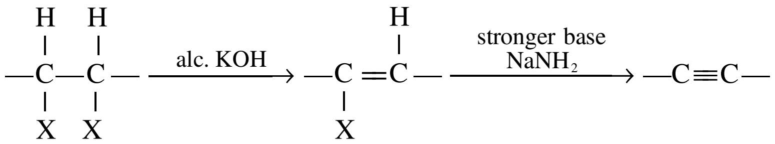
Saytzeff's rule is followed to give predominant isomer.

Alcohol to Alkene



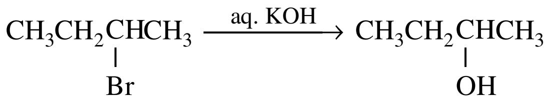
$$CH_3CH_2\underset{\substack{|\\ OH}}{C}HCH_3 \xrightarrow[\text{or } Al_2O_3 \text{ at high temperature}]{H_2SO_4\text{, heat}} CH_3CH{=}CHCH_3$$

Alkyl vicinal dihalide to alkyne



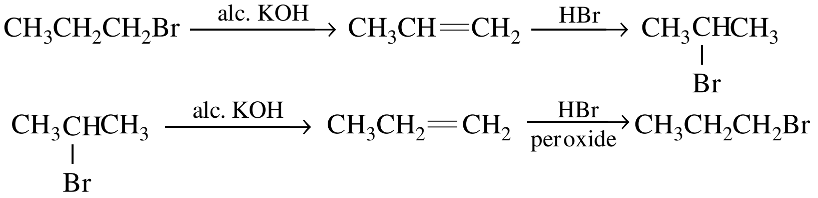
$$-\overset{\substack{H\\|}}{\underset{\substack{|\\X}}{C}}-\overset{\substack{H\\|}}{\underset{\substack{|\\X}}{C}}- \xrightarrow{\text{alc. KOH}} -\underset{\substack{|\\X}}{C}=\overset{\substack{H\\|}}{C}- \xrightarrow[\text{NaNH}_2]{\text{stronger base}} -C\equiv C-$$

Alkyl bromide to alcohol



$$CH_3CH_2\underset{\substack{|\\ Br}}{C}HCH_3 \xrightarrow{\text{aq. KOH}} CH_3CH_2\underset{\substack{|\\ OH}}{C}HCH_3$$

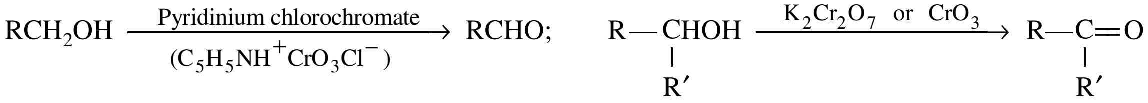
Position isomers of alkyl bromide



$$CH_3CH_2CH_2Br \xrightarrow{\text{alc. KOH}} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\underset{\substack{|\\ Br}}{C}HCH_3$$

$$CH_3\underset{\substack{|\\ Br}}{C}HCH_3 \xrightarrow{\text{alc. KOH}} CH_3CH_2{=}CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br$$

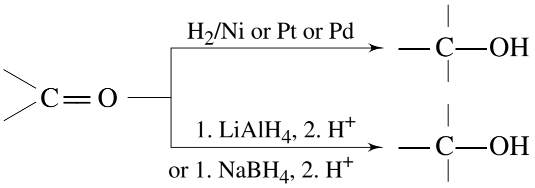
Alcohols to aldehydes and ketones (oxidation)



$$RCH_2OH \xrightarrow[(C_5H_5NH^+CrO_3Cl^-)]{\text{Pyridinium chlorochromate}} RCHO;\quad R-\underset{\substack{|\\ R'}}{C}HOH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3} R-\underset{\substack{|\\ R'}}{C}=O$$

Primary alcohol of carboxylic acid (oxidation) $RCH_2OH \xrightarrow{KMnO_4} RCOOH$

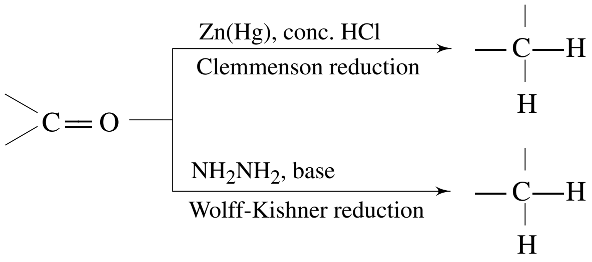
Aldehydes or *ketones to alcohols* (reduction)



$$>C=O \xrightarrow{H_2/\text{Ni or Pt or Pd}} -\overset{|}{\underset{|}{C}}-OH$$

$$>C=O \xrightarrow[\text{or 1. NaBH}_4\text{, 2. H}^+]{\text{1. LiAlH}_4\text{, 2. H}^+} -\overset{|}{\underset{|}{C}}-OH$$

Aldehydes to hydrocarbons

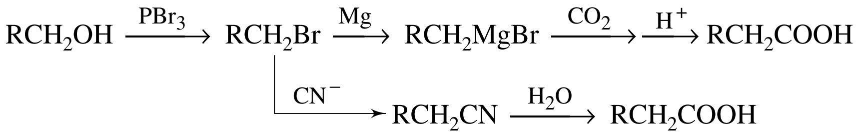


$$>C=O \xrightarrow[\text{Clemmenson reduction}]{\text{Zn(Hg), conc. HCl}} -\overset{|}{\underset{\substack{|\\ H}}{C}}-H$$

$$>C=O \xrightarrow[\text{Wolff-Kishner reduction}]{NH_2NH_2\text{, base}} -\overset{|}{\underset{\substack{|\\ H}}{C}}-H$$

Carboxylic acid to alcohol $RCOOH \xrightarrow{LiAlH_4} RCH_2OH$

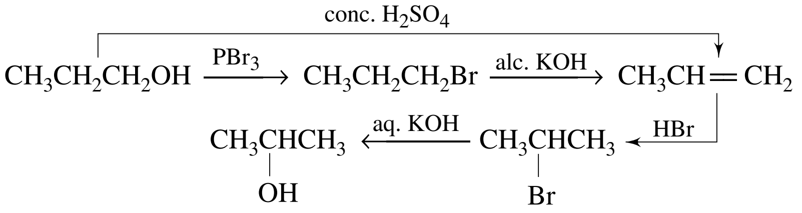
Alcohol to carboxylic acid containing higher carbon number



$$RCH_2OH \xrightarrow{PBr_3} RCH_2Br \xrightarrow{Mg} RCH_2MgBr \xrightarrow{CO_2}\xrightarrow{H^+} RCH_2COOH$$

$$RCH_2Br \xrightarrow{CN^-} RCH_2CN \xrightarrow{H_2O} RCH_2COOH$$

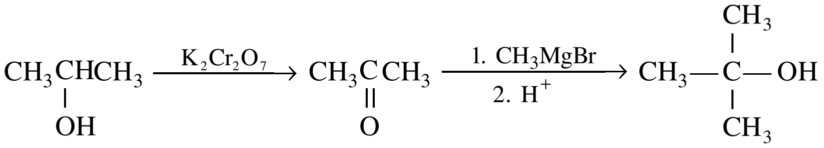
Primary alcohol to secondary alcohol



$$CH_3CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2Br \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \qquad (CH_3CH_2CH_2OH \xrightarrow{conc.\ H_2SO_4} CH_3CH{=}CH_2)$$

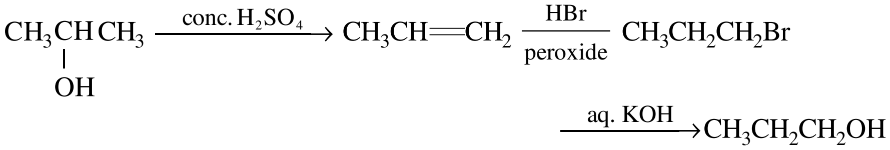
$$CH_3CH{=}CH_2 \xrightarrow{HBr} \underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} \xrightarrow{aq.\ KOH} \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}$$

Secondary alcohol to tertiary alcohol



$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3} \xrightarrow{K_2Cr_2O_7} \underset{\displaystyle O}{CH_3\underset{\|}{C}CH_3} \xrightarrow[2.\ H^+]{1.\ CH_3MgBr} CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$$

Secondary alcohol to primary alcohol



$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3} \xrightarrow{conc.\ H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[peroxide]{HBr} CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH} CH_3CH_2CH_2OH$$

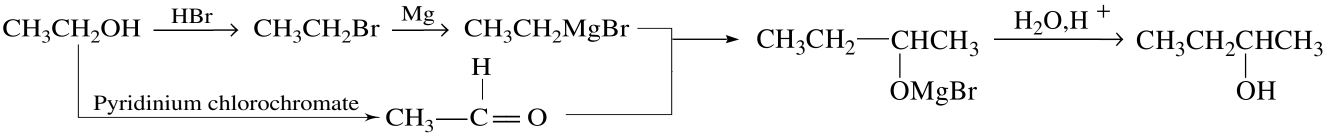
Alcohol to alcohol containing one carbon more

$$CH_3OH \xrightarrow{PBr_3} CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{[H]} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH$$

Alcohol to alcohol containing one carbon less

$$CH_3CH_2OH \xrightarrow[K_2\,Cr_2\,O_7]{[O]} CH_3COOH \xrightarrow{soda\ lime} CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{aq.\ KOH} CH_3OH$$

Simple alcohol to complicated alcohol



$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br \xrightarrow{Mg} CH_3CH_2MgBr$$

$$CH_3CH_2OH \xrightarrow{Pyridinium\ chlorochromate} CH_3—\overset{\displaystyle H}{\overset{|}{C}}{=}O$$

$$CH_3CH_2MgBr + CH_3CHO \longrightarrow \underset{\displaystyle OMgBr}{CH_3CH_2—\underset{|}{C}HCH_3} \xrightarrow{H_2O,H^+} \underset{\displaystyle OH}{CH_3CH_2\underset{|}{C}HCH_3}$$

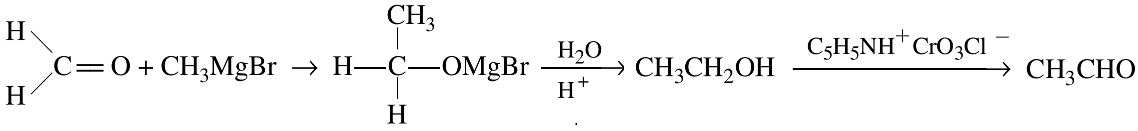
Amine to amine containing one carbon more

$$RCH_2NH_2 \xrightarrow[0\,°C]{HNO_2} RCH_2OH \xrightarrow{PBr_3} RCH_2Br \xrightarrow{NaCN} RCH_2CN \xrightarrow{H_2/Ni} RCH_2CH_2NH_2$$

Amine to amine containing one carbon less

$$RCH_2NH_2 \xrightarrow[0\,°C]{HNO_2} RCH_2OH \xrightarrow[KMnO_4]{[O]} RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{NH_3} RCONH_2 \xrightarrow{OBr^-} RNH_2$$

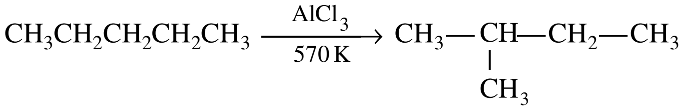
Aldehyde to aldehyde containing one carbon more



$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C{=}O + CH_3MgBr \rightarrow H—\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—OMgBr \xrightarrow[H^+]{H_2O} CH_3CH_2OH \xrightarrow{C_5H_5NH^+CrO_3Cl^-} CH_3CHO$$

4. Isomerization

(a) *Normal to branched chain in alkane* n-Alkane is heated with $AlCl_3$ at 570 K to give branched chain.



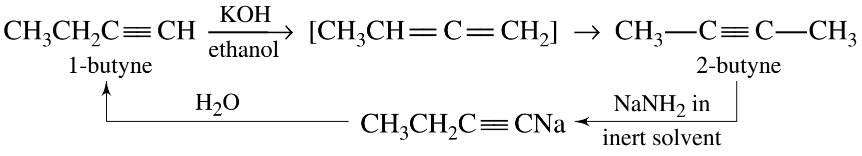
$$CH_3CH_2CH_2CH_2CH_3 \xrightarrow[570\,K]{AlCl_3} CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_2—CH_3$$

(b) *Shift of double bond*

In the presence of catalyst like $Al_2(SO_4)_3$, alkene undergo isomerization at high temperature (770 – 970 K).

$$CH_3CH_2CH_2CH{=}CH_2 \rightarrow CH_3CH_2CH{=}CHCH_3$$

(c) *Shift of triple bond*



$$\underset{1\text{-butyne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[ethanol]{KOH} [CH_3CH{=}C{=}CH_2] \rightarrow \underset{2\text{-butyne}}{CH_3—C{\equiv}C—CH_3}$$

$$CH_3—C{\equiv}C—CH_3 \xrightarrow[inert\ solvent]{NaNH_2\ in} CH_3CH_2C{\equiv}CNa \xrightarrow{H_2O} CH_3CH_2C{\equiv}CH$$

Heating with ethanolic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodamide in an inert solvent shifts the bond towards the end of chain.

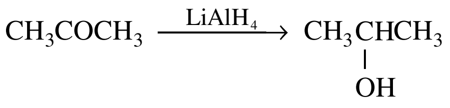
5. Reduction

(a) $CH_3CH{=}CHCHO \xrightarrow{H_2,\,Ni} CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH{=}CHCHO \xrightarrow{\text{9-BBN}} \xrightarrow{HOCH_2CH_2NH_2} CH_3CH{=}CHCH_2OH$; 9-BBN is 9-Borabicyclo[3.3.1]nonane.

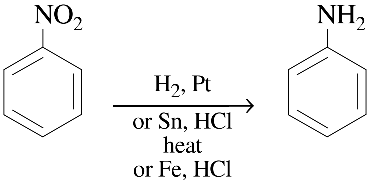
(c) $CH_3CH_2CHO \xrightarrow[\text{Clemmensen reduction}]{\text{Zn + Conc. HCl}} CH_3CH_2CH_3$

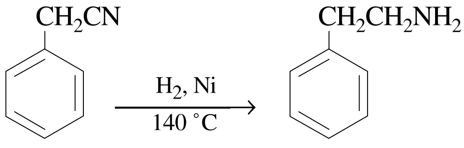
$CH_3CH_2CHO \xrightarrow[\text{Wolff-Kishner reduction}]{NH_2NH_2 + KOH} CH_3CH_2CH_3$

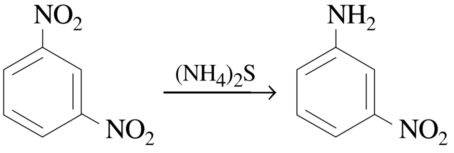
(d) 

$CH_3COCH_3 \xrightarrow{LiAlH_4} CH_3\underset{OH}{\underset{|}{C}}HCH_3$

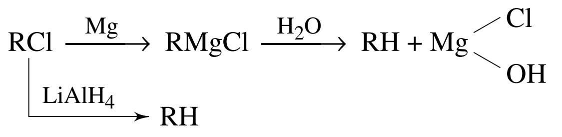
(e) $RCOOH \xrightarrow[2.\,H_2O]{1.\,LiAlH_4} RCH_2OH$

(f) 

(g) 

(h) 

Only one nitro group is reduced.

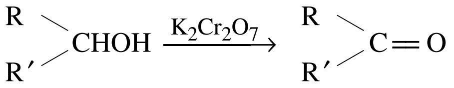
(i) 

(j) *Rosenmund's reduction*

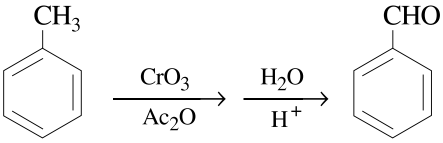
$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$

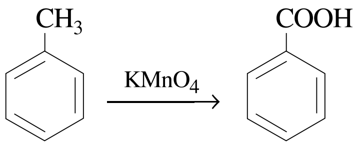
6. Oxidation

(a) $RCH_2OH \xrightarrow[C_5H_5NH^+CrO_3Cl^-]{\text{Pyridinium chlorochromate}} RCHO$

(b) 

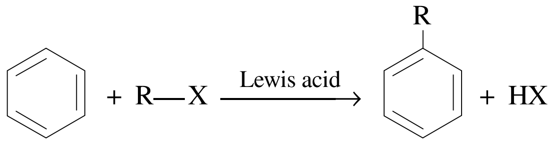
(c) $RCH_2OH \xrightarrow{KMnO_4} RCOOH$

(d) 

(e) 

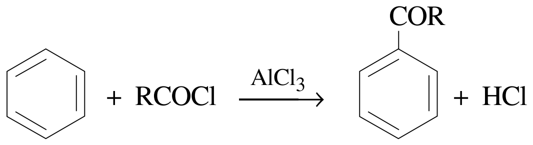
(f) $RCH{=}CHCHO \xrightarrow[\text{reagent}]{\text{Tollens}} RCH{=}CHCOOH$

7. Monosubstituted Benzenes

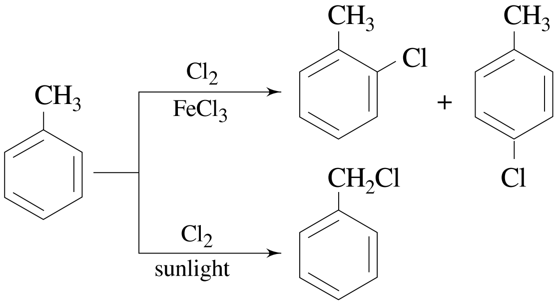
Alkylation of benzene 

Lewis acid: $AlCl_3$, BF_3 Ar—X cannot be used in place of R—X

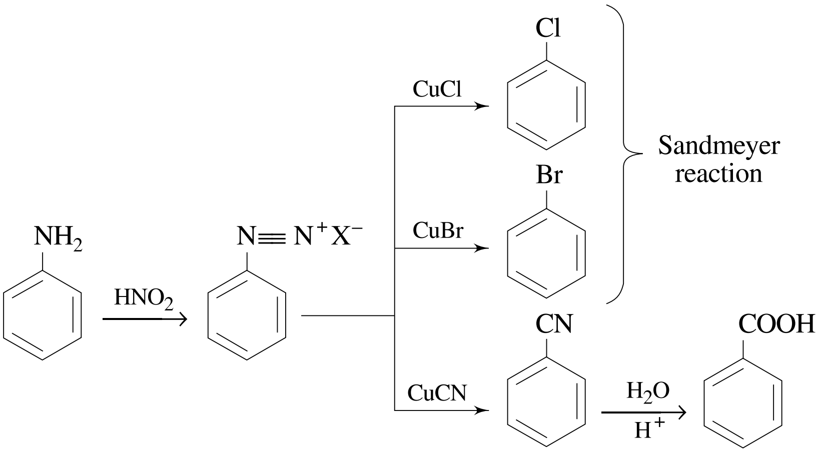
Acylation of benzene

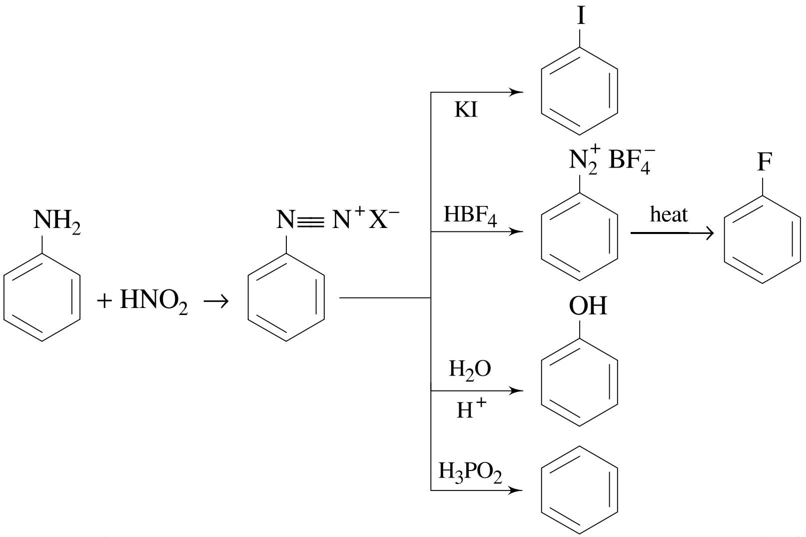


Halogenation in benzene and its alkyl derivatives



Substitution via diazonium salts



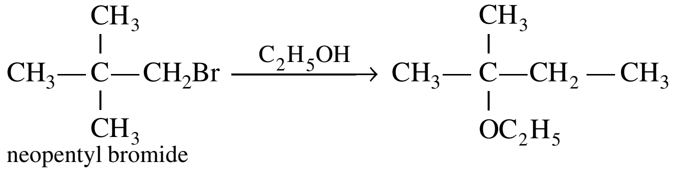


Many other groups such as —Ar, —NO_2, —OR, —SH, —NCS, —NCO, etc. can be introduced via diazotization.

8. Reactions Involving Rearrangement

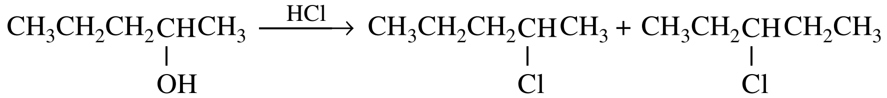
Many organic reactions are accompanied by the rearrangement of carbon skeleton. The main types of reactions in which rearrangement occurs are (1) nucleophilic substitution reactions involving S_N1 mechanism, (2) elimination reactions involving E1 mechanism, (3) electrophilic addition reactions, and (4) Friedel-Crafts alkylation. In all these reactions, a carbocation is formed. The rearrangement of carbon skeleton is basically due to the transformation of a lesser stable carbocation to the more stable carbocation.

1. Nucleophilic Substitution Reactions Involving S_N1 Mechanism

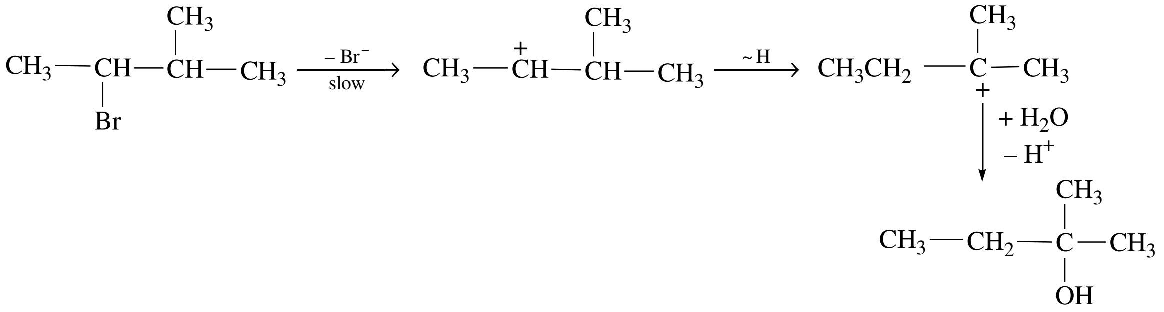


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br \xrightarrow{C_2H_5OH} CH_3-\underset{OC_2H_5}{\overset{CH_3}{C}}-CH_2-CH_3$$

neopentyl bromide



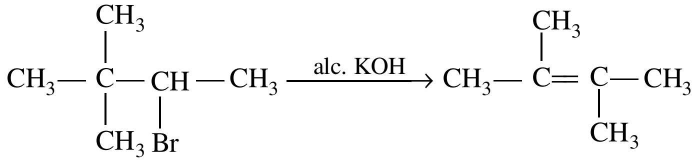
$$CH_3CH_2CH_2\underset{OH}{CH}CH_3 \xrightarrow{HCl} CH_3CH_2CH_2\underset{Cl}{CH}CH_3 + CH_3CH_2\underset{Cl}{CH}CH_2CH_3$$



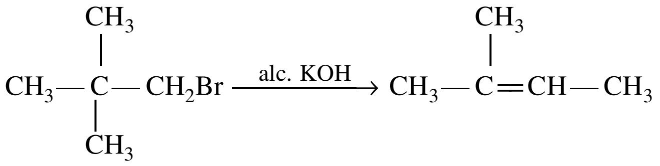
$$CH_3-\underset{Br}{CH}-\overset{CH_3}{CH}-CH_3 \xrightarrow[slow]{-Br^-} CH_3-\overset{+}{CH}-\overset{CH_3}{CH}-CH_3 \xrightarrow{\sim H} CH_3CH_2-\underset{+}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-H^+]{+H_2O} CH_3-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

2. Elimination Reactions Involving E1 Mechanism

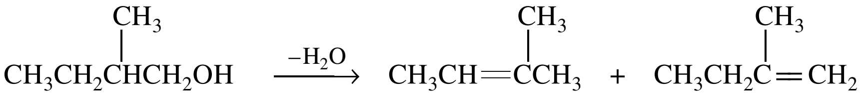
In general, the E1 mechanism is encountered only with secondary or tertiary substrates, and in solution where the base is either in low concentration or weak.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow{alc.\ KOH} CH_3-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

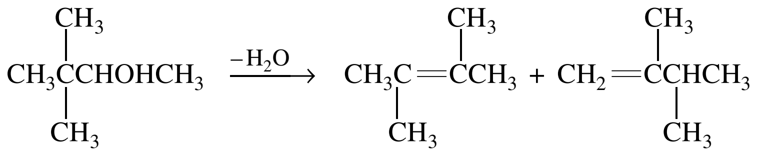


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br \xrightarrow{alc.\ KOH} CH_3-\overset{CH_3}{C}=CH-CH_3$$



$$CH_3CH_2\overset{CH_3}{CH}CH_2OH \xrightarrow{-H_2O} CH_3CH=\overset{CH_3}{C}CH_3 + CH_3CH_2\overset{CH_3}{C}=CH_2$$

main product

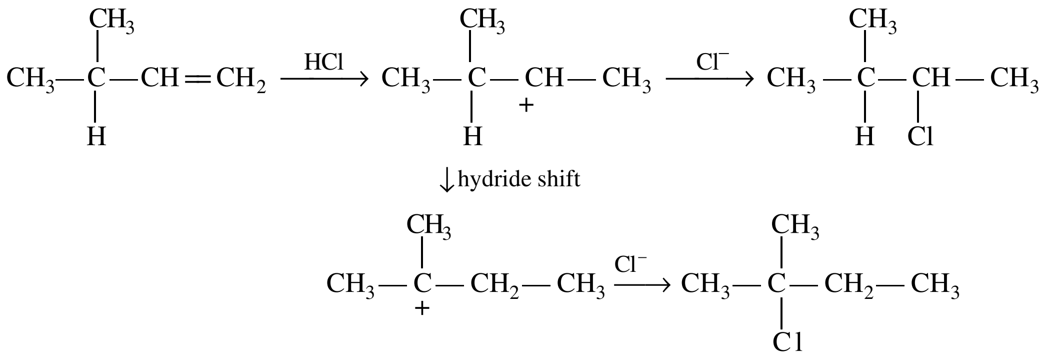


$$CH_3\underset{CH_3}{\overset{CH_3}{C}}CHOHCH_3 \xrightarrow{-H_2O} CH_3\underset{CH_3}{C}=\overset{CH_3}{C}CH_3 + CH_2=\underset{CH_3}{\overset{CH_3}{C}}CHCH_3$$

main product

3. Electrophilic Addition Reactions

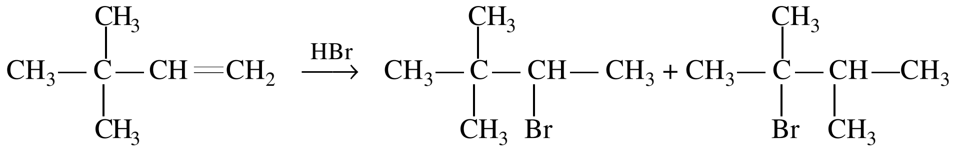
Because of the formation of carbocation as an intermediate, rearrangement of this may lead to a different carbon skeleton or the same skeleton with the shift of centre of position charge leading to a product which otherwise is not expected.



$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{HCl} CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{+}{CH}-CH_3 \xrightarrow{Cl^-} CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_3$$

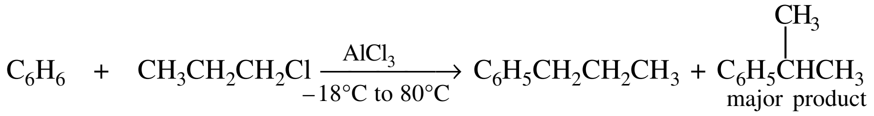
↓ hydride shift

$$CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{Cl^-} CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2-CH_3$$



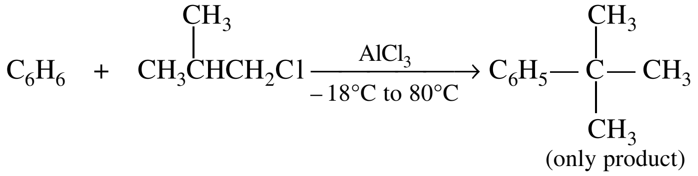
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 + CH_3-\underset{Br}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3$$

4. Friedel-Crafts Reaction



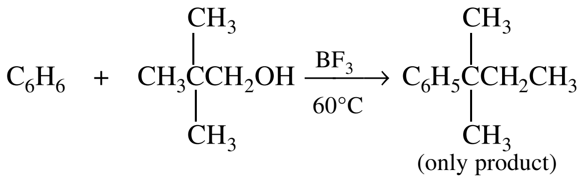
$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[-18^\circ C \text{ to } 80^\circ C]{AlCl_3} C_6H_5CH_2CH_2CH_3 + C_6H_5\overset{CH_3}{C}HCH_3$$

major product



$$C_6H_6 + CH_3\overset{CH_3}{C}HCH_2Cl \xrightarrow[-18^\circ C \text{ to } 80^\circ C]{AlCl_3} C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

(only product)

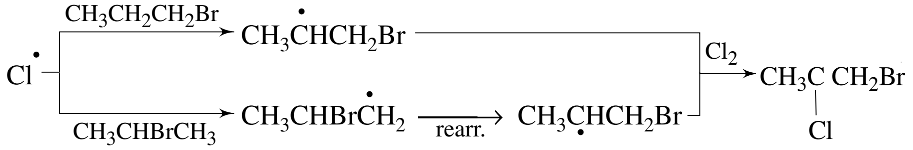


$$C_6H_6 + CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2OH \xrightarrow[60^\circ C]{BF_3} C_6H_5\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_3$$

(only product)

5. Rearrangement, by migration of Br, of initially formed 1° radical into more stable 2° or 3° radical.

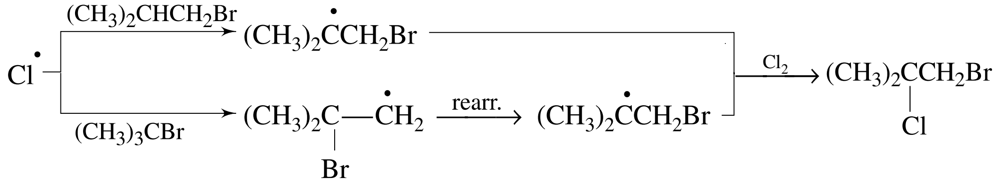
Chlorination of either *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane.



$$\overset{\bullet}{Cl} \xrightarrow{CH_3CH_2CH_2Br} CH_3\dot{C}HCH_2Br \xrightarrow{Cl_2} CH_3\underset{Cl}{C}CH_2Br$$

$$\overset{\bullet}{Cl} \xrightarrow[CH_3CHBrCH_3]{} CH_3CHBr\dot{C}H_2 \xrightarrow[\text{rearr.}]{} CH_3\underset{\bullet}{C}HCH_2Br \xrightarrow{Cl_2} CH_3\underset{Cl}{C}CH_2Br$$

Chlorination of either isobutyl or *tert*-butyl bromide gives 1-bromo-2-chloro-2-methylpropane.



$$\overset{\bullet}{Cl} \xrightarrow{(CH_3)_2CHCH_2Br} (CH_3)_2\dot{C}CH_2Br \xrightarrow{Cl_2} (CH_3)_2\underset{Cl}{C}CH_2Br$$

$$\overset{\bullet}{Cl} \xrightarrow[(CH_3)_3CBr]{} (CH_3)_2\underset{Br}{C}-\dot{C}H_2 \xrightarrow{\text{rearr.}} (CH_3)_2\dot{C}CH_2Br \xrightarrow{Cl_2} (CH_3)_2\underset{Cl}{C}CH_2Br$$

A Few Conversions

1. Methane to butane

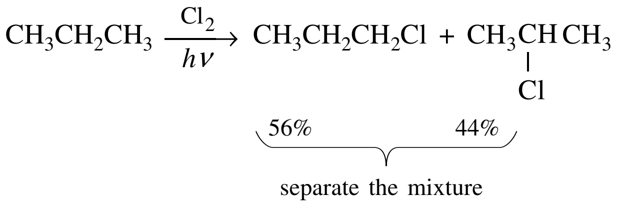
$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[\substack{2.\ Cu\,I\\3.\ CH_3Cl}]{1.\ Li} CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow[\substack{2.\ Cu\,I\\3.\ CH_3CH_2Cl}]{1.\ Li} CH_3CH_2CH_2CH_3$$

2. Ethane to methane

$$C_2H_6 \xrightarrow[h\nu]{Cl_2} C_2H_5Cl \xrightarrow{aq.\ KOH} C_2H_5OH \xrightarrow{Cr_2O_7^{2-}/H^+} CH_3COOH$$

$$CH_4 \xleftarrow{soda\ lime} CH_3COONa \xleftarrow{NaOH}$$

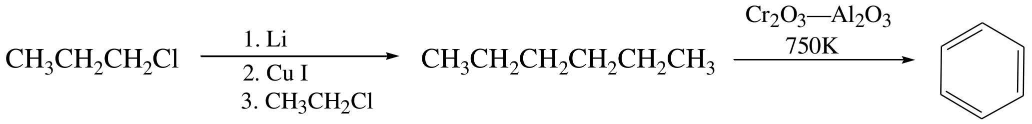
3. Propane to benzene



$$CH_3CH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2CH_2Cl + \underset{\displaystyle Cl}{CH_3CHCH_3}$$

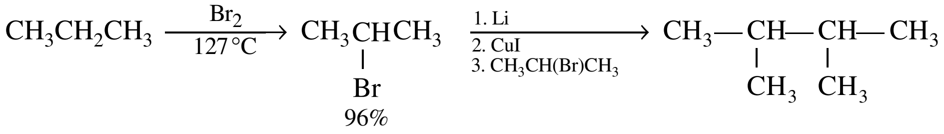
56% 44%

separate the mixture



$$CH_3CH_2CH_2Cl \xrightarrow[\substack{2.\ Cu\,I\\3.\ CH_3CH_2Cl}]{1.\ Li} CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow{\substack{Cr_2O_3—Al_2O_3\\750K}}$$

4. Propane to 2, 3-dimethylbutane

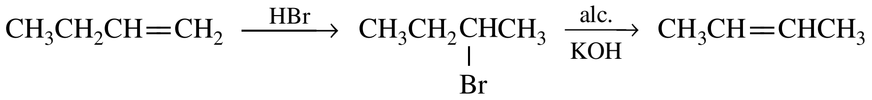


$$CH_3CH_2CH_3 \xrightarrow[127\,°C]{Br_2} \underset{\substack{\displaystyle Br\\96\%}}{CH_3CHCH_3} \xrightarrow[\substack{2.\ CuI\\3.\ CH_3CH(Br)CH_3}]{1.\ Li} CH_3—\underset{\displaystyle CH_3}{CH}—\underset{\displaystyle CH_3}{CH}—CH_3$$

5. Methane to propane

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[\substack{2.\ Cu\,X\\3.\ CH_3Cl}]{1.\ Li} CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow[\substack{2.\ Cu\,X\\3.\ CH_3Cl}]{1.\ Li} CH_3CH_2CH_3$$

6. 1-Butene to 2-butene



$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} \underset{\displaystyle Br}{CH_3CH_2CHCH_3} \xrightarrow[KOH]{alc.} CH_3CH{=}CHCH_3$$

7. 2-Butyne to 1-butyne

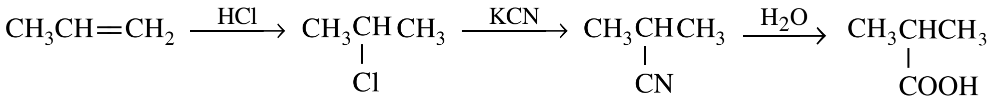
$$CH_3C{\equiv}CCH_3 + NaNH_2 \xrightarrow{paraffin} NH_3 + CH_3CH_2C{\equiv}CNa \xrightarrow{H^+} CH_3CH_2C{\equiv}CH$$

8. Propene to 1, 5-hexadiene

$$CH_3CH{=}CH_2 \xrightarrow[500\,°C]{Cl_2} ClCH_2CH{=}CH_2$$

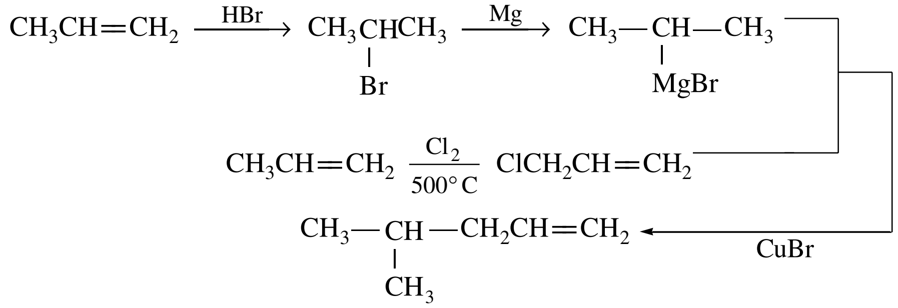
$$CH_2{=}CHCH_2Cl + Na + ClCH_2CH{=}CH_2 \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2$$

9. Propene to 2-methylpropanoic acid



$$CH_3CH{=}CH_2 \xrightarrow{HCl} \underset{\displaystyle Cl}{CH_3CHCH_3} \xrightarrow{KCN} \underset{\displaystyle CN}{CH_3CHCH_3} \xrightarrow{H_2O} \underset{\displaystyle COOH}{CH_3CHCH_3}$$

10. Propene to 4-methyl-1-pentene



$$CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\underset{\underset{Br}{|}}{CH}CH_3 \xrightarrow{Mg} CH_3{-}\underset{\underset{MgBr}{|}}{CH}{-}CH_3$$

$$CH_3CH{=}CH_2 \xrightarrow[500^\circ C]{Cl_2} ClCH_2CH{=}CH_2$$

$$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2CH{=}CH_2 \xleftarrow[CuBr]{}$$

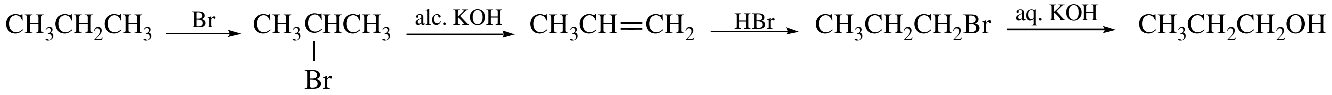
11. Propene to allene

$$CH_3CH{=}CH_2 \xrightarrow[500\,^\circ C]{Br_2} BrCH_2CH{=}CH_2 \xrightarrow[\Delta]{alc.KOH} CH_2{=}C{=}CH_2$$

12. Ethane to ethene

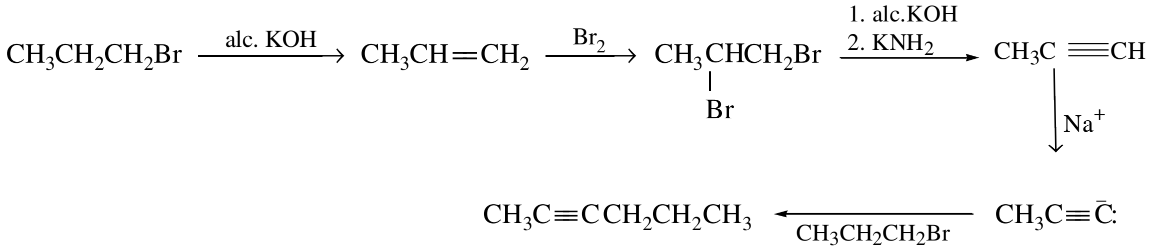
$$CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow{aq.\ KOH} CH_3CH_2OH \xrightarrow[620\,K]{Al_2O_3} CH_2{=}CH_2$$

13. Propane to 1-propanol



$$CH_3CH_2CH_3 \xrightarrow{Br} CH_3\underset{\underset{Br}{|}}{CH}CH_3 \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH} CH_3CH_2CH_2OH$$

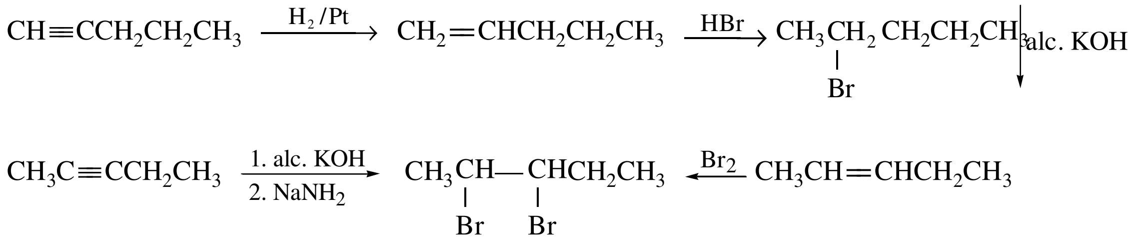
14. *n*-propyl bromide to 2-hexyne



$$CH_3CH_2CH_2Br \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\underset{\underset{Br}{|}}{CH}CH_2Br \xrightarrow{\substack{1.\ alc.KOH\\ 2.\ KNH_2}} CH_3C\equiv CH \xrightarrow{Na^+} CH_3C\equiv\bar{C}{:}$$

$$CH_3C\equiv CCH_2CH_2CH_3 \xleftarrow[CH_3CH_2CH_2Br]{} CH_3C\equiv\bar{C}{:}$$

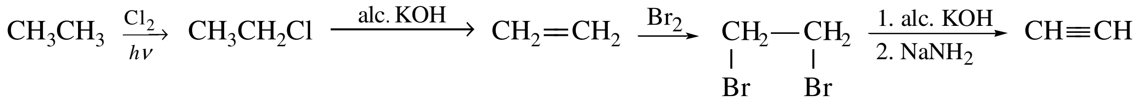
15. 1-Pentyne to 2-pentyne



$$CH\equiv CCH_2CH_2CH_3 \xrightarrow{H_2/Pt} CH_2{=}CHCH_2CH_2CH_3 \xrightarrow{HBr} CH_3\underset{\underset{Br}{|}}{CH_2}CH_2CH_2CH \xrightarrow{alc.\ KOH}$$

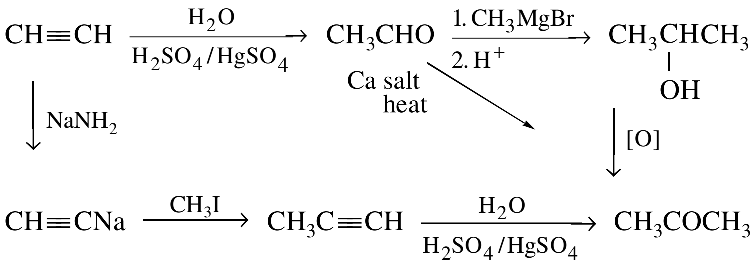
$$CH_3C\equiv CCH_2CH_3 \xleftarrow[2.\ NaNH_2]{1.\ alc.\ KOH} CH_3\underset{\underset{Br}{|}}{CH}{-}\underset{\underset{Br}{|}}{CH}CH_2CH_3 \xleftarrow{Br_2} CH_3CH{=}CHCH_2CH_3$$

16. Ethane to ethyne



$$CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow{alc.KOH} CH_2{=}CH_2 \xrightarrow{Br_2} \underset{\underset{Br}{|}}{CH_2}{-}\underset{\underset{Br}{|}}{CH_2} \xrightarrow[2.\ NaNH_2]{1.\ alc.\ KOH} CH\equiv CH$$

17. Ethyne to acetone



$$CH\equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3CHO \xrightarrow[2.\ H^+]{1.\ CH_3MgBr} CH_3\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow{[O]} CH_3COCH_3$$

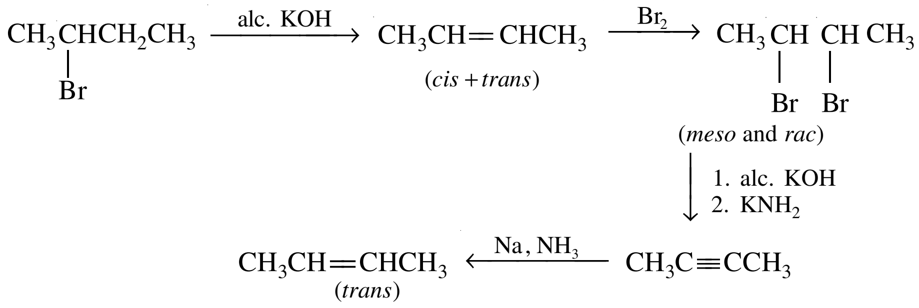
$$CH_3CHO \xrightarrow{\text{Ca salt, heat}} CH_3COCH_3$$

$$CH\equiv CH \xrightarrow{NaNH_2} CH\equiv CNa \xrightarrow{CH_3I} CH_3C\equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3COCH_3$$

18. 2-Butyne to racemic 2, 3-dibromobutane

$$\mathrm{CH_3C{\equiv}CCH_3} \xrightarrow{H_2/Pt} \underset{cis\text{-but-2-ene}}{\mathrm{CH_3CH{=}CHCH_3}} \xrightarrow{Br_2} \underset{\substack{trans\text{ addition}\\ \text{(racemic mixture)}}}{\mathrm{CH_3CHBrCHBrCH_3}}$$

19. 2-Bromobutane to *trans*-2-butene

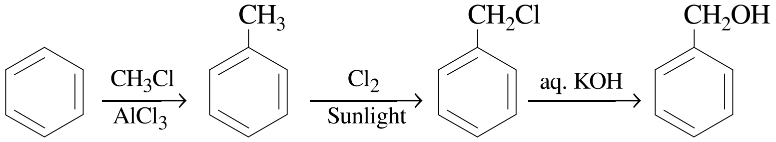


$$\underset{\mathrm{Br}}{\mathrm{CH_3CHCH_2CH_3}} \xrightarrow{\text{alc. KOH}} \underset{(cis+trans)}{\mathrm{CH_3CH{=}CHCH_3}} \xrightarrow{Br_2} \underset{(meso\text{ and }rac)}{\mathrm{CH_3\,\underset{Br}{CH}\,\underset{Br}{CH}\,CH_3}} \xrightarrow[\text{2. KNH}_2]{\text{1. alc. KOH}} \mathrm{CH_3C{\equiv}CCH_3} \xrightarrow{Na,\ NH_3} \underset{(trans)}{\mathrm{CH_3CH{=}CHCH_3}}$$

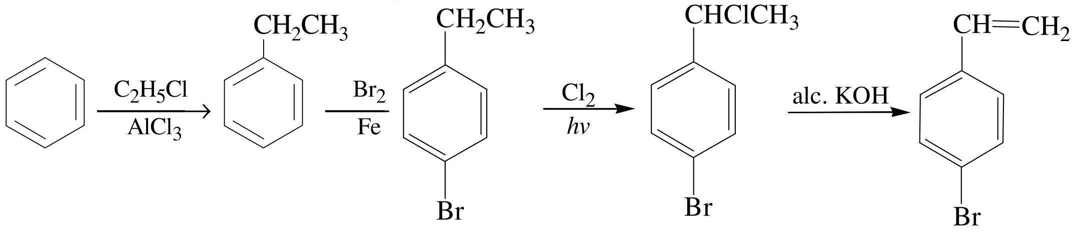
20. Ethyne to iodoform

$$\mathrm{HC{\equiv}CH} \xrightarrow[H_2SO_4/HgSO_4]{H_2O} \mathrm{CH_3CHO} \xrightarrow{I_2/NaOH} \mathrm{CHI_3}$$

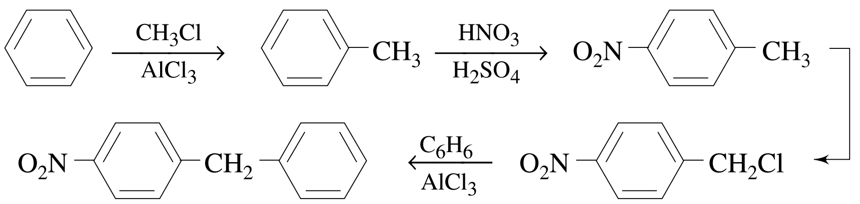
21. Benzene to benzyl alcohol



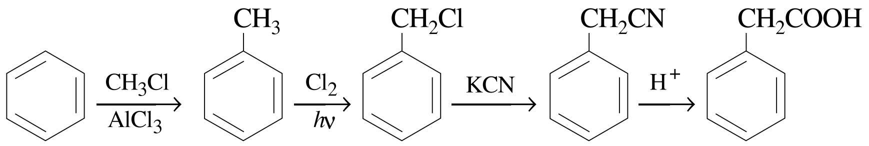
22. Benzene to *p*-bromostyrene



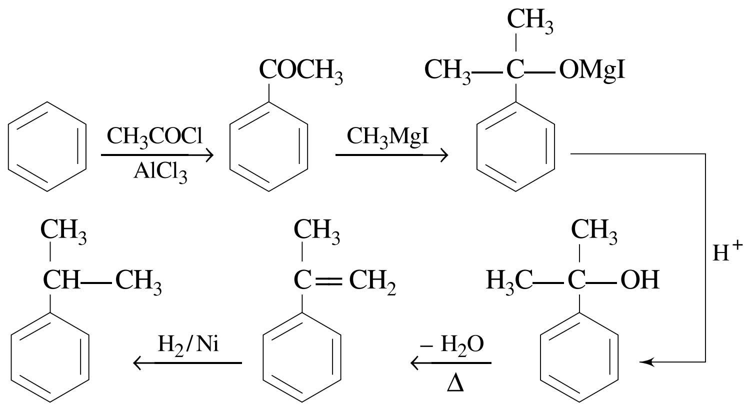
23. Benzene to $p\text{-}O_2NC_6H_4\text{—}CH_2\text{—}C_6H_5$



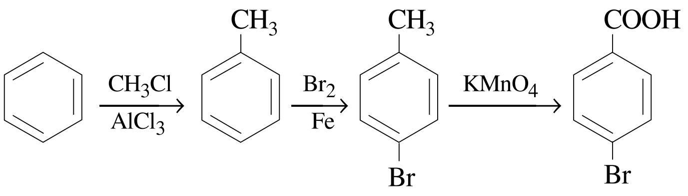
24. Benzene to phenylacetic acid



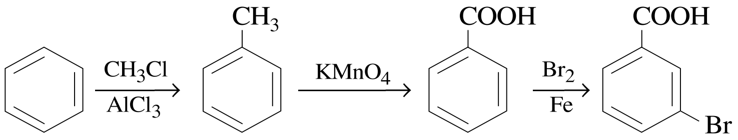
25. Benzene to isopropylbenzene



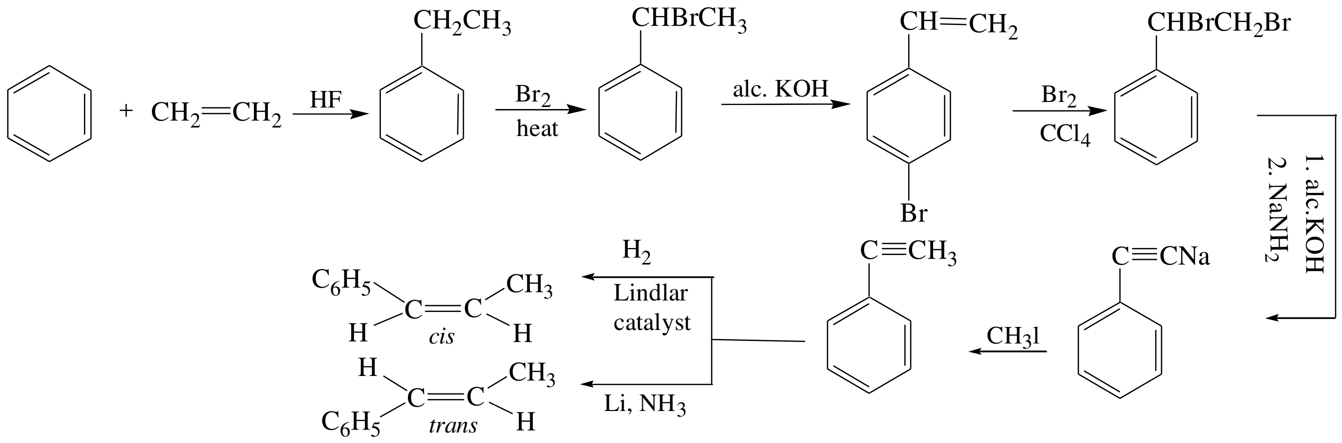
26. Benzene to *p*-bromobenzoic acid



27. Benzene to *m*-bromobenzoic acid



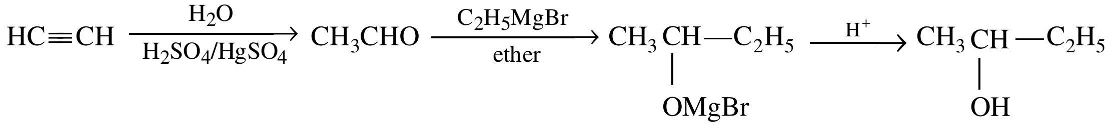
28. Benzene to *cis*- or *trans*-methylphenylethylene



29. Ethane to 1-propanol

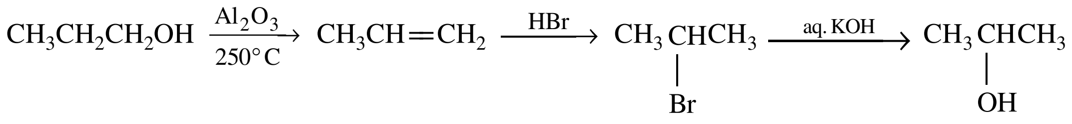
$$CH_3CH_3 \xrightarrow[h\nu]{Cl} CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{H_2,\,Ni} CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2CH_2OH$$

30. Ethyne to 2-butanol



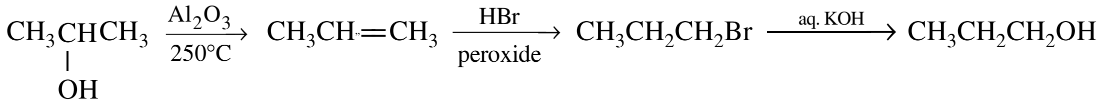
$$HC\equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3CHO \xrightarrow[ether]{C_2H_5MgBr} CH_3\underset{OMgBr}{CH}{-}C_2H_5 \xrightarrow{H^+} CH_3\underset{OH}{CH}{-}C_2H_5$$

31. 1-Propanol to 2-propanol



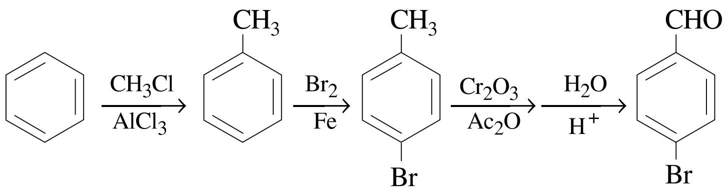
$$CH_3CH_2CH_2OH \xrightarrow[250°C]{Al_2O_3} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\underset{Br}{CH}CH_3 \xrightarrow{aq. KOH} CH_3\underset{OH}{CH}CH_3$$

32. 2-Propanol to 1-propanol

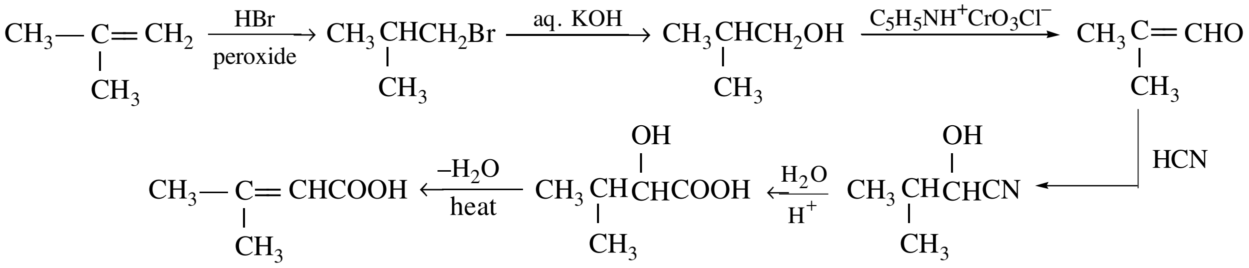


$$CH_3\underset{OH}{CH}CH_3 \xrightarrow[250°C]{Al_2O_3} CH_3CH{=}CH_3 \xrightarrow[peroxide]{HBr} CH_3CH_2CH_2Br \xrightarrow{aq. KOH} CH_3CH_2CH_2OH$$

33. Benzene to *p*-bromobenzaldehyde



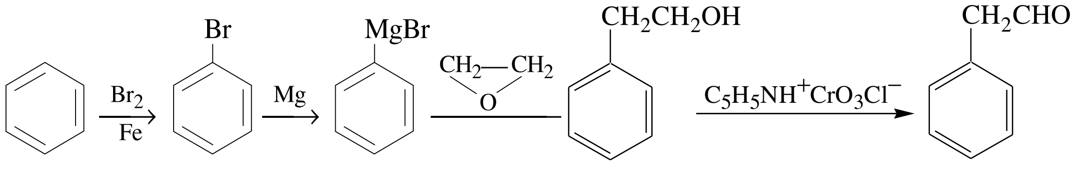
34. 2-Methylpropene to 3-methyl-2-butenoic acid



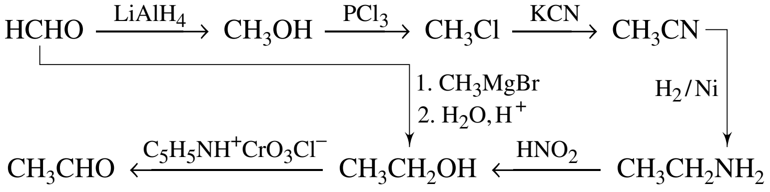
$$CH_3{-}\underset{CH_3}{C}{=}CH_2 \xrightarrow[peroxide]{HBr} CH_3\underset{CH_3}{CH}CH_2Br \xrightarrow{aq. KOH} CH_3\underset{CH_3}{CH}CH_2OH \xrightarrow{C_5H_5NH^+CrO_3Cl^-} CH_3\underset{CH_3}{C}{=}CHO$$

$$\xrightarrow{HCN} CH_3\underset{CH_3}{CH}\overset{OH}{CH}CN \xrightarrow[H^+]{H_2O} CH_3\underset{CH_3}{CH}\overset{OH}{CH}COOH \xrightarrow[heat]{-H_2O} CH_3{-}\underset{CH_3}{C}{=}CHCOOH$$

35. Benzene to phenylacetaldehyde



36. Formaldehyde to acetaldehyde



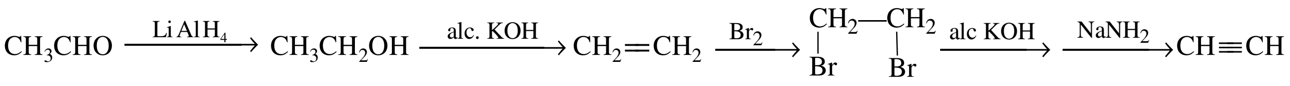
$$HCHO \xrightarrow{LiAlH_4} CH_3OH \xrightarrow{PCl_3} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{H_2/Ni} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{C_5H_5NH^+CrO_3Cl^-} CH_3CHO$$

$$HCHO \xrightarrow{1.\ CH_3MgBr\quad 2.\ H_2O, H^+} CH_3CH_2OH$$

37. Acetaldehyde to formaldehyde

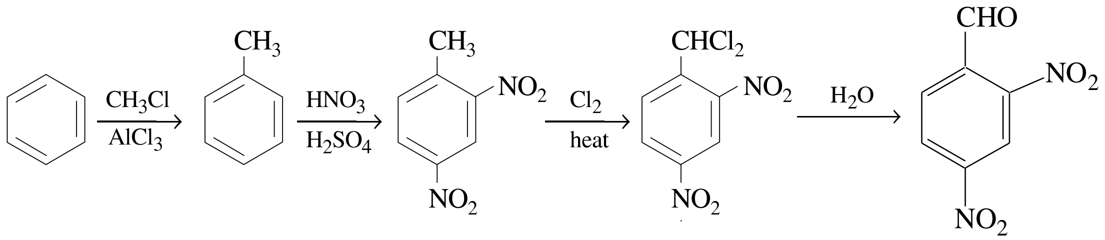
$$CH_3CHO \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH \xrightarrow[heat]{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow[heat]{Cu} HCHO$$

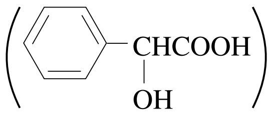
38. Acetaldehyde to acetylene

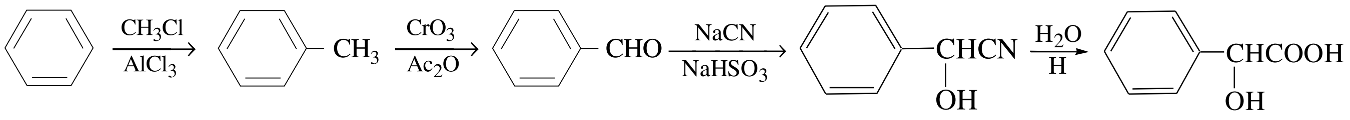


$$CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{alc.\ KOH} CH_2{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH_2} \xrightarrow{alc\ KOH} \xrightarrow{NaNH_2} CH{\equiv}CH$$

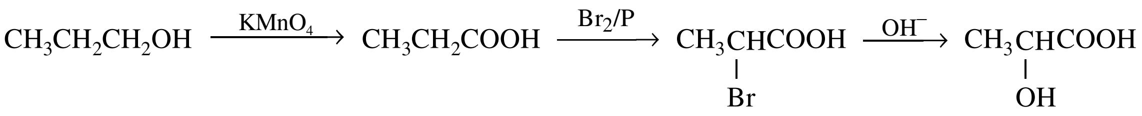
39. Benzene to 2,4-dinitrobenzaldehyde



40. Benzene to Mandelic acid 



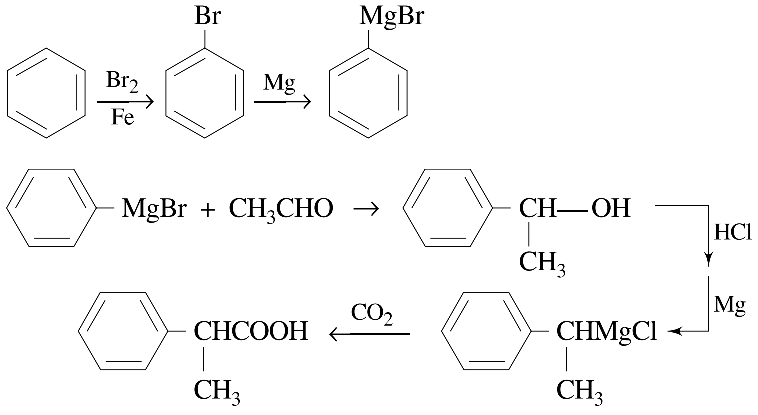
41. Propanol to α-hydroxypropionic acid



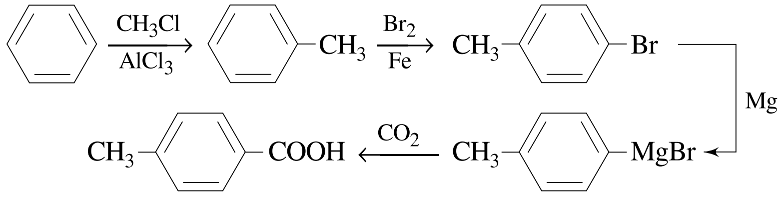
$$CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2COOH \xrightarrow{Br_2/P} CH_3\underset{Br}{C}HCOOH \xrightarrow{OH^-} CH_3\underset{OH}{C}HCOOH$$

42. Benzene + alcohol to α-methylphenylacetic acid

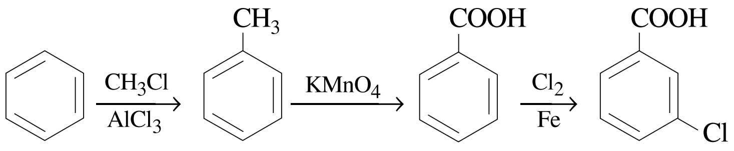
$$C_2H_5OH \xrightarrow{C_5H_5NH^+CrO_3Cl^-} CH_3CHO$$



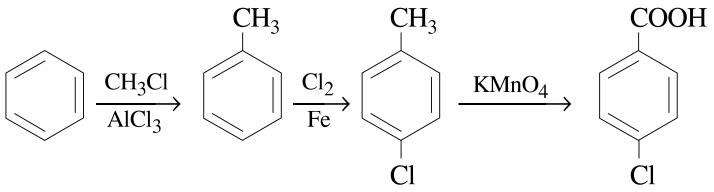
43. Benzene to *p*-toluic acid



44. Benzene to *m*-chlorobenzoic acid



45. Benzene to *p*-chlorobenzoic acid



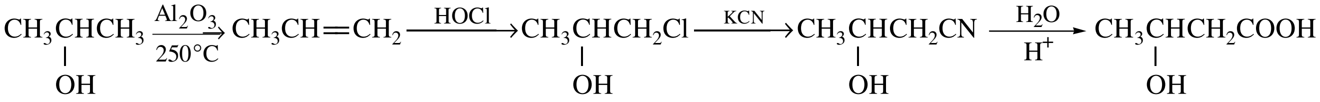
46. Acetic acid to malonic acid

$$CH_3COOH \xrightarrow{Br_2,\,P} BrCH_2COOH \xrightarrow{KCN} CNCH_2COOH \xrightarrow[H^+]{H_2O} HOOCCH_2COOH$$

47. Ethyne to propanoic acid

$$HC\equiv CH \xrightarrow[\text{catalyst}]{\text{Lindlar}} H_2C=CH_2 \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow[H^+]{H_2O} C_2H_5COOH$$

48. Isopropyl alcohol to β-hydroxybutyric acid



$$\underset{OH}{CH_3CHCH_3} \xrightarrow[250°C]{Al_2O_3} CH_3CH=CH_2 \xrightarrow{HOCl} \underset{OH}{CH_3CHCH_2Cl} \xrightarrow{KCN} \underset{OH}{CH_3CHCH_2CN} \xrightarrow[H^+]{H_2O} \underset{OH}{CH_3CHCH_2COOH}$$

49. Acetic acid to propanoic acid

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_3} CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2COOH$$

50. Propanoic acid to acetic acid

$$CH_3CH_2COOH \xrightarrow[\text{heat}]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH$$

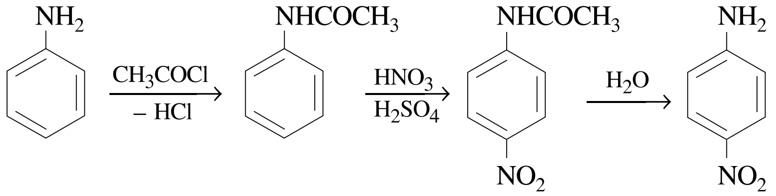
51. Methylamine to ethylamine

$$CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_3} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{Sn/HCl} CH_3CH_2NH_2$$

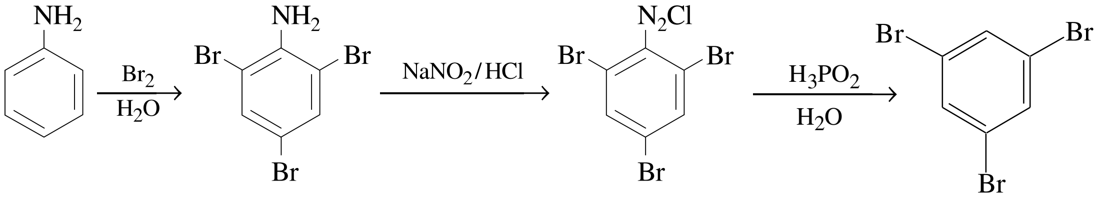
52. Ethylamine to methylamine

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH \xrightarrow[\text{heat}]{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

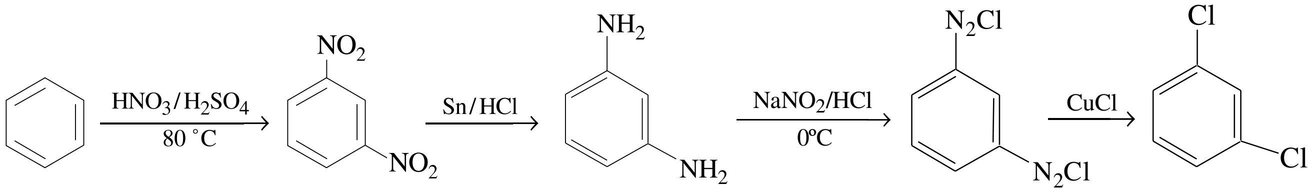
53. Aniline to *p*-nitroaniline



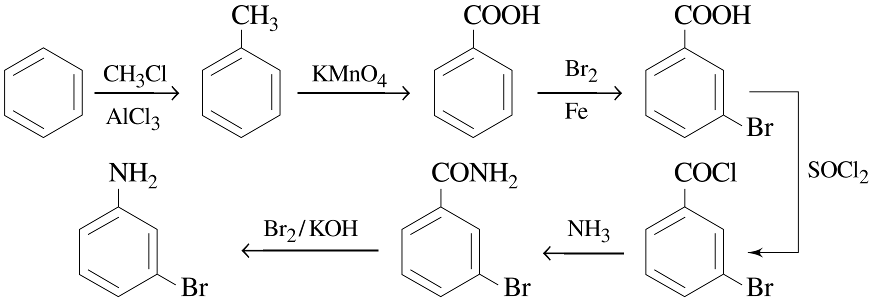
54. Aniline to *sym*-tribromobenzene



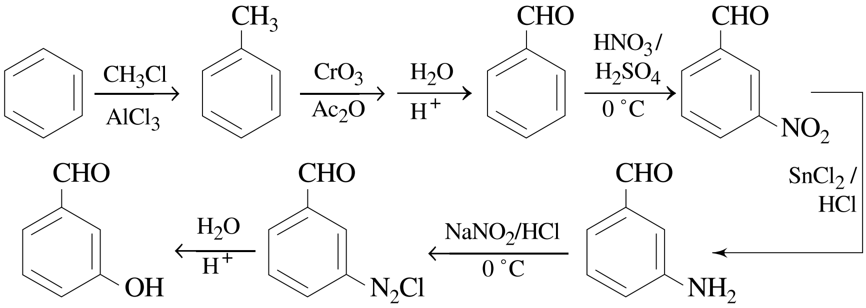
55. Benzene to *m*-dichlorobenzene



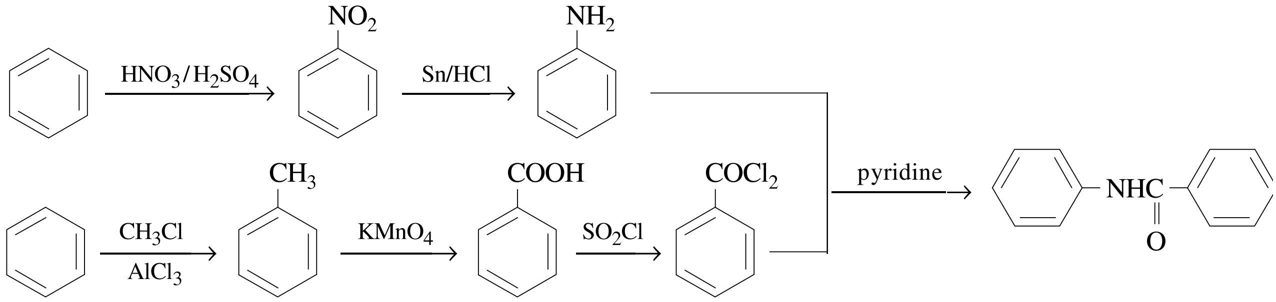
56. Benzene to *m*-bromoaniline



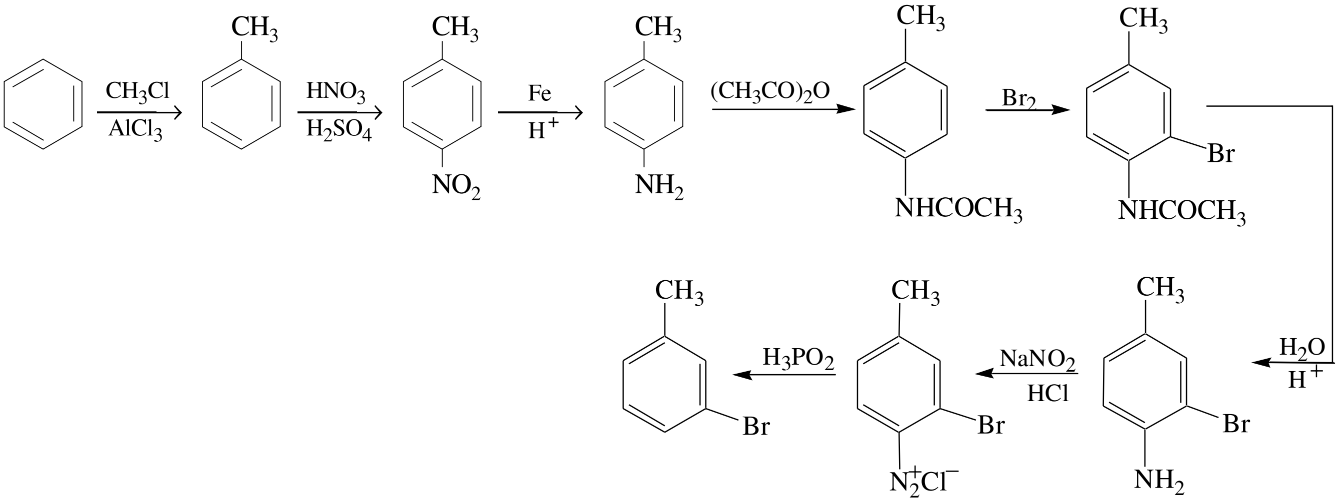
57. Benzene to *m*-hydroxybenzaldehyde



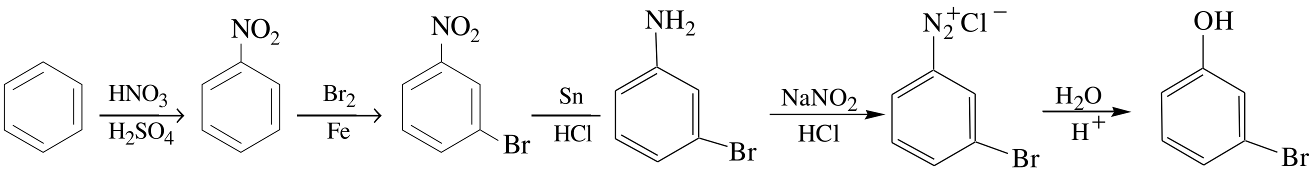
58. Benzene to benzanilide



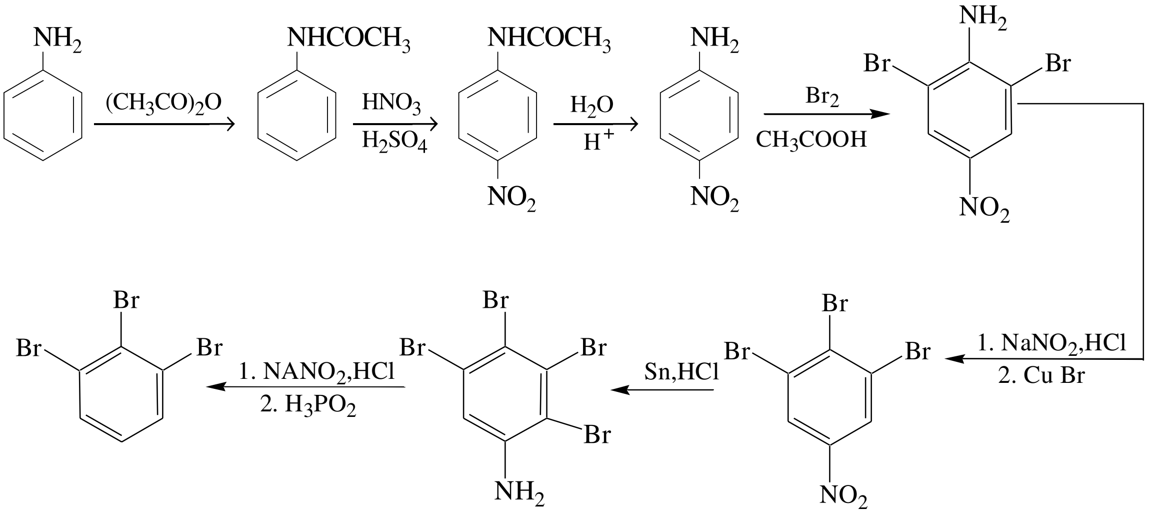
59. Benzene to *m*-bromotoluene



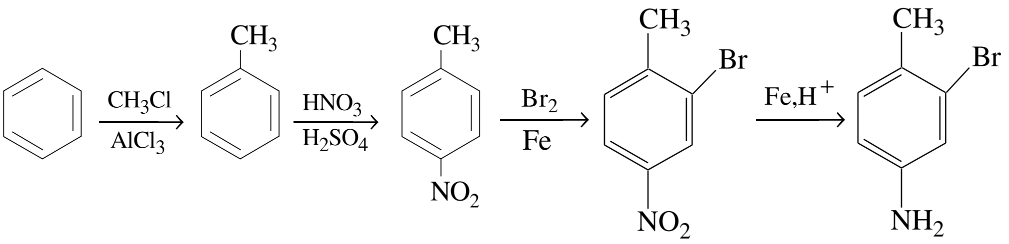
60. Benzene to *m*-bromophenol



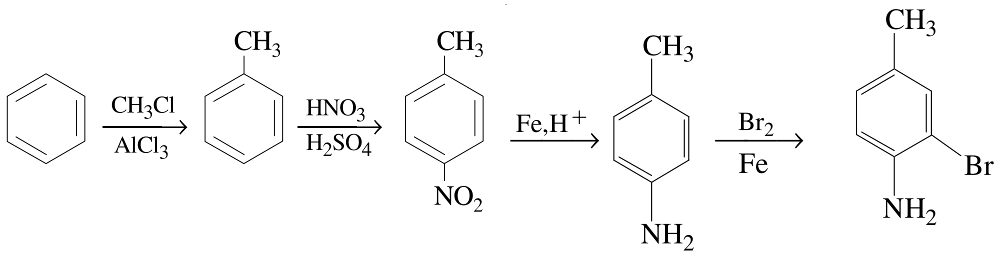
61. Aniline to 1, 2, 3-tribromobenzene [1990]



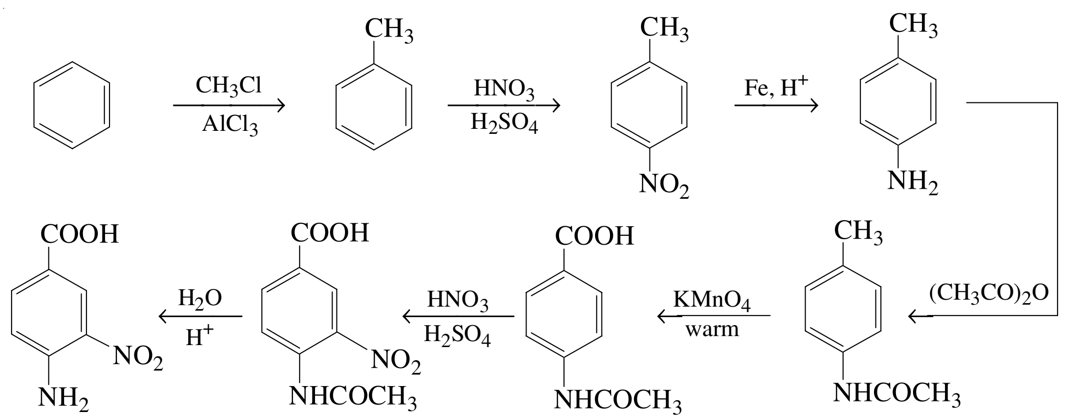
62. Benzene to 4-amino-2-bromotoluene



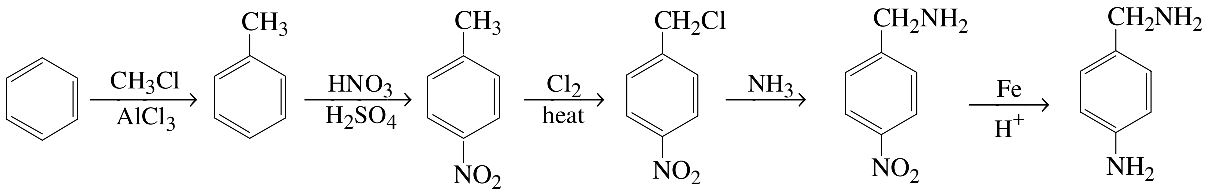
63. Benzene to 4-amino-3-bromotoluene



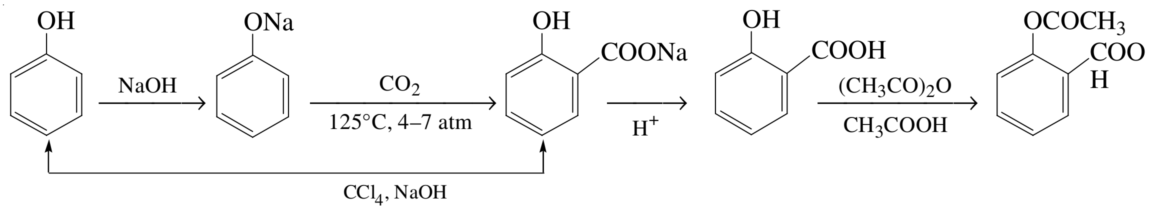
64. Benzene to 4-amino-3-nitrobenzoic acid



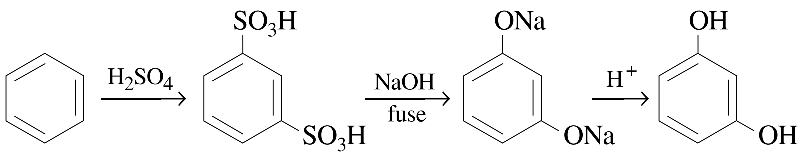
65. Benzene to *p*-aminobenzylamine



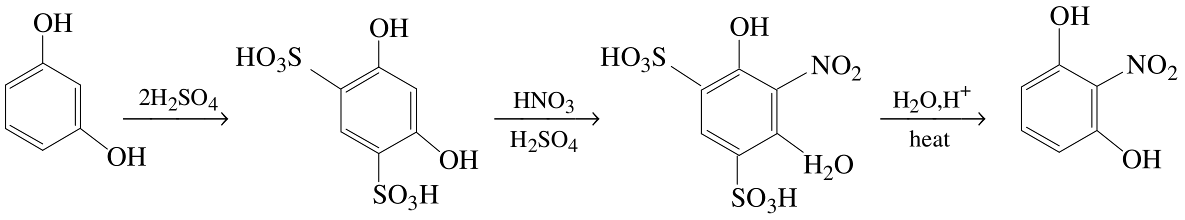
66. Phenol to aspirin [2003]



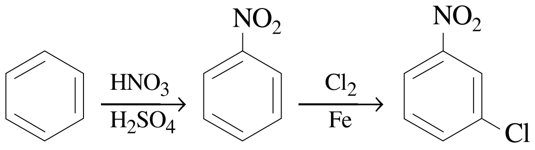
67. Benzene to resorcinol



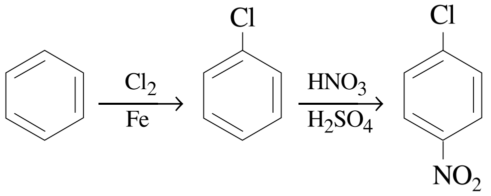
68. Resorcinol to 2-nitro-1, 3-dihydroxybenzene



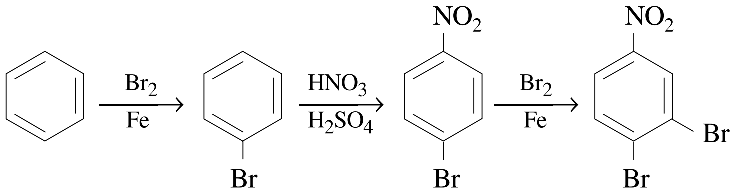
69. Benzene to *m*-chloronitrobenzene



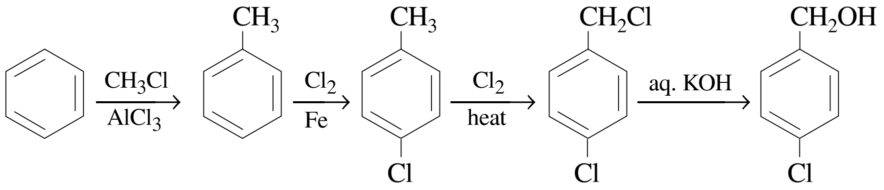
70. Benzene to *p*-chloronitrobenzene



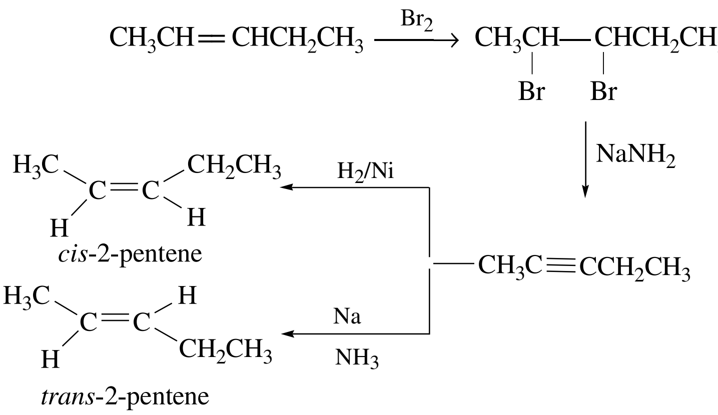
71. Benzene to 3, 4-dibromonitrobenzene



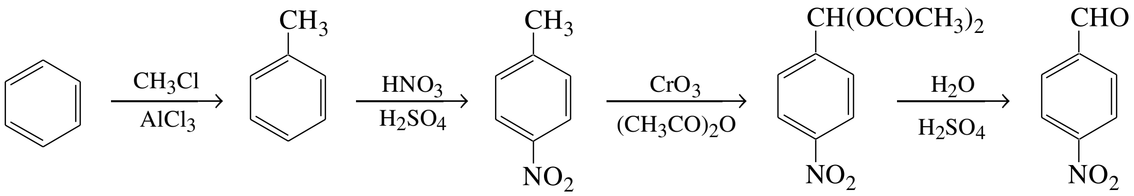
72. Benzene to *p*-chlorobenzylalcohol



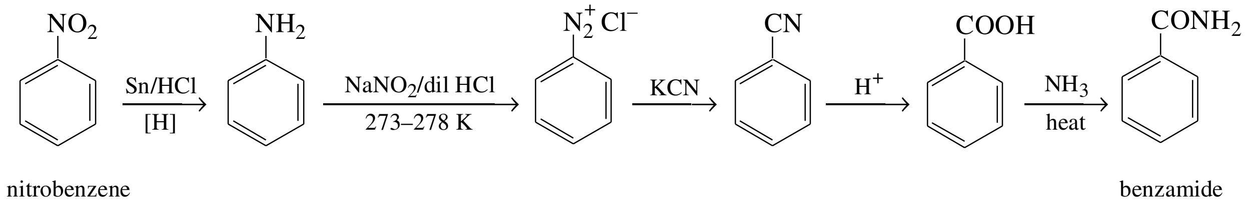
73. A mixture of *cis*-2-pentene and *trans*-2-pentene into *cis*-2-pentene or *trans*-2-pentene.



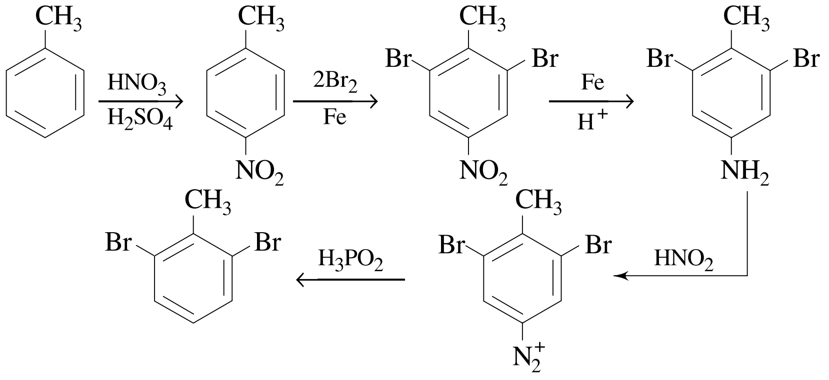
74. Benzene to 4-nitrobenzaldehyde [1994]



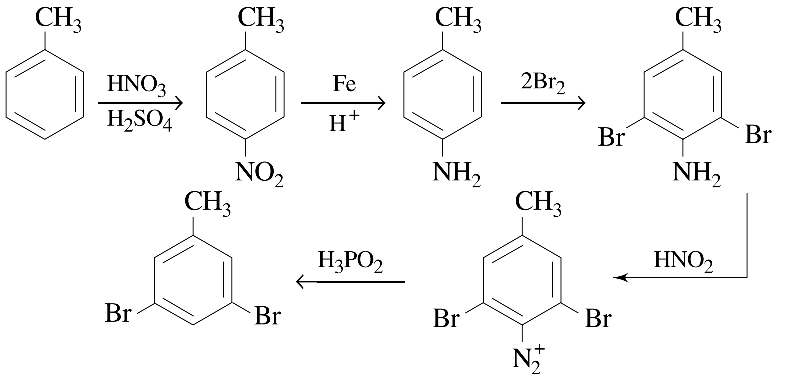
75. Nitrobenzene to benzamide [1994]



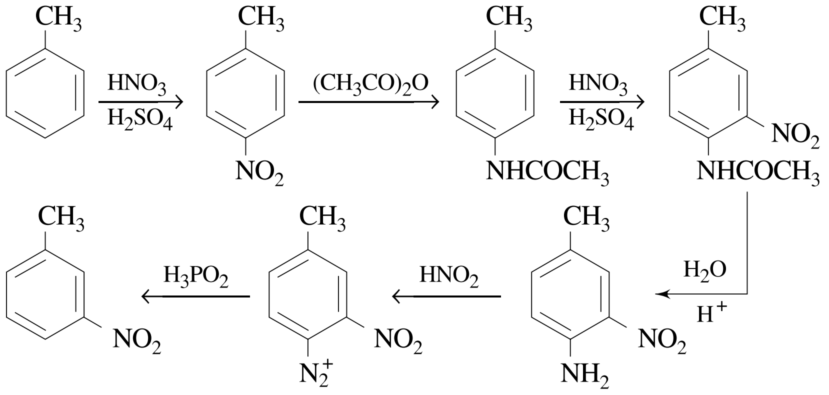
76. Toluene to 2, 6-dibromotoluene



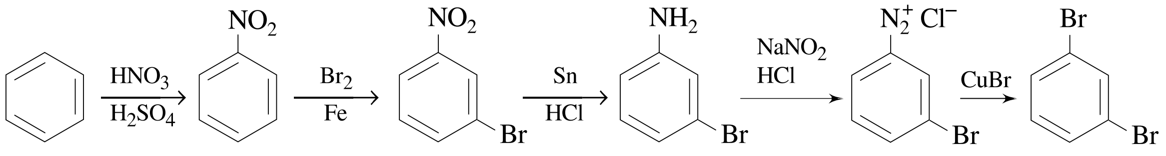
77. Toluene to 3, 5-dibromotoluene



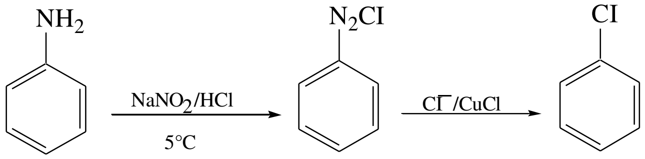
78. Toluene to *m*-nitrotoluene



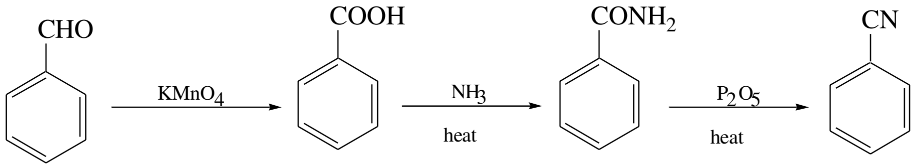
79. Benzene to *m*-dibromobenzene



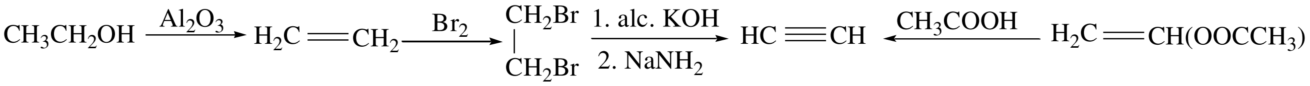
80. Aniline to Chlorobenzene (1985)



81. Benzaldehyde to cyanobenzene



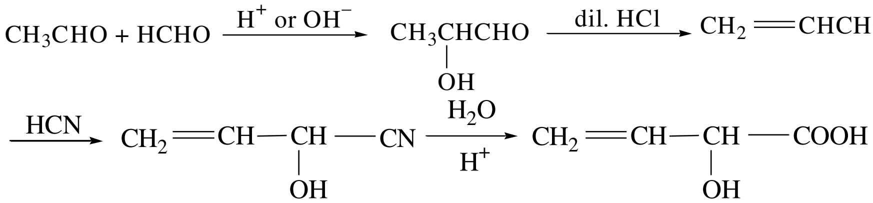
82. Ethyl alcohol to vinyl acetate (1986)



$$CH_3CH_2OH \xrightarrow{Al_2O_3} H_2C{=}CH_2 \xrightarrow{Br_2} \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} \xrightarrow[2.\ NaNH_2]{1.\ alc.\ KOH} HC{\equiv}CH \xleftarrow{CH_3COOH} H_2C{=}CH(OOCCH_3)$$

83. Carry out the following conversions.

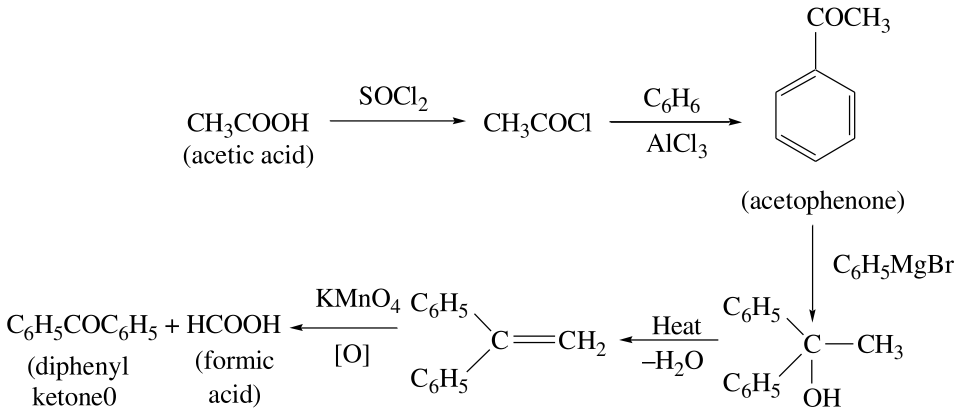
(i) Ethanal to 2-hydroxy-3-butenoic acid



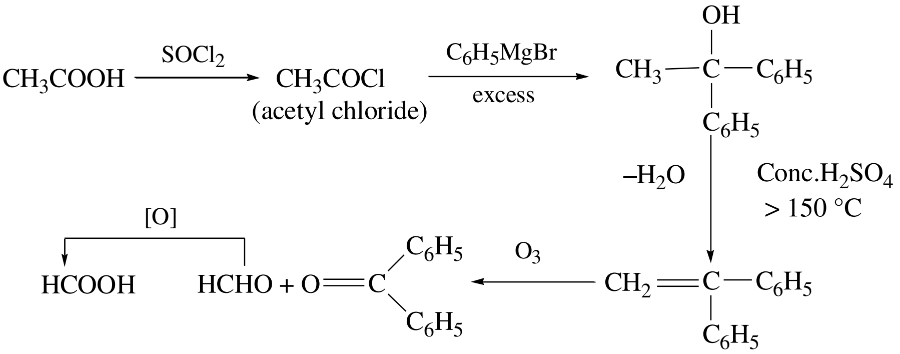
$$CH_3CHO + HCHO \xrightarrow{H^+ \text{ or } OH^-} CH_3\underset{\overset{|}{OH}}{C}HCHO \xrightarrow{dil.\ HCl} CH_2{=}CHCHO$$

$$\xrightarrow{HCN} CH_2{=}CH{-}\underset{\overset{|}{OH}}{CH}{-}CN \xrightarrow[H^+]{H_2O} CH_2{=}CH{-}\underset{\overset{|}{OH}}{CH}{-}COOH$$

(ii) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone



Alternatively, we may proceed as follows.

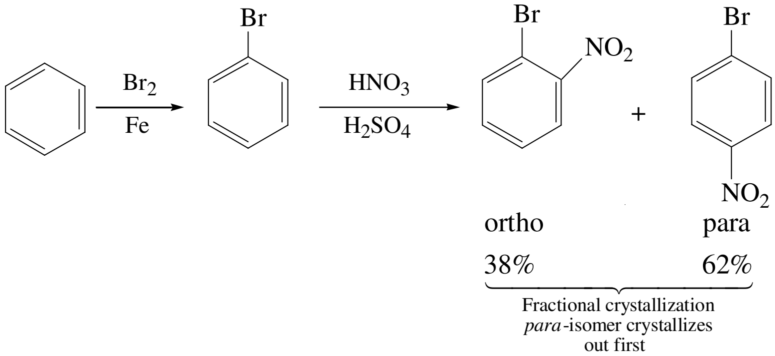


$$CH_3COOH \xrightarrow{SOCl_2} \underset{\text{(acetyl chloride)}}{CH_3COCl} \xrightarrow[\text{excess}]{C_6H_5MgBr} CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}{-}C_6H_5$$

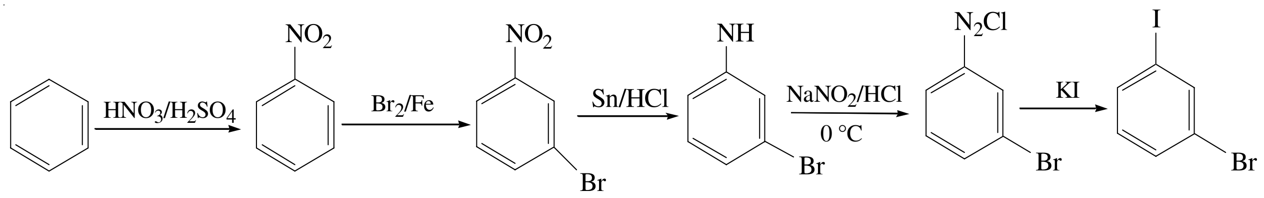
$$\xrightarrow[\text{Conc.}H_2SO_4\ > 150\ °C]{-H_2O} CH_2{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}C_6H_5$$

$$HCOOH \xleftarrow{[O]} HCHO + O{=}C\begin{array}{l}C_6H_5\\ C_6H_5\end{array} \xleftarrow{O_3} CH_2{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{-}C_6H_5$$

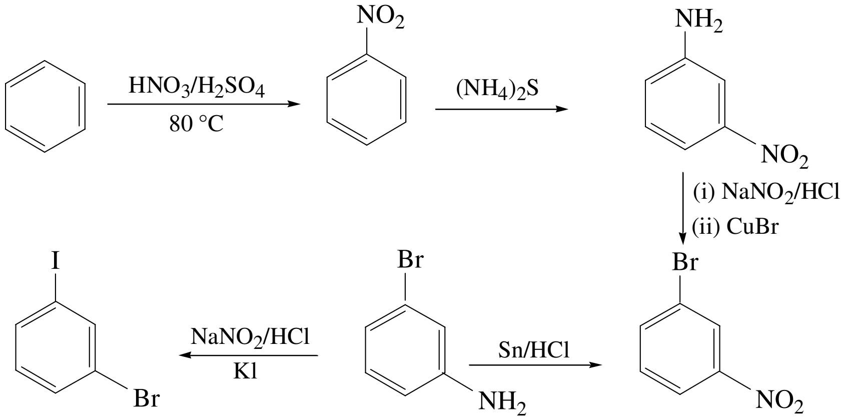
84. Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. (1993)



85. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)? (1996)

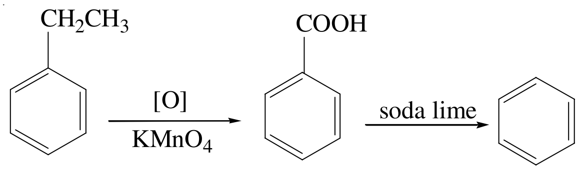


Alternatively, we may proceed as follows:

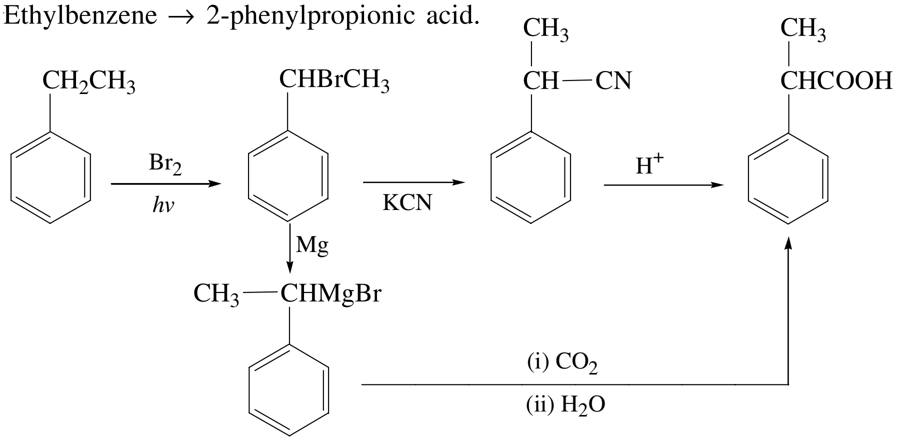


86. Show the steps to carry out the following transformations.

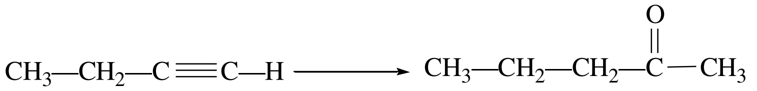
(i) Ethylbenzene → benzene



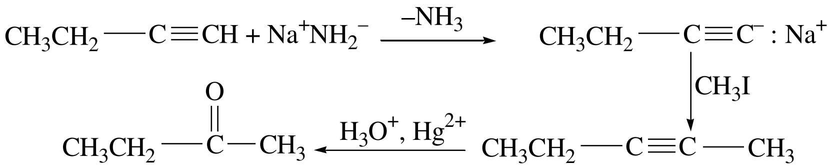
(ii) Ethylbenzene → 2-phenylpropionic acid. (1998)



87. Carry out the following transformation in not more than three steps.

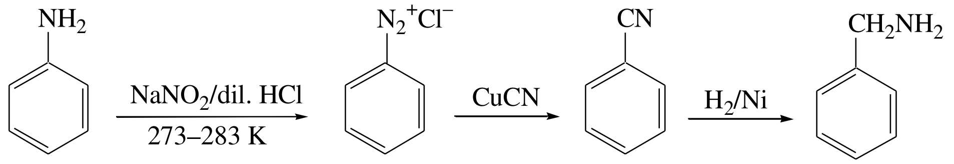


$$CH_3{-}CH_2{-}C{\equiv}C{-}H \longrightarrow CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

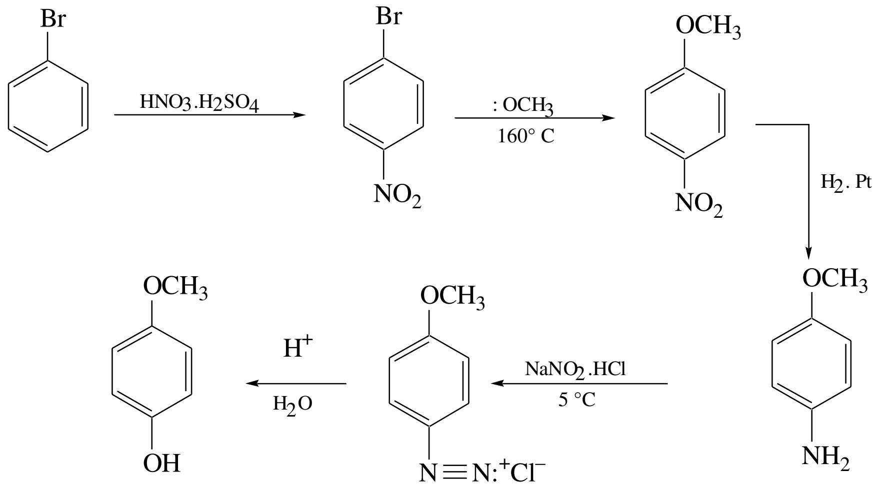


(1999)

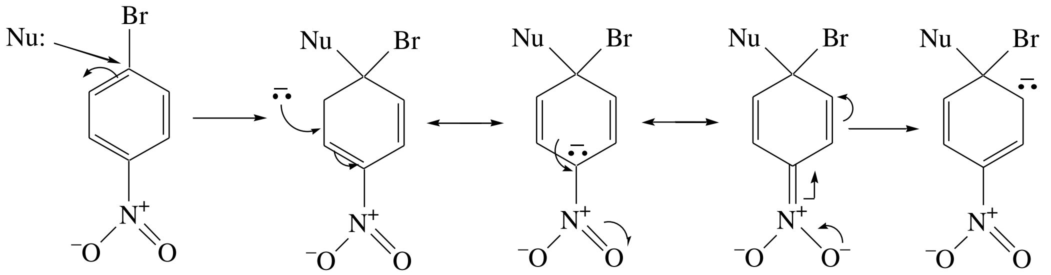
88. How would you bring about the following conversion (in 3 steps)?
Aniline → Benzylamine (2000)



89. How would you synthesise 4-methoxyphenol from bromobenzene is NOT more than five steps? State clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme. (2001)

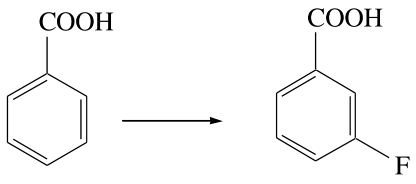


The introduction of —NO_2 group at *para* position in bromobenzene facilitates the nucleophilic replacement of —Br by —OCH_3.

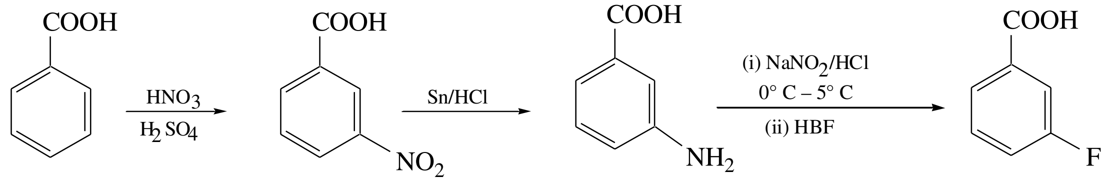


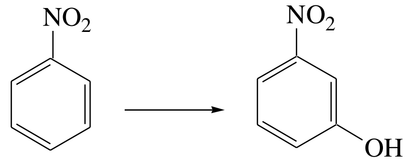
The negative charge is strongly stabilised by resonance involving *para*-nitro group.

90. Convert

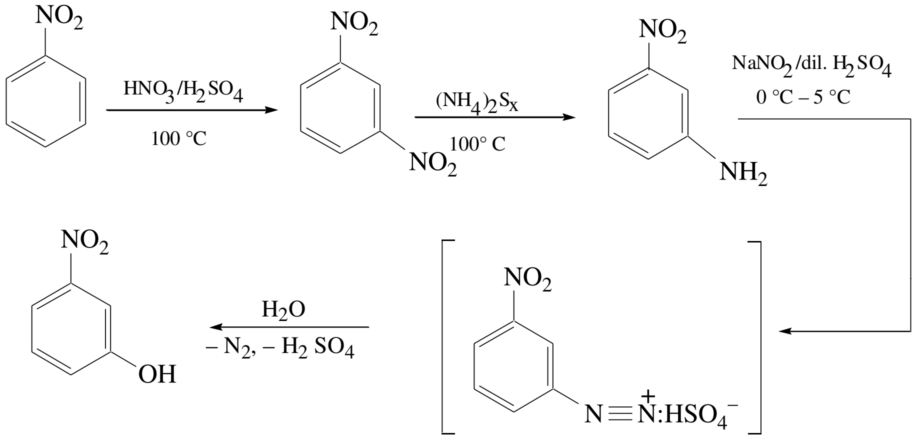


(not more than 3 steps)



91. Convert  in not more than 4 steps mentioning the reagents, reaction conditions and intermediates in the above conversion. (2004)

The given conversion can be carried out as follows.



diazonium salt
(an intermediate compound)

92. Write down the reactions involved in the preparation of the following using the reagents indicated against each in paranthesis

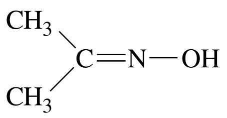
(i) Ethylbenzene from benzene [C_2H_5OH, PCl_5, anhydrous $AlCl_3$]
(ii) Propanoic anhydride from propanol [$AgNO_3/NH_4OH$, P_2O_5]
(iii) Acetoxime from acetaldehyde [$K_2Cr_2O_7/H^+$, $Ca(OH)_2$ and $NH_2OH.HCl$] (1984)

(i) $C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$

$C_6H_6 + C_2H_5Cl \xrightarrow[AlCl_3]{} C_6H_5C_2H_5 + HCl$

(ii) $C_3H_7OH \xrightarrow{AgNO_3/NH_4OH} C_2H_5COOH$; $2C_2H_5COOH \xrightarrow[\Delta]{P_2O_5} (C_2H_5CO)_2O$

(iii) $CH_3CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$; $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$



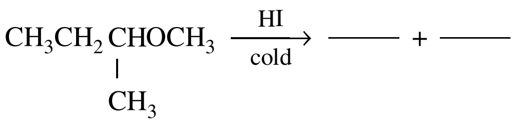
$(CH_3COO)_2Ca \xrightarrow{heat} CH_3COCH_3 + CaCO_3$; $CH_3COCH \xrightarrow{NH_2OH} (CH_3)_2C{=}N{-}OH$

Completing the Reactions

1. $HC{\equiv}CH + CH_3CO_2H \xrightarrow{Hg^+}$ —— $\xrightarrow[Hg^{2+}]{CH_3CO_2H}$ ——

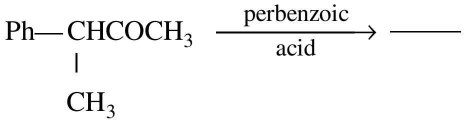
2. $HC{\equiv}CH + HOCl \rightarrow$ —— $\xrightarrow{HOCl}$ ——

3. $CH_3CHO \xrightarrow{NaOH}$ —— $\xrightarrow{heat}$ —— $\xrightarrow{H_2/Ni}$ ——

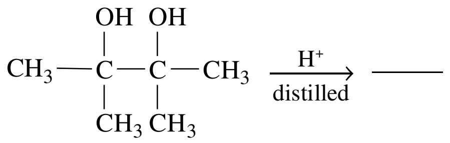
4. 
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_3 \xrightarrow[cold]{HI}$ —— + ——

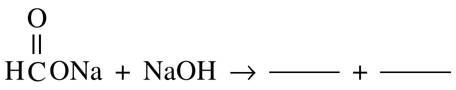
5. $CH_3COCH_3 \overset{HCl}{\rightleftharpoons}$ —— $\overset{CH_3COCH_3}{\rightleftharpoons}$ ——

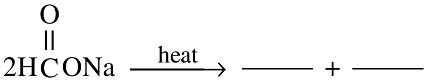
6. $RCOR \xrightarrow[acid]{perbenzoic}$ —— $\xrightarrow{H}$ —— + ——

7. 
$Ph{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCH_3 \xrightarrow[acid]{perbenzoic}$ ——

8. $C_6H_5CHO + HCHO \xrightarrow{NaOH}$ —— + ——

9. 
$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}{-}\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}{-}CH_3 \xrightarrow[distilled]{H^+}$ ——

10. 
$H\overset{\displaystyle O}{\overset{\|}{C}}ONa + NaOH \rightarrow$ —— + ——

11. 
$2H\overset{\displaystyle O}{\overset{\|}{C}}ONa \xrightarrow{heat}$ —— + ——

12. $CH_2{=}C{=}O + CH_3CO_2H \rightarrow$ ——

13. $CH_3CHO + (CH_3CO)_2O \rightarrow$ ——

14. $CH_2{=}CHCOOH + \underset{\text{in acetic acid}}{HBr} \rightarrow$ ——

15. $CH_2ClCH_2CH_2COOH \xrightarrow[reflux]{NaOH}$ ——

16. $\underset{vapour}{CH_3CHO} + \underset{vapour}{HCHO} \xrightarrow[silicate]{sodium}$ —— + ——

17. $CH_3CH{=}CHCHO \xrightarrow{LiAlH_4}$ ——

18. $HCHO + CH_3COCH_3 \xrightarrow{NaOH}$ —— $\xrightarrow{-H\ O}$ ——

19. $CH_2{=}CH_2 + (CH_3CO)_2O \xrightarrow{ZnCl_2}$ —— + ——

20. $RCHO + CH_2(CO_2C_2H_5)_2 \xrightarrow{pyridine}$ —— $\xrightarrow[2.\ HCl]{1.\ KOH}$ $\xrightarrow{heat}$ —— + ——

21. $CH_2{=}CHCH_2Br \xrightarrow{CuCN}$ —— $\xrightarrow{NaOH}$ [——] $\xrightarrow{NaOH}$ ——

22. $RCOOH + NH_3 \rightarrow$ —— $\xrightarrow{Al_2O_3}$ —— + —— $\xrightarrow{Al_2O_3}$ —— + ——

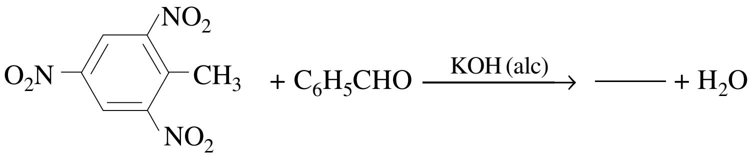
23. $RCN + R'MgX \longrightarrow$ —— $\xrightarrow{H_2O}$ ——

24. $RX + KCN \rightarrow$ —— + ——

25. $RI + AgCN \rightarrow$ —— + ——

26. $RNH_2 + CHCl_3 + 3KOH \rightarrow$ —— + —— + ——

27. $C_6H_5COCH_3 + CH_3MgI \rightarrow$ —— $\xrightarrow{H^+}$ —— $\xrightarrow{heat}$ —— $\xrightarrow{H_2/Ni}$ ——

28. 

29. $C_6H_5OH + RCOCl \rightarrow HCl +$ ——— $\xrightarrow[60°C]{AlCl_3}$ ———

30. $C_6H_5OH + RCOCl \rightarrow HCl +$ ——— $\xrightarrow[160°C]{AlCl_3}$ ———

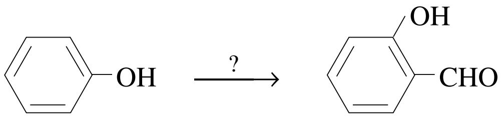
31. $C_6H_5CH_3 \xrightarrow[(CH_3CO)_2O]{Cr_2O_3}$ ——— $\xrightarrow{H^+}$ ——— + ———

32. $C_6H_5CHO + CH_3COCH_3$ ——— $+ H_2O \xrightarrow{C_6H_5CHO}$ ——— $+ H_2O$

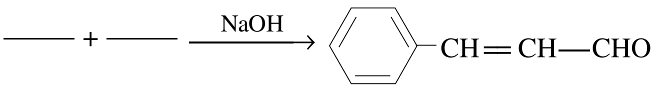
33. $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH\cdot CO\ Na}$ ———

34. $C_6H_5CH{=}CHCOOH \xrightarrow{LiAlH_4}$ ———

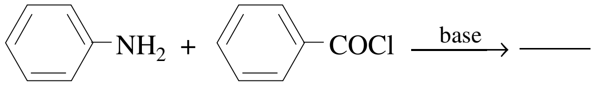
35. $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH +$ ——— (1986)

36. 

(1986)

37. 

(1986)

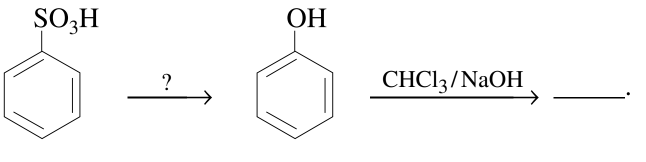
38. 

(1986)

39. $H_3CCHO \xrightarrow{CH_3MgBr} ? \longrightarrow H_3C{-}\underset{H}{\overset{OH}{C}}{-}CH_3$ (1988)

40. $CH_3COOH \xrightarrow{?} ClCH_2COH \xrightarrow[excess]{NH_3}$ ———. (1988)

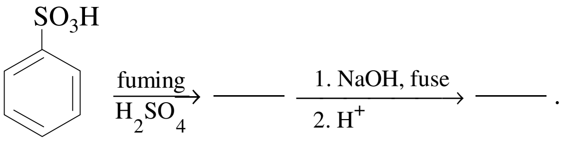
41. $2\ CH_3COCH_3 \xrightarrow{base}$ ——— $\xrightarrow{acid}$ ——— . (1988)

42. 

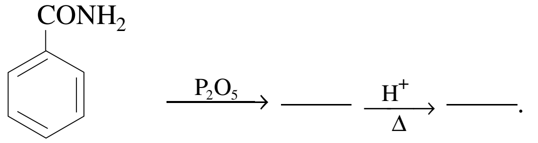
(1988)

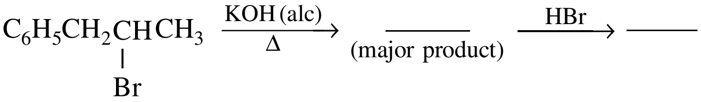
43. $C_6H_5COOH \xrightarrow{PCl_5}$ ——— $\xrightarrow{NH_3}$ ——— $\xrightarrow{P_2O_5}$ ——— $\xrightarrow{H_2/Ni}$ ——— (1991)

44. $H_3C{-}CH{=}CH{-}CHO \xrightarrow{NaBH_4}$ ——— $\xrightarrow[ZnCl_2]{HCl}$ ——— $\xrightarrow[H^+]{KCN}$ ———. (1991)

45. 

(1992)

46.  (1992)

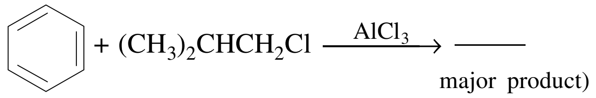
47. 

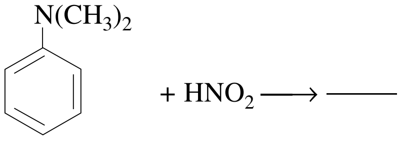
$$\underset{\displaystyle\text{Br}}{C_6H_5CH_2CHCH_3} \xrightarrow[\Delta]{\text{KOH (alc)}} \underset{\text{(major product)}}{\text{———}} \xrightarrow{\text{HBr}} \text{———}$$

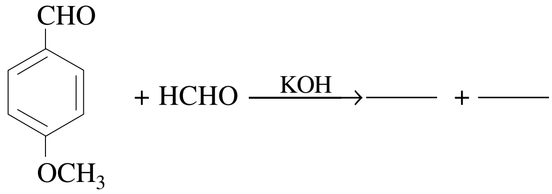
(1992)

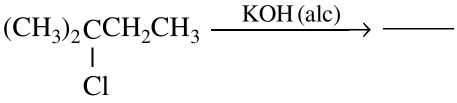
48. $C_6H_5COOC_6H_5 \xrightarrow[\text{mononitration}]{HNO_3/H_2SO_4}$. ——— (1993)

49. $C_6H_5COOH + CH_3MgI \longrightarrow$ ——— + ——— (1993)

50. 

51.  (1992)

52.  (1992)

53. 

$$\underset{\displaystyle\text{Cl}}{(CH_3)_2CCH_2CH_3} \xrightarrow{\text{KOH (alc)}} \text{———}$$

(1992)

54. $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}}$ ——— (1992)

55. $C_6H_5CH_2CO_2CH_3 \xrightarrow[\text{excess}]{CH_3MgBr}$ ——— $\longrightarrow$ ——— $\xrightarrow{H^+}$ ———

(1994)

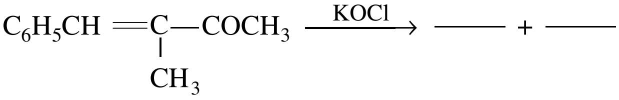
56. $C_6H_5CH_2CH_3 \xrightarrow[\text{heat, light}]{Br_2}$ ——— $\xrightarrow{\text{NaCN}}$ ———. (1994)

57. $CH_3CH_2COOH \xrightarrow[Br_2]{P}$ ——— $\xrightarrow[\text{2. }H^+]{\text{1. alc. KOH}}$ ——— (1995)

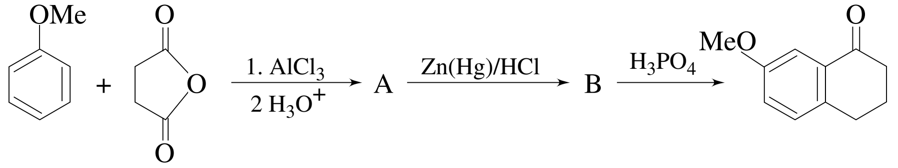
58. 2, 4-dinitroaniline $\xrightarrow[\text{((i) anisol}]{\text{1. }NaNO_2 + HCl\text{ at }5°C}$ ——— (1995)

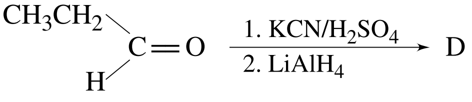
59. $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH\text{ and heat}]{NaOC_2H_5\text{ in absolute}}$ ——— (1995)

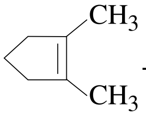
60. *o*-HOOC $C_6H_4CH_2C_6H_5 \xrightarrow{SOCl_2}$ ——— $\xrightarrow[AlCl_3]{\text{anhydrous}}$ ——— $\xrightarrow[HCl]{Zn-Hg}$ ——— (1995)

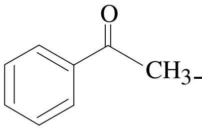
61. 

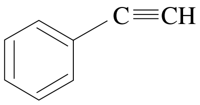
$$C_6H_5CH{=}\underset{\displaystyle CH_3}{C}{-}COCH_3 \xrightarrow{\text{KOCl}} \text{———} + \text{———}$$

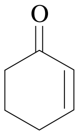
62.  (1996)

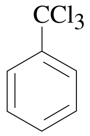
63.  (1996)

64.  $\xrightarrow{\text{dil. KMnO}_4} A \xrightarrow{\text{HIO}_4} B \xrightarrow{\text{HO}^-} C$ (1996)

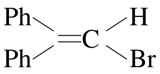
65.  $\xrightarrow{\text{Br}_2\text{(1 equivalent)}} A \xrightarrow{\text{NaBH}_4} B \xrightarrow{\text{Base}} C$ (1997)

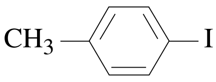
66.  $\xrightarrow{\text{1. HgSO}_4\text{, H}_3\text{O}^+} A \xrightarrow{\text{NH}_2\text{OH}} B + C$ (1997)

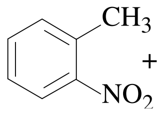
67.  $\xrightarrow[\text{2. aq HCl}]{\text{1. Me MgBr}} A$ (1997)

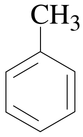
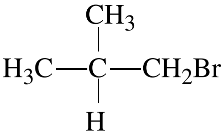
68.  $\xrightarrow{\text{Cl}_2\text{/Fe}} A$ (1997)

69. $\text{PhC}\equiv\text{CH} \xrightarrow[\text{MeI}]{\text{NaNH}_2} A \xrightarrow{\text{Na/NH}_3\text{(l)}} B$ (1997)

70.  $+ \text{KNH}_2 \longrightarrow A$ (1997)

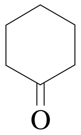
71.  $+ \text{Cu} \xrightarrow[\text{heat}]{} A$ (1997)

72.  $+ \text{(COOEt)}_2 + \text{EtONa} \longrightarrow A$ (1997)

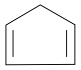
73.  + 

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2\text{Br}$$

$\xrightarrow{\text{AlCl}_3} A$ (1997)

74.  $+ \text{Ph}_3\text{P}=\text{CH}_2 \longrightarrow E$ (1997)

75. $\text{(COOH)}_2 + \text{(CH}_2\text{OH)}_2 \xrightarrow[\text{conc. H}_2\text{SO}_4]{} F$ (1997)

76.  $+ \text{CHBr}_3 \xrightarrow{\text{t-BuOK}} A$ (1997)

77. $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COPh} \xrightarrow[\text{KOH}]{\text{methanolic}} A$ (1997)

78. $\text{H}_3\text{C}-\text{CO}-\text{CO}-\text{C}_6\text{H}_5 \xrightarrow{\text{NaOH/H}_3\text{O}^+} A$ (1997)

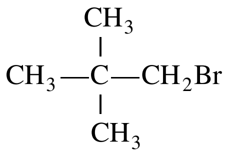
79. $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \xrightarrow{\text{Br}_2} A \xrightarrow[\text{2. CH}_3\text{I}]{\text{1. NaNH}_2\text{(3 equiv)}} B$ (1998)

80. $\text{C}_6\text{H}_5\text{CH}_2\text{CHClC}_6\text{H}_5 \xrightarrow[\text{heat}]{\text{alc. KOH}} A$ (1998)

81. $\text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow[\text{heat}]{\text{(CH}_3\text{CO)}_2\text{O}} A + B$ (1998)

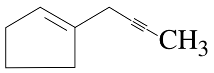
82. $\text{(CH}_3\text{)}_2\text{CHOCH}_3 \xrightarrow[\text{heat}]{\text{(HI) (excess)}} A + B$ (1998)

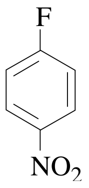
83. $\text{CH}_3\text{CONHC}_6\text{H}_5 \xrightarrow{\text{Br}_2\text{, Fe}} A + B$ (1998)

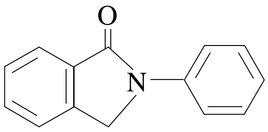
84. 

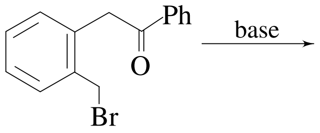
$$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2\text{Br} \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{———}$$

(2000)

85.  $\xrightarrow[\text{Lindlar catalyst}]{\text{H}_2}$ ——— (2000)

86.  $\xrightarrow[\Delta]{\text{NaOCH}_3}$ ——— (2000)

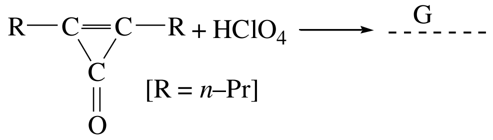
87.  $\xrightarrow[\text{(1 equv)}]{\text{Br}_2\text{/Fe}}$ (2000)

88. 

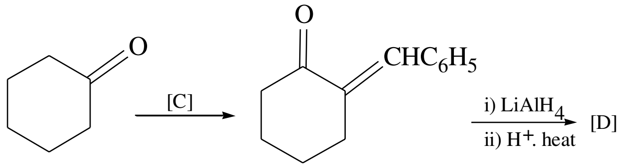
(2000)

89. $(CH_3CO)_2O + C_6H_5OH \xrightarrow[\text{base}]{} \text{—} + \text{—}$ (1982)

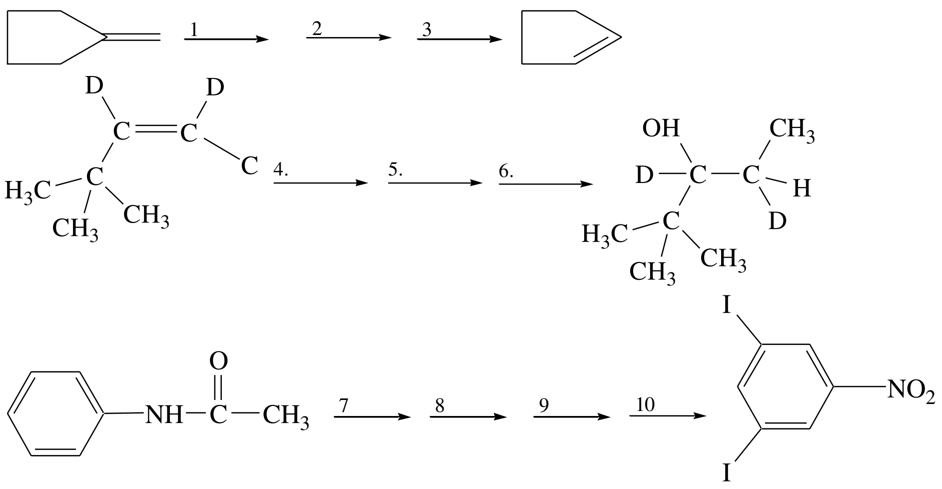
90. $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_5}$ (1994)

91. 

(1997)

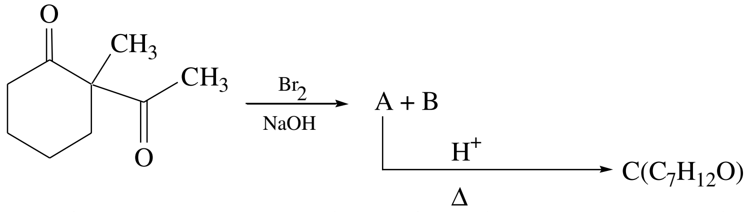
92. 

(1998)

93. 

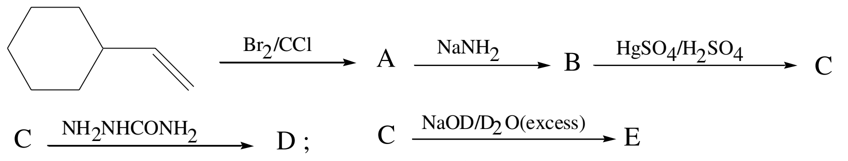
(1999)

94. Identify A, B and C, and give their structures.



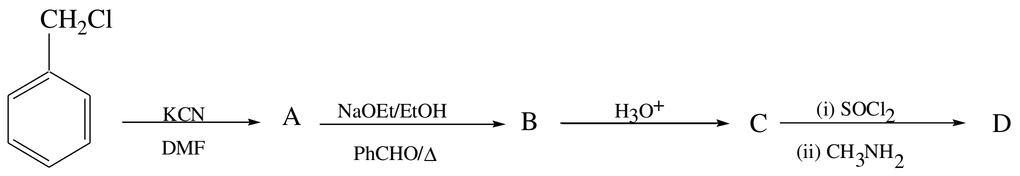
(2000)

95. Identify A, B, C, D, and E in the following schemes and write their structures:



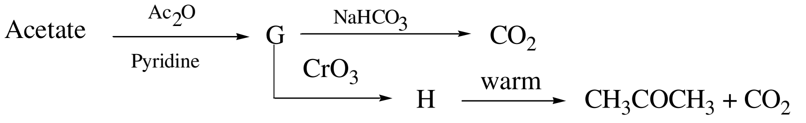
(2001)

96. Identify the compounds A to D in the following reactions.



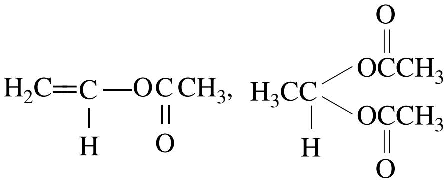
(2004)

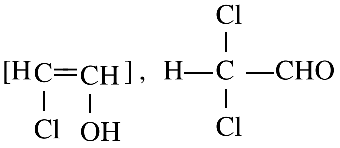
97. Write down the structure of G and H where G is $C_4H_8O_3$.

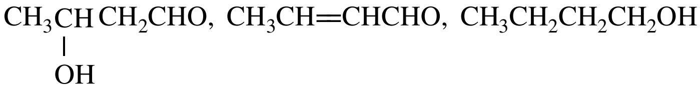


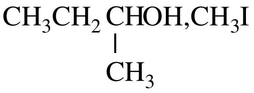
(1997)

ANSWERS

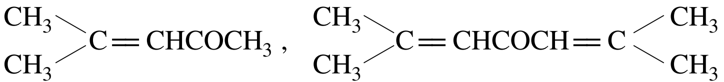
1. 
$H_2C{=}C(H){-}OCOCH_3$, $H_3CC(H)(OCOCH_3)_2$

2. 
$[HC(Cl){=}CH(OH)]$, $H{-}CCl_2{-}CHO$

3. 
$CH_3CH(OH)CH_2CHO$, $CH_3CH{=}CHCHO$, $CH_3CH_2CH_2CH_2OH$

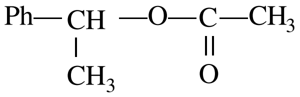
4. 
$CH_3CH_2CH(CH_3)OH, CH_3I$

4. In ethers, if one of the alkyl group is methyl, it always produces methyl iodide.

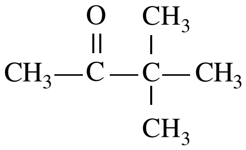
5. 
$(CH_3)_2C{=}CHCOCH_3$, $(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2$

mesityl oxide phorone

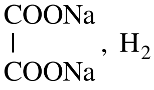
6. RCOOR, RCO_2H, ROH

7. 
$Ph{-}CH(CH_3){-}O{-}C({=}O){-}CH_3$

8. $C_6H_5CH_2OH$, HCO_2Na

9. 
$CH_3{-}C({=}O){-}C(CH_3)_2{-}CH_3$

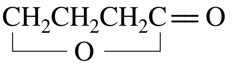
10. H_2, Na_2CO_3

11. 
$COONa{-}COONa$, H_2

12. $(CH_3CO)_2O$

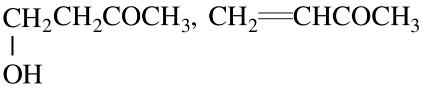
13. $CH_3CH(OCOCH_3)_2$ ethylidene acetate

14. $BrCH_2CH_2COOH$

15. 
, γ-butyrolactone

16. $CH_2{=}CHCHO$, H_2O

17. $CH_3CH{=}CHCH_2OH$

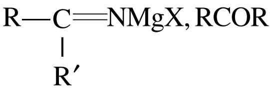
18. 
$CH_2(OH)CH_2COCH_3$, $CH_2{=}CHCOCH_3$

19. $CH_2{=}CHCOCH_3$, CH_3COOH

20. $RCH{=}C(CO_2C_2H_5)_2$, $RCH{=}C(COOH)_2$, $RCH{=}CHCOOH$, CO_2

21. $CH_2{=}CHCH_2CN$, $CH_2{=}CHCH_2COOH$, $CH_3CH{=}CHCOOH$

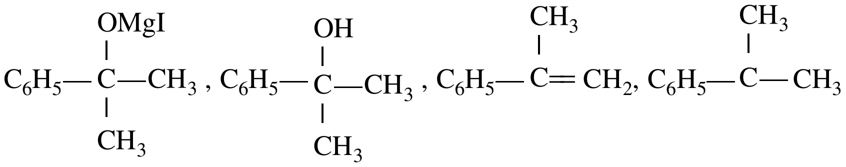
22. RCO_2NH_4, $H_2O + RCONH_2$, $H_2O + RCN$

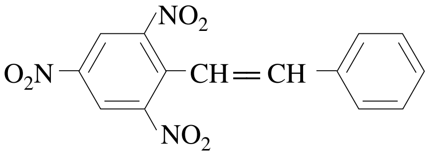
23. 
$R{-}C(R'){=}NMgX$, $RCOR'$

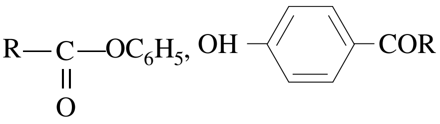
24. $R{-}C{\equiv}N$, KX

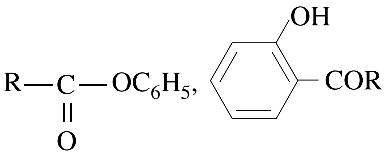
25. $R{\equiv}NC$, KI

26. RNC, 3KCl, $3H_2O$

27. 
$C_6H_5{-}C(OMgI)(CH_3){-}CH_3$, $C_6H_5{-}C(OH)(CH_3){-}CH_3$, $C_6H_5{-}C(CH_3){=}CH_2$, $C_6H_5{-}CH(CH_3){-}CH_3$

28. 

29. 

30. 

$R-\underset{\underset{O}{\|}}{C}-OC_6H_5$,

31. $C_6H_5CH(OCOCH_3)_2$, $C_6H_5CHO + CH_3COOH$

32. $C_6H_5CH{=}CHCOCH_3$, $C_6H_5CH{=}CHCOCH{=}CHC_6H_5$

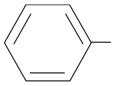
33. $C_6H_5CH{=}CHCO_2H$

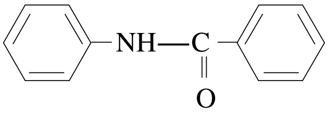
34. $C_6H_5CH_2CH_2CH_2OH$

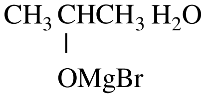
When a phenyl group is attached to the β-carbon atom of an α, β- unsaturated carbonyl compound, both the double bond and carbonyl group are reduced by $LiAlH_4$.

35. $CH_3COOC_2H_5$.

36. $CHCl_3 + NaOH$

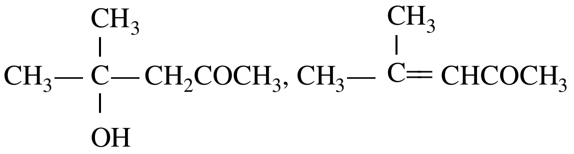
37.  , CH_3CHO

38. 

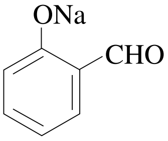
39. 

$\underset{\underset{OMgBr}{|}}{CH_3CHCH_3}$ H_2O

40. P/Cl_2, H_2NCH_2COOH

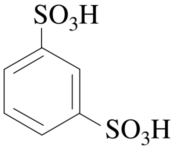
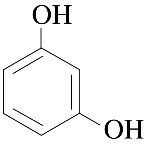
41. 

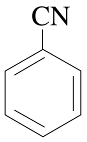
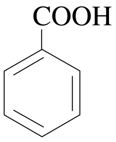
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2COCH_3$, $CH_3-\overset{\overset{CH_3}{|}}{C}{=}CHCOCH_3$

42. fusion with NaOH followed by H^+, 

43. C_6H_5COCl, $C_6H_5CONH_2$, C_6H_5CN, $C_6H_5CH_2NH_2$

44. $H_3C-CH{=}CH-CH_2OH$, $CH_3-CH{=}CH-CH_2Cl$, $CH_3-CH{=}CH-CH_2COOH$

45.  , 

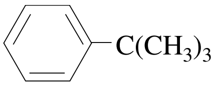
46.  , 

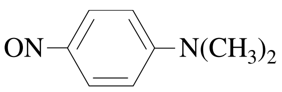
47. $C_6H_5CH{=}CHCH_3$, 

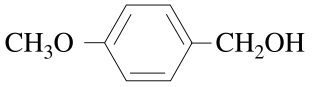
$\underset{\underset{Br}{|}}{C_6H_5CH}\,CH_2CH_3$

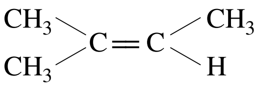
48. $C_6H_5COOC_6H_4NO_2$ (*para*)

49. $CH_4 + C_6H_5COOMgBr$

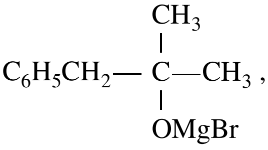
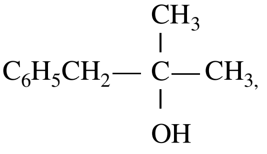
50. 

51. 

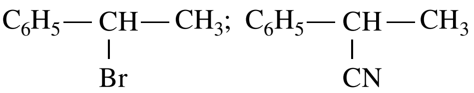
52.  + HCOOK

53. 

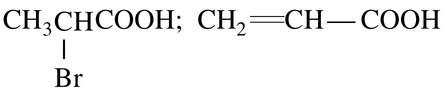
54. CH_3CH_2CHO

55. $C_6H_5CH_2COCH_3$,  , 

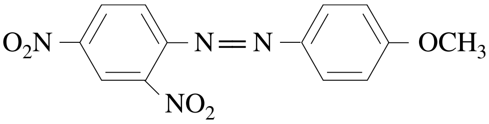
$C_6H_5CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OMgBr}{|}}{C}}-CH_3$, $C_6H_5CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$,

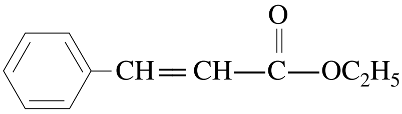
56. 

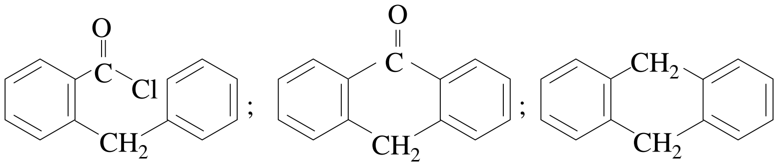
$C_6H_5-\underset{\substack{|\\ Br}}{CH}-CH_3;\ C_6H_5-\underset{\substack{|\\ CN}}{CH}-CH_3$

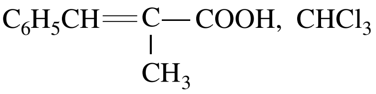
57. 

$CH_3\underset{\substack{|\\ Br}}{CH}COOH;\ CH_2=CH-COOH$

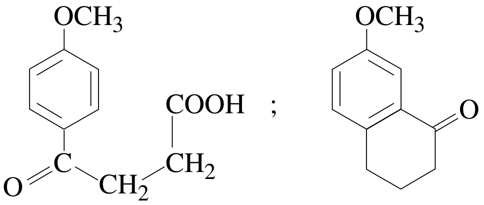
58. 

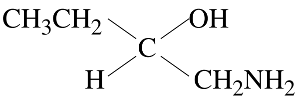
59. 

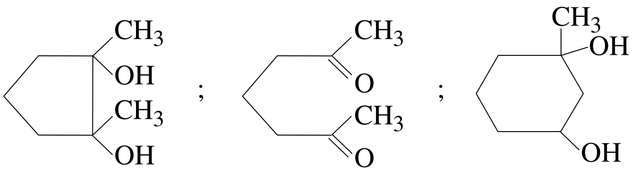
60. 

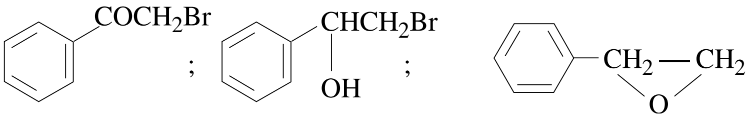
61. 

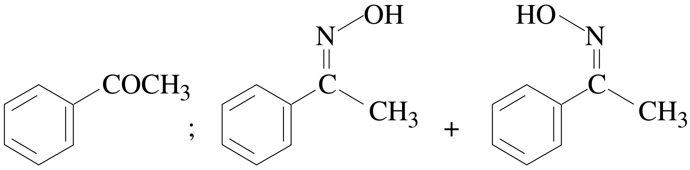
$C_6H_5CH=\underset{\substack{|\\ CH_3}}{C}-COOH,\ CHCl_3$

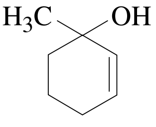
62. 

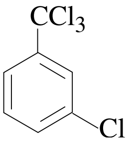
63. 

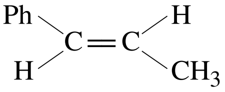
64. 

65. 

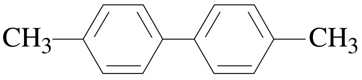
66. 

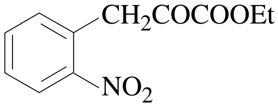
67. 

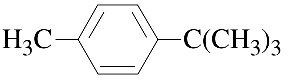
68. 

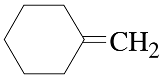
69. $PhC\equiv CCH_3;$ 

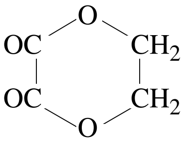
70. $Ph-C\equiv C-Ph$

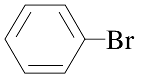
71. 

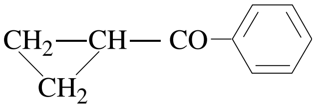
72. 

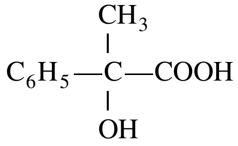
73. 

74. 

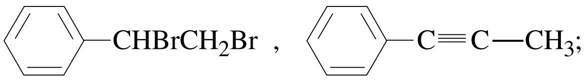
75. 

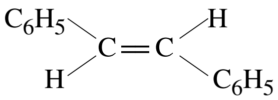
76. 

77. 

78. 

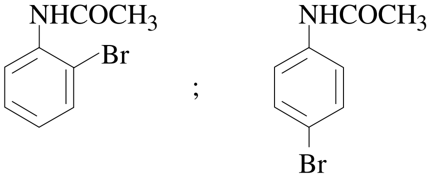
$$C_6H_5-\underset{OH}{\overset{CH_3}{C}}-COOH$$

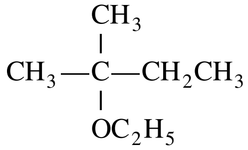
79. 

80. 

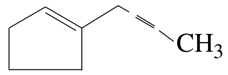
81. $CH_3CH_2NHCOCH_3$, CH_3COOH

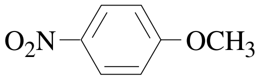
82. CH_3CHICH_3, CH_3I

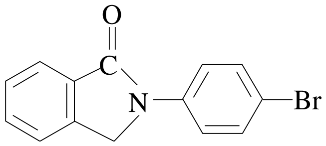
83. 

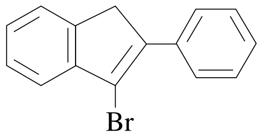
84. 

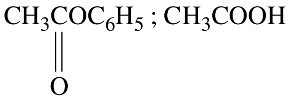
$$CH_3-\underset{OC_2H_5}{\overset{CH_3}{C}}-CH_2CH_3$$

85. 

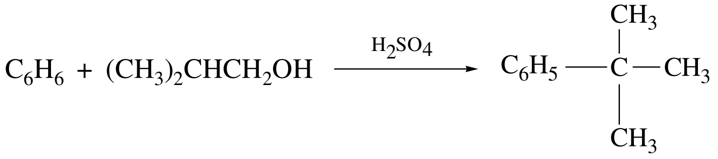
86. 

87. 

88. 

89. 

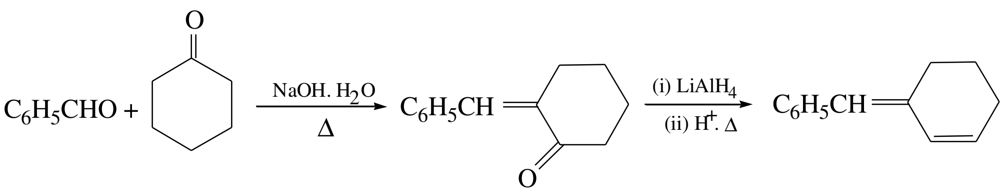
$CH_3\underset{O}{\underset{\|}{C}}OC_6H_5$; CH_3COOH

90. 

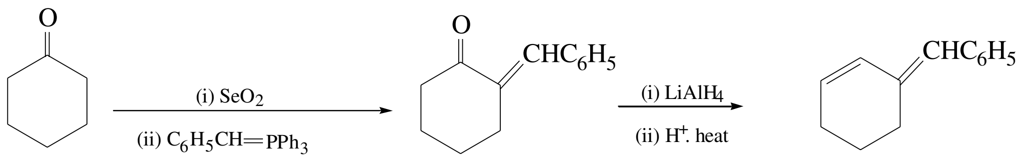
$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

2-methy1-2-phenylpropane

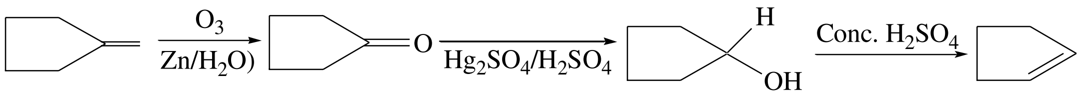
91. RCOOH

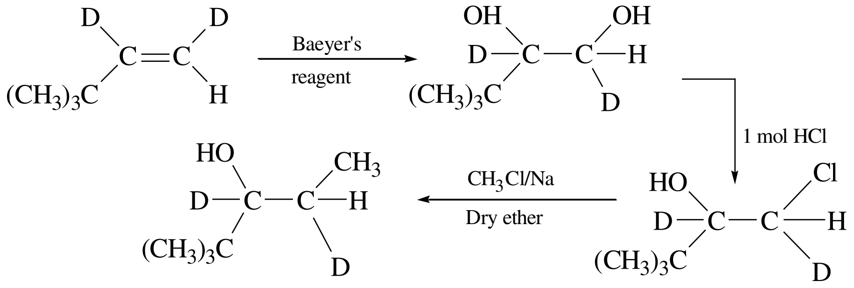
92. 

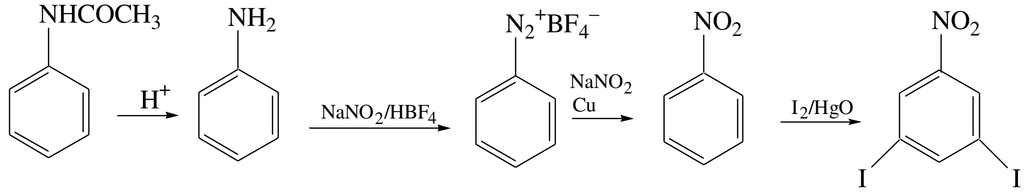
Alternatively, we may proceed as follows.



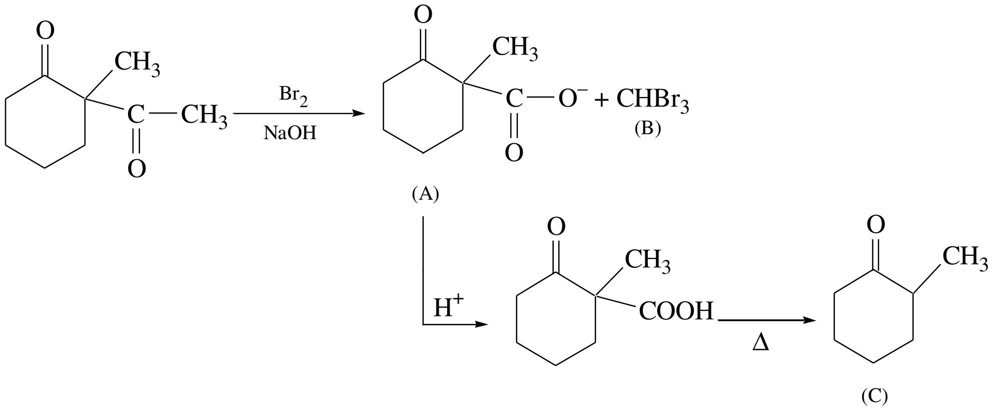
93.



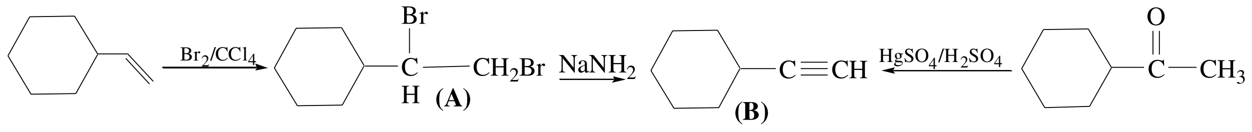


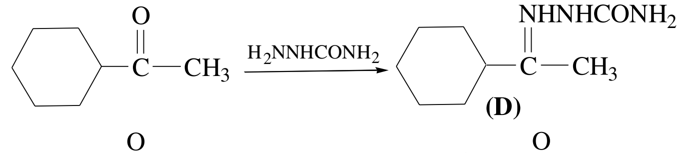


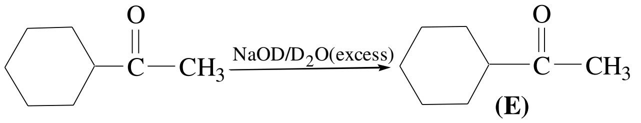
94.



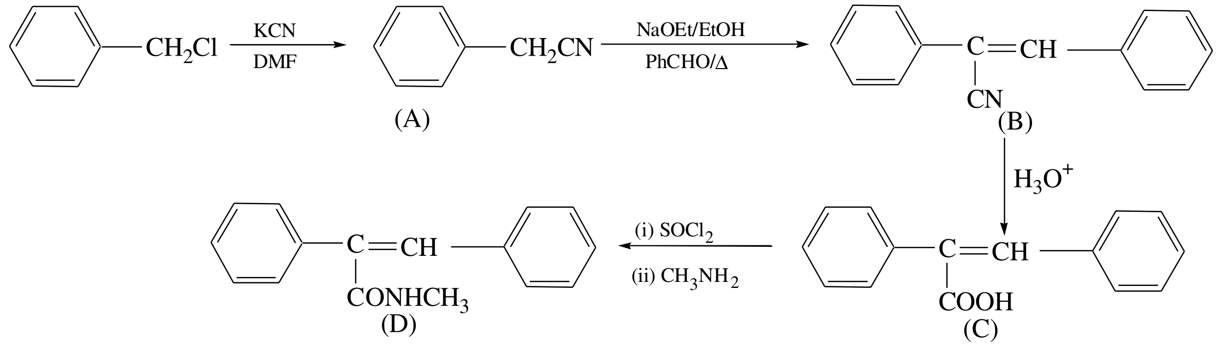
95.

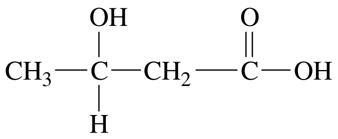




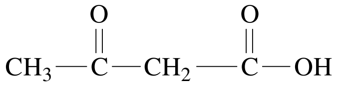


96. The sequence of reactions is follows.



97. G is 

$CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

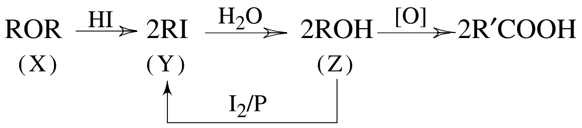
H is 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(III) SOLVED PROBLEMS

1. A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, X yields only one organic product Y. On hydrolysis Y yields a new compound Z which can be converted to Y by reaction with red phosphorus and iodine. The compound Z on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds X, Y and Z? Write chemical equations leading to the conversion of X to Y. (1981)

Solution Since the compound is unreactive towards sodium, it is neither alcohol (including phenol) nor carboxylic acid. It is also not an aldehyde. It may be a symmetrical ether because on refluxing with excess of HI, it gives only one product. Thus, we have



$$\underset{(X)}{ROR}\xrightarrow{HI}\underset{(Y)}{2RI}\xrightarrow{H_2O}\underset{(Z)}{2ROH}\xrightarrow{[O]}2R'COOH$$

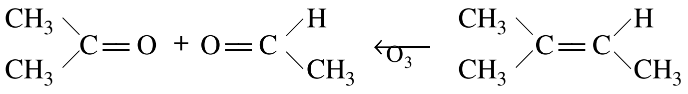
I_2/P

Now the equivalent weight of R′COOH is 60. From this, it follows that R′ is —CH_3 group and hence R is —CH_2CH_3 group. Thus, the compounds X, Y and Z are

X : $CH_3CH_2OCH_2CH_3$; Y : CH_3CH_2I; Z : CH_3CH_2OH

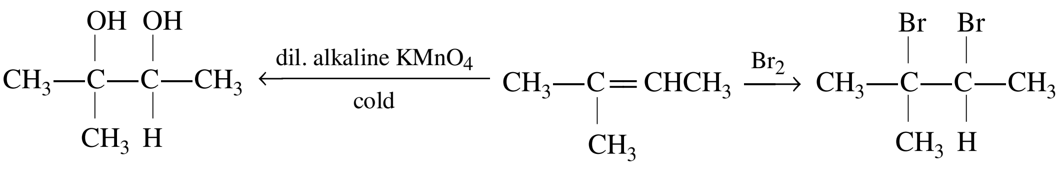
2. One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. Substance A on treatment with cold, dilute alkaline potassium permanganate solution forms a compound $C_5H_{12}O_2$. On ozonolysis, A gives equimolar quantities of propanone and ethanal. Deduce the structural formula of A. (1981)

Solution From the products of ozonolysis, we conclude that



propanone ethanal (A) 2-methylbut-2-ene

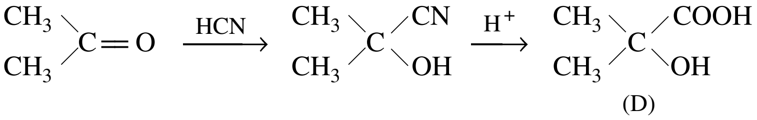
The compound A contains a double bond. This is also confirmed from the fact that the compound A reacts with one mole of bromine. Thus, the given reactions are



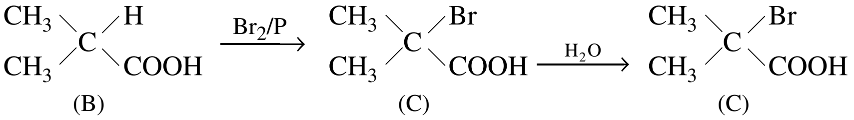
$$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3 \xleftarrow[\text{cold}]{\text{dil. alkaline KMnO}_4} CH_3-\underset{CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{Br_2} CH_3-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$$

3. An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with bromine in presence of phosphorus, it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D. (1982)

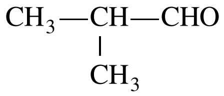
Solution The structure of compound D is easily deduced from the fact that it is obtained by the combination of acetone with hydrogen cyanide followed by hydrolysis.



The conversion B to C and then C to D indicates that the reaction B to C is Hell-Volhard-Zelinsky reaction. Thus, we have



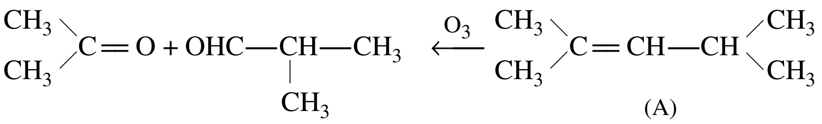
Hence, we conclude that the aldehyde from which compound B is obtained by oxidation has the structure



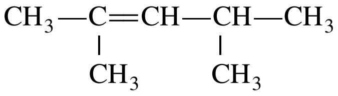
$$\underset{\displaystyle CH_3}{CH_3—\underset{|}{C}H—CHO}$$

2-methylpropanal

Now, the ozonolysis of the compound A gives acetone and 2-methyl-propanal, i.e.

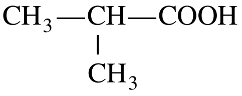


Hence, the compound A, B, C and D are

A: 

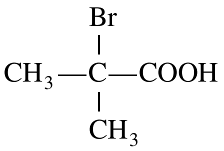
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CH—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_3$$

2, 4-dimethylpent-2-ene

B: 

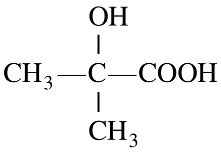
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}H}—COOH$$

2-methylpropanoic acid

C: 

$$CH_3—\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—COOH$$

2-bromo-2-methylpropanoic acid

D: 

$$CH_3—\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—COOH$$

2-hydroxy-2-methylpropanoic acid

4. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molar mass is 121 g mol^{-1}. Draw two possible structures for this compound. (1982)

Solution The reactions involved are

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$
$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Amount of sodium hydroxide to neutralize excess of sulphuric acid $= (25\ \text{mL})\left(\dfrac{0.1\ \text{mol}}{1000\ \text{mL}}\right) = \dfrac{1}{400}\ \text{mol}$

Amount of sulphuric acid neutralized with sodium hydroxide $= \dfrac{1}{2}\left(\dfrac{1}{400}\ \text{mol}\right) = \dfrac{1}{800}\ \text{mol}$

Amount of sulphuric acid taken to start with $= (50\ \text{mL})\left(\dfrac{0.05\ \text{mol}}{1000\ \text{mL}}\right) = \dfrac{1}{400}\ \text{mol}$

Amount of sulphuric acid neutralized by ammonia = $\left(\dfrac{1}{400}-\dfrac{1}{800}\right)\text{mol}=\dfrac{1}{800}\ \text{mol}$

Amount of ammonia evolved = $2\left(\dfrac{1}{800}\ \text{mol}\right)=\dfrac{1}{400}\ \text{mol}$

Mass of nitrogen in the evolved ammonia = $\left(\dfrac{1}{400}\ \text{mol}\right)(14\ \text{g mol}^{-1})=\dfrac{7}{200}\ \text{g}$

Per cent of nitrogen in the given aromatic compound = $\dfrac{(7/200)\ \text{g}}{0.303\ \text{g}}\times 100=11.6$

Per cent of oxygen in the given aromatic compound = 100 – (69.4 + 5.8 + 11.6) = 13.2
The ratios of atoms present in the given compound are

$$\text{C : H : N : O} \ :: \ \frac{69.4}{12}:\frac{5.8}{1}:\frac{11.6}{14}:\frac{13.2}{16}\ ::\ 5.8 : 5.8 : 0.83 : 0.83 :: 7 : 7 : 1 : 1$$

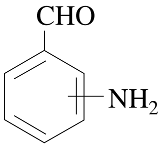
Hence, for the given compound, we have

Empirical formula = C_7H_7NO Empirical molar mass = 121 g mol^{-1}

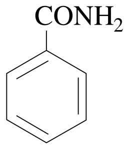
It is given that 121 g mol^{-1} is also the molar mass. Hence,

Molecular formula = C_7H_7NO

Since, the given compound is aromatic, the two possible structures are



and



5. An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983)

Solution The combustion reaction is $C_xH_{2y}O_y + x\,O_2 \rightarrow x\,CO_2 + y\,H_2O$

To start with, the amount of O_2 taken is $2x$. Hence, after the combustion reaction, we will be left with the following amounts.

Amount of oxygen left unreacted = x; Amount of carbon dioxide = x; Amount of water = y

When this mixture is cooled to 0 °C and 1 atm, we will be left with oxygen and carbon dioxide. Hence, the amount $2x$ occupies the given volume of 2.24 L at STP. Hence,

$$\text{Amount } x=\frac{(2.24/2)\ \text{L}}{22.4\ \text{L mol}^{-1}}=0.05\ \text{mol}$$

Now, Mass of water collected = 0.9 g Amount of water collected, $y=\dfrac{0.9\ \text{g}}{18\ \text{g mol}^{-1}}=0.05\ \text{mol}$

Thus, the empirical formula of the compound is $C_{0.05}H_{2\times 0.05}O_{0.05}$, i.e. CH_2O. Now, according to Raoult's law

$$-\frac{\Delta p}{p^*}=x_2 \quad \text{i.e.} \quad \frac{0.104\ \text{mmHg}}{17.5\ \text{mmHg}}=\frac{(50\ \text{g}/M)}{(50\ \text{g}/M)+(1000\ \text{g}/18\ \text{g mol}^{-1})}$$

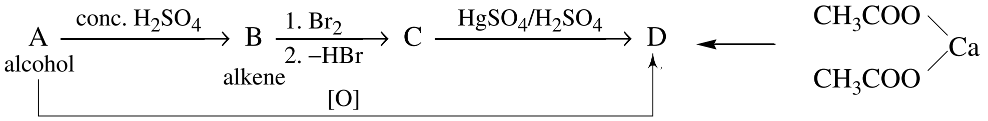
Solving for M, we get M = 150.5 g mol^{-1}

$$\text{Number of repeating units of CH}_2\text{O in the molecular formula}=\frac{150.5}{12+2+16}\simeq 5$$

Hence, Molecular formula of the compound is $C_5H_{10}O_5$.

6. An alcohol A, when heated with concentrated H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. D can also be obtained either by oxidizing A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D. (1983)

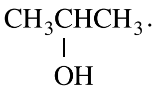
Solution The given reactions are as follows.



The reaction of obtaining D from calcium acetate is

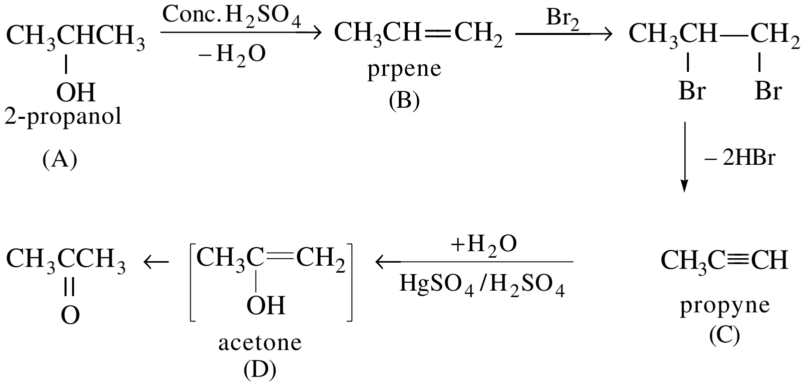
$$(CH_3COO)_2Ca \rightarrow \underset{(D)}{CH_3COCH_3} + CaCO_3$$

Hence, D is acetone. Since the latter is also obtained from the oxidation of alcohol A, compound A will be



$\underset{\displaystyle OH}{\overset{}{CH_3\underset{|}{C}HCH_3}}$.

Hence, the reactions depicted above are as follows.



7. A certain hydrocarbon A was found to contain 85.7 per cent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.0 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by mass) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula C_4H_8O) and compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of A and deduce the structures A, B and C. (1984)

Solution The ratio of atoms in the compound A is $C : H : : \frac{85.7}{12} : \frac{14.3}{1} : : 7.14 : 14.3 : : 1 : 2$

Thus, Empirical formula of A is CH_2.

Since the compound A consumes 1 mol of hydrogen, the molecule of A contains only one carbon-carbon double bond. From the data on the absorption of bromine, we can calculate the molar mass of A as shown in the following.

$$\text{Mass of bromine absorbed by 1.0 g of hydrocarbon} = \frac{5}{100} \times 38.05 \text{ g}$$

$$\text{Mass of hydrocarbon absorbing 160 g (= 1 mol) of } Br_2 = \frac{1.0}{(5 \times 38.05/100)} \times 160 \text{ g} = 84.1 \text{ g.}$$

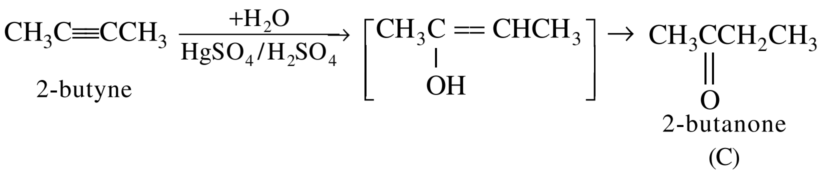
Hence, Molar mass of A is 84.1 g mol^{-1}.

The number of repeating CH_2 group in one molecule of A will be 6(= 84.1/14). Hence,

Molecular formula of A is C_6H_{12}. Now, it is given that

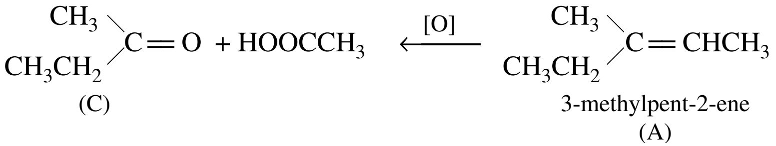
$$\underset{(A)}{C_6H_{12}} \xrightarrow{\text{conc. } KMnO_4} \underset{(C)}{C_4H_8O} + CH_3COOH$$

The compound C is obtained by the hydration of 2-butyne. Hence, its structure obtained from the reaction is



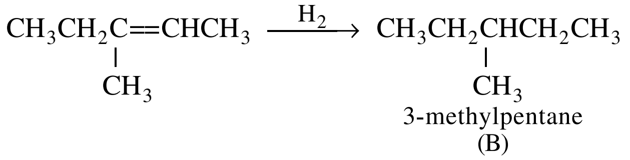
$$\underset{\text{2-butyne}}{CH_3C{\equiv}CCH_3} \xrightarrow[HgSO_4/H_2SO_4]{+H_2O} \left[\underset{\displaystyle OH}{CH_3\underset{|}{C}} = CHCH_3\right] \rightarrow \underset{\substack{\text{2-butanone}\\ (C)}}{CH_3\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_3}$$

Finally, the structure of A would be



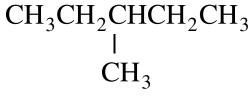
$$\underset{\text{(C)}}{\overset{CH_3}{\underset{CH_3CH_2}{>}}C{=}O} + HOOCCH_3 \xleftarrow{[O]} \underset{\substack{\text{3-methylpent-2-ene}\\ \text{(A)}}}{\overset{CH_3}{\underset{CH_3CH_2}{>}}C{=}CHCH_3}$$

The structure of B is

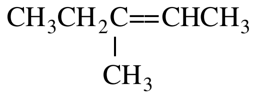


$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3 \xrightarrow{H_2} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_3$$

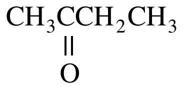
3-methylpentane
(B)

Hence, Molecular formula of A is C_6H_{12} Structure of B is  $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_3$

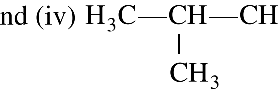
3-methylpentane

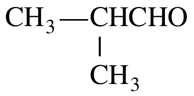
Structure of A is  $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3$

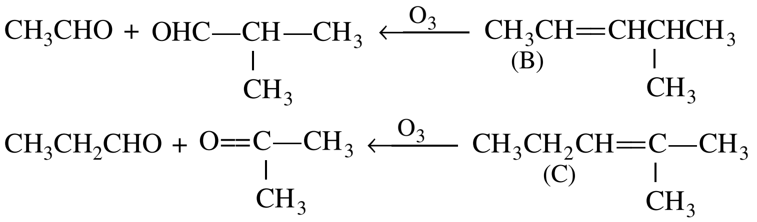
3-methylpent-2-ene

Structure of C is  $CH_3\underset{\displaystyle O}{\underset{\|}{C}}CH_2CH_3$

2-butanone

8. A white precipitate was formed slowly when silver nitrate was added to compound A with molecular formula $C_6H_{13}Cl$. Compound A on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes B and C, having formula C_6H_{12}. The mixture of B and C on ozonolysis, furnished four compounds: (i) CH_3CHO, (ii) C_2H_5CHO, (iii) CH_3COCH_3 and (iv)  $H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CHO$. What are the structures of A, B and C? (1986)

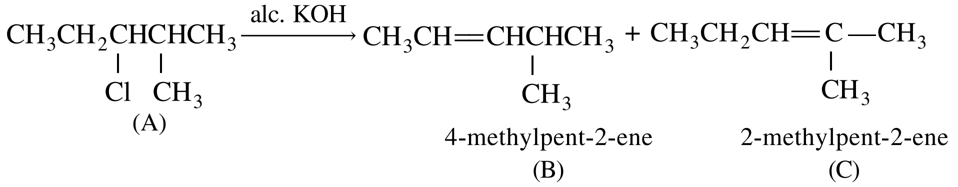
Solution Since during ozonolysis, no loss of carbon occurs, we conclude that CH_3CHO and  $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}CHO$ are the products of one of the compounds (say, B) and C_2H_5CHO and CH_3COCH_3 are the products of the other compound (i.e. C). Thus, we have



$$CH_3CHO + OHC{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3 \xleftarrow{O_3} \underset{\text{(B)}}{CH_3CH{=}CH}\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_3$$

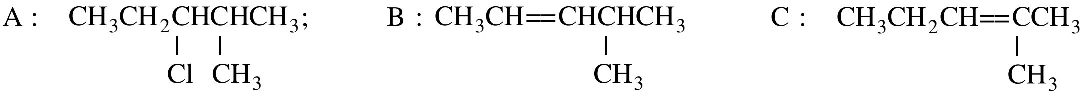
$$CH_3CH_2CHO + O{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xleftarrow{O_3} \underset{\text{(C)}}{CH_3CH_2CH}{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$$

Since the compounds B and C are obtained when A is treated with hot alocholic potassium hydroxide, we will have



$$\underset{\text{(A)}}{CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}H}\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_3} \xrightarrow{\text{alc. KOH}} \underset{\substack{\text{4-methylpent-2-ene}\\ \text{(B)}}}{CH_3CH{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_3} + \underset{\substack{\text{2-methylpent-2-ene}\\ \text{(C)}}}{CH_3CH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3}$$

Since the chlorine atom in A is an aliphatic chlorine, it will be slowly precipitated with silver nitrate. Hence, the structures of A, B and C are



A : $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}H}\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_3$; B : $CH_3CH{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_3$ C : $CH_3CH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_3$

3-chloro-2-methylpentane 4-methylpent-2-ene 2-methylpent-2-ene

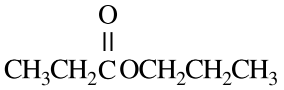
9. A liquid X, having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid, Y, and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z? (1986)

Solution Since the hydrolysis of X gives a carboxylic acid (Y) and an alcohol (Z), the compound X must be an ester. Let it be RCOOR′. The compounds Y and Z will be RCOOH and R′OH, respectively, Since the oxidation of Z gives Y, we will have

$$R'OH \xrightarrow{[O]} RCOOH \quad \text{or} \quad RCH_2OH \xrightarrow{[O]} RCOOH$$

Hence, the given compound X may be written as $RCOOCH_2R$. From this it follows that

$$2R \equiv C_6H_{12}O_2 - C_2H_2O \equiv C_4H_{10} \quad \text{or} \quad R \equiv C_2H_5$$



$$X : CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2CH_3 \quad \text{Propylpropanate} \qquad Y : CH_3CH_2COOH \quad \text{Propanoic acid}$$

$$Z : CH_3CH_2CH_2OH \quad \text{Propanol}$$

10. An unknown compound of carbon, hydrogen, and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molar mass of 86 g mol^{-1}. It does not reduce Fehling's solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures? (1987)

Solution The given compound is a ketone as it does not reduce Fehling's solution, but forms a bisulphite addition compound. It will also contain CH_3CO group as it shows positive iodoform test.

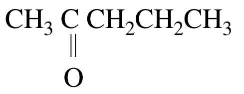
The ratios of atoms in the compound are

$$C : O : H :: \frac{69.77}{12} : \frac{18.60}{16} : \frac{11.63}{1} :: 5.81 : 1.16 : 11.63 :: 5 : 1 : 10$$

Hence Empirical formula is $C_5H_{10}O$. Molar empirical mass = 86 g mol^{-1}; same as the given molar mass

Thus, Molecular formula is $C_5H_{10}O$.

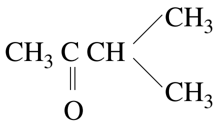
The structure of the compound will be



$$CH_3\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$

2-pentanone

or



3-methylbutan-2-one

11. An organic compound A on treatment with acetic acid in the presence of sulphuric acid produces an ester B. The compound A on mild oxidation gives C. The compound C with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates A and D. The compound D with phosphorus pentachloride followed by reaction with ammonia gives E. The compound E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E. (1987)

Solution The given reactions are

$$A + CH_3COOH \xrightarrow{H_2SO_4} \underset{(B)}{\text{ester}}; \qquad A \xrightarrow[\text{oxidation}]{\text{mild}} C \xrightarrow{50\%\ KOH} A + D$$

$$D \xrightarrow{PCl_5} \xrightarrow{NH_3} E \xrightarrow{-H_2O} HCN$$

The reaction $C \xrightarrow{50\%\ KOH} A + D$ is a Cannizzaro reaction and thus the compound C is an aldehyde with no α-hydrogen, C must be HCHO. From this it follows that A must be CH_3OH as its mild oxidation gives HCHO.

With this fact, we can write the given reactions as shown below.

$$\underset{(A)}{CH_3OH} + CH_3COOH \rightarrow \underset{\underset{(B)}{\text{methyl acetate}}}{CH_3COOCH_3}; \qquad \underset{[A]}{CH_3OH} \xrightarrow{[O]} HCHO \xrightarrow{50\%\ KOH} \underset{(A)}{CH_3OH} + \underset{(D)}{HCOOH}$$

$$HCOOH \xrightarrow{PCl_5} HCOCl \xrightarrow{NH_3} HCONH_2 \xrightarrow{-H_2O} HCN$$

Hence,

A : CH_3OH	methanol	B : CH_3COOCH_3	methylethonate
C : HCHO	methanal	D : HCOOH	methanoic acid
E : $HCONH_2$	methanamide		

12. An organic compound A, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B. (1988)

Solution The ratios of atoms present in the molecule are

$$\mathrm{C : H : N : O} :: \frac{49.32}{12} : \frac{9.59}{1} : \frac{19.18}{14} : \frac{21.91}{16} :: 4.11 : 9.58 : 1.37 : 1.37 :: 3 : 7 : 1 : 1$$

Hence, Empirical formula; C_3H_7NO.

Since A on boiling with NaOH gives of NH_3 and salt of monobasic nitrogen free acid, the compound A must be an amide. Let it be $RCONH_2$. The reaction is

$$\mathrm{RCONH_2} \xrightarrow{\mathrm{NaOH}} \underset{\text{(B)}}{\mathrm{RCOONa}} + \mathrm{NH_3}; \qquad \mathrm{RCOONa} \xrightarrow{\mathrm{H^+}} \mathrm{RCOOH}$$

Let M be the molar mass of RCOO. From the data on silver salt, we get

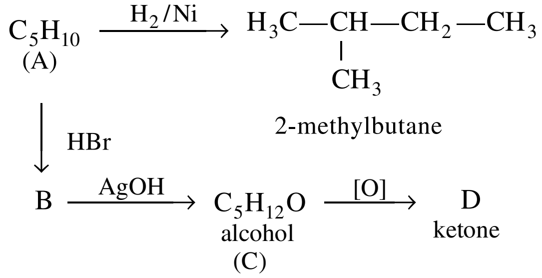
$$\frac{M_{\mathrm{Ag}}}{M_{\mathrm{Ag}} + M_{\mathrm{RCOO}}} \times 100 = 59.67 \quad \text{or} \quad M_{\mathrm{RCOO}} = M_{\mathrm{Ag}} \left(\frac{0.4033}{0.5967}\right) = (108 \text{ g mol}^{-1}) \left(\frac{0.4033}{0.5967}\right) = 73 \text{ g mol}^{-1}.$$

$$\text{Molar mass of R} = (73 - 12 - 32) \text{ g mol}^{-1} = 29 \text{ g mol}^{-1}$$

Hence, the alkyl group R is C_2H_5 and the compounds A and B are $C_2H_5CONH_2$ and C_2H_5COOH, respectively.

13. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markovnikov's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the structures A, B, C and D and show the reactions involved. (1988)

Solution The given reactions are



$$\underset{\text{(A)}}{C_5H_{10}} \xrightarrow{H_2/\mathrm{Ni}} \underset{\text{2-methylbutane}}{\mathrm{H_3C{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}CH_3}}$$

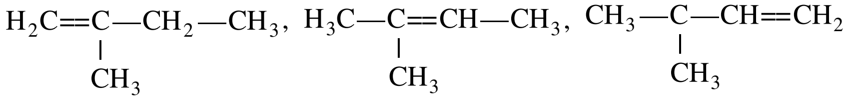
$$\big\downarrow \mathrm{HBr}$$

$$\mathrm{B} \xrightarrow{\mathrm{AgOH}} \underset{\substack{\text{alcohol}\\ \text{(C)}}}{C_5H_{12}O} \xrightarrow{[\mathrm{O}]} \underset{\text{ketone}}{\mathrm{D}}$$

The compound C must be a secondary alcohol as it gives ketone on oxidation.

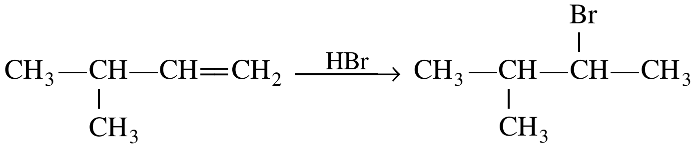
The compound B will be a secondary bromo derivative.

Since the compound A gives 2-methylbutane on reduction, it must have any one of the following structures.



$$\mathrm{H_2C{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2{-}CH_3}, \quad \mathrm{H_3C{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_3}, \quad \mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{C}{-}CH{=}CH_2}$$

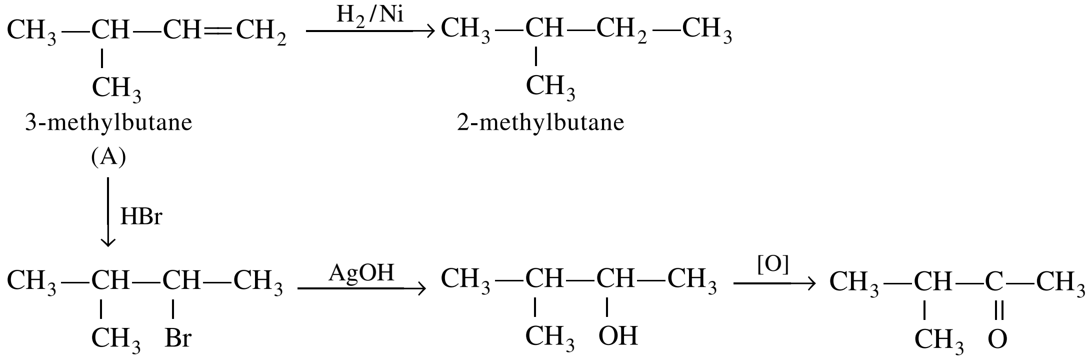
Of these structures, only the last one will produce secondary bromo derivative when HBr adds in accordance with Markovnikov's rule:



$$\underset{\text{(A)}}{\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH{=}CH_2}} \xrightarrow{\mathrm{HBr}} \underset{\text{(B)}}{\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{Br}{|}}{CH}{-}CH_3}}$$

(A) (B)

Thus, the reactions involved are as follows.



$$\underset{\text{3-methylbutane (A)}}{\underset{\displaystyle CH_3}{CH_3\text{—}\underset{|}{C}H}\text{—}CH{=}CH_2} \xrightarrow{H_2/Ni} \underset{\text{2-methylbutane}}{CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{—}CH_2\text{—}CH_3}$$

$$(A)\ \xrightarrow{HBr}\ \underset{\text{2-bromo-3-methylbutane}}{CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{—}\underset{\displaystyle Br}{\underset{|}{C}H}\text{—}CH_3} \xrightarrow{AgOH} CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{—}\underset{\displaystyle OH}{\underset{|}{C}H}\text{—}CH_3 \xrightarrow{[O]} \underset{\text{3-methylbutan-2-one}}{CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CH_3}$$

3-methylbutane (A); 2-methylbutane; 2-bromo-3-methylbutane; 3-methylbutan-2-one

14. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. The compound Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound, while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z. (1989)

Solution Mass per cent of chlorine in the organic compound X

$$= \frac{M_{Cl}}{M_{AgCl}}\frac{m_{AgCl}}{m_{compound}} \times 100 = \frac{35.5}{143.5}\times\frac{2.90}{1.0} \times 100 = 71.21$$

The ratios of atoms in the molecule of X are

$$C:H:Cl::\frac{24.24}{12}:\frac{4.04}{1}:\frac{71.72}{35.5}::2:4:2::1:2:1$$

Empirical formula of X is CH_2Cl

Since the isomer Y of the compound gives a dihydroxy compound on treating with aqueous KOH, it follows that the compound must contain two Cl atoms. Hence,

Molecular formula of X is $C_2H_4Cl_2$.

Its two isomers are $\underset{(Z)}{CH_3CHCl_2}$ and $\underset{(Y)}{ClCH_2CH_2Cl}$.

The reaction are

$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow{\text{aq. KOH}} [CH_3CH(OH)_2] \rightarrow \underset{\text{ethanal}}{CH_3CHO}$$

$$ClCH_2CH_2Cl \xrightarrow{\text{aq. KOH}} \underset{\text{ethylene glycol}}{HOCH_2CH_2OH}$$

15. *n*-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at STP required to produce 55 g *n*-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. (1989)

Solution The equation are

$$CH_3CH_3 \xrightarrow{\text{bromination}} CH_3CH_2Br \qquad \text{yield} = 90\%$$

$$2CH_3CH_2Br \xrightarrow[\text{reaction}]{\text{Wurtz}} CH_3CH_2CH_2CH_3 \qquad \text{yield} = 85\%$$

Mass of *n*-butane to be produced = 55 g

$$\text{Amount of } n\text{-butane to be produced} = \frac{m_{butane}}{M_{butane}} = \frac{55\ g}{58\ g\ mol^{-1}} = 0.948\ mol$$

Amount of C_2H_5Br required to obtain 0.948 mol of C_4H_{10} would be 2 × 0.948 mol = 1.896 mol. But the per cent conversion is 85. Thus, the amount of C_2H_5Br required would be

$$(1.896 \text{ mol}) \left(\frac{100}{85}\right) = 2.23 \text{ mol}$$

Amount of C_2H_6 required would also be 2.23 mol. But the per cent conversion of C_2H_6 to C_2H_5Br is 90. Thus, the actual amount of C_2H_6 required would be $(2.23 \text{ mol}) \left(\frac{100}{90}\right) = 2.478 \text{ mol}$

Volume of C_2H_6 required at STP would be $(2.478 \text{ mol}) (22414 \text{ mL mol}^{-1}) = 55.54 \times 10^3 \text{ mL}$.

16. A ketone A which undergoes a haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms mono-ozonide D. The compound D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. (1989)

Solution We are given that

$$\text{A} \xrightarrow{\text{reduction}} \text{B}; \quad \text{B} \xrightarrow{H_2SO_4} \text{C}; \quad \text{C} \quad \text{forms mono-ozonoide, D}$$

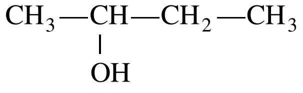
$$\text{D} \xrightarrow{H_2O/Zn} CH_3CHO$$

Solution The compound A gives a haloform reaction; it must contain CH_3CO group. The compound C contains a double bond as it forms mono-ozonoide D. Since, the compound D on hydrolysis gives only CH_3CHO, the structure of C would be

$CH_3CH{=}CHCH_3$ 2-butene

(C)

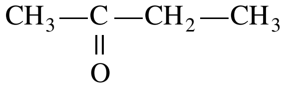
The compound C is obtained by dehydration of B, the latter should be



$CH_3{-}CH(OH){-}CH_2{-}CH_3$ 2-butanol

(B)

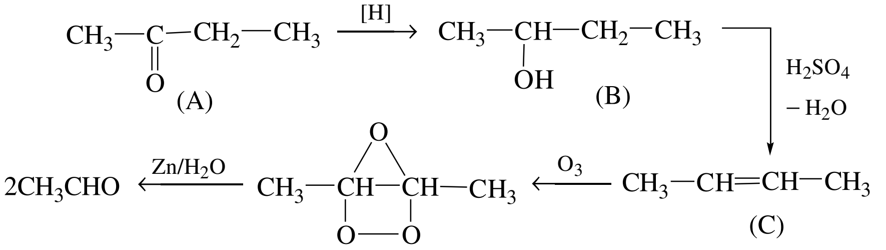
Finally, B is obtained by the reduction of A. Hence, the compound A should be



$CH_3{-}C({=}O){-}CH_2{-}CH_3$ 2-butanone

(A)

The equations involved are as follows.



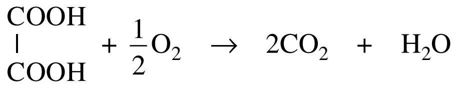
17. The sodium salt of a carboxylic acid, A, was produced by passing a gas, B, into an aqueous solution of caustic alkali at an elevated temperature and pressure. A, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, C. A sample of 0.4 g of acid C, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B and C. (1990)

Solution From the given data, we can determine the molar mass of dicarboxylic acid. Since on ignition, 2 mol of Ag (≡ 215.8 g Ag) will be left per mole of dicarboxylic acid, we have

$$\frac{1.0 \text{ g of silver salt of dicarboxylic acid}}{0.71 \text{ g Ag}} \times 215.8 \text{ g Ag} = 303.94 \text{ g of silver salt of dicarboxylic acid.}$$

Hence, $M_{\text{acid}} = 303.94 \text{ g mol}^{-1} - 2\,M_{\text{Ag}} + 2M_{\text{H}} = 303.94 \text{ g mol}^{-1} - 215.8 \text{ g mol}^{-1} + 2 \text{ g mol}^{-1}$
$= 90.14 \text{ g mol}^{-1}$

Now, since the molar mass of two carboxylic groups (2COOH) is 90 g mol^{-1}, the dicarboxylic acid (C) is oxalic acid (HCOOH—COOH). The nature of dicarboxylic acid may be confirmed from the combustion data.



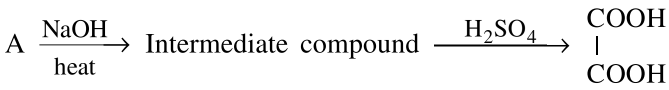
$$\begin{array}{lcccc} & \begin{array}{c}\text{COOH}\\ | \\ \text{COOH}\end{array} + \frac{1}{2}O_2 & \rightarrow & 2CO_2 & + \quad H_2O \\ \textit{Molar mass} & 90\ \text{g mol}^{-1} & & 44\ \text{g mol}^{-1} & 18\ \text{g mol}^{-1} \\ \textit{Given data} & 0.4\ \text{g} & & 0.39\ \text{g} & 0.08\ \text{g} \end{array}$$

The calculated values of masses of CO_2 and H_2O produced during the combustion of 0.4 g of oxalic acid are

$$\frac{2 \times 44\ \text{g}\ CO_2}{90\ \text{g oxalic acid}} \times 0.4\ \text{g oxalic acid} = 0.39\ \text{g}\ CO_2$$

$$\frac{18\ \text{g}\ H_2O}{90\ \text{g oxalic acid}} \times 0.4\ \text{g oxalic acid} = 0.08\ \text{g}\ H_2O$$

These values tally with the given data. Hence, the compound C is confirmed to be oxalic acid. The production of C from A is as follows.



$$\text{A} \xrightarrow[\text{heat}]{\text{NaOH}} \text{Intermediate compound} \xrightarrow{H_2SO_4} \begin{array}{c}\text{COOH}\\ | \\ \text{COOH}\end{array}$$

The compound A must be formic acid as the above reactions are used in the manufacture of oxalic acid. The reactions are

$$\text{2HCOOH} \rightarrow \text{2HCOONa} \xrightarrow{-H_2} (\text{COONa})_2 \xrightarrow{H^+} \underset{\text{(C)}}{(\text{COOH})_2}$$

The sodium salt of A is produced by passing a gas B into an aqueous solution of caustic alkali at an elevated temperature and pressure. The reaction involved here is

$$\text{NaOH} + \text{CO} \xrightarrow[\text{and pressure}]{\text{High temperature}} \text{HCOONa}$$

Hence, the gas B is carbon monoxide. Thus, the structures of A, B and C are

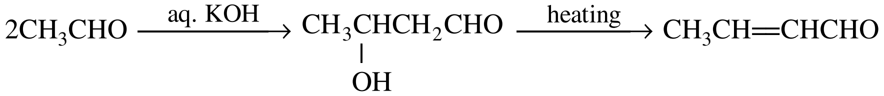
A is HCOOH; B is CO, C is $(COOH)_2$.

18. Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave C. The compound D was oxidized further to give F which was found to be a monobasic acid (molar mass : 60.0 g mol^{-1}). Deduce the structures of A, B, C, D and E. (1990)

Solution The compound A is an ester. The equations involved in the given reactions are as follows.

The compound F is a monobasic acid (molar mass = 60 g mol^{-1}). This may be represented as RCOOH. From the molar mass of F, it is evident that the molar mass of R is 15 g mol^{-1} [= (60 – 45) g mol^{-1}]. Hence, the compound F is CH_3COOH (ethanoic acid).

F is obtained by the oxidation of D. Hence, the compound D must be an aldehyde with the structure CH_3CHO (ethanal). The compound D was obtained from the oxidation of B which must be an alcohol. Hence, the structure of B is CH_3CH_2OH (ethanol). D undergoes an aldol condensation (treatment with aqueous alkali) which subsequently gives E on heating. The reactions involved here are



$$2CH_3CHO \xrightarrow{\text{aq. KOH}} CH_3\underset{\displaystyle\overset{|}{OH}}{C}HCH_2CHO \xrightarrow{\text{heating}} CH_3CH{=}CHCHO$$

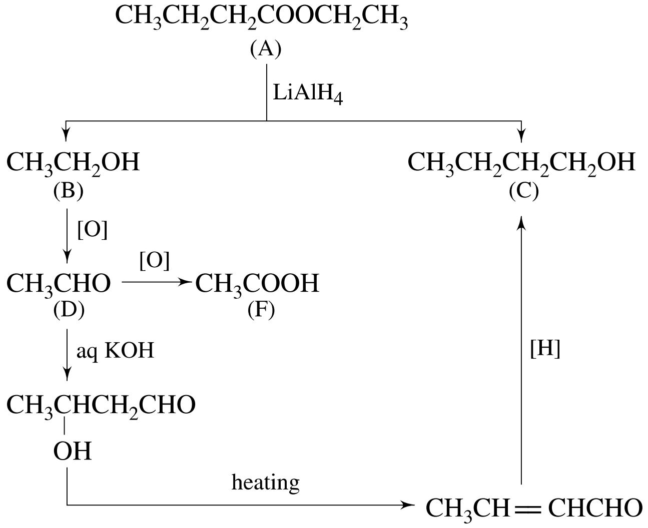
The reduction of E gives compound C. Hence, we have

$$CH_3CH{=}CHCHO \xrightarrow{[H]} \underset{\text{(C)}}{CH_3CH_2CH_2CH_2OH}$$

Finally, the structure of A can be obtained from the two alcohols (CH_3CH_2OH and $CH_3CH_2CH_2CH_2OH$) produced on treating A with $LiAlH_4$. Thus, we have

$$\underset{\text{(A)}}{CH_3CH_2CH_2COOCH_2CH_3} \xrightarrow{LiAlH_4} \underset{\text{(C)}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{(B)}}{CH_3CH_2OH}$$

Thus, the reactions involved are as follows.

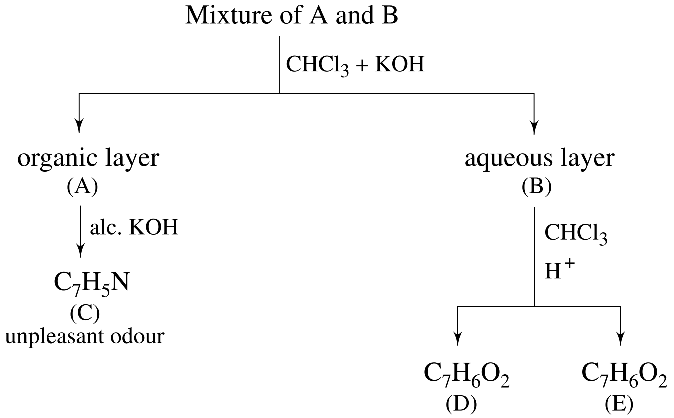


Alternatively, the compound A may be

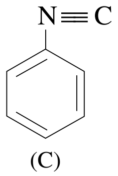
$CH_3COOCH_2CH_2CH_2CH_3$
(butylacetate)

19. A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula $C_7H_6O_2$. Identify the compounds A, B, C, D, and E and write their structures. (1990)

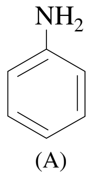
Solution We have



The compound C is an isocyanide which is produced from a primary amine. Hence, the structures of C and A are

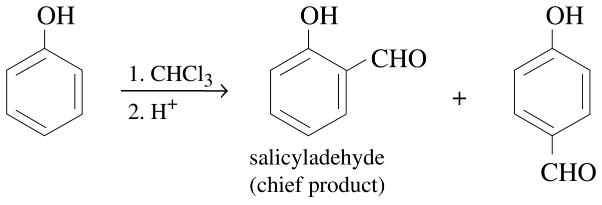


(C)



(A)

The compound B exhibits Reimer-Tiemann reaction. Thus, the compound B must be phenol. The reaction is



20. An organic compound containing C, H and O exists in two isomeric forms A and B. A mass of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. A is insoluble NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with concentrated HI to give compounds C and D. C can be separated from D by the ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula, $C_7H_5OBr_3$. Identify A, B, C, D and E with justification and give their structures. (1991)

Solution We have

$$\text{Per cent of carbon in the compound} = \frac{M_C}{M_{CO_2}}\frac{m_{CO_2}}{m_{\text{compound}}} \times 100 = \left(\frac{12}{44}\right)\left(\frac{0.308}{0.108}\right)(100) = 77.78$$

$$\text{Per cent of hydrogen in the compound} = \frac{2\,M_H}{M_{H_2O}}\frac{m_{H_2O}}{m_{\text{compound}}} \times 100 = \left(\frac{2}{18}\right)\left(\frac{0.072}{0.108}\right)(100) = 7.41$$

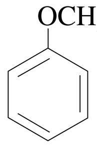
Per cent of oxygen in the compound = 100 – (77.78 + 7.41) = 14.81.

The ratios of atoms in the compound are

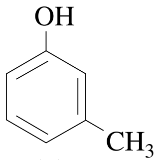
$$C : H : O :: \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} :: 6.48 : 7.41 : 0.926 :: 7 : 8 : 1$$

Hence, Empirical formula of the compound is C_7H_8O.

Since the isomer B on reacting with bromine water gives compound E ($C_7H_5OBr_3$), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and $NaHCO_3$ and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are

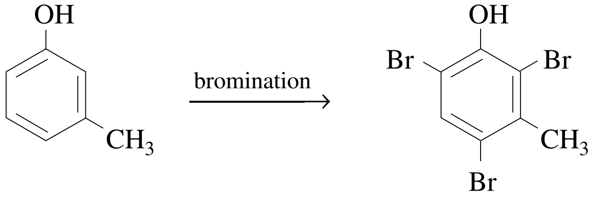


(A)
anisol

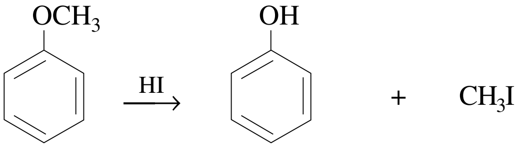


(B)
m-cresol

The bromination of B gives

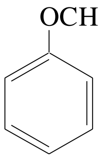


The reaction of compound A with HI is



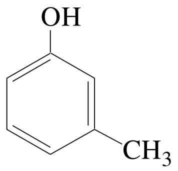
(A) (D) (C)

The compound C can be separated from D by use of ethanolic $AgNO_3$ solution as it is soluble in it whereas D will remain insoluble. The compound D will be soluble in NaOH as it is phenol. Hence, the structures of A, B, C, D and E are



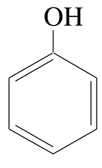
(A)
anisol

;



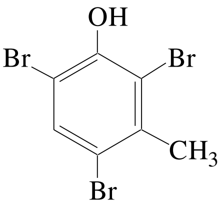
(B)
m-cresol

; CH_3I ;
(C)



(D)

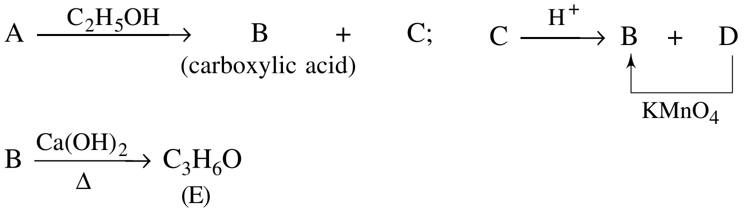
;



(E)

21. An organic compound A on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with $KMnO_4$ also gives B. The compound B on heating with $Ca(OH)_2$ gives E (molecular formula C_3H_6O). E does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify A, B, C, D and E. (1992)

Solution The given reaction are as follows.



$$\begin{tikzcd} A \arrow[r, "C_2H_5OH"] & \underset{\text{(carboxylic acid)}}{B} + C; & C \arrow[r, "H^+"] & B & + & D \arrow[ll, bend left, "KMnO_4"] \end{tikzcd}$$

$$B \xrightarrow[\Delta]{Ca(OH)_2} \underset{(E)}{C_3H_6O}$$

The compound E must be a ketonic compound as it does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Therefore, its structure would be CH_3COCH_3 (acetone).

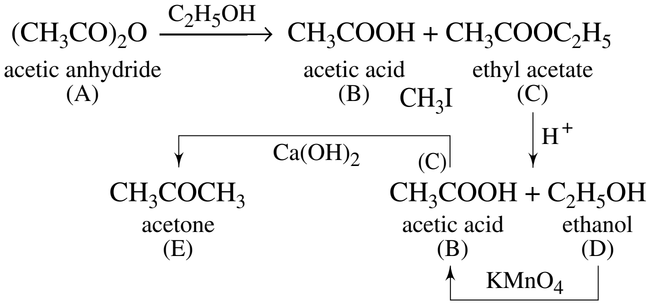
Since E is obtained by heating B with $Ca(OH)_2$, the compound B must be CH_3COOH (acetic acid).

Since B is obtained by oxidation of D with $KMnO_4$, the compound D must be an alcohol with molecular formula CH_3CH_2OH (ethanol).

Since B and D are obtained by acid hydrolysis of C, the compound C must be an ester $CH_3COOC_2H_5$ (ethyl acetate).

Since the compounds B (acetic acid) and C (ethyl acetate) are obtained by treating A with ethanol, the compound A must be an anhydride $(CH_3CO)_2O$ (acetic anhydride).

The given reactions are



$$\begin{tikzcd} \underset{\substack{\text{acetic anhydride}\\ \text{(A)}}}{(CH_3CO)_2O} \arrow[r, "C_2H_5OH"] & \underset{\substack{\text{acetic acid}\\ \text{(B)}\ CH_3I}}{CH_3COOH} + \underset{\substack{\text{ethyl acetate}\\ \text{(C)}}}{CH_3COOC_2H_5} \arrow[dl, "Ca(OH)_2"', "(C)"] \arrow[d, "H^+"] \\ \underset{\substack{\text{acetone}\\ \text{(E)}}}{CH_3COCH_3} & \underset{\substack{\text{acetic acid}\\ \text{(B)}}}{CH_3COOH} + \underset{\substack{\text{ethanol}\\ \text{(D)}}}{C_2H_5OH} \arrow[loop below, "KMnO_4"] \end{tikzcd}$$

22. Compound X (C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess CH_3MgBr, 0.42 g of X gives 22.4 mL of CH_4 at STP. Treatment of X and H_2 in presence of Pt catalyst followed by boiling with excess HI gives *n*-pentane. Suggest structure of X and write the equations involved. (1992)

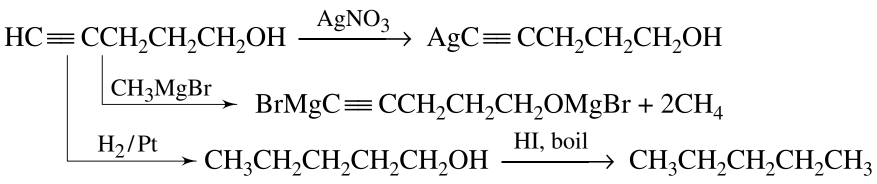
Solution Since the given compound does not react appreciably with Lucas reagent, it may be primary alcohol.

It is given that 0.42 g of the compound (which is 0.005 mol) produces 22.4 mL of CH_4 at STP (which is 0.01 mol) with excess CH_3MgBr. This shows that the compound X contains two active hydrogen atoms. Of these, one is due to hydroxyl group and the other must be due to acetylinic hydrogen, i.e. the compound must contain a triple bond with one hydrogen directly attached to it. This is possible only if —C≡C— group is present at one of the extreme ends of the molecule. The presence of acetylinic hydrogen is also supported by the fact that the compound X gives a precipitate with ammoniacal silver nitrate.

Moreover, the treatment of X with H_2/Pt followed by boiling with excess of HI gives *n*-pentane. This shows that the compound X contains a straight chain. With these facts, we can write the structure of X as

$$\underset{\text{4-pentyn-1-ol}}{HC{\equiv}CCH_2CH_2CH_2OH}$$

The equations are



$$\begin{tikzcd}[column sep=small] HC{\equiv}CCH_2CH_2CH_2OH \arrow[r, "AgNO_3"] \arrow[dr, "CH_3MgBr"] \arrow[ddr, "H_2/Pt"'] & AgC{\equiv}CCH_2CH_2CH_2OH & \\ & BrMgC{\equiv}CCH_2CH_2CH_2OMgBr + 2CH_4 & \\ & CH_3CH_2CH_2CH_2CH_2OH \arrow[r, "\text{HI, boil}"] & CH_3CH_2CH_2CH_2CH_3 \end{tikzcd}$$

23. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aqueous HCl, and treated with $NaNO_2$ solution at 0 °C liberated a colourless, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. (1993)

Solution Since the compound gives a foul smelling gas on treating with $CHCl_3$ and alcoholic KOH, the compound must be a primary amine.

$$RNH_2 + CHCl_3 + 3KOH \rightarrow \underset{\substack{\text{alkyl isocyanide} \\ \text{(foul smelling gas)}}}{RNC} + 3KCl + 3H_2O \qquad (1)$$

Since the compound on treating with $NaNO_2/HCl$ at 0 °C produces a colourless gas, the compound must be an aliphatic primary amine.

$$RNH_2 + HNO_2 \rightarrow ROH + N_2 + H_2O \qquad (2)$$

Thus, the gas produced is nitrogen.

$$\text{Amount of gas liberated} = \frac{112\ \text{mL}}{22400\ \text{mL mol}^{-1}} = \frac{1}{200}\ \text{mol}$$

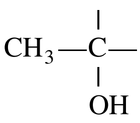
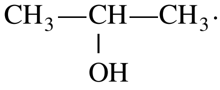
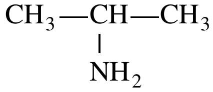
From the above equation, it is obvious that

$$\text{Amount of compound } RNH_2 = \frac{1}{200}\ \text{mol}$$

If M is the molar mass of RNH_2, then

$$\frac{2.295\ \text{g}}{M} = \frac{1}{200}\ \text{mol} \qquad \text{or} \qquad M = 0.295 \times 200\ \text{g mol}^{-1} = 59\ \text{g mol}^{-1}.$$

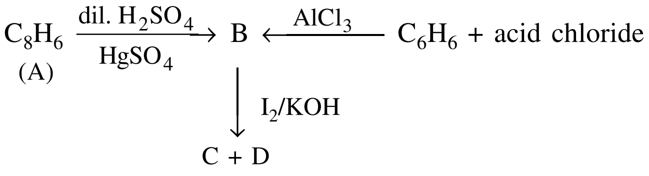
Thus, the molar mass of alkyl group R is (59 – 16) g mol^{-1}, i.e. 43 g mol^{-1}. Hence, R must be C_3H_7.

From Eq. (2), it is obvious that the liquid obtained after distillation is ROH. Since this gives yellow precipitate with alkali and iodine (iodoform test), it must contain  $CH_3—\overset{|}{\underset{\substack{| \\ OH}}{C}}—$ group. Hence, it is concluded that ROH is  $CH_3—\underset{\substack{| \\ OH}}{CH}—CH_3$. Thus, the original compound is  $CH_3—\underset{\substack{| \\ NH_2}}{CH}—CH_3$

isopropylamine

24. An organic compound A, C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A. (1994)

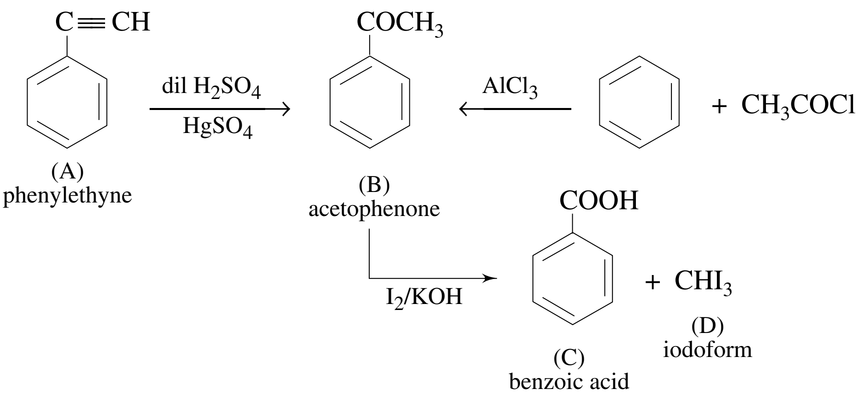
Solution The given reactions are



$$\begin{tikzcd} \underset{(A)}{C_8H_6} \arrow[r, "\text{dil. } H_2SO_4", "HgSO_4"'] & B \arrow[d, "I_2/KOH"] & C_6H_6 + \text{acid chloride} \arrow[l, "AlCl_3"'] \\ & C + D & \end{tikzcd}$$

The reaction of B with I_2 in KOH is iodoform reaction. The compound D is iodoform, CHI_3. The compound B must contain $—COCH_3$ group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone ($C_6H_5COCH_3$). The compound C must be an acid.

The compound A may be represented as $C_6H_5C_2H$. Since it gives $C_6H_5COCH_3$ on treating with dilute H_2SO_4 and $HgSO_4$, it must contain a triple bond ($—C{\equiv}CH$) in the side chain. Hence, the given reactions may be represented as

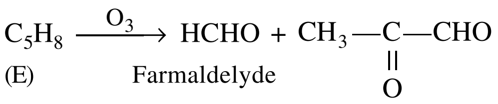


25. An organic compound E (C_5H_8) on hydrogenation gives compound F(C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-keto-propanal. Deduce the structure of compound E. (1995)

Solution Since there are four hydrogen atoms added in the reaction

$$\underset{(E)}{C_5H_8} \xrightarrow{4H} \underset{(F)}{C_5H_{12}}$$

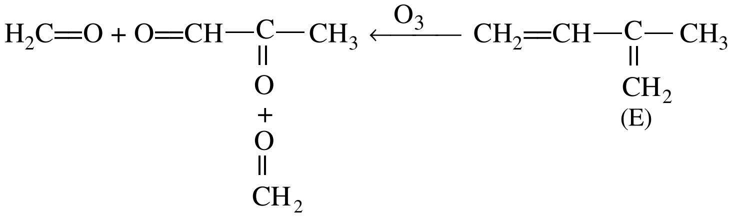
the compound E may contain two double bonds. The ozonolysis reaction is



$$\underset{(E)}{C_5H_8} \xrightarrow{O_3} \underset{\text{Farmaldelyde}}{HCHO} + CH_3—\underset{\underset{O}{\|}}{C}—CHO$$

2-ketopropanal

Since there is no loss of carbon atoms in an ozonolysis reaction, probably 2 molecules of formaldehyde are formed. In 2-ketopropanal, $—\underset{\underset{O}{\|}}{C}—$ and —CHO groups must have resulted due to the cleavage of double bonds. Hence, the net reaction can be explained as follows.



$$H_2C{=}O + O{=}CH—\underset{\underset{\underset{\underset{\underset{CH_2}{\|}}{O}}{+}}{O}}{\underset{\|}{C}}—CH_3 \xleftarrow{O_3} CH_2{=}CH—\underset{\underset{\underset{(E)}{CH_2}}{\|}}{C}—CH_3$$

Hence, the compound E is 2-methyl-1, 3-butadiene.

26. An organic compound A contains 69.42% C, 5.78% H and 11.57% N. Its vapour density is 60.5. It evolves ammonia when boiled with caustic potash. On heating with P_2O_5, it gives a compound B containing 81.55% C, 4.85% H and 13.59% N. On reduction with sodium and alcohol, B forms a base which reacts with HNO_2 giving off nitrogen and yielding an alcohol, C. The alcohol can be oxidized to benzoic acid. Explain the above reactions and assign structural formulae to A, B and C.

Solution The ratios of atoms in the molecule of A are

$$C : H : N : O :: \frac{69.42}{12} : \frac{5.78}{1} : \frac{11.57}{14} : \frac{13.23}{16} :: 5.785 : 5.78 : 0.826 : 0.827 :: 7 : 7 : 1 : 1$$

Empirical formula of A : C_7H_7NO

$$\text{Molar empirical formula mass} = (12 \times 7 + 7 + 14 + 16)\ \text{g mol}^{-1} = 121\ \text{g mol}^{-1}$$

Molar mass of the compound = 2×60.5 g mol^{-1}

Since molar empirical formula mass is the same as the molar mass, we have

Molecular formula of compound A: C_7H_7NO.

Since the compound A evolves NH_3 when boiled with caustic potash, the compound A may be an amide.

The ratios of atoms in the compound B are

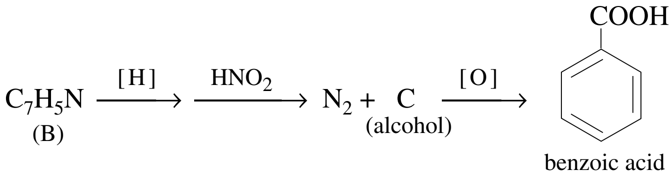
$$\mathrm{C : H : N} :: \frac{81.55}{12} : \frac{4.85}{1} : \frac{13.59}{14} :: 6.80 : 4.85 : 0.97 :: 7 : 5 : 1$$

Empirical formula of B is C_7H_5N.

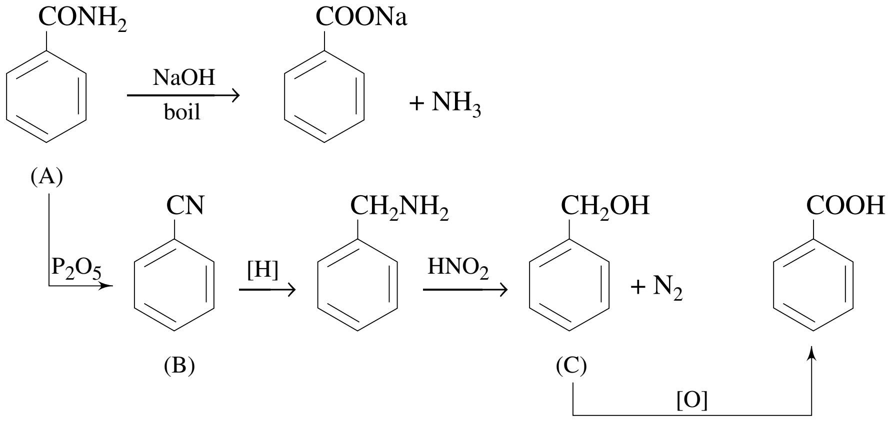
Since the compound B is obtained by heating A with P_2O_5, the reaction involved is

$$\underset{\text{(A)}}{C_7H_7NO} \xrightarrow{P_2O_5} \underset{\text{(B)}}{C_7H_5N}$$

This is dehydration reaction confirming that the compound A is an amide. The remaining reactions are



The formation of benzoic acid indicates that the compound A is an aromatic amide. Hence, the given reactions are



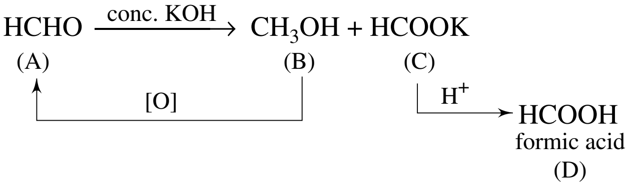
27. An organic compound A contains 40% C and 6.7% H. Its vapour density is 15. On reacting with a concentrated solution of potassium hydroxide, it gives two compounds B and C. When B is oxidized, the original compound A is obtained. When C is treated with concentrated HCl, it gives a compound D which reduces Fehling and ammoniacal silver nitrate solution and also give effervescence with aqueous sodium bicarbonate solution. Write the structures of A, B, C and D and explain the reactions.

Solution The ratios of atoms present in the compound A are

$$\mathrm{C : H : O} :: \frac{40}{12} : \frac{6.7}{1} : \frac{53.3}{16} :: 3.33 : 6.7 : 3.33 :: 1 : 2 : 1$$

Empirical formula of A is CH_2O. Molar empirical formula mass = 30 g mol^{-1}

This is twice of the given vapour density. Hence, Molecular formula of A is CH_2O. The compound A is formaldehyde, HCHO. The given reactions are



$$\underset{\text{(A)}}{HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{(B)}}{CH_3OH} + \underset{\text{(C)}}{HCOOK} \xrightarrow{H^+} \underset{\text{(D)}}{\underset{\text{formic acid}}{HCOOH}}$$

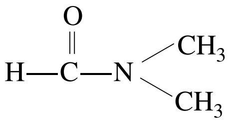
Formic acid reduces Fehling solution and ammoniacal silver nitrate solution and also give effervescence with aqueous sodium bicarbonate solution.

28. A compound A (C_3H_7NO) on hydrolysis gives an amine B and a carboxylic acid C. Amine B reacts with benzenesulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution. Acid C on reaction with Tollens reagent gives a silver mirror. Write the structures of A, B and C by writing the chemical equations involved.

Solution The amine B must be a secondary amine as the product obtained with benzenesulphonyl chloride is insoluble in aqueous sodium hydroxide.

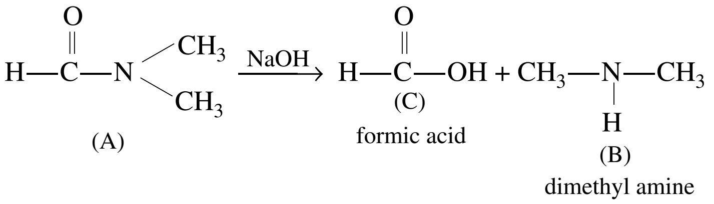
The acid C must be formic acid as it reduces Tollens reagent to give silver mirror.

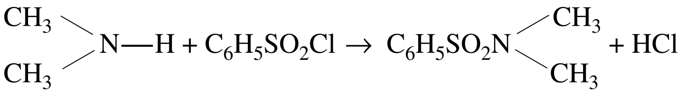
The compound A must be an amide having the structure



N, *N*-dimethylformamide

The involved chemical reactions are





N, *N*-dimethylbenzene sulphonamide

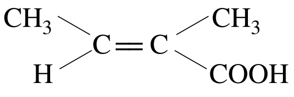
$$\underset{\text{Tollens reagent}}{HCOOH + Ag_2O} \longrightarrow H_2O + CO_2 + \underset{\text{silver mirror}}{Ag}$$

29. Compound A($C_5H_8O_2$) liberated carbon dioxide on reacting with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields compound B ($C_5H_{10}O_2$) on hydrogenation. Compound B can be separated into enantiomorphs. Write the structural formulae for A and B giving reasons.

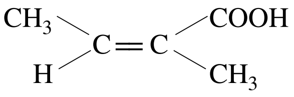
Solution From the reaction

$$\underset{(A)}{C_5H_8O_2} \xrightarrow{[H]} \underset{(B)}{C_5H_{10}O_2}$$

we conclude that the compound A contains a carbon-carbon double bond. The compound A also contains carboxylic group as it liberated CO_2 on reacting with $NaHCO_3$. Since A exists in two forms, we conclude that A contains two methyl groups attached to different carbon atoms of double bond. Hence, the structures of A are

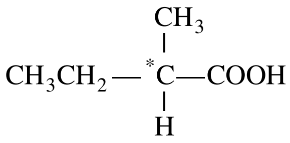


cis-form



trans-form

Reduction of A generates B containing one asymmetric carbon and thus compound B exists in two enantiomorphs.



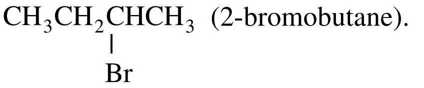
$$CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{{}^{*}C}}-COOH$$

30. It required 0.70 g of a hydrocarbon A to react completely with Br_2 (2.0 g). On treatment of A with HBr, it yielded monobromo alkane B. The same compound B was obtained when A was treated with HBr in the presence of peroxide. Write down the structural formulae of A and B and explain the reactions involved.

Solution Since the compound A on reacting with HBr gives monobromo alkane, the compound A must be an alkene. Since the same product is obtained in the presence of peroxide, the alkene A must be symmetrical in nature. Now, the molar mass of A is the mass of the hydrocarbon reacting with 1 mol of Br_2 (= 160 g). Hence,

$$\text{Molar mass of A} = \frac{0.70\ \text{g}}{2.0\ \text{g}} \times 160\ \text{g mol}^{-1} = 56\ \text{g mol}^{-1}$$

Hence, the compound A is C_4H_8 with the structure $CH_3CH{=}CHCH_3$ (2-butene). The compound B is $CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{C}HCH_3$ (2-bromobutane).



31. 0.90 g of an organic compound A ($C_4H_{10}O_2$) when treated with sodium, 224 mL of hydrogen was evolved at STP. Compound A could be separated into two fractions B and C by crystallization, of which fraction B could only be resolved into optical isomers. Write down the structural formula for A with proper reasoning.

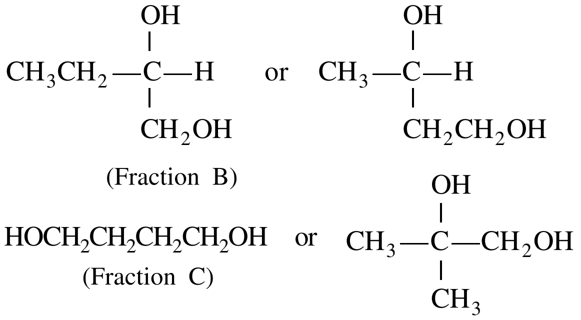
Solution Sodium reacts with active hydrogen (—OH, —COOH) in the molecule to give hydrogen gas.

$$\text{Amount of compound A taken} = \frac{0.90\ \text{g}}{90\ \text{g mol}^{-1}} = 0.01\ \text{mol}$$

$$\text{Amount of } H_2 \text{ evolved at STP} = \frac{224\ \text{mL}}{22400\ \text{mL mol}^{-1}} = 0.01\ \text{mol}$$

Since 0.01 mol of H_2 is equivalent to 0.02 mol of H atoms, it implies that 0.02 mol of active H atoms are present in 0.01 mol of compound A. This implies the presence of two —OH groups in the molecule as the latter contains two oxygen atoms. Hence, the structure of A will be $C_4H_8(OH)_2$.

Since the compound A can be separated into two fractions B and C in which only fraction B can be resolved into optical isomers, it implies that the molecules of fraction C does not contain any chiral carbon whereas those of fraction B will contain one chiral atom. Consistent with this fact, the structures of B and C would be



$$CH_3CH_2{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}{-}H \quad \text{or} \quad CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2CH_2OH}{|}}{C}}{-}H$$

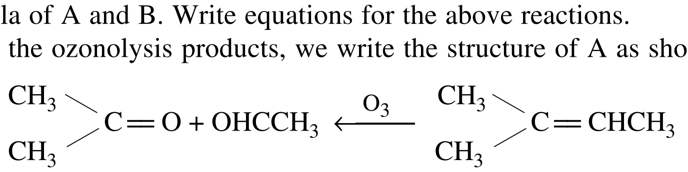
(Fraction B)

$$HOCH_2CH_2CH_2CH_2OH \quad \text{or} \quad CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_2OH$$

(Fraction C)

32. A compound A with molecular formula C_5H_{10} reacts with alkaline potassium permanganate to form compound B ($C_5H_{12}O_2$). A on reduction yields 2-methylbutane and on ozonolysis forms acetone and acetaldehyde. Deduce the structural formula of A and B. Write equations for the above reactions.

Solution From the ozonolysis products, we write the structure of A as shown in the following equation.



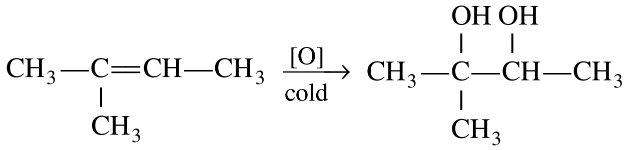
$$(CH_3)_2C{=}O + OHCCH_3 \xleftarrow{O_3} (CH_3)_2C{=}CHCH_3$$

2-methylbut-2-ene

(A)

The structure of A is further confirmed from the fact that it gives 2-methylbutane on reduction.

The reaction of A with alkaline $KMnO_4$ giving B is



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_3 \xrightarrow[\text{cold}]{[O]} CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_3$$

33. Compound A with molar mass 108 g mol^{-1} contained 88.89% C and 11.11% H. It gave a white precipitate with ammoniacal silver nitrate. Complete hydrogenation of A gave another compound B with molar mass 112 g mol^{-1}. Oxidation of A gave an acid with equivalent mass 128 g eq^{-1}. Decarboxylation of this acid gave cyclohexane. Give structures of A and B and write the equations of the reactions involved.

Solution The ratio of atoms in a molecule of A is

$$C : H :: \frac{88.89}{12} : \frac{11.11}{1} :: 7.4 : 11.11 :: 2 : 3$$

Hence Empirical formula of A = C_2H_3; Molar mass of A = 108 g mol^{-1}

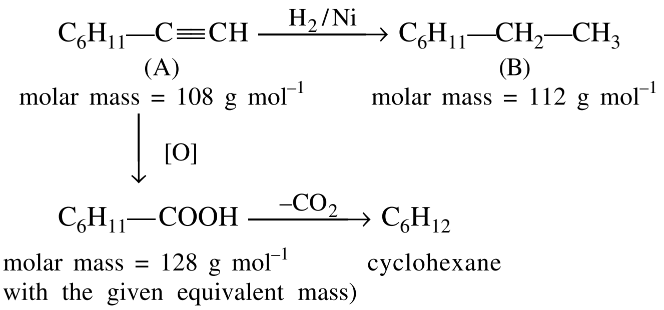
$$\text{Number of repeating } C_2H_3 \text{ unit in one molecule of A} = \frac{108}{27} = 4$$

Hence, Molecular formula of A = C_8H_{12}.

Since there is an increase of 4 g mol^{-1} (≡ 2 mol H_2) in the molar mass of A on hydrogenation and also it gives white precipitate with Tollens reagent, it may be concluded that the molecule of A contains one terminal carbon-carbon triple bond. Thus, the compound A may be written as

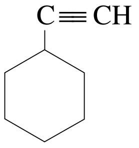
$$C_6H_{11}—C{\equiv}CH$$

The given observations are as under:

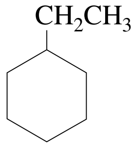


$$\begin{tikzcd}[column sep=large] \underset{\substack{\text{(A)}\\ \text{molar mass = 108 g mol}^{-1}}}{C_6H_{11}—C{\equiv}CH} \arrow[r, "H_2/Ni"] \arrow[d, "{[O]}"] & \underset{\substack{\text{(B)}\\ \text{molar mass = 112 g mol}^{-1}}}{C_6H_{11}—CH_2—CH_3} \\ \underset{\substack{\text{molar mass = 128 g mol}^{-1}\\ \text{(tally with the given equivalent mass)}}}{C_6H_{11}—COOH} \arrow[r, "-CO_2"] & \underset{\text{cyclohexane}}{C_6H_{12}} \end{tikzcd}$$

Thus, the group C_6H_{11} in A represents a cyclic structure involving six carbon atoms. Hence, the structures of A and B are



(A)



(B)

34. 448 mL of a hydrocarbon A having C, 87.80%; H, 12.19% has a mass of 1.64 g at STP. On hydrogenation it gives 2-methylpentane. Treatment of A with acidic $HgSO_4$ gives a new compound B ($C_6H_{12}O$). Compound A does not react with ammoniacal $AgNO_3$. Find out the structure of A and explain the reaction involved.

Solution The ratio of atoms in one molecule is

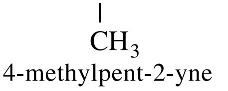
$$C : H :: \frac{87.80}{12} : \frac{12.19}{1} :: 7.32 : 12.19 :: 1 : 1.666 :: 3 : 5$$

Hence, Empirical formula of A is C_3H_5. Molar empirical formula mass of A = 41 g mol^{-1}

$$\text{Molar Mass of A} = \left(\frac{1.64\ g}{448\ mL}\right) (22400\ mL\ mol^{-1}) = 82\ g\ mol^{-1}$$

Thus Molecular formula of A is C_6H_{10}.

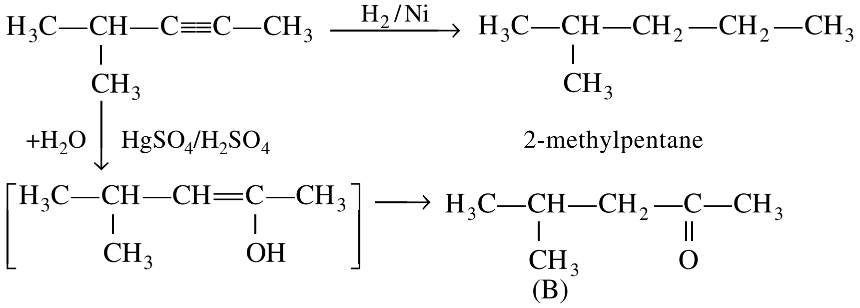
The molecular formula C_6H_{10} (= C_nH_{2n-2}) of A indicates that it is an alkyne. Since on hydrogenation, A gives 2-methylpentane, the carbon skelton of A would be  $C—C—\underset{\substack{|\\C}}{C}—C—C$. Now since A does not react with ammoniacal $AgNO_3$, the functional group —C≡C— is not present at the terminals. Hence, the structure of A would be



$$H_3C—\underset{\substack{|\\CH_3}}{CH}—C{\equiv}C—CH_3$$

4-methylpent-2-yne

The given reactions are



$$\underset{\underset{\displaystyle CH_3}{|}}{H_3C-CH}-C{\equiv}C-CH_3 \xrightarrow{H_2/Ni} \underset{\underset{\displaystyle CH_3}{|}}{H_3C-CH}-CH_2-CH_2-CH_3$$

2-methylpentane

$$\xrightarrow[HgSO_4/H_2SO_4]{+H_2O} \left[\underset{\underset{\displaystyle CH_3}{|}}{H_3C-CH}-\underset{\underset{\displaystyle OH}{|}}{CH{=}C}-CH_3\right] \longrightarrow \underset{\underset{\displaystyle CH_3}{|}}{H_3C-CH}-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$$

(B)

35. An organic compound A has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with $FeCl_3$ solution. The compound A when treated with CO_2 and NaOH at 140 °C under pressure gives B which on being acidified gives C. The compound C reacts with acetyl chloride to give D which is a well known pain killer. Identify A, B, C and D and explain the reactions involved.

Solution The ratios of atoms present in one molecule of A are

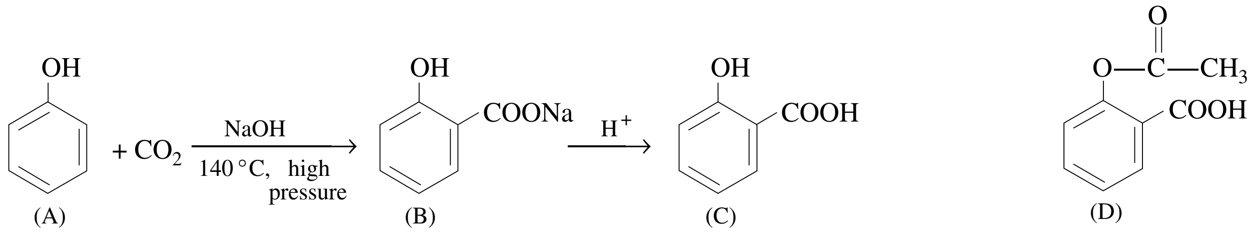
$$C : H : O \ :: \ \frac{76.6}{12} : \frac{6.38}{1} : \frac{17.02}{16} \ :: \ 6.38 : 6.38 : 1.064 :: 6 : 6 : 1$$

Hence, Empirical formula of A is C_6H_6O. Molar empirical formula mass of A = 94 g mol^{-1}

This tallies with the given molar mass (= 2 × 47 g mol^{-1}). Thus Molecular formula of A is C_6H_6O.

Since, the compound A gives characteristic colour with $FeCl_3$, it must be a phenol.

The given reactions are



(A) (B) (C) (D)

Aspirin (pain killer)

36. An organic compound A of molar mass 140.5 g mol^{-1} has 68.32% C, 6.4% H and 25.26% Cl. Hydrolysis of A with dilute acid gives compound B, $C_8H_{10}O$. Compound B can be oxidized under mild conditions to compound C, C_8H_8O. Compound C forms a phenylhydrazone D with $PhNHNH_2$ and gives a positive iodoform test. Deduce the structures of compounds A to D with proper reasoning.

Solution The ratios of atoms in a molecule of A are

$$C : H : Cl \ :: \ \frac{68.32}{12} : \frac{6.4}{1} : \frac{25.26}{35.5} \ :: \ 5.69 : 6.4 : 0.71 :: 8 : 9 : 1$$

Hence, Empirical formula of A is C_8H_9Cl. Molar empirical formula mass of A = 140.5 g mol^{-1}

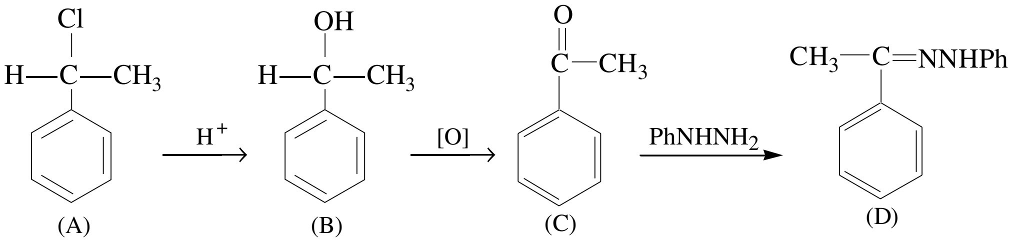
This tallies with the given molar mass. Thus Molecular formula of A is C_8H_9Cl.

The high content of carbon indicates the presence of aromatic (or benzene) ring in the molecule.

Since Cl atom in the compound A is easily replaced during hydrolysis of A with dilute acid, the Cl atom must be attached to the aliphatic portion of the molecule.

Since the compound C gives a positive iodoform test, it must contain—$COCH_3$ group.

Since the compound C is obtained by mild oxidation of B, the latter must be a secondary alcohol. Hence, the compound A also contains secondary chlorine atom. Consistent with this, the given reactions are as follows.



(A) (B) (C) (D)

JEE Advanced

Model Test Paper I

(with Solutions)

SECTION–I

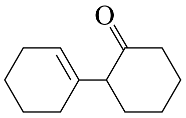
(Only One option correct)

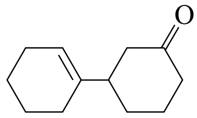
This section contains **10 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

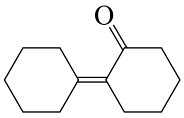
1. The aldol condensation between PhCHO and $CH_3COC_2H_5$ in basic condition and in acidic condition give respectively

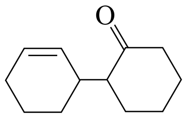
(a) $PhCH{=}CHCOCH_2CH_3$ and $PhCH{=}CHCOCH_2CH_3$
(b) $PhCH{=}CHCOCH_2CH_3$ and $PhCH{=}C(CH_3)COCH_3$
(c) $PhCH{=}C(CH_3)COCH_3$ and $PhCH{=}CHCOCH_2CH_3$
(d) $PhCH{=}C(CH_3)COCH_3$ and $PhCH{=}C(CH_3)COCH_3$

2. The dehydrated aldol condensation product of cyclohexanone is

(a) 

(b) 

(c) 

(d) 

3. The end products in the oxidation of a mixture of 1-nitronaphthalene and α-naphthylamine, respectively, is/are

(a) 3-nitrophthalic acid and phthalic acid
(b) 3-nitrophthalic acid and 3-aminophthalic acid
(c) phthalic acid and phthalic acid
(d) phthalic acid and 3-aminophthalic acid

4. Which of the following statements regarding P_4O_{10} is **not** correct?

(a) Each P atom is bonded to four O atoms
(b) P atoms are arranged tetrahedrally with respect to each other
(c) Each P—O bond has identical bond lengths
(d) Each P is bounded to one O atom with considerable pπ-dπ back bounding.

5. Hypophosphorous acid is a

(a) monobasic acid
(b) dibasic acid
(c) tribasic acid
(d) tetrabasic acid

6. The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ respectively involve

(a) sp^3 and dsp^2 hydridizations
(b) dsp^2 and sp^3 hybridizations
(c) sp^3 and sp^3 hybridizations
(d) dsp^2 and dsp^2 hybridizations

7. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_c^\circ = 66.9$ at 350 °C and $K_c^\circ = 50$ at 448 °C. The reaction has

(a) ΔH = +ve
(b) ΔH = –ve
(c) ΔH = zero
(d) ΔH whose sign cannot be predicted.

8. The standard potential of $2H_2O + 2e^- = H_2 + 2OH^-$ at 298 K is about

(a) 0.414 V
(b) –0.414 V
(c) 0.828 V
(d) –0.828 V

9. Which of the following unit cells has the crystallographic parameters $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$?

(a) Orthorhombic
(b) Tetragonal
(c) Rhombohedral
(d) Monoclinic

10. Which of the following orders regarding acid strength of isomers of nitrobenzoic acid is correct?

(a) *para > meta > ortho*
(b) *para > ortho > meta*
(c) *ortho > para > meta*
(d) *ortho > meta > para*

SECTION – II

(One or more Options Correct Type)

This section contains **5 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONE or MORE** are correct.

11. Which of the following polymers classify as copolymer?
(a) Saran (b) Teflon (c) Buna-S (d) Orlon

12. 10 mL of a given H_2O_2 sample in water (density 1.4 g/mL) required 50 mL of M/20 $KMnO_4$ in acidic medium for its oxidation. Which of the following facts regarding H_2O_2 in the sample is/are correct.
(a) Molarity of H_2O_2 in the solution = 0.625 M
(b) Molarity of H_2O_2 in the solution = 0.453 mol kg^{-1}
(c) Mole fraction of H_2O_2 in the solution = 0.1
(d) Volume strength at STP of the solution = 7.0

13. The correct statement(s) regarding defects in solids is/are
(a) Frenkel defect is usually favoured by a small difference in sizes of cations and anions.
(b) Frenkel effect is a dislocation effect
(c) Trapping of an electron in the lattice leads to the formation of F-centre
(d) Schottky defect has no effect on the physical properties of solids.

14. When $NaNO_3$(s) is heated in a closed vessel, O_2(g) is liberated and $NaNO_2$(s) is left behind. Which of the following is/are correct when the reaction is at equilibrium.
(a) Addition of $NaNO_2$(s) favours the reverse reaction
(b) Addition of $NaNO_3$(s) favours the forward reaction
(c) Increasing temperature favours forward reaction
(d) Increasing pressure favours reverse reaction

15. Which of the following statements are **not** correct?
(a) Nitric Oxide is a diamagnetic molecule
(b) Bond order of nitrosonium ion is 2.5
(c) N_2O_3 is a stable molecule in the gaseous phase
(d) Nitric oxide is easily dimerized to N_2O_4

16. Which of the following statements is/are not correct?
(a) NF_3 is less basic than NH_3
(b) Guanidine, $HN{=}C(NH_2)_2$, is a weak base
(c) The bond angle in NH_3 is greater than NF_3
(d) The decreasing base strength of the amines $CH_3(CH_2)NH_2$, $CH_2{=}CH\,CH_2NH_2$ and $HC{\equiv}C\,CH_2NH_2$ is $CH_3(CH_2)_2NH_2 > H_2C{=}CCH_2NH_2 > HC{\equiv}CCH_2NH_2$

SECTION – III

(Paragraph Type)

This section contains **2 paragraphs** each describing theory, experiment, data, etc. Each paragraph includes three multiple-choice questions with four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

Paragraph or Questions Nos. 17 to 19

Given the following informations.

$[Cd(NH_3)_4]^{2+} + 2e^- = Cd + 4NH_3$; $E° = -0.61$ V
$[Cu(NH_3)_4]^{2+} + 2e^- = Cu + 4NH_3$; $E° = -0.12$ V
$[Ag(NH_3)_2]^{+} + e^- = Ag + 2NH_3$; $E° = 0.37$ V

$Cl_2 + 2e^- = 2Cl^-$; $E^\circ = 1.36$ V

$Fe^{2+} + 2e^- = Fe$; $E^\circ = -0.44$ V

$Fe^{3+} + 3e^- = Fe$; $E^\circ = -0.04$ V

Answer the following.

17. Which of the following statements regarding oxidation ability in ammoniacal medium of Cl_2 is correct?

(a) Oxidises only Cd (b) Oxidises only Cu

(c) Oxidises only Ag (d) Oxidises all the three Cu, Cd and Ag

18. Which of the following statements regarding oxidation ability in ammoniacal medium of Fe^{2+} ion is correct?

(a) Oxidises only Cd (b) Oxidises only Cu

(c) Oxidises only Ag (d) Oxidises all the three Cu, Cd and Ag

19. Which of the following statements regarding oxidation ability in ammoniacal medium of Fe^{3+} ion is correct?

(a) Oxidises only Cd (b) Oxidises both Cu and Cd

(c) Oxidises only Ag (d) Oxidises all the three Cu, Cd and Ag

Paragraph or Questions Nos. 20 to 22

The well known complex ions of iron are ferrocyanide and ferricyanide. Identify the correct choice in the following.

20. Which of the following is correct regarding the hybridization of iron in the complex?

(a) $[Fe(CN)_6]^{4-}$ involves d^2sp^3 while $[Fe(CN)_6]^{3-}$ involves sp^3d^2

(b) $[Fe(CN)_6]^{4-}$ involves sp^3d^2 while $[Fe(CN)_6]^{3-}$ involves d^2sp^3

(c) both the ions involve d^2sp^3

(d) both the ions involve sp^3d^2

21. Which one is correct regarding magnetic properties?

(a) $[Fe(CN)_6]^{4-}$ is paramagnetic while $[Fe(CN)_6]^{3-}$ diamagnetic

(b) $[Fe(CN)_6]^{4-}$ is diamagnetic while $[Fe(CN)_6]^{3-}$ paramagnetic

(c) Both are paramagnetic

(d) Both are diamagnetic

22. Blue coloration is obtained by both the ions when

(a) $[Fe(CN)_6]^{4-}$ is mixed with Fe^{3+} ions and $[Fe(CN)_6]^{3-}$ is mixed with Fe^{2+} ions

(b) $[Fe(CN)_6]^{4-}$ is mixed with Fe^{2+} ions and $[Fe(CN)_6]^{3-}$ is mixed with Fe^{3+} ions

(c) both are mixed with Fe^{2+} ions

(d) both are mixed with Fe^{3+} ions

SECTION – IV

(Matching List Type)

This section contains 3 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c, d) in Column-I have to be matched with statements (p, q, r, s) in Column-II.

23. Match the crystal systems/unit cells mentioned in Column-I with their characteristic features mentioned in Column-II.

Column I	**Column II**
(a) Cube	(p) $a = b = c$
(b) Rhombohedral	(q) $a = \beta = \gamma$
(c) Tetragonal	(r) $\gamma = 120^\circ$
(d) Monoclinic	(s) $a = b \neq c$

24. Match disaccharides listed in Column-I with their properties in Column-II.

Column I	**Column II**
(a) Cellobiose	(p) 1, 2′-glycosidic linkage
(b) Maltose	(q) 1, 4′-glycosidic linkage
(c) Lactose	(r) Reducing sugar
(d) Sucrose	(s) Two different monosaccharides units

25. Match the complexes in Column-I with their properties listed in Column-II.

Column I	**Column II**
(a) $[Cr(en)_2Cl_2]^+$	(p) optical isomers
(b) $[Fe(CN)_6]^{3-}$	(q) d^2sp^3 hydridization
(c) $[Ni(NH_3)_6]^{2-}$	(r) paramagnetic
(d) $[CoF_6]^{3-}$	(s) sp^3d^2 hybridization

ANSWERS

1. (b)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (a)	**6.** (a)
7. (b)	**8.** (d)	**9.** (c)	**10.** (d)	**11.** (a), (c)	**12.** (a), (b), (d)
13. (b), (c)	**14.** (c), (d)	**15.** (a), (b), (c)	**16.** (b)	**17.** (d)	**18.** (a)
19. (b)	**20.** (c)	**21.** (b)	**22.** (a)		

23. a–p, q; b–p, q; c–r,s; d–r

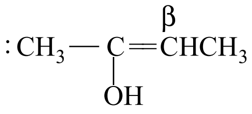
24. a–q,r; b–q,r; c–q,r,s; d–r,s

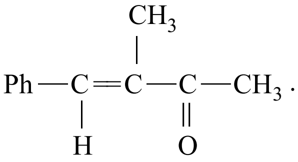
25. a–p,q,r; b–q,r; c–r,s; d–r,s

Solutions

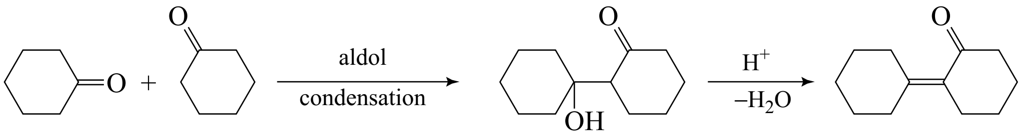
1. In basic medium, the more acidic 1° H from the CH_3 of $CH_3COCH_2CH_3$ is removed to give $:\overline{C}H_2COCH_2CH_3$. This adds to PhCHO followed by dehydration to give $PhCH{=}CHCOCH_2CH_3$

In acidic medium, H^+ adds to PhCHO to give $PhCH{=}OH^+$. This adds to the βC of the more stable (i.e. more substituated) enol $:CH_3-\underset{OH}{C}=\overset{\beta}{C}HCH_3$ followed by dehydration to give $Ph-\underset{H}{C}=\overset{CH_3}{C}-\underset{O}{\overset{\|}{C}}-CH_3$.

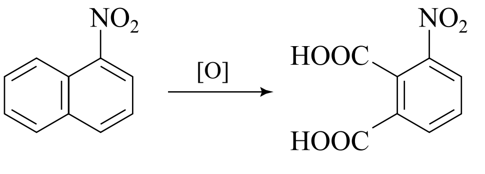




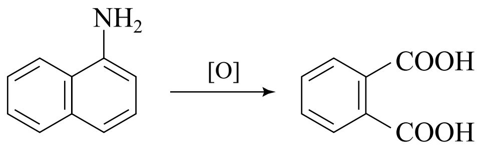
2.



3. The more active benzene ring is oxidized.

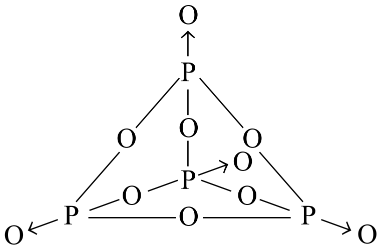


3-nitrophthalic acid



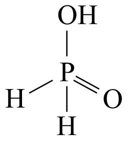
Phthalic acid

4. The structure of P_4O_{10} is



Each P atom forms three bonds to oxygen atoms and also an additional coordinate bond with an oxygen atom. Terminal coordinate P—O bond is much shorter than the expected P—O bond length. This shows the presence of considerable pπ–dπ back bonding because of the lateral overlap of full p orbital on oxygen with empty d orbital on phosphorus.

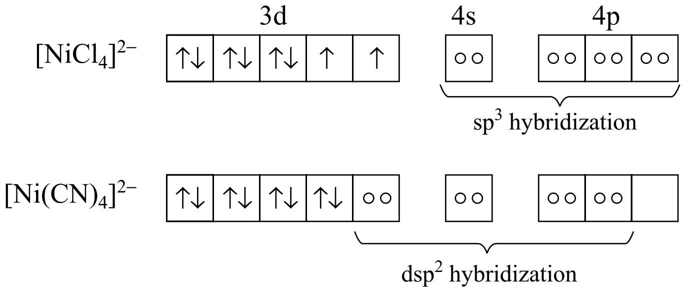
5. Hypophosphorous acid is



(H_3PO_2)

It is a monobasic acid as it contains one —OH group attached to P.

6. The configurations are



Cl^- is a weak ligand, it has no effect on pairing 3d electrons, thus forms high-spin complex.
CN^- is a strong ligand. It can paired 3d electrons, thus forms low-spin complex.

7. Since the equilibrium constant decreases on increasing temperature, the reaction must be exothermic and thus have $\Delta_r H = -\text{ve}$

8. For the reaction $2H^+(aq) + 2e^- \rightarrow H_2(g)$, we have

$$E = -\frac{RT}{2F}\ln\frac{p_{H_2}}{[H^+]^2}$$

Multiplying and dividing right hand side by $[OH^-]^2$, we get

$$\begin{aligned} E &= -\frac{RT}{2F}\ln\frac{p_{H_2}[OH^-]^2}{[H^+]^2[OH^-]} = -\frac{RT}{2F}\ln\frac{p_{H_2}[OH^-]^2}{K_w^2} \\ &= \frac{RT}{F}\ln K_w - \frac{RT}{2F}\ln\left(p_{H_2}[OH^-]^2\right) \\ &= (0.5915\,\text{V})(-14) - \frac{RT}{2F}\ln\left(p_{H_2}[OH^-]^2\right) \\ &= -0.828\,\text{V} - \frac{RT}{2F}\ln\left(p_{H_2}[OH^-]^2\right) \end{aligned}$$

This expression corresponds to the reaction $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$. Hence $E^\circ = -0.828\text{V}$

9. Rhombohedral has the structural parameters $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$

10. —NO_2 is acid strengthening. Its affect at *para* position is more than at *meta* position. This is due to the fact at *para* position, nitro group generates. Some positive charge on the carbon bearing —COOH group. This causes electron-with drawing effect making *para* isomer more acidic than *meta* isomer. *Ortho* isomer is most acidic due to the *ortho* effect.

11. Copolymers are formed from two or more repeating monomer units. Examples are Saran (formed from vinyl chloride and vinylidene choloride) and Buna–S (formed from styrene (25%) and butadiene (75%)).

Teflon and orlon are homopolymer formed from acrylonitrile and tetrafluoroethene, respectively.

12. The reactions to be considered are:

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2 \\ H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-] \times 5 \\ \hline 2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^2 + 5O_2 + 4H_2O \end{array}$$

From the relation $(2)(M_{H_2O_2})(V_{H_2O_2}) = 5(M_{MnO_4^-})(V_{MnO_4^-})$

we get $$M_{H_2O_2} = \frac{(5)(M/20)(50.0\,mL)}{(2)(10\text{ mL})} = 0.625\,M$$

Mass of 1000 mL of H_2O_2 sample = (1000 mL) (1.4 g mL^{-1}) = 1400 g

Mass of H_2O_2 in the solution = (0.625 mol) (32 g mol^{-}) = 20 g

Mass of water in the solution = (1400 – 20) g = 1380 g

Molality of the solution = $\dfrac{n_2}{m_1} = \dfrac{0.625\,mol}{1.380\text{ kg}} = 0.453\text{ mol kg}^{-1}$

Mole fraction of H_2O in the solution = $\dfrac{n_2}{n_1 + n_2} = \dfrac{0.625}{(1380/18) + 0.625} = 0.008$

The volume strength of H_2O_2 is based on the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$.

2 mol H_2O_2 gives 1 mol of O_2 or 22:414 L of O_2 at STP

Hence, 0.625 mol per litre of solution of H_2O_2 will liberate $\left(\dfrac{22.414}{2\text{ M}}\right)(0.625\,M) = 7.00$

13. In Frenkel defect, the ion, instead of being in its expected location, is found in one of the interstices. This defect is favoured by a large difference in size between the cation and anion of the solid. Schottky defect involves the absence of cation or anion from the position which it is expected to occupy in the periodic arrangement of ions. This affects the physical properties of solids.

14. The reaction is $2NaNO_3(s) \rightleftharpoons 2NaNO_2(s) + O_2(g)$; $\Delta H = +ve$

Since the reaction is endothermic, increase in temperature will shift the reaction in the forward direction.

Since, Δv_g is positive, increasing pressure will cause the reaction to move in reverse direction.

Adding either $NaNO_3(s)$ or $NaNO_2(s)$ has no effect on equilibrium.

15. Nitric oxide is paramagnetic as it contains one unpaired electron.

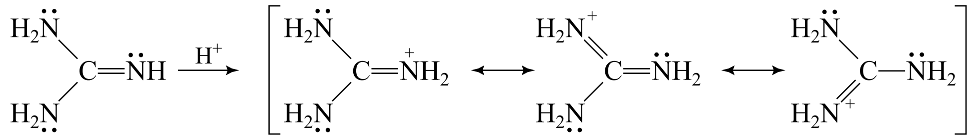
NO^+ contains10 valence electrons. Its valence electronic configuration is $(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2$.

Its bond order is $\frac{1}{2}$ (8 bonding electrons –2 antibonding electrons) = $\frac{1}{2}$ (8–2)=3

N_2O_3 is stable in the liquid phase. It decomposes to NO and NO_2 in the gaseous phase.

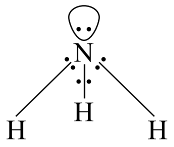
16. (a) In NF_3, nitrogen acquires δ^+ charge because it is less electronegative than fluorine. With positive charge on nitrogen, the lone pair of electrons are more tightly held in NF_3.

(b) In guanidine, the imino (=NH) nitrogen is sp^2 hybridised while amino ($-NH_2$) is sp^3 hybridised. The proton is likely to be attached to $-NH_2$ as its nitrogen has less s-character. Actually the imino nitrogen is protonated because this leads to the stable symmetrical resonating cation with very high delocalization energy as there are three contributing structures.

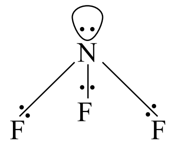


Because of the large delocalization energy, the cation is very much stabilised leading the guanidine to act as a strong base.

(c) Ammonia involves more bonding pair-bonding pair electronic repulsion as the pairs are located near the nitrogen atom due to its more electronegative character. In NF_3, F is more electronegative and thus bonding pair lies more near F leading to less electronic repulsion.



more electronic repulsion, more bond angle



less electronic repulsion, less bond angle

(d) The larger the s-character of a hybrid orbital of carbon, the larger electron-withdrawing (by induction) effect it has, consequently, the larger is its base-weakening effect.

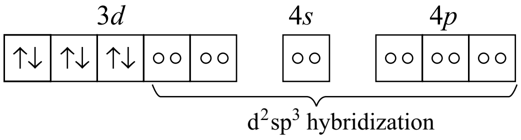
17. The reduction potential of Cl_2 to Cl^- is more positive than those of $[Cd(NH_3)_4]^{2+}$ to Cd, $[Cu(NH_3)_4]^{2+}$ to Cu and $Ag[(NH_3)_2]^+$ to Ag. Hence, Cl_2 will be able to oxidise all the three metals to the corresponding ammonical ions.

18. The reduction potential of Fe^{2+} to Fe is only more positive than that of $[Cd(NH_3)_4]^{2+}$ to Cd. Hence, Fe^{2+} will be able to oxidise only Cd to its ammonical ion.

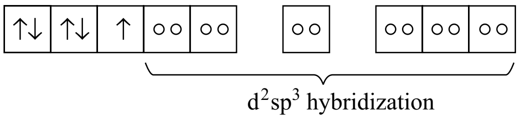
19. The reduction potential of Fe^{3+} to Fe is more positive than those of $[Cd(NH_3)_4]^{2+}$ to Cd and $[Cu(NH_3)_4]^{2+}$ to Cu. Hence, Fe^{3+} will be able to oxidise only Cd and Cu to their ammonical ions.

20. The electronic configurations of the complexes are as follows.

$[Fe(CN)_6]^{4-}$



$[Fe(CN)_6]^{3-}$



Both the ions involve d^2sp^3 hybridization.

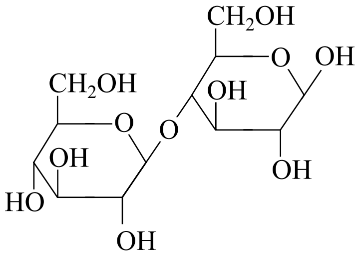
21. From the electronic configurations given in Q.20, it follows that $[Fe(CN)_6]^{4-}$ is diamagnetic while $[Fe(CN)_6]^{3-}$ is paramagnetic as the former has no unpaired 3d electrons while the latter has one 3d unpaired electron.

22. Ferrocyanide, $[Fe(CN)_6]^{4-}$ with Fe^{3+} ion and ferricyanide $[Fe(CN)_6]^{3-}$ with Fe^{2+} ions give blue coloration.

23. The structural parameters are as follows.

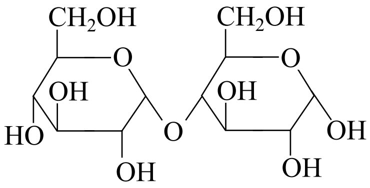
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$

24. Cellobiose is 1, 4′-β-glycoside and is a reducing sugar



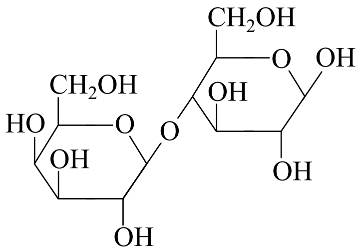
4-O-(β-D-Glucopyranosyl)-D-glucopyranos

Maltose is 1, 2′-α-glycoside and is a reducing sugar.



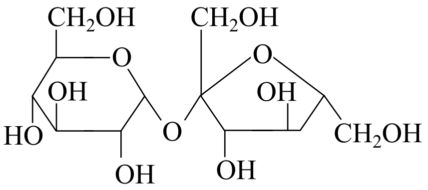
4-O-(α-D-Glucopyranosyl)-D-glucopyranos

Lactose is 1, 4′-β-glycoside and is reducing sugar. It contains glucose and galactose units.



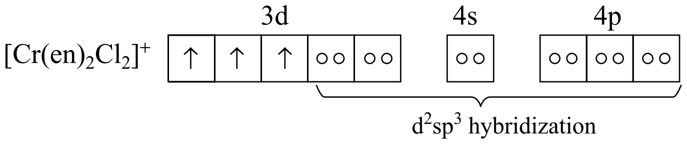
4-O-(β-D-Glucopyranosyl)-Dglucopyranos

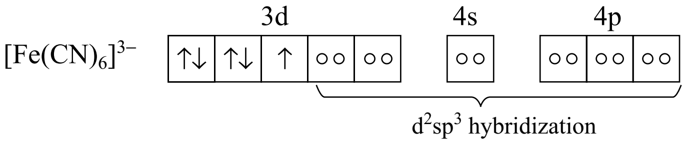
Surose is 1, 2′-α-glycoside and is reducing sugar. Its contains glucose and fructose units.

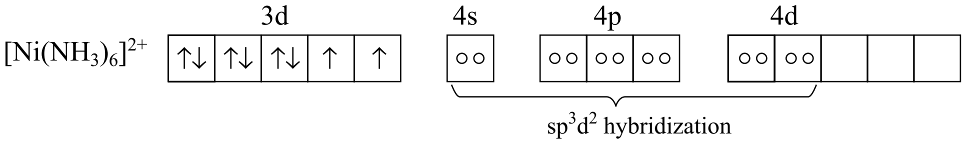


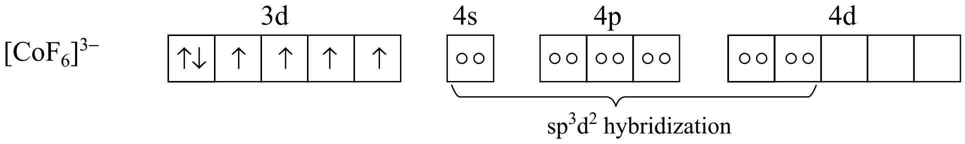
4-O-(α-D-Glucopyranosyl)-β-D-fructofuranoside

25. The electronic configurations are as follows.

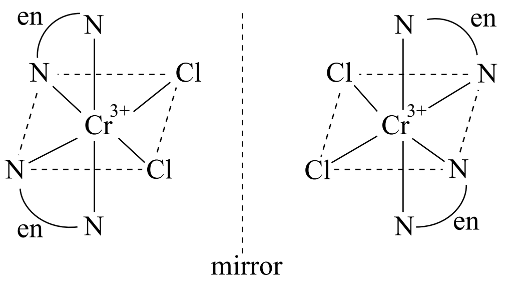








The *cis* - isomer of the complex $[Cr(en)_2Cl_2]^+$ shows optical isomers.



JEE ADVANCED

MODEL TEST PAPER II

(with Solutions)

SECTION–I

(Only one Option Correct)

This section contains **10 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

1. Which of the following salts is expected to have minimum value of standard solubility product constant?

(a) HgS (b) CuS (c) SnS (d) Bi_2S_3

2. Which of the following crystal systems has four Bravais lattices?

(a) Cubic (b) Tetragonal (c) Orthorhombic (d) Monoclinic

3. If the standard potentials of Cl^- |AgCl| Ag and $Ag(NH_3)_2^-$, NH_3|Ag are 0.222 V and 0.373 V, respectively, the value of standard equilibrium constant of the reaction $AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$ is about

(a) 1.28 (b) 0.0525 (c) 19.05 (d) 0.782

4. Phenol is added slowly to water with continuous stirring in increasing amount. Initially phenol dissolves completely and soon two layers are formed. The system continues to exist in two layers till it is again converted to a single layer. During the existence of two layers, which of the following statements is correct?

(a) Masses of the two layers change in a continuous manner without change in their compositions.

(b) Compositions of two layers change in a continuous manner without change in their masses.

(c) Both masses and compositions of the two layers change in a continuous manner.

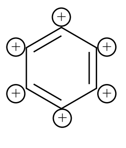
(d) Both masses and compositions of two layers change in a discontinuous manner.

5. In a binary solution, mole fraction of solute (x_2) is related to the molality (m) of the solution by the expression

(a) $x_2 = \dfrac{mM_1}{1 - mM_1}$ (b) $x_2 = \dfrac{mM_1}{1 + mM_1}$ (c) $x_2 = \dfrac{1 - mM_1}{mM_1}$ (d) $x_2 = \dfrac{1 + mM_1}{1 + mM_2}$

where M_1 and M_2 are the molar masses of solvent and solute, respectively.

6. The sign of coefficients of 2p atomic orbitals in three molecular orbitals of benzene are as follows.



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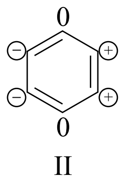
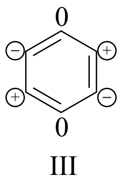


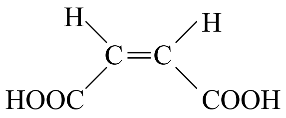
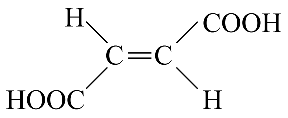
II



III

The correct order of their energies is

(a) I > II > III (b) I > III > II (c) II > III > I (d) III > II > I

7. Which of the following statements regarding maleic acid  and fumaric acid  is correct?

(a) Maleic acid is a stronger acid than fumaric acid but maleate monoanion is a weaker acid than fumarate monoanion.
(b) Maleic acid is a stronger acid than fumaric acid but maleate monoanion is a stronger acid than fumarate monoanion.
(c) Maleic acid is a weaker acid than fumaric acid but maleate monoanion is a stronger acid than fumarate monoanion.
(d) Maleic acid is a weaker acid than fumaric acid but maleate monoanion is a weaker acid than fumarate monoanion.

8. The correct order of reducing power of $GeCl_2$, $SnCl_2$ and $PbCl_2$ is
(a) $GeCl_2 < SnCl_2 < PbCl_2$ (b) $GeCl_2 > PbCl_2 > SnCl_2$
(c) $GeCl_2 > SnCl_2 > PbCl_2$ (d) $GeCl_2 < PbCl_2 < SnCl_2$

9. Which of the following statements is **not** correct for $Ni(CO)_4$ and $[NiCl_4]^{2-}$.
(a) Both differ in the state of hybridization (b) Both differ in magnetic properties
(c) Both differ in the oxidation state of Ni (d) Both differ stability on heating

10. Which of the following statements is not correct?
(a) Phenol is a stronger acid than ROH.
(b) PhO^- is a stronger base than RO^-
(c) $NaHCO_3$ does not react with phenol because it is less acidic than phenol.
(d) Na_2CO_3 reacts with phenol because it is more acidic than phenol.

SECTION — II

(Integer Answer Type)

This Section contains 6 **questions**. The answer to each question is a **single digit integer** ranging from 0 to 9. (both inclusive).

11. A solution containing 2.92×10^{-2} mol of B^{n+} ions requires 1.75×10^{-2} mol of MnO_4^- for the oxidation of B^{n+} to BO_3^- in acidic medium. The value of n is ___.

12. The per cent loss in mass of $K_2Cr_2O_7$ (molar mass of Cr = 52 g mol^{-1}) on heating is about ____ per cent.

13. A spherical balloon of 20 cm diameter is to be filled with hydrogen at 1 atm and 300 K from a cylinder containing the gas at 10 atm at 300 K. It the cylinder can hold 2.33 L of water, the number of balloons that can be filled up is____.

14. In a mixture of H and He^+ gases, H atoms and H^+ ions are excited to their first excited states. Subsequently, H atoms transfer its excitation energy to He^+ ion (by collision). The quantum number n of He^+ ion after the energy transferred is ____.

15. 0.30 g of an organic compound gave 18.68 mL of moist N_2 collected over NaOH solution at 27 °C and 760 mm Hg. If aqueous tension of water is 10 mmHg, the per cent of nitrogen in the compound is about ___.

16. An aldose requires ___ molecules of phenylhydrazine to form an osazone.

SECTION – III

(Paragraph Type)

This section contains 2 paragraphs each describing theory, experiment, data, etc. Each paragraph includes three multiple-choice questions with four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

Paragraph or Questions Nos. 17 to 19

Given:

$Cu(OH)_2 + 2e^- = Cu + 2OH^-$; $E° = -0.224$ V

$O_2 + 4H^+ + 4e^- = 2H_2O$; $E° = 1.229$ V

Answer the following.

17. The standard reduction potential of the reaction $Cu(OH)_2 + 2H^+ + 2e^- = Cu + 2H_2O$ will be
(a) – 1.050 V (b) 0.224 V (c) – 0.602 V (d) 0.602 V

18. The standard reduction potential of the reaction $O_2 + 2H_2O + 4e^- = 4OH^-$ will be

(a) 1.229 V (b) – 1.229 V (c) 0.403 V (d) – 0.403 V

19. Amongst the following four oxidizing agents, the strongest oxidizing ability is shown by

(a) O_2 in acidic medium
(b) O_2 in alkaline medium
(c) $Cu(OH)_2$ in acidic medium
(d) $Cu(OH)_2$ in alkaline medium

Paragraph for Question Nos. 20 to 22

Cobalt(III) forms complexes with various ligands. Hexacoordinate complexes of cobalt(III) may involve same or different hybridization of cobalt(III) in the complex. Their magnetic properties may also differ depending on the electronic configuration of the ion in the complexes. Also, they may acquire different colour depending upon the ligand coordinated to the ion. Identify the correct answer in each of the following questions.

20. Which of the following choices is correct regarding the hybridization of Co(III) in the complexes?

(a) d^2sp^3 in $[Co(CN)_6]^{3-}$ and sp^3d^2 in $[CoF_6]^{3-}$
(b) sp^3d^2 in $[Co(CN)_6]^{3-}$ and d^2sp^3 in $[CoF_6]^{3-}$
(c) Both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ involve d^2sp^3
(d) Both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ involve sp^3d^2

21. Which of the following choices is correct regarding magnetic properties of the given complexes?

(a) $[Co(CN)_6]^{3-}$ is paramagnetic while $[CoF_6]^{3-}$ is diamagnetic
(b) $[Co(CN)_6]^{3-}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic
(c) Both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ are paramagnetic
(d) Both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ are diamagnetic

22. Which of the following choices is correct regarding colour of the given complexes?

(a) Both $[CoF_6]^{3-}$ and $[Co(en)_3]^{3+}$ are yellow
(b) Both $[CoF_6]^{3-}$ and $[Co(en)_3]^{3+}$ are blue
(c) $[CoF_6]^{3-}$ is blue while $[Co(en)_3]^{3+}$ is yellow
(d) $[CoF_6]^{3}$ is yellow while $[Co(en)_3]^{3+}$ blue

SECTION – IV

(Matching List Type)

This section contains 3 questions. Each questions contain statements given in two columns which have to be matched. Statements (a, b, c, d) in Column-I have to be matched with statements (p, q, r, s) in Column-II.

23. Match the crystal systems mentioned in **Column-I** with their Bravais lattices mentioned in **Column-II**.

Column I	**Column II**
(a) Monoclinic	(p) P
(b) Tetragonal	(q) I
(c) Orthorhomic	(r) C
(d) Trigonal	(s) F

24. Match the chemical substance in **Column-I** with type of polymer/type of bonds in **Column-II.**

Column I	**Column II**
(a) Polystyrene	(p) Step-growth polymer
(b) Dacron	(q) Chain-growth polymer
(c) Nylon-6, 6	(r) Amide linkages
(d) Proteins	(s) Ester linkages

25. Match the physical quantities in **Column-I** with their characteristics in **Column-II.**

Column I	**Column II**
(a) Molarity	(p) Temperature dependent
(b) Molality	(q) Temperature independent
(c) Mole fraction	(r) Unit less
(d) Density	(s) Intensive property

ANSWERS

1. (b)
2. (c)
3. (b)
4. (a)
5. (b)
6. (d)
7. (a)
8. (c)
9. (a)
10. (b)
11. (2)
12. (8)
13. (5)
14. (4)
15. (7)
16. (3)
17. (d)
18. (c)
19. (a)
20. (a)
21. (b)
22. (c)
23. a–p, r; b–p, q; c–p,q,r,s; d–p
24. a–q; b–p, s; c–p, r; d–r,
25. a–p,s; b–q,s; c–q,r,s; d–p,s

Solutions

1. $HgS(s) \rightleftharpoons Hg^{2+} + S^{2-}$ $K_{sp} = [Hg^{2+}]\,[S^{2-}]$ $SnS(s) \rightleftharpoons Sn^{2+} + S^{2-}$ $K_{sp} = [Sn^{2+}]\,[S^{2-}]$

$CuS(s) \rightleftharpoons Cu^{2+} + S^{2-}$ $K_{sp} = [Cu^{2+}]\,[S^{2-}]$ $Bi_2S_3(s) \rightleftharpoons 2Bi^{3+} + 3S^{2-}$ $K_{sp} = [Bi^{3+}]\,[S^{2-}]^3$

Since K_{sp} of Bi_2S_3 involves square and cubic expressions, its solubility product is expected to have minimum value.

2. Orthorhombic lattice has four Bravais lattices. These are primitive (P), body-centred (I), face-centred (F) and end-centred (c).

Cubic lattice has three Bravais lattices, namely, P, I and F.

Monoelinic lattice has two Bravais lattices, namely, P and C

Tetragonal lattice also, has two Bravais lattices, nomely, P and I

3. We have

$$\begin{array}{lll} & AgCl + e^- \rightarrow Ag + Cl^-; & E_1^\circ = 0.222\ V \\ \text{Subtract} & Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3; & E_2^\circ = 0.373\ V \\ \hline & AgCl + 2NH_3 \rightarrow Ag\,(NH_3)_2^+ + Cl^- & \end{array}$$

$$E^\circ = E_1^\circ - E_2^\circ = (0.222 - 0.373)\ V = -0.151\ V$$

Now $\Delta G^\circ = -nFE^\circ = -RT \ln K_{eq}^\circ$

Thus, $\ln K_{eq}^\circ = \dfrac{E^\circ}{(RT/nF)} = \dfrac{-0.151\,V}{0.5915\,V} = -0.2553$

$$K_{eq}^\circ = 0.77$$

(Note : $\ln K_{eq}^\circ$ is negative, K_{eq}° will be less that 1.)

4. So long two layers exist, their compositions will remain constant irrespective of their masses.

5. By diffinition, molatity m is

$$m = \frac{n_2}{m_1}$$

where n_2 is the amount of solute and m_1 is the mass of solvent. Since $m_1 = n_1M_1$, we have

$$m = \frac{n_2}{n_1M_1} \quad \text{or} \quad \frac{n_1}{n_2} = \frac{1}{mM_1}$$

Adding 1 on both sides, we get

or $$\frac{n_1 + n_2}{n_2} = \frac{1 + mM_1}{mM_1}$$

Taking inverse, we have

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{mM_1}{1 + mM_1}$$

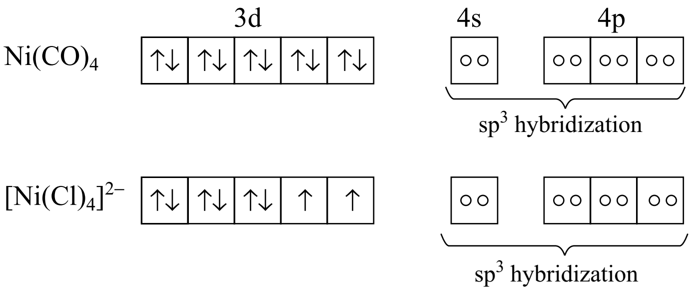
6. Larger the nodal planes, larger the energy.
Structure I has no nodal plane
Structure II has one nodal plane
Structure III has two nodal planes
Hence, the energies follows the order III > II > I

7. The maleic acid is a stronger acid because of the stabilization of its monoanion due to H-bonding between the *cis* COOH and COO^- groups. This is not present in fumaric acid.

H-Bonding in maleate monoanion makes the removal of H more difficult as compared to fumarate monoanion where H-bonding is not present.

8. Due to inter-pair effect, M^{2+} ion of Group 14 is more stabilised on descending the group. Hence, the reducing power follows the order $GeCl_2 > SnCl_2 > PbCl_2$

9. The electronic configurations are.



Both the complexes have the same hybridization. They have different magnetic properties, oxidation state of Ni and stability.

10. (b) The negative charge on the alkoxide anion, RO^-, is completely localised, but the negative charge on PhO^- is delocalised by extended π-bonding to the *ortho* and *para* ring positions. This makes PhO^- weaker base than RO^- and PhOH a stronger acid than ROH.

(c) The reaction of phenol with $NaHCO_3$ would produce the following reaction

$$\begin{array}{ccccccc} \text{PhOH} & + & HCO_3^- & \not\longrightarrow & PhO^- & + & H_2CO_3 \\ pK_a^\circ = 10 & & pK_b^\circ = 7.6 & & pK_b^\circ = 4 & & pK_a^\circ = 6.4 \\ \text{(weaker)} & & \text{(weaker)} & & \text{(stronger)} & & \text{(stronger)} \end{array}$$

Both the reactants are weaker than the corresponding species on the right side. Thus, the reaction would not proceed to the right side.

(d) The reaction would be

$$\begin{array}{ccccccc} \text{PhOH} & + & CO_3^{2-} & \longrightarrow & PhO^- & + & HCO_3^- \\ pK_a^\circ = 10 & & pK_b^\circ = 3.7 & & pK_b^\circ = 4 & & pK_a^\circ = 10.3 \\ \text{(stronger)} & & \text{(stronger)} & & \text{(weaker)} & & \text{(weaker)} \end{array}$$

Both the products are weaker than the corresponding species on the left side. Thus, the reaction proceeds to the right side.

11. The reactions are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$B^{n+} + 3H_2O \rightarrow BO_3^- + 6H^+ + (5-n)e^-$$

Hence, we have

$$5(1.75 \times 10^{-2}\ \text{mol}) = (5 - n)\ (2.92 \times 10^{-2}\ \text{mol})$$

which gives $n = 5 - 5\ (1.75 \times 10^{-2}\ \text{mol})/\ (2.92 \times 10^{-2}\ \text{mol}) = 5 - 3 = 2$

12. The reactions to be considered is:

$$4\,K_2\,Cr_2O_7 \rightarrow 4\,K_2CrO_4 + 2\,CrO_3 + 3\,O_2$$

The loss of mass is due to the escape of O_2. For 1 mol $K_2\,Cr_2O_7$, (3/4) mol of O_2 is escaped. Hence

$$\frac{\text{Mass of (3/4) mol } O_2}{\text{Mass of 1 mol of } K_2Cr_2O_7}\times 100 = \frac{\left(\frac{3}{4}\right)(32\text{ g mol}^{-1})}{(294\text{ g mol}^{-1})}\times 100 = 8.16 \simeq 8$$

13. Volume of balloon = $\frac{4}{3}\pi r^3 = \left(\frac{4}{3}\right)\left(\frac{22}{7}\right)\left(\frac{20\text{ cm}}{2}\right)^2 = 4190.5\text{ cm}^3$

Volume of gas available at 1 atm

$$V = \frac{V_1 p_1}{p} = \frac{(2.33\text{ L})(10\text{ atm})}{1\text{ atm}} = 23.3\text{ L}$$

During the filling of the gas, 2.33 L of the gas will remain in the cylinder. Hence, the volume of gas available for filling the balloons is

$$V = 23.3\text{ L} - 2.33\text{ L} = 20.97\text{ L}$$

Number of balloons that can be filled is

$$\frac{20.97\times 10^3\text{ cm}^3}{4190.5\text{ cm}^3} = 5$$

14. The energy difference between two orbits of hydrogen-like species is

$$\Delta E = Z_2\, R_H\, hc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For hydrogen atom, $\Delta E_{1\rightarrow 2} = R_H hc\left(\frac{1}{1} - \frac{1}{4}\right) = \frac{3}{4}R_H hc$

When this energy is transferred to the first excited state of He^+, we will have

$$\frac{3}{4}R_H hc = (2^2)R_H hc\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

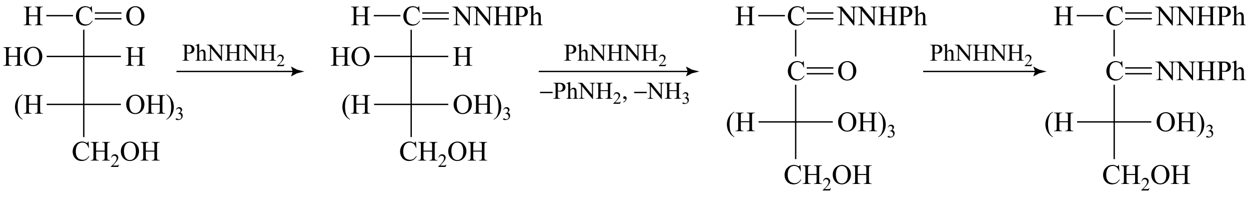
Solving for n, we get $n = 4$.

15. Volume collected at STP is

$$V_2 = \left(\frac{p_1V_1}{T_1}\right)\left(\frac{T_2}{p_2}\right) = \frac{\{(760-10)\text{ mmHg}\}(18.68\text{ mL})(273\text{ K})}{(300\text{ K})(760\text{ mmHg})} = 16.77\text{ mL}$$

Per cent of $N = \frac{M_{N_2}}{(V_m)_{STP}}\left\{\frac{(V_{N_2})_{STP}}{m_{\text{compound}}}\times 100\right\} = \left(\frac{28g\text{ mol}^{-1}}{22400\text{ mL mol}^{-1}}\right)\left(\frac{16.77\text{ mL}}{0.30\text{ g}}\times 100\right) = 6.99 \simeq 7$

16.



on osazone

17. For the half-cell reaction

$Cu(OH_2) + 2e^- \rightarrow Cu + 2OH^-$

Nernst equation is

$$E = E^\circ - \frac{RT}{2F}\ln[OH^-]^2 = E^\circ - \frac{RT}{2F}\ln\left([OH^-]^2\frac{[H^+]^2}{[H^+]^2}\right)$$

$$= E^\circ - \frac{RT}{2F}\ln\frac{K_w^2}{[H^+]^2} = \left(E^\circ - \frac{RT}{2F}\ln K_w^2\right) - \frac{RT}{2F}\ln\frac{1}{[H^+]^2}$$

This expression represents the Nernst equation for $Cu(OH)_2 + 2H^+ + 2e^- \rightarrow Cu + 2H_2O$.
Hence, its E_1° is

$$E_1^\circ = E^\circ - \frac{RT}{2F}\ln K_w^2 = -0.224\text{ V} + 0.059 \times 14 = -0.224\text{ V} + 0.826\text{ V} = 0.602\text{ V}$$

18. For the half-call reaction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Nernst equation is $$E = E^\circ - \frac{RT}{4F}\ln\frac{1}{[H^+]^4 p_{O_2}} = E^\circ - \frac{RT}{4F}\ln\left(\frac{1}{[H^+]^4}\frac{[OH^-]^4}{[OH^-]^4}\frac{1}{p_{O_2}}\right)$$

$$= E^\circ - \frac{RT}{4F}\ln\left(\frac{[OH^-]^4}{K_w^4}\frac{1}{p_{O_2}}\right) = \left(E^\circ + \frac{RT}{4F}\ln K_w\right) - \frac{RT}{4F}\ln\frac{[OH^-]^4}{p_{O_2}}$$

This expression reprents the Nernst equation for $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Hence, its E_1° is

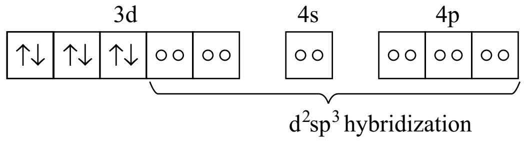
$$E_1^\circ = E^\circ + \frac{RT}{F}\ln K_w$$

$$= 1.229\text{ V} - (0.059\text{ V}) \times 14 = 1.229\text{ V} - 0.826\text{ V} = 0.403\text{ V}$$

19. Larger the reduction potential of a species, larger its oxidizing ability. Hence, O_2 in acidic medium is the strongest oxidizing agent.

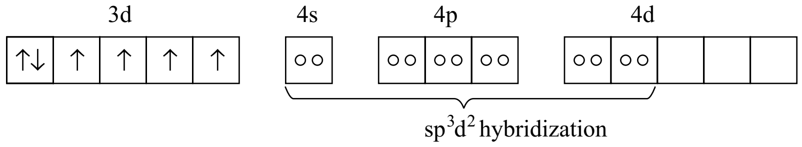
20. The electronic configurations of Co^{3+} in the given complexes are as follows

Co^{3+} ($3d^6$) in $[Co(CN)_6]^{3-}$



CN^- is a strong ligand. It can couse pairing of electrons

Co^{3+} ($3d^6$) in $[CoF_6]^{3-}$



F^- is a weak ligand. It is unable to cause pairing the electrons.

21. $[CoF_6]^{3-}$ is paramagnetic because of the presence of four unpaired electrons.
$[Co(CN)_6]^{3-}$ is diagmagnetic as there no unpaired electron.

22. en being a strong ligand, the splitting of 3d orbitals is larger and thus the complex requires larger energy to excite electron within 3d orbitals. The complementary colour will be of lesser energy.
F^- being a weak ligand, the splitting of 3d orbitals is not large, and thus the complex requires lesser energy to excite electrons within 3d orbitals. The complementary colour will be of larger energy. Thus $[CoF_6]^{3-}$ is expected to be blue while $[Co(en)_3]^{3-}$ is expected to be yellow.

23. Monoclinic has P and C Bravais lattices
Tetragonal has P and I Bravais lattices
Orthorhombic has P, I C and F Broavais lattices
Trigonal has only P lattice.

24. Polystyrene is a chain-growth polymer formed from styrene ($H_2C{=}CHC_6H_5$)
Dacron is a step-growth polymer formed by the condensation of ethylene glycol and terephthalic acid. It contains ester linkages.
Nylon-6, 6 is a step-growth polymer formed by the condensation of hexamethylene diamine and adipic acid. It contains amide linkages.
Proteins contains amide linkages.

25. Molarity and density are temperature dependent while molality and mole fraction are temperature independent. All the four concentration terms are intensive property as their values remains the same on dividing the solution in two or more portions. Only mole fraction is unit less.

MODEL SOLUTIONS

IIT-JEE CHEMISTRY PAPER I—2012

SECTION–I

(Single Correct Answer Type)

This section contains **10 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

1. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ?

(a) HNO_3, NO, NH_4Cl, N_2 (b) HNO_3, NO, N_2, NH_4Cl

(c) HNO_3, NH_4Cl, NO, N_2 (d) NO, HNO_3, NH_4Cl, N_2

Solution :

The oxidation states of nitrogen in the given compounds are as follows.

HNO_3 : $+1 + x + 3(-2) = 0 \Rightarrow x = +5$ NO : $x + (-2) = 0 \Rightarrow x = +2$

NH_4Cl : $x + 4(+1) + (-1) = 0 \Rightarrow x = -3$ N_2 : $2(x) = 0 \Rightarrow x = 0$

Thus, the decreasing oxidation numbers of nitrogen is HNO_3, NO, N_2 and NH_4Cl.

Therefore, the **choice (b)** is correct.

2. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom (a_0 is Bohr radius) is

(a) $h^2/(4\pi^2 m a_0^2)$ (b) $h^2/(16\pi^2 m a_0^2)$ (c) $h^2/(32\pi^2 m a_0^2)$ (d) $h^2/(64\pi^2 m a_0^2)$

Solution :

Bohr model of an atom satisfies the following two requirements.

- Equality of centripetal and centrifugal forces, i.e.

$$\frac{(Ze)(e)}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r}$$

- Quantization of angular momentum, i.e.

$$mvr = n\left(\frac{h}{2\pi}\right)$$

Eliminating v in these two expressions, we get

$$r = n^2\left[\frac{h^2}{4\pi^2 m\left(Ze^2/4\pi\varepsilon_0\right)}\right] = \frac{n^2}{Z}a_0$$

where a_0 is the Bohr radius. The kinetic energy of the electron in Bohr orbit of an atom is

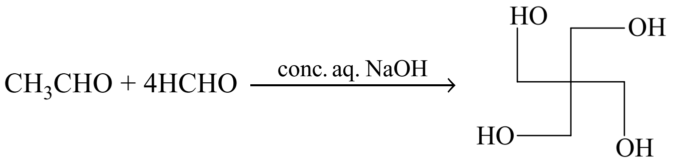
$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m\left[\frac{n}{mr}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{1}{2}m\left[\frac{n}{m\left(n^2 a_0/Z\right)}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{Z^2}{n^2}\left(\frac{h^2}{8\pi^2 m a_0^2}\right)$$

For the second Bohr orbit of hydrogen atom, $Z = 1$, and $n = 2$. Hence

$$\text{KE} = \frac{1}{32}\left(\frac{h^2}{\pi^2 m a_0^2}\right)$$

Therefore, the **choice (c)** is correct.

3. The number of aldol reaction(s) that occurs in the given transformation



$$CH_3CHO + 4HCHO \xrightarrow{\text{conc. aq. NaOH}}$$

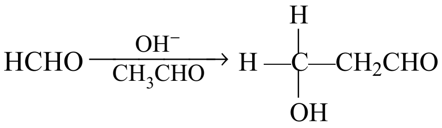
is

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

Solution :

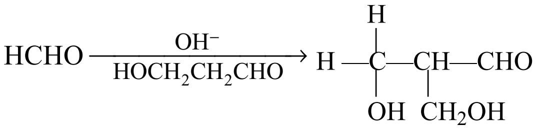
The given reaction may be formulated as follows.

- *First aldol condensation*



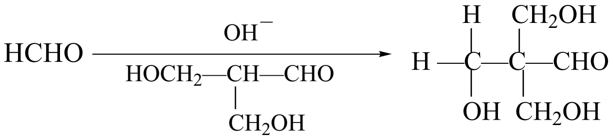
$$HCHO \xrightarrow[CH_3CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-CH_2CHO$$

- *Second aldol condensation*



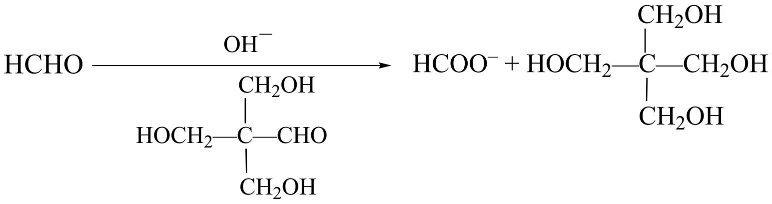
$$HCHO \xrightarrow[HOCH_2CH_2CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-\underset{CH_2OH}{CH}-CHO$$

- *Third aldol condensation*



$$HCHO \xrightarrow[HOCH_2-\underset{CH_2OH}{CH}-CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CHO$$

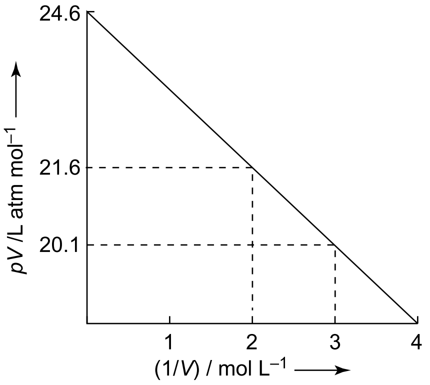
- *Cannizzaro reaction*



$$HCHO \xrightarrow[HOCH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CHO]{OH^-} HCOO^- + HOCH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2OH$$

There are three aldol condensations and one Cannizzaro reaction.
Therefore, the **choice (c)** is correct

4. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the plot of pV versus $1/V$ is shown below.



The value of the van der Waals constant a is

(a) 1.0 L^2 atm mol^{-2} (b) 4.5 L^2 atm mol^{-2} (c) 1.5 L^2 atm mol^{-2} (d) 3.0 L^2 atm mol^{-2}

Solution :

For one mole of a gas, the van der Waals equation is $\left(p+\frac{a}{V^2}\right)(V-b) = RT$

When $b = 0$, we have $\left(p+\frac{a}{V^2}\right)V = RT$ i.e. $pV = RT - \frac{a}{V}$

The plot of pV versus $1/V$ will be a straight line with slope equal to $-a$. Hence

Slope of the given straight line is $\dfrac{(20.1-21.6)\,\text{L atm mol}^{-1}}{(3.0-2.0)\,\text{mol L}^{-1}} = -1.5\ \text{L}^2\ \text{atm mol}^{-2}$

Equating this to $-a$, we get $a = 1.5\ \text{L}^2\ \text{atm mol}^{-2}$

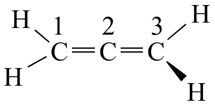
Therefore, the **choice (c)** is correct.

5. In allene (C_3H_4), the type(s) of hybridization of the carbon atom is (are)

(a) sp and sp^3 (b) sp and sp^2 (c) sp^3 only (d) sp^2 and sp^3

Solution :

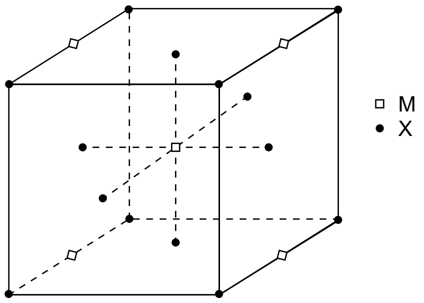
The structure of allene is



In this molecule, carbon atoms 1 and 3 are sp^2 hybridized while the carbon atom 2 is sp hybridized.

Therefore, the **choice (b)** is correct.

6. A compound M_pX_q has cubic close packing (CCP) arrangement of X. Its unit cell structure is shown below.



The empirical formula of the compound is

(a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}

Solution :

The atom at the corner of the cube is shared amongst 8 unit cells; the atom at the centre of a face is shared between 2 unit cells, the atom at the centre of edges is shared amongst 4 unit cells and that at the centre of the cube belongs wholly to the unit cell.

There are eight X atoms at the corners and six X atoms at the centre of faces. Thus, the number of X atoms per unit cell is

$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 1 + 3 = 4$$

There are four M atoms at the centre of edges and one M atom at the centre of the cube.

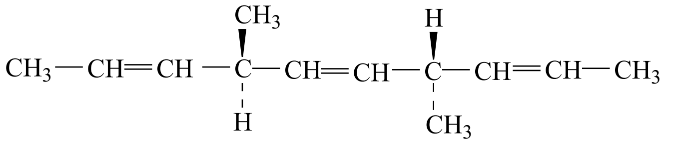
Thus, the number of M atoms per unit cell is

$$4\left(\frac{1}{4}\right) + 1(1) = 1+1 = 2$$

The formula of the compound will be M_2X_4 and the empirical formula will be MX_2.

Therefore, the **choice (b)** is correct.

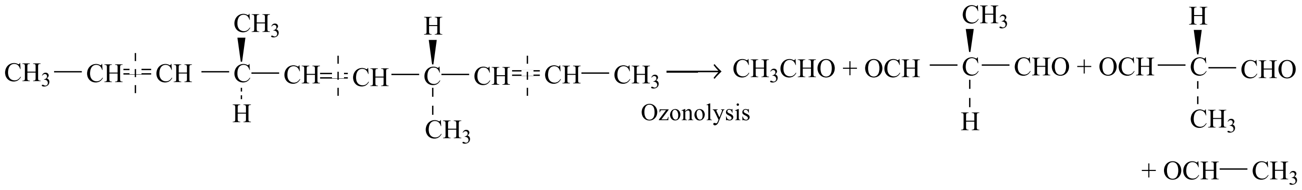
7. The number of optically active products obtained from the complete ozonolysis of the given compound



$$CH_3-CH=CH-\underset{H}{\overset{CH_3}{C}}-CH=CH-\underset{CH_3}{\overset{H}{C}}-CH=CH-CH_3$$ is

(a) 0 (b) 1 (c) 2 (d) 4

Solution :



$$CH_3-CH=CH-\overset{CH_3}{\underset{H}{C}}-CH=CH-\overset{H}{\underset{CH_3}{C}}-CH=CH-CH_3 \xrightarrow[\text{Ozonolysis}]{} CH_3CHO + OCH-\overset{CH_3}{\underset{H}{C}}-CHO + OCH-\overset{H}{\underset{CH_3}{C}}-CHO + OCH-CH_3$$

None of the products will be optically active.
Therefore, the **choice (a)** is correct.

8. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]\,Cl_3$ is
(a) Tetraaquadiaminecobalt(III) chloride (b) Tetraaquadiamminecobalt(III) chloride
(c) Diaminetetraaquacobalt(III) chloride (d) Diamminetetraaquacobalt(III) chloride

Solution :

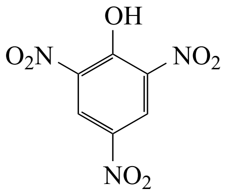
While naming a complex, the ligands are quoted in alphabetical order, regardless of their charges (followed by the metal). The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the metal name without any intervening blank. NH_3 is named as ammine and not as amine. Hence, the IUPAC name of the given compound is Diamminetetraaquacobalt(III) chloride.
Therefore, the **choice (d)** is correct.

9. The carboxylic functional group (—COOH) is present in
(a) picric acid (b) barbituric acid (c) ascorbic acid (d) aspirin

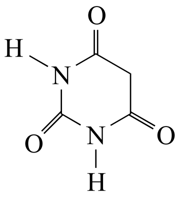
Solution :

The structures of the given compounds are as follows.

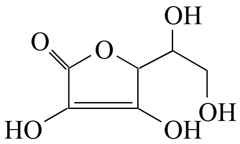
Picric acid



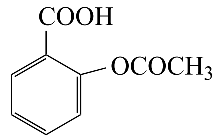
Barbituric acid



Ascorbic acid



Aspirin



Therefore, the **choice (d)** is correct.

10. The colour of light absorbed by an aqueous solution of $CuSO_4$ is
(a) orange-red (b) blue-green (c) yellow (d) violet

Solution :

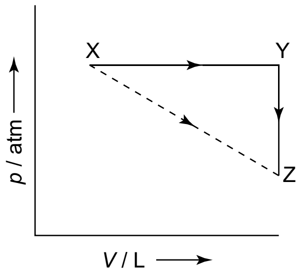
An aqueous solution of $CuSO_4$ is blue. The colour of light absorbed by this solution is that of complimentary colour which is orange-red.
Therefore, the **choice (a)** is correct

SECTION – II

Multiple Correct Answers(s) Type

This section contains **5 multiple** choice questions. Each question has four choices (a), (b), (c) and (d) out of which **ONE** or **MORE** is/are correct.

11. For an ideal gas, consider only *p–V* work in going from an initial state X to the final state Z. The final state can be reached by either of the two paths shown in the figure. Which of the following choice (s) is/are correct ? (Take ΔS as the change in entropy and *w* as work done.)



(a) $\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$ (b) $w_{X\to Z} = w_{X\to Y} + w_{Y\to Z}$

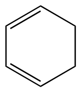
(c) $w_{X\to Y\to Z} = w_{X\to Y}$ (d) $\Delta S_{X\to Y\to Z} = \Delta S_{X\to Y}$

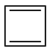
Solution :

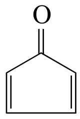
Entropy *S* is a state function. The entropy change in going from one state to another does not depend upon the path(s) followed. The work done is path-dependent function. The change of state from Y to Z is a constant volume process and the work involved ($-p\,dV$) will be zero.

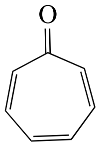
The choice (a) is correct as *S* is a state function. The choice (c) is also correct as $w_{Y\to Z}$ is zero. The choices (b) and (d) are incorrect. Therefore, the **choices (a) and (c)** are correct.

12. Which of the following molecules, in pure form, is (are) unstable at room temperature?

(a) 

(b) 

(c) 

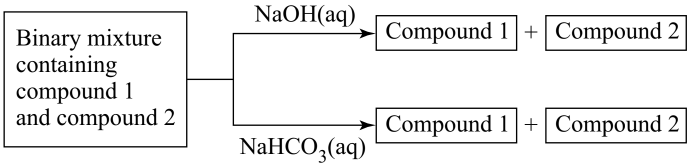
(d) 

Solution :

Cyclobutadiene (choice b) is an unstable due to much strain in the ring because of the shorter double-bond length and larger deviation from the stable bond angles. This molecule has not been isolated and has only a lifetime shorter than 5s in the free state. Cyclopentadienone (choice c) is also very reactive and has not been isolated. Its life time is about 15s. The cyclopentadiene ring with the formaion of the carbocation at the carbonyl carbon in its resonance structure has an anti-aromatic character due to which it is destabilised. Cycloheptatrienone (choice d) is quite stable due to the aromatic character of the ring with the formation of carbocation at the carbonyl carbon in its resonance structure.

Therefore the **choices (b) and (c)** are correct.

13. Identify the binary mixture(s) that can be separated into individual compounds by differential extraction as shown in the scheme.



(a) $C_6H_5OH + C_6H_5COOH$ (b) $C_6H_5COOH + C_6H_5CH_2OH$

(c) $C_6H_5CH_2OH + C_6H_5OH$ (d) $C_6H_5CH_2OH + C_6H_5CH_2COOH$

Solution :

We have the following facts.

C_6H_5OH is solube in NaOH(aq) and not in $NaHCO_3$(aq). C_6H_5COOH is soluble in both NaOH(aq) and $NaHCO_3$(aq). $C_6H_5CH_2OH$ is insoluble in both NaOH(aq) and $NaHCO_3$(aq). $C_6H_5CH_2COOH$ is soluble in both NaOH(aq) and $NaHCO_3$(aq). Thus, we have

Only in the choices (b) and (d), one compound is soluble and the other one is insoluble in both NaOH(aq) and $NaHCO_3$(aq) solutions.

In choice (a), C_6H_5OH and C_6H_5COOH are soluble in NaOH(aq) while C_6H_5OH is insoluble and C_6H_5COOH is soluble in $NaHCO_3$(aq).

In choice (c), $C_6H_5CH_2OH$ and C_6H_5OH are insoluble in $NaHCO_3$(aq) while $C_6H_5CH_2OH$ is insoluble and C_6H_5OH is soluble in NaOH(aq).

Thus, only in choices (b) and (d), the two components can be separated as one is soluble while the second one is insoluble in both NaOH(aq) and $NaHCO_3$(aq).

Therefore, the **choices (b) and (d)** are correct.

14. Choose the correct reason(s) for the stability of lyophobic colloidal particles.
(a) Preferential adsorption of ions on their surface from the solution.
(b) Preferential adsorption of solvent on their surface from the solution.
(c) Attraction between different particles having opposite charges on their surface.
(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

Solution :

The stability of lyophobic colloidal particles is due to the preferential adsorption of common ion from the solution. Each colloidal particle has the same charge and are thus kept away from each other due to electronic repulsion (choice a).
There exists potential difference between the fixed and diffused layer of opposite charge (choice d).
Therefore, the **choice (a) and (d)** are correct.

15. Which of the following halides react(s) with $AgNO_3$(aq) to give a precipitate that dissolves in $Na_2S_2O_3$(aq) ?

(a) HCl (b) HF (c) HBr (d) HI

Solution :

The precipitates of AgCl, AgBr and AgI are soluble in $Na_2S_2O_3$(aq) forming the complex $Na_3[Ag(S_2O_3)_2]$. For example,

$$Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 + 2NaBr$$
$$Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3\,[Ag(S_2O_3)_2]$$

AgF is soluble in water.
Therefore, the **choices (a), (c) and (d)** are correct.

SECTION – III

Integer Answer type

This section contains 5 questions. The answer to each question is single-digit integer, ranging from 0 to 9 (both inclusive).

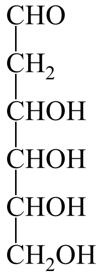
16. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$, respectively. What is the value of $(t_{1/8}/t_{1/10})*10$? (log 2 = 0.3.)

Solution :
For first-order decomposition of A, the rate law is $\ln([A]/[A]_0) = -kt$
Hence $\ln(1/8) = -k\,t_{1/8}$ and $\ln(1/10) = -k\,t_{1/10}$

Thus $$\frac{\ln(1/8)}{\ln(1/10)} = \frac{t_{1/8}}{t_{1/10}} \quad \text{or} \quad \frac{\log 8}{\log 10} = \frac{t_{1/8}}{t_{1/10}}$$

Hence $(t_{1/8}/t_{1/10}) = \log 8 = \log 2^3 = 3\log 2 = 3 \times 0.3 = 0.9$ or $10(t_{1/8}/t_{1/10}) = 10 \times 0.9 = 9$
Therefore, the answer is **9**.

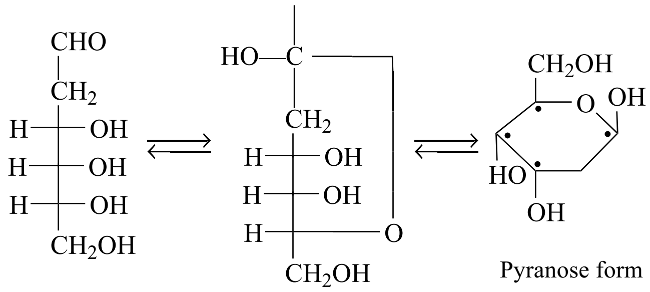
17. When the following aldohexose exists in D–configuration, the total number of stereoisomers in its pyranose form is



$$\begin{array}{l} CHO \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Solution:

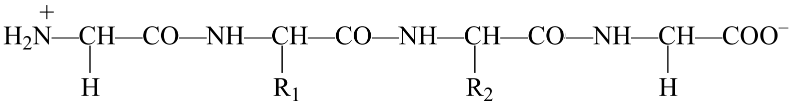
In D-configuration, the hydroxyl group at the assymmetric carbon placed at the bottom of Fischer projection lies to the right of the straight skeleton. Thus, we will have


Pyranose form

There are four chiral carbon atoms in the pyranose form of the given aldohexose. Thus, there will be 16 (= 2^4) stereoisomers, out of which 8 are of D-configurations (CH_2OH group above the ring) and 8 are of L-configurations (CH_2OH group below the ring).

Therefore, the correct answer is **8**.

18. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many these peptides are positively charged at pH = 7.0 ?



$$\overset{+}{H_2N}—\underset{H}{CH}—CO—NH—\underset{R_1}{CH}—CO—NH—\underset{R_2}{CH}—CO—NH—\underset{H}{CH}—COO^-$$

Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4\ NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

Solution:

In general, the pH of the solution at which amino acids exist as zwitterion follows the order :

$$\underset{(pH \simeq 3)}{\text{Acidic side chain}} < \underset{(pH = 5.5 – 6.0)}{\text{neutral chain}} < \underset{(pH = 9–10)}{\text{basic side chain}}$$

This pH is known as isoelectric point.

At pH = 7, the acidic side chain (for which isoelectric point < 7) exists as a negatively–charged species (e.g. $—COO^-$) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g. $—NH_3^+$). Since peptides IV, VI, VIII and IX contain $—NH_2$ group in R_1 or/and R_2 group(s), these are expected to exist as positively–charged species.

Therefore, the correct answer is **4**.

19. The periodic table consits of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table ?

$$^{63}_{29}\text{Cu} + {}^1_1\text{H} \rightarrow 6\,{}^1_0\text{n} + \alpha + 2\,{}^1_1\text{H} + \text{X}$$

Solution :

The reaction is $^{63}_{29}\text{Cu} + {}^1_1\text{H} \rightarrow 6\,{}^1_0\text{n} + {}^4_2\text{He} + 2\,{}^1_1\text{H} + {}_Z\text{X}$

Balancing the atomic numbers on both sides, we get $29 + 1 = 6(0) + 1(2) + 2(1) + 1(Z)$

which gives $Z = 26$

Copper belongs to Group 11 of the periodic table as shown in the following.

Atomit number	29
Elements in First period	–2
Elements in Second period	–8
Elemens in Third period	–8
Number in Fourth period	11th Group

The element with atomic number 26 will belong to the following group. 26 – 2 – 8 – 8 = 8th Group

Therefore, the Group number of X is **8**.

20. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molar mass of HCl is 36.5 g mol^{-1}. The volume in mL of stock solution required to prepare a 200 mL solution of 0.4 M HCl is _______ .

Solution :

Amount of HCl required to prepare 200 mL (= 0.2 L) solution of 0.4 M HCl is

$$n = MV = (0.4 \text{ mol L}^{-1})\ (0.2 \text{ L}) = 0.08 \text{ mol}$$

Mass of HCl required to prepare the said solution is

$$m = nM_\text{m} = (0.08 \text{ mol})\ 36.5 \text{ g mol}^{-1}) = 2.92 \text{ g}.$$

Mass of HCl solution containing 2.92 g of HCl is

$$m_1 = \left(\frac{\text{mass of solution}}{\text{mass of HCl}}\right)(m) = \left(\frac{100 \text{ g}}{29.2 \text{ g}}\right)(2.92 \text{ g}) = 10 \text{ g}$$

Volume of HCl solution required to prepare the given HCl solution is $V = \dfrac{m_1}{\rho} = \dfrac{10 \text{ g}}{1.25 \text{ g mL}^{-1}} = 8 \text{ mL}$

Therefore, the correct answer is **8**.

MODEL SOLUTIONS

IIT-JEE CHEMISTRY PAPER II—2012

SECTION–I

(Single Correct Answer Type)

This section contains **8 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

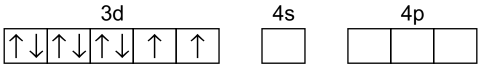
1. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

Solution :

In the paramagnetic state, the complex will have unpaired 3d electrons in Ni^{2+} ion, whereas no such electrons (i.e. all the 3d elctrons will be paired) are present in the diamagnetic state.

The electronic configuration of $_{28}Ni^{2+}$ is



If the two unpaired electrons remain present in the ion, it will undergo sp^3 hybridization to accommodate ligands and the geometry of the complex ion will be tetrahedral.

If the two unpaired electrons are coupled, the ion will be diamagnetic and it can undergo dsp^2 hybridization to accommodate ligands leading to the square planar geometry to the complex ion.

Therefore, the **choice (c)** is correct.

2. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product, respectively, are

(a) redox reaction, –3 and –5
(b) redox reaction, 3 and +5
(c) disproportionation reaction, –3 and +5
(c) disproportionation reaction, –3 and +3

Solution :

The reaction is $\overset{0}{P}_4 + 3NaOH + 3H_2O \rightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{P}O_2$

The salt NaH_2PO_2 undergoes the following changes on heating.

$$4NaH_2\overset{+1}{P}O_2 \rightarrow Na_4\overset{+5}{P_2}O_7 + 2\overset{-3}{P}H_3 + H_2O$$

The reaction is disproportionation reaction and the oxidation states of phosphorus are –3 (in phosphine) and +5 in the second product.

Therefore, the **choice (c)** is correct.

3. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

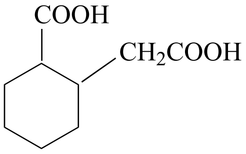
(a) O_2 and CO, respectively
(b) O_2 and Zn dust, respectively
(c) HNO_3 and Zn, respectively
(d) HNO_3 and CO, respectively

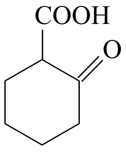
Solution :

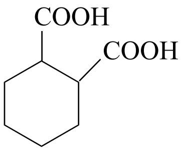
The argentite ore contains Ag_2S. After crushing and concentration by froth flotation process, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated with a current of air.

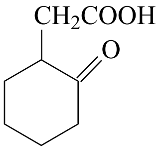
Silver passes into the solution as argentocyanide. $Ag_2S + 4NaCN \rightleftharpoons 2Na\,[Ag(CN)_2] + Na_2S$
The air blown removes Na_2S as $Na_2S_2O_3$ and Na_2SO_4 causing the above reaction to proceed to completion. Silver is recovered by adding zinc into argentocyanide. $2Ag(CN)_2^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag$
Thus, oxidizing agent is O_2 (from air) and the reducing agent is Zn.
Therefore, the **choice (b)** is correct.

4. The compound that undergoes decarboxylation most readily under mild condition is

(a) 

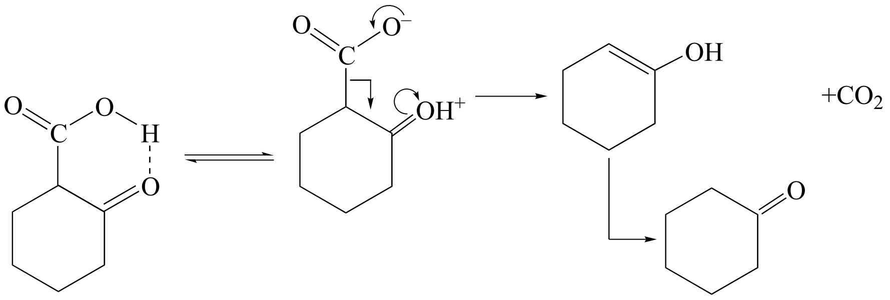
(b) 

(c) 

(d) 

Solution :

β-Ketocarboxylic acid is unstable acid. It readily undergoes decarboxylation through a cyclic transition state.



Therefore, the **choice (b)** is correct.

5. Using the data provided, calculate the multiple bond energy of a C≡C bond in C_2H_2.

$2C(s) + H_2(g) \rightarrow C_2H_2(g) \qquad \Delta H_1 = 225\ \text{kJ mol}^{-1}$

$2C(s) \rightarrow 2C(g) \qquad \Delta H_2 = 1410\ \text{kJ mol}^{-1}$

$H_2(g) \rightarrow 2H(g) \qquad \Delta H_3 = 330\ \text{kJ mol}^{-1}$

Take the bond energy of C—H bond equal to 350 kJ mol^{-1}.

(a) 1165 kJ mol^{-1} (b) 837 kJ mol^{-1} (c) 865 kJ mol^{-1} (d) 815 kJ mol^{-1}

Solution:

Consider the following transformations.

$$\begin{tikzcd}
2C(s) \arrow[d, "\Delta H_2"'] & + & H_2(g) \arrow[d, "\Delta H_3"] \arrow[r, "\Delta H_1"] & H\text{—}C\equiv C\text{—}H \\
2C(g) & + & 2H(g) \arrow[r, leftrightarrow] & H\text{---}C\,\vdots\vdots\vdots\,C\text{---}H \arrow[u, "-2\varepsilon_{C-H}-\varepsilon_{C\equiv C}"']
\end{tikzcd}$$

According to Hess's law $\Delta H_1 = \Delta H_2 + \Delta H_3 - 2\varepsilon_{C\text{–}H} - \varepsilon_{C\,\equiv\,C}$
This gives

$$\varepsilon_{C\,\equiv\,C} = \Delta H_2 + \Delta H_3 - \Delta H_1 - 2\varepsilon_{C\text{–}H} = (1410 + 330 - 225 - 2 \times 350)\ \text{kJ mol}^{-1} = 815\ \text{kJ mol}^{-1}$$

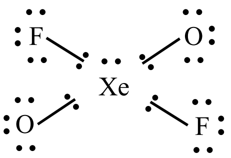
Therefore, the **choice (d)** is correct.

6. The shape of XeO_2F_2 molecule is

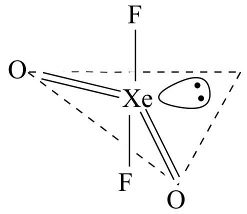
(a) trigonal bipyramidal (b) square planar (c) tetrahedral (d) see-saw

Solution :

The number of valence electrons in XeO_2F_2 is $8 + 2 \times 6 + 2 \times 7 = 34$. These are distributed as shown in the following.



There are five paires of electrons around Xe. To accommodate these, Xe undergoes dsp^3 hybridization leading to the trigonal bipyramidal arrangement of five paires of electrons. The structure of XeO_2F_2 is

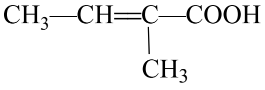


The shape of XeO_2F_2 is sea-saw.
Therefore, the **choice (d)** is correct.

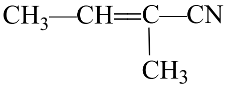
7. The major product H in the given reaction sequence

$$CH_3-CH_2-CO-CH_3 \xrightarrow[HCN]{CN^-} G \xrightarrow[Heat]{95\%\ H_2SO_4} H$$

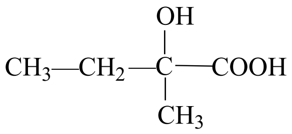
is

(a) 

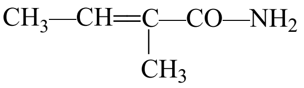
$CH_3—CH{=}\underset{\substack{|\\CH_3}}{C}—COOH$

(b) 

$CH_3—CH{=}\underset{\substack{|\\CH_3}}{C}—CN$

(c) 

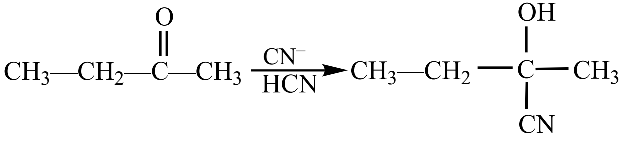
$CH_3—CH_2—\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}—COOH$

(d) 

$CH_3—CH{=}\underset{\substack{|\\CH_3}}{C}—CO—NH_2$

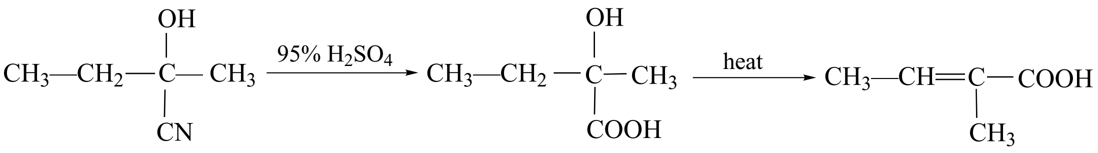
Solution :

The first reaction is nucleophilic addition reaction across the —C═O bond.



$$CH_3—CH_2—\overset{\substack{O\\||}}{C}—CH_3 \xrightarrow[HCN]{CN^-} CH_3—CH_2—\overset{\substack{OH\\|}}{\underset{\substack{|\\CN}}{C}}—CH_3$$

In the second reaction, —CN is hydrolysed to —COOH. The resultant molecule undergoes dehydration on heating.



$$CH_3—CH_2—\overset{\substack{OH\\|}}{\underset{\substack{|\\CN}}{C}}—CH_3 \xrightarrow{95\%\ H_2SO_4} CH_3—CH_2—\overset{\substack{OH\\|}}{\underset{\substack{|\\COOH}}{C}}—CH_3 \xrightarrow{heat} CH_3—CH{=}\underset{\substack{|\\CH_3}}{C}—COOH$$

Therefore, the **choice (a)** is correct.

8. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation of boiling point at 1 atm pressure is 2 °C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure of the solution (take $K_b = 0.76$ K kg mol^{-1}) is

(a) 724 mmHg (b) 740 mmHg (c) 736 mmHg (d) 718 mmHg

Solution :

From the expression $\Delta T_b = K_b m$, we find that the molality of solute (m) in the solution is

$$m = \frac{\Delta T_b}{K_b} = \frac{2\ \text{K}}{0.76\ \text{K kg mol}^{-1}} = \frac{2}{0.76}\ \text{mol kg}^{-1}$$

Since $m = n_2/m_1$ (where n_2 is the amount of solute and m_1 is the mass of solvent expressed in kg), we get

$$n_2 = mm_1 = \left(\frac{2}{0.76}\,\text{mol kg}^{-1}\right)(0.1\ \text{kg}) = \frac{2}{7.6}\ \text{mol}$$

From the expression $-\Delta p = x_2\, p_1^*$ of the relative lowering of vapour pressure of solvent (whose vapour pressure is 1 atm as the solute is non-volatile), we find that

$$x_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} = \frac{n_2}{m_1 / M_1} = \frac{(2/7.6)\ \text{mol}}{\left(100\,\text{g}/18\ \text{g mol}^{-1}\right)} = \frac{36}{76}$$

$$\text{Hence } -\Delta p = \left(\frac{36}{760}\right)(760\ \text{mmHg}) = 36\ \text{mmHg}$$

$$p = p_1^* + \Delta p = 760\ \text{mmHg} - 36\ \text{mmHg} = 724\ \text{mmHg}$$

Therefore, the **choice (a)** is correct.

Section–II

Paragraph Type

This section contains **6 multiple choice questions** relating to three paragraphs with two questions on each paragraph. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

Paragraph for Questions No. 9 and 10

The electrochemical cell shown below is a concentration cell.

$\text{M}|\text{M}^{2+}$(saturated solution of a sparingly soluble salt, MX_2) || $\text{M}^{2+}(0.001\ \text{mol dm}^{-3})|\text{M}$

The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

9. The solubility product (K_{sp}) of MX_2 at 298 K based on the information available for the given concentration cell (take $2.303\, RT/F = 0.059$ V at 298 K) is

(a) $1 \times 10^{-15}\ \text{mol}^3\ \text{dm}^{-9}$ (b) $4 \times 10^{-15}\ \text{mol}^3\ \text{dm}^{-9}$

(c) $1 \times 10^{-12}\ \text{mol}^3\ \text{dm}^{-9}$ (d) $4 \times 10^{-12}\ \text{mol}^3\ \text{dm}^{-9}$

10. The value of ΔG for the given cell reaction (take $1F = 96\,500\ \text{C mol}^{-1}$) is

(a) $-5.7\ \text{kJ mol}^{-1}$ (b) $5.7\ \text{kJ mol}^{-1}$ (c) $11.4\ \text{kJ mol}^{-1}$ (d) $-11.4\ \text{kJ mol}^{-1}$

Solutions :

The cell reaction may be obtained as follows.

LHC: Oxidation	$\text{M(s)} \rightarrow (\text{M}^{2+})_\text{L} + 2\text{e}^-$
RHC: Reduction	$(\text{M}^{2+})_\text{R} + 2\text{e}^- \rightarrow \text{M(s)}$
Overall reaction	$(\text{M}^{2+})_\text{R} \rightarrow (\text{M}^{2+})_\text{L}$

The cell potential is

$$E = -\frac{RT}{2F}\ln\left\{\frac{[\text{M}^{2+}]_\text{L} / \text{mol dm}^{-3}}{[\text{M}^{2+}]_\text{R} / \text{mol dm}^{-3}}\right\} \quad \text{i.e.,} \quad 0.059\ \text{V} = -\left(\frac{0.059\ \text{V}}{2}\right)\log\left\{\frac{[\text{M}^{2+}]_\text{L} / \text{mol dm}^{-3}}{0.001}\right\}$$

This gives $\log([\text{M}^{2+}]_\text{L}/\text{mol dm}^{-3}) = -2 + \log(0.001) = -2 - 3 = -5$ i.e., $[\text{M}^{2+}]_\text{L} = 1.0 \times 10^{-5}\ \text{mol dm}^{-3}$

From the reaction

$$\text{MX}_2(\text{s}) \rightleftharpoons \text{M}^{2+}(\text{aq}) + 2\ \underset{2s}{\text{X}^-}(\text{aq});$$ (s is solubility of the salt)

$$K_{sp} = [\text{M}^{2+}][\text{X}^{2-}] = (s)(2s)^2 = 4s^3 = 4\,(1.0 \times 10^{-5}\ \text{mol dm}^{-3})^3 = 4 \times 10^{-15}\ \text{mol}^3\ \text{dm}^{-9}$$

The ΔG of the cell reaction is

$$\Delta G = -\,nFE = -\,(2)\,(96500\ \text{C mol}^{-1})\,(0.059\ \text{V}) = -\,11\,387\ \text{J mol}^{-1} = -\,11.4\ \text{kJ mol}^{-1}$$

Hence, we have

9. The **choice (b)** is correct.

10. The **choice (d)** is correct.

Paragraph for Questions 11 and 12

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.

11. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

12. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

(a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

Solutions :

For Q.11, we may write

$$\text{Household bleach} + 2\,\text{KI} \rightarrow I_2 + \text{products}$$
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Amount of $Na_2S_2O_3$ used $= VM = (48 \times 10^{-3}\ \text{L})\ (0.25\ \text{mol L}^{-1}) = 12 \times 10^{-3}$ mol

Amount of I_2 generated $= \frac{1}{2}\ (12 \times 10^{-3}\ \text{mol}) = 6 \times 10^{-3}$ mol

Assuming 1 mol of household bleach produces 1 mol I_2, we will have

Amount of household bleach in 25 mL solution $= 6 \times 10^{-3}$ mol

$$\text{Molarity of household bleach} = \frac{n}{V} = \frac{6 \times 10^{-3}\,\text{mol}}{25 \times 10^{-3}\,\text{L}} = 0.24\ \text{M}$$

For Q 12, we have

Bleaching powder contains Ca(OCl)Cl.

The oxoacid of this salt is HOCl. The formation of this acid through its anhydride is $\underset{\text{anhydride}}{Cl_2O} + H_2O \rightarrow \underset{\text{oxoacid}}{2HOCl}$

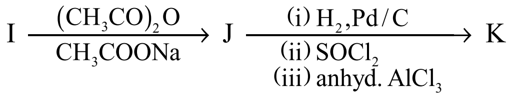
Hence, we have

11. The **choice (c)** is correct

12. The **choice (a)** is correct.

Paragraph for Questions No. 13 and 14

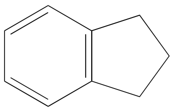
In the following reaction sequence, the compound J is an intermediate

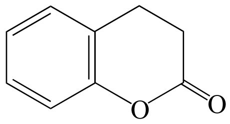


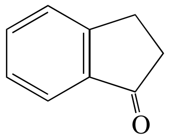
$$\text{I} \xrightarrow[\text{CH}_3\text{COONa}]{(\text{CH}_3\text{CO})_2\text{O}} \text{J} \xrightarrow[\substack{\text{(ii) SOCl}_2 \\ \text{(iii) anhyd. AlCl}_3}]{\text{(i) H}_2\text{,Pd/C}} \text{K}$$

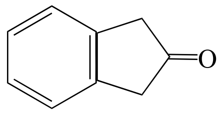
$J(C_9H_8O_2)$ gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test.

13. The compound K is

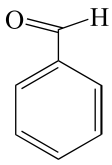
(a) 

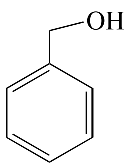
(b) 

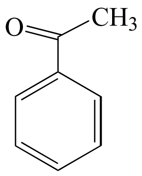
(c) 

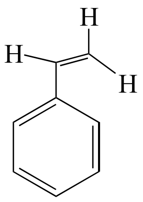
(d) 

14. The compound I is

(a) 

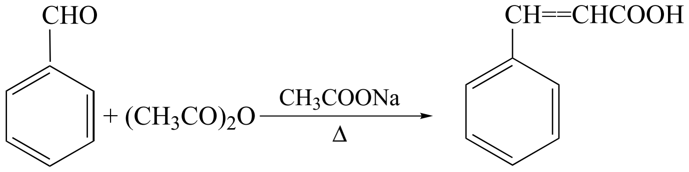
(b) 

(c) 

(d) 

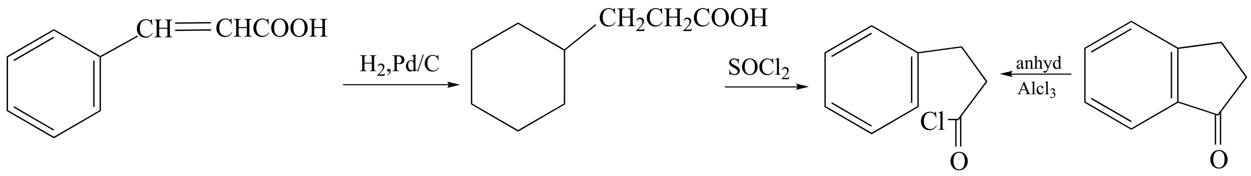
Solutions :

The compound J must contain a —COOH group as it gives effervescence with $NaHCO_3$. Also, it is an unsaturated compound as it gives positive Baeyer's test (decolourization of pink colour of alkaline $KMnO_4$). Since the compound J is obtained by treating the compound I with $(CH_3CO)_2O$ and CH_3COONa, and more over the compound J seems to be aromatic (high carbon content), the compound I amongst the choices given in Q.14 seems to be benzaldehyde as it shows Perkin condensation shown in the following



α, β- unsaturated
carboxylic acid

The conversion J to K is as follows.



choice (c) of 2.13

Hence, we have

13. The **choice (c)** is correct.

14. The **choice (a)** is correct.

SECTION–III

Multiple Correct Answer(s) type

This section contains **6 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONE** or **MORE** is/are correct.

15. With respect to graphite and diamond, which of the following statement(s) given below is(are) correct?

(a) Graphite is harder than diamond.
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C—C bond order than diamond.

Solution :

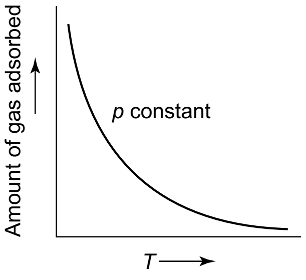
The given facts about graphite and diamond are as follows.

Graphite is less hard than diamond. Graphite has higher electrical and thermal conductivities than diamond. This is due to highly delocalized nature of π electrons. Graphite has higher C—C bond order (due to σ and π bonds) than that of diamond (which has only σ bonds)

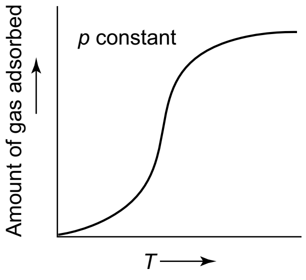
Therefore, the **choices (b), (c) and (d)** are correct.

16. The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is(are) correct.

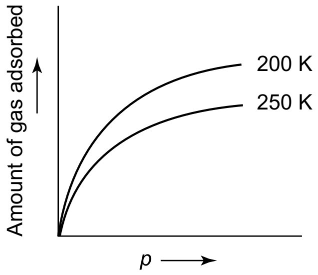
(I)



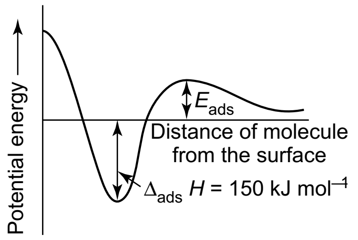
(II)



(III)



(IV)



(a) I is physisorption and II is chemisorption
(b) I is physisorption and III is chemisorption
(c) IV is chemisorption and II is chemisorption
(d) IV is chemisorption and III is chemisorption

Solution:

We have the following facts.

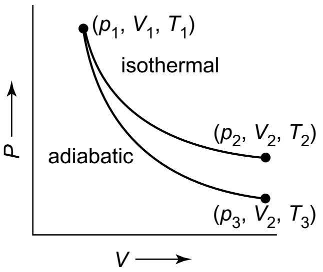
- Adsorption decreases with increase in temperature at constant pressure in case of physisorption
- Adsorption increases initially with increase in temperature at constant pressure in case of chemisorption as more molecules satisfy the energy of activation.
- The enthalpy change during chemisorptions is high due to the bond formation between adsorbent and adsorbate.

With these guidelines, we will have

Graph I represents physisorption	Graph II represents chemisorption
Graph III represents physisorption	Graph IV represents chemisorptions

Therefore, The **choices (a) and (c)** are correct.

17. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?



(a) $T_1 = T_2$
(b) $T_2 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Solution :

We will have

$T_1 = T_2$ as the expansion is isothermal.

$T_3 < T_1$ as the adiabatic expansion involves cooling.

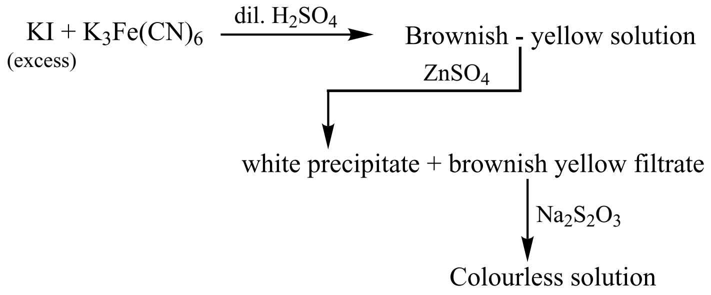
$|w_{\text{isothermal}}| > |w_{\text{adiabatic}}|$ as the area under the isothermal curve is greater than that under adiabatic curve.

$\Delta U_{\text{isothermal}} = 0$ as temperature remains constant while $\Delta U_{\text{adiabatic}} < 0$ as the expansion occurs at the expanse of internal energy.

Therefore, the **choices (a) and (d)** are correct.

Note: The choice (c) is correct if the magnitude of the work is considered. Since expansion carries negative sign as per IUPAC recommendations, the choice (c) will not be correct if the negative sign is also considered.

18. For the given aqueous solutions, which of the following statement(s) is(are) correct?



(a) The first reaction is a redox reaction.
(b) White precipitate is $Zn_3[Fe(CN)_6]_2$.
(c) Addition of filtrate to starch solution gives blue coloration.
(d) White precipitate is soluble in NaOH solution.

Solution

The given reactions are as follows.

$$\underset{\text{(excess)}}{2KI} + 2K_3[Fe(CN)_6] \xrightarrow{\text{dil } H_2SO_4} \underset{\text{(Brownish - yellow solution)}}{I_2 \text{ dissolved in KI}} + K_4[Fe(CN)_6]$$

$$K_4[Fe(CN)_6] + 2\,ZnSO_4 \rightarrow \underset{\text{(white precipitate)}}{Zn_2[Fe(CN)_6]} + 2K_2SO_4$$

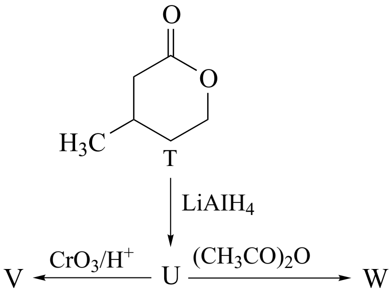
$$I_2 \text{ dissolved in KI} + 2\,Na_2S_2O_3 \rightarrow \underset{\text{colourless solution}}{Na_2S_4O_6} + 2NaI$$

$$Zn_2[Fe(CN)_6] + 8NaOH \rightarrow \underset{\text{soluble}}{2Na_2[Zn(OH)_4]} + Na_4[Fe(CN)_6]$$

The first reaction is a redox reaction. Filtrate contains free iodine, so it gives blue colouration with starch solution.

Therefore, the **choices (a), (c) and (d)** are correct.

19. With reference to the scheme given, which of the given statement(s) about T, U, V and W is(are) correct?



(a) T is soluble in hot aqueous NaOH.

(b) U is an optically active compound.

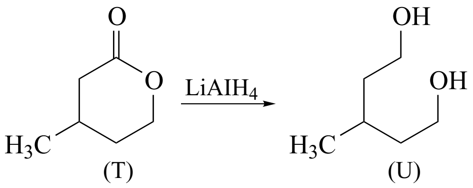
(c) Molecular formula of W is $C_{10}H_{18}O_4$.

(d) V gives effervescence with aqueous $NaHCO_3$.

Solution

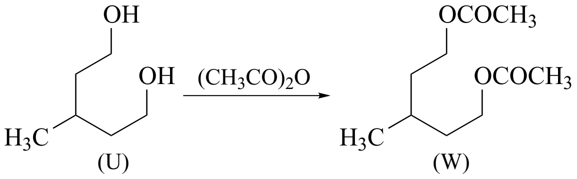
The compound T is a cyclic ester. It is soluble in hot aqueous NaOH

The treatment of ester T with $LiAlH_4$ produces diol compound



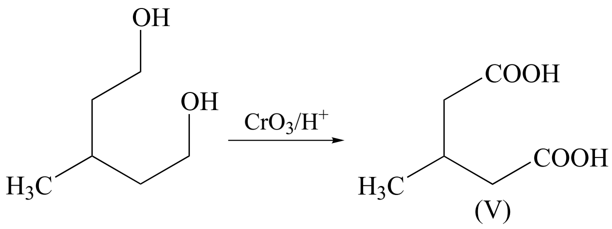
The compound U is not optically active as carbon bearing —CH_3 group contains two identical groups — CH_2CH_2OH.

The conversion of U to W is the acetylation of the two hydroxyl groups.



The molecular formula of W is $C_{10}H_{18}O_4$.

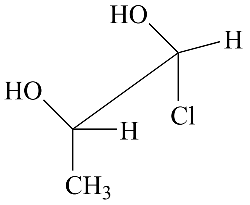
The conversion of U to V is the oxidation of the two —CH_2OH groups to —COOH groups.



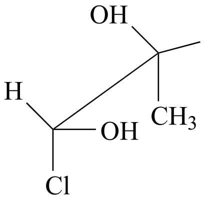
(V)

Being a dicarboxylic acid, it gives effervescence with $NaHCO_3$(aq).
Therefore, the **choices (a), (c) and (d)** are correct.

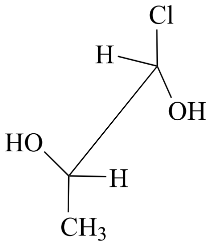
20. Which of the given statement(s) about N, O, P and Q with respect to M is(are) correct?



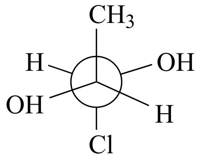
(M)



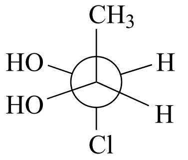
(N)



(O)



(P)

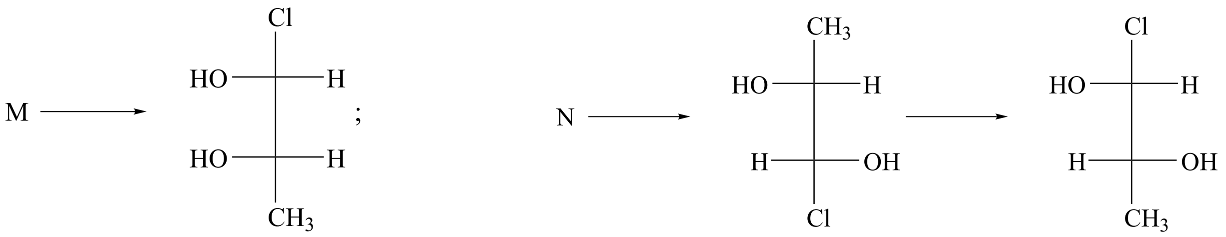


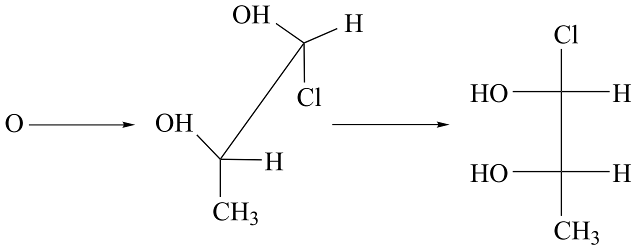
(Q)

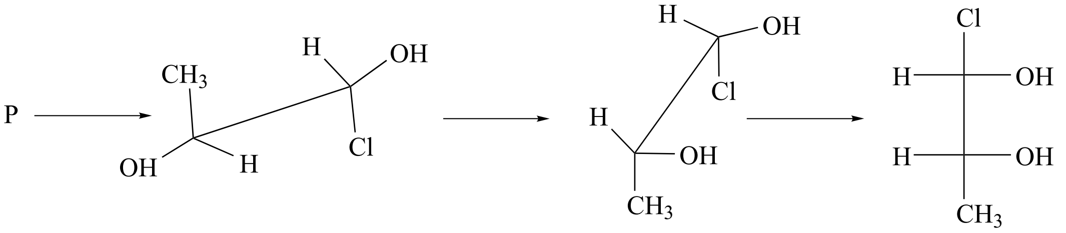
(a) M and N are non-mirror image stereoisomers. (b) M and O are identical
(c) M and P are enantiomers (d) M and Q are identical

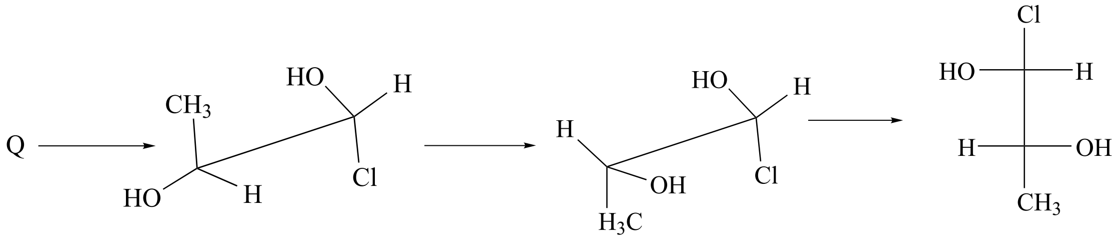
Solution :

First of all, we may draw Fischer projections of the given compounds









From the Fischer projections, it follows that

M and N are non-mirror images.

M and O are identical.

M and P are enantiomers.

M and Q are not identical.

Therefore the **chioces (a) ,(b) and (c)** are correct.

Model Solutions

JEE (Advanced)—2013

Paper I

SECTION–I

(Only One Option Correct Type)

This section contains **10 multiple choice questions.** Each question has four choices (a), (b) (c) and (d) out of which **ONLY ONE** is correct.

1. Consider the following complex ions P, Q and R.

$P = [FeF_6]^{3-}$; $Q = [V(H_2O)_6]^{2+}$; $R = [Fe(H_2O)_6]^{2+}$

The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.), is

(a) R < Q < P (b) Q < R < P (c) R < P < Q (c) Q < P < R

Solution :

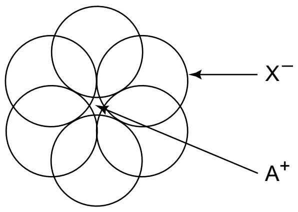
The electronic configurations of $_{23}V^{2+}$, $_{26}Fe^{2+}$ and $_{26}Fe^{3+}$ are $(3d)^3$, $(3d)^6$ and $(3d)^5$, respectively. Since F^- and H_2O are weak ligands, there occurs no rearrangement of d elctrons in the formation of the given complex ions. Thus, the number of unpaired electrons of V^{2+}, Fe^{2+} and Fe^{3+} ions in the complex ions are 3, 4 and 5, respectively. The expression of magnetic moment is $\sqrt{n(n+2)}\,\mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton. Hence, the magnetic moment of the given complexes follows the order Q < R < P.

Therefore, the **choice (b)** is correct.

2. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not shown in scale). If the radius of X^- is 250 pm, the radius of A^+ is

(a) 104 pm (b) 125 pm

(c) 183 pm (d) 57 pm



Solution :

The cation A^+ occupy the octahedral void created by six X^- anions. The size of A^+ that can be fitted in the void is related to those of X^- by the relation

$$\frac{r_{A^+}}{r_{X^-}} = 0.414 \qquad \text{Thus} \quad r_{A^+} = 0.414\ r_{X^-} = (0.414)\ (250\ \text{pm}) = 103.5\ \text{pm}$$

Therefore, the **choice (a)** is correct.

3. Sulphides ores are common for the metals

(a) Ag, Cu and Pb (b) Ag, Cu and Sn (c) Ag, Mg and Pb (d) Al, Cu and Pb

Solution :

Ag, Cu and Pb occur as sulphide ores while Sn, Mg and Al occur in non-sulphide ores.

Therefore, the **choice (a)** is correct.

4. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25 °C are $-400\ \text{kJ mol}^{-1}$, $-300\ \text{kJ mol}^{-1}$ and $-1300\ \text{kJ mol}^{-1}$, respectively. The standard enthalpy of combustion per gram of glucose at 25 °C is

(a) +2900 kJ (b) –2900 kJ (c) –16.11 kJ (d) +16.11 kJ

Solution :

The combustion reaction of glucose is $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$

Hence
$$\begin{aligned} \Delta_c H^\circ &= 6\ \Delta_f H^\circ(CO_2) + 6\ \Delta_f H^\circ(H_2O) - \Delta_f H^\circ(C_6H_{12}O_6) \\ &= [6(-400) + 6(-300) - (-1300)]\ \text{kJ mol}^{-1} \\ &= -2900\ \text{kJ mol}^{-1} \end{aligned}$$

The molar mass of glucose is
$$\begin{aligned} M &= 6\ M_C + 12\ M_H + 6\ M_O = (6 \times 12 + 12 \times 1 + 6 \times 16)\ \text{g mol}^{-1} \\ &= 180\ \text{g mol}^{-1} \end{aligned}$$

Hence, the standard enthalpy of combustion per gram of glucose is

$$\Delta H^\circ = \frac{\Delta_c H^\circ}{M} = \frac{-2900\ \text{kJ mol}^{-1}}{180\ \text{g mol}^{-1}} = -16.11\ \text{kJ g}^{-1}$$

Therefore, the **choice (c)** is correct.

5. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as sulphide is

(a) Fe(III) (b) Al(III) (c) Mg(II) (d) Zn(II)

Solution :

Zn(II) precipitates as ZnS when H_2S is passed through the ammoniacal solution of Zn(II) salt.
Therefore, the **choice (d)** is correct.

6. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25 °C. For this process, the correct statement is

(a) The adsorption requires activation at 25 °C
(b) The adsorption is accompanied by a decrease in enthalpy
(c) The adsorption increases with increase of temperature
(d) The adsorption is irreversible.

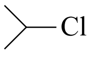
Solution :

The adsorption of methylene blue on activated charcoal is a physical adsorption which requires no activation. This process is reversible and the adsorption decreases with increase of temperature. It is accompanied with decrease of enthalpy due to the attraction between adsorbent and adsorbate.
Therefore, the **choice (b)** is correct.

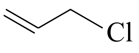
7. KI in acetone undergoes S_N2 reaction with each of P, Q, R and S.

$H_3C—Cl$

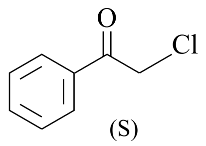
(P)



(Q)



(R)



(S)

The rates of the reaction vary as

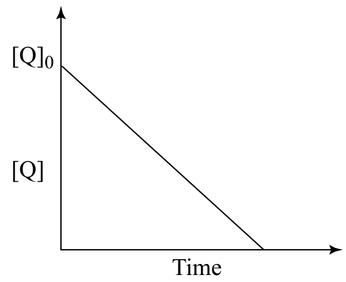
(a) P > Q > R > S (b) S > P > R > Q (c) P > R > Q > S (d) R > P > S > Q

Solution :

The compound Q will have least rate of reaction as its transition state will be more crowded.

The compound S will have the maximum rate of reaction as the π-electronic cloud of $C_6H_5CO—$ group reduces the energy of transition state. In the transition state, the carbon undergoing reaction changes from the sp^3-hybrid state to the sp^2-hybrid state and thus has a p orbital. This p orbital forms partial bonds with both the incoming nucleophile and the leaving group. The entire grouping of atoms carries a negative charge. Adjacent p orbitals of $C_6H_5CO—$ or $CH_2 = CH—$ group undergo partial overlap with the transitional p orbital. In this way, negative charge is delocalized resulting lowering of energy of the transition state and thus enhancing the rate of reaction.
Therefore, the **choice (b)** is correct.

8. In the reaction $P + Q \rightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50 % reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



(a) 2 (b) 3

(c) 0 (d) 1

Solution :

With respect to P, the reaction is first order as the successive decrease in concentration of P to a half value is independent of its initial concentration, i.e.

$$\begin{tikzcd}[P]_0 \arrow[r, "50\% \text{ reaction}", "t_{1/2}"'] \arrow[rr, bend right, "75\% \text{ reaction}", "2t_{1/2}"'] & {[P]_0/2} \arrow[r, "50\% \text{ reaction}", "t_{1/2}"'] & {[P]_0/4}\end{tikzcd}$$

With respect to Q, the reaction is zero order as its concentration follows the rate equation

$$[Q] - [Q]_0 = -kt \quad \text{i.e} \quad [Q] = [Q]_0 - kt.$$

Thus, the overall order of the reaction is one.
Therefore, the **choice (d)** is correct.

9. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of

(a) NO (b) NO_2 (c) N_2O (d) N_2O_4

Solution :

The concentrated nitric acid acquires yellow-brown colour due to the decomposition of nitric acid into NO_2 and O_2.

$$4\ HNO_3 \rightarrow 4\ NO_2 + O_2 + 2H_2O$$

Therefore, the **choice (b)** is correct.

10. The compound that does not liberate CO_2 on treating with aqueous sodium bicarbonate solution is

(a) Benzoic acid (b) Benzene sulphonic acid

(c) Salicyclic acid (d) Carbolic acid (phenol)

Solution :

The compound containing —COOH group or —SO_3H group react with $NaHCO_3$, liberating CO_2. Phenol does not react with $NaHCO_3$ because it is a weaker acid as compared to H_2CO_3.
Therefore, the **choice (d)** is correct.

SECTION–II

(One or More Option Correct Type)

This section contains **5 multiple choice questions.** Each question has four choices (a), (b), (c) and (d) out of which **ONE or MORE** are correct.

11. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid HA (1 M) is 1/100th of that of a strong acid HX (1 M) at 25 °C. The K_a° of HA is

(a) 1×10^{-4} (b) 1×10^{-5} (c) 1×10^{-6} (d) 1×10^{-3}

Solution :

Acid hydrolysis of an ester is first order with respect to the concentration of $H^+(aq)$. Since the initial rate of hydrolysis with weak acid HA(1M) is 1/100th of that of a strong acid HX (1 M, assumed to be completely dissociated), it follows that $[H^+]$ in the weak acid solution will be (1/100) M.

Since $K_a = \dfrac{[H^+][A^-]}{[HA]_0 - [H^+]} \simeq \dfrac{[H^+]^2}{[HA]_0}$, we have $K_a = \dfrac{\{(1/100)M\}^2}{1\,M} = 10^{-4}\ M$

Therefore, the **choice (a)** is correct.

12. The hyperconjugative of *tert*-butyl cation and 2-butene, respectively, are due to

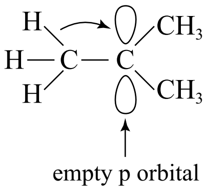
(a) $\sigma \rightarrow$ p (empty) and $\sigma \rightarrow \pi^*$ electron delocalization

(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalization

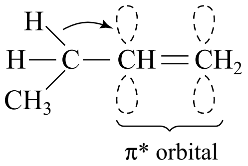
(c) $\sigma \rightarrow$ p (filled) and $\sigma \rightarrow \pi$ electron delocalization

(d) p(filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalization

Solution :



$\sigma \rightarrow$ p (empty) electron delocolization



$\sigma \rightarrow \pi^*$
electron delocolization

Therefore the **choice (a)** is correct.

13. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is (are)

(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$

(b) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$

(c) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$

(d) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

Solution :

The complex $[Cr(NH_3)_5Cl]Cl_2$ in the choice (a) will not show either structural or stereoisomerism whereas $[Cr(NH_3)_4Cl_2]Cl$ exhibits geometrical (*cis-trans*) isomerism.

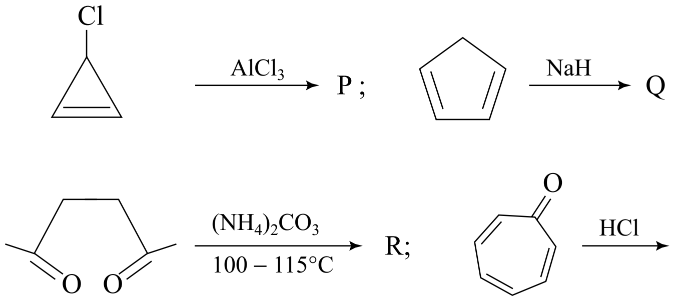
In the choice (b), the complex $[Co(NH_3)_4 Cl_2]^+$ is octahedral whereas $[Pt(NH_3)_2(H_2O)Cl]^+$ is a square planar. Both these complexes will exhibit geometrical (*cis-trans*) isomerism.

In the choice (c), $[CoBr_2Cl_2]^{2-}$ is tetrahedral while $[PtBr_2Cl_2]^{2-}$ is square planar. There is no isomerism of the same type in these complexes.

In the choice (d), both are square planar and can exhibit ionization isomerism.

Therefore, the **choices (b) and (d)** are correct.

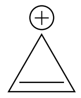
14. Among P, Q, R and S, the aromatic compound(s) is/are

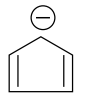


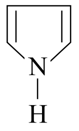
(a) P (b) Q (c) R (d) S

Solution :

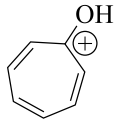
The resultant compounds are as follows.


(P)


(Q)



(R)



(S)

All these compounds satisfy $4n + 2$ rule, where n is the number of π-electrons. Hence, all of them will be aromatic.

Therefore, the **choices (a), (b), (c) and (d)** are correct.

15. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)

(a) ΔG is positive
(b) ΔS_{system} is positive
(c) $\Delta S_{\text{surroundings}} = 0$
(d) $\Delta H = 0$

Solution :

In the formation of an ideal solution, $\Delta H = 0$, $\Delta G = -\text{ve}$ and $\Delta S_{\text{system}} = +\text{ve}$.
Also, since $q = 0$, $\Delta S_{\text{surroundings}} = 0$.

Therefore, the **choices (b), (c) and (d)** are correct.

SECTION–III

(Interger Value Correct Type)

This section contains **5 questions**. The answer to each question is a single digit integer ranging from 0 to 9 (both inclusive).

16. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de Broglie wavelength of He gas at –73 °C is "M" times that of the de Broglie wavelength of Ne at 727 °C. The value of "M" is

Solution :

We have de Broglie relation $\lambda = h/m\upsilon$

Average kinetic energy $\frac{1}{2}m\upsilon^2 = \frac{3}{2}kT$

Hence $\lambda = \frac{h}{m\upsilon} = \frac{h}{m}\sqrt{\frac{m}{3kT}} = \frac{h}{\sqrt{3\,m\,k\,T}}$

Thus $\lambda \propto 1/(mT)^{1/2}$. Hence

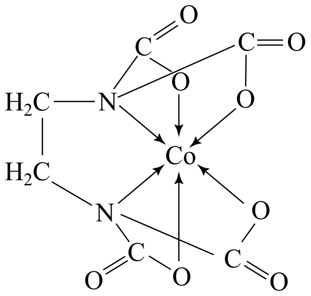
$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \left[\frac{(20\text{ amu})(1000\text{ K})}{(4\text{ amu})(200\text{ K})}\right]^{1/2} = 5$$

Therefore, the value of M is **5**.

17. EDTA^{4-} is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in $[\text{Co(EDTA)}]^-$ complex ion is_________.

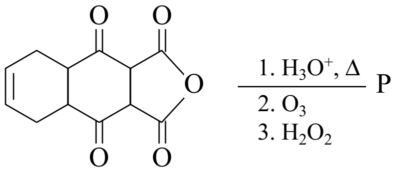
Solution :

Ethylenediaminetetraacetate ion is a hexadentate. It is linked to the central Co(III) ion via two nitrogen atoms of amines and four oxygen atoms of acetate ions. Hence, there will be eight (= 2 × 4) N – Co – O bond angles. The structure for the complex ion is



Therefore, there are **8** N – Co – O bonds.

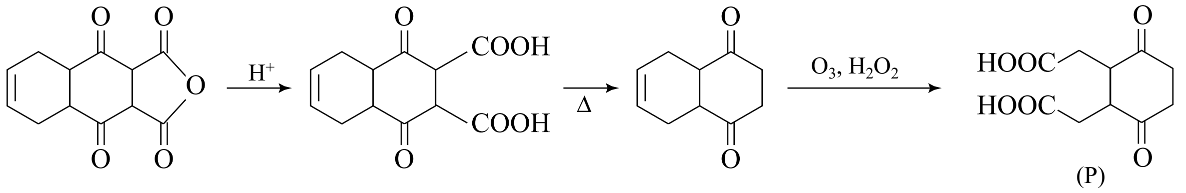
18. The Total number of carboxylic acid groups in the product P is ___________.



Solution :

The treatment with H_3O^+ will cause the opening of anhydride bonds. The resultant compound contains two β-keto-carboxylic acids. These are easily decarboxylated by heating. The resultant compound undergoes ozonolysis followed by oxidation of —CHO groups to give —COOH groups.

The reactions are



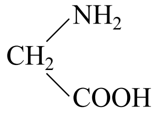
(P)

Therefore, the total number of carboxylic acid in the compound is **2**.

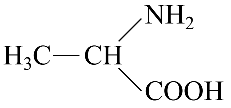
19. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (val), phenyl alanine (Phe) and alanine (Al), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structure) with —NH_2 group attached to a chiral centre is__________.

Solution :

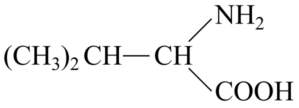
The structures of four amino acids are as follows.



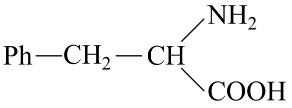
(Gly)



(Al)



(Val)



(Phe)

The given tetrapeptide has —COOH group on alanine. Thus, alanine occupy right-most position in tetrapeptide. Since —NH_2 group is attached to a chiral centre, the left-most position will not be occupied by glycine (which has no chiral centre). This left-most position will be occupied by any of the two remaining acids, i.e. valine and phenyl alanine. Thus, the following will be the primary structures.

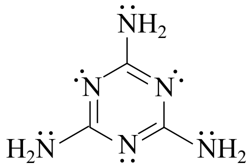
Val – Phe – Gly – Ala
Val – Gly – Phe – Ala
Phe – Val – Gly – Ala
Phe – Gly – Val – Ala

Therefore, there are **4** primary structures.

20. The total number of lone pairs in melamine is _____________.

Solution :

The structure of melamine is



There are **six pairs** of lone pairs of electrons.

MODEL SOLUTIONS

JEE (ADVANCED)—2013

PAPER II

SECTION–I

(One or more options correct type)

This section contains **8 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONE or MORE** are correct.

1. The carbon-based reduction method is **NOT** used for the extraction of

(a) tin from SnO_2
(b) iron from Fe_2O_3
(c) aluminium from Al_2O_3
(d) magnesium from $MgCO_3 \cdot CaCO_3$

Solution :

Tin and iron are extracted by carbon-based reduction method whereas aluminium and magnesium are extracted by electrolytic method.

Therefore, the **choices (c) and (d)** are correct.

2. The thermal dissociation equilibrium of $CaCO_3$(s) is studied under different conditions.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

For this equilibrium, the correct statement(s) is (are)

(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of the catalyst

Solution:

The equilibrium constant of the reaction is

$$K_p = p_{CO_2}$$

Since K_p is a constant at a given T, the value of p_{CO_2} will be independent of p_{CO_2} at a given T. The remaining three statements are correct.

Therefore, the **choices (a), (b) and (d)** are correct.

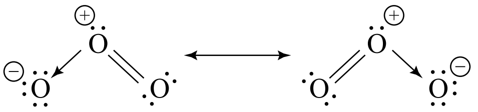
3. The correct statement(s) about ozone is (are)

(a) O – O bond lengths are equal
(b) Thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure.

Solution :

The reaction $O_3 \rightleftharpoons (3/2)\, O_2$ is an exothermic reaction.

Because of resonating structures



Both the O — O bond lengths are equal.

Ozone has a bent structure and is diamagnetic in nature.

Therefore, the **choices (a), (c) and (d)** are correct.

4. In the nuclear transmutation

$$ {}^{9}_{4}\mathrm{Be} + \mathrm{X} \rightarrow {}^{8}_{4}\mathrm{Be} + \mathrm{Y} $$

(X, Y) is (are)

(a) (γ, n) (b) (p, D) (c) (n, D) (d) (γ, p)

Solution :

The given transmutation involves (i) no change in atomic number and (ii) a decrease of one in mass number. The choices (a) and (b) satisfy this requirement as shown in the following.

$$ {}^{9}_{4}\mathrm{Be} + \gamma \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{1}_{0}\mathrm{n} $$

$$ {}^{9}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{D} $$

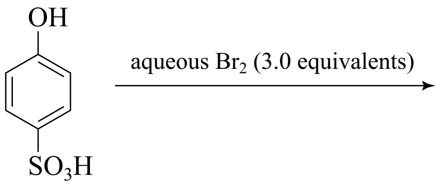
The choices (c) and (d) involve an increase in atomic number

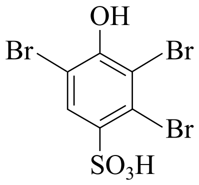
$$ {}^{9}_{4}\mathrm{Be} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{D} $$

$$ {}^{9}_{4}\mathrm{Be} + \gamma \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{p} $$

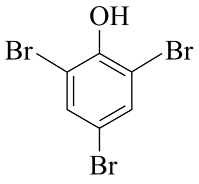
Therefore, the **choices (a) and (b)** are correct.

5. The major product(s) of the following reaction is (are).

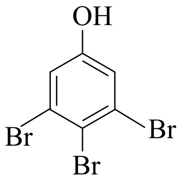




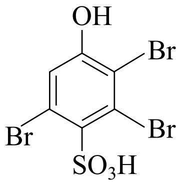
(P)



(Q)



(R)

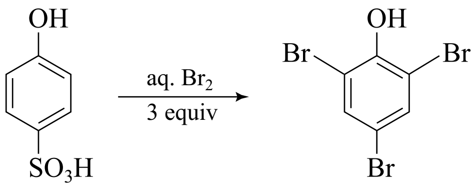


(S)

(a) (P) (b) Q (c) R (d) S

Solution :

The reaction is

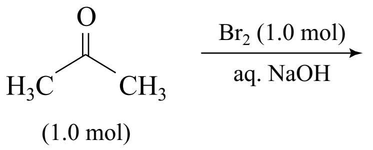


(Q)

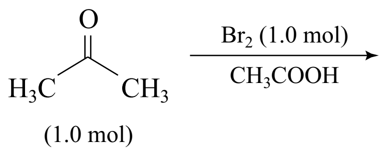
Therefore, the **choice (b)** is correct.

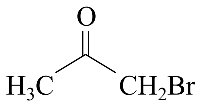
6. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are)

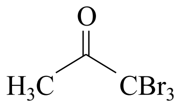
Reaction I:

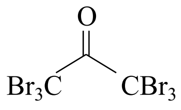


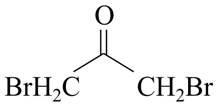
Reaction II:

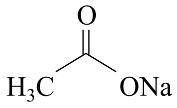



(P)


(Q)


(R)


(S)


(T)

$CHBr_3$

(U)

(a) Reaction I: P and Reaction II : P
(b) Reaction I : U, acetone and Reaction II: Q, acetone
(c) Reaction I: T, U, acetone and Reaction II : P
(d) Reaction I: R and Reaction II: S, acetone.

Solution :

Since both acetone and Br_2 are present in equal amounts, it is expected that the product P would be formed in both the cases. However, in the base-promoted α-halogenation, the second and third halogenation occur with much faster than the first one. Consequently, the product T, U and remaining acetone will be found in the reaction I. This does not occur in the acid-catalysed halogenation of ketone because the second and third halogenation occur with much slower speed than the first one. The reaction are :

(I)

$$\begin{tikzcd} CH_3COCH_3 \arrow[r, "{OH^-, Br_2}", "{-H_2O, -Br^-}"'] & CH_3COCH_2Br \arrow[r, "{OH^-, Br_2}", "{-H_2O, -Br^-}"'] & CH_3COCHBr_2 \arrow[d, "{OH^-, Br_2}", "{-H_2O, -Br^-}"'] \\ & CH_3COO^- + CHBr_3 & CH_3COCBr_2 \arrow[l, "OH^-"'] \end{tikzcd}$$

(II) $CH_3COCH_3 \xrightarrow[Br_2]{CH_3COOH} CH_3COCH_2Br$

Therefore, the **choice (c)** is correct.

7. The K^o_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol L^{-1}) of Ag_2CrO_4 in 0.1 M $AgNO_3$ solution is

(a) 1.1×10^{-11} (b) 1.1×10^{-10} (c) 1.1×10^{-12} (d) 1.1×10^{-9}

Solution :

Given that $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

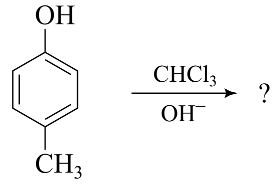
$$K_{sp}\ [Ag^+(aq)]^2[CrO_4^{2-}(aq)]$$

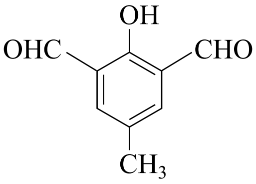
The concentration of CrO_4^{2-} in 0.1 M solution of $AgNO_3$ would be

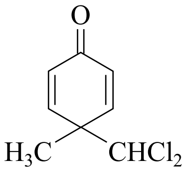
$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.1 \times 10^{-12}\ M^3}{(0.1\ M)^2} = 1.1 \times 10^{-10} M$$

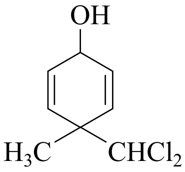
Therefore, the **choice (b)** is correct.

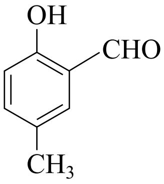
8. In the following reaction, the product(s) formed is (are)




(P)


(Q)


(R)

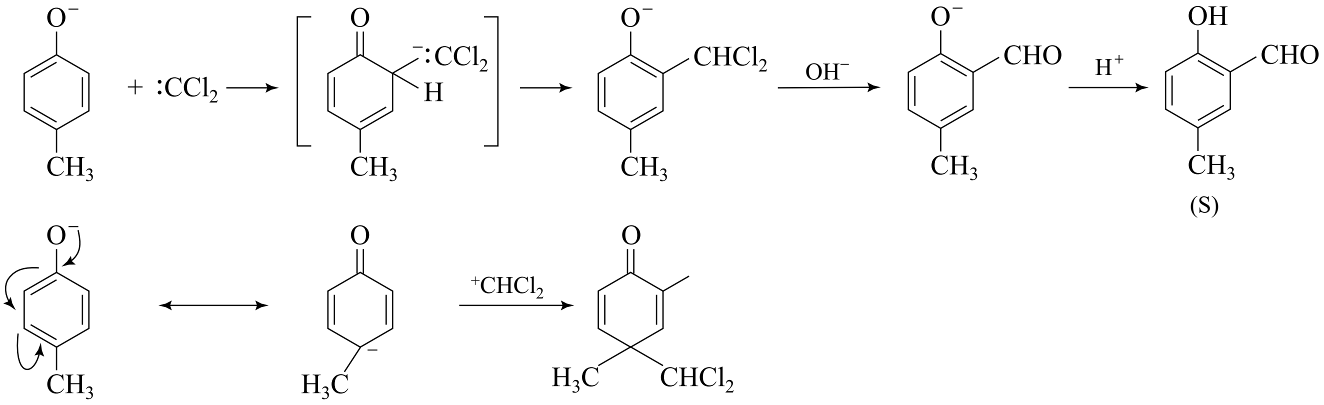

(S)

(a) (P) major (b) (Q) minor (c) R (minor) (d) S (major)

Solution:

The reaction is known as Reimer – Tiemann reaction. It proceeds as follows.

$$HCCl_3 \xrightarrow[-H^+]{OH^-} {}^-:CCl_3 \longrightarrow Cl^- + :CCl_2$$



(Q)

Therefore, the **choices (b) and (d)** are the correct answer.

SECTION–II

(Paragraph Type)

This section contains **4 paragraphs,** each describing theory, experiment, data, etc. **Eight questions** relate to four paragraphs with two questions on each paragraph. Each question of a paragraph has **only one correct answer** among the four choices (a), (b), (c) and (d).

Using the following Paragraph, solve Q. No. 9 and 10

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (**P**) and a filtrate (**Q**). The precipitate **P** was found to dissolve in hot water. The filtrate (**Q**) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (**R**) with H_2S in an ammoniacal medium. The precipitate **R** gave a coloured solution (**S**) when treated with H_2O_2 in an aqueous NaOH medium.

9. The precipitate P contains

(a) Pb^{2+} (b) Hg_2^{2+} (c) Ag^+ (d) $1 + Hg^{2+}$

10. The coloured solution S contains

(a) $Fe_2(SO_4)_3$ (b) $CuSO_4$ (c) $ZnSO_4$ (d) Na_2CrO_4

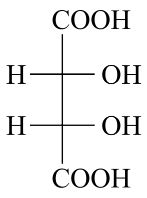
Solutions :

The precipitate P contains Pb^{2+} ions as it gives white precipitate with dilute HCl which is soluble in hot water and reappears when the solution is cooled.
The coloured solution S is of Na_2CrO_4. The filtrate Q contains Cr^{3+} ions which get precipitated in an ammoniacal H_2S medium and is oxidised to CrO_4^{2-} when treated with H_2O_2 in alkaline medium.

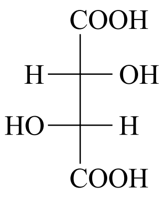
Therefore, the **choice (a) for Q. 9** and **choice (d) for Q. 10** are correct.

Using the following paragraph, solve Q. No. 11 and 12

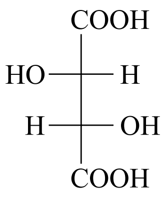
P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorized Br_2/H_2O. On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U.



(S)



(T)

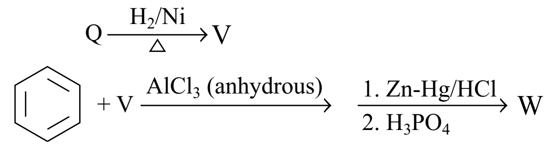


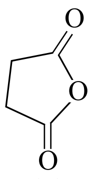
(U)

11. Compounds formed from P an Q, respectively, are

(a) Optically active S and optically active pair (T ,U)
(b) Optically inactive S and optically inactive pair (T, U)
(c) Optically active pair (T, U) and optically active S
(d) Optically inactive pair (T, U) and optically inactive S

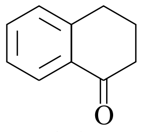
12. In the following reaction sequences V and W are, respectively



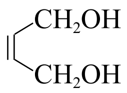
(a)


(V)

and

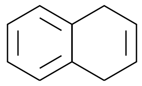


(W)

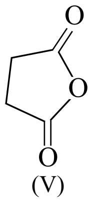
(b)


(V)

and

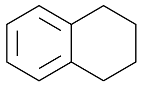


(W)

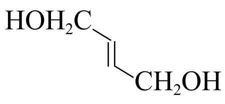
(c)


(V)

and

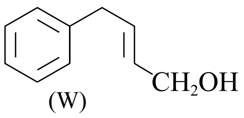


(W)

(d)


(V)

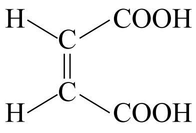
and

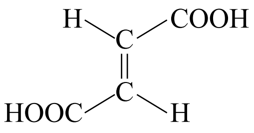


(W)

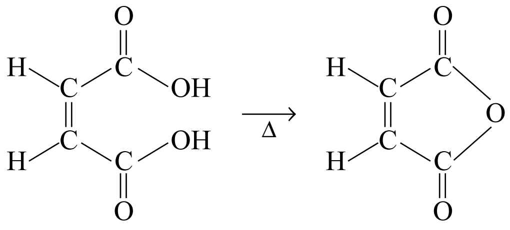
Solutions :

Q. 11 The compounds P and Q are

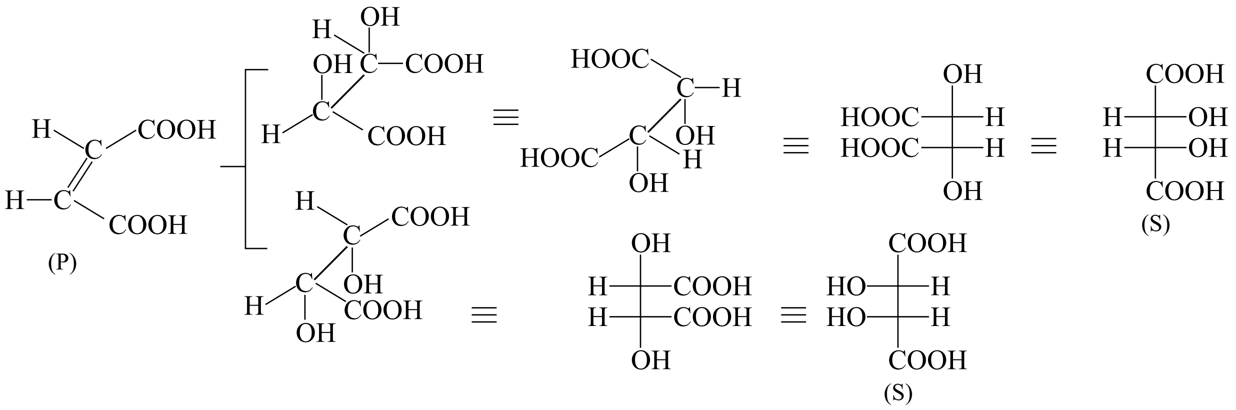

(P)

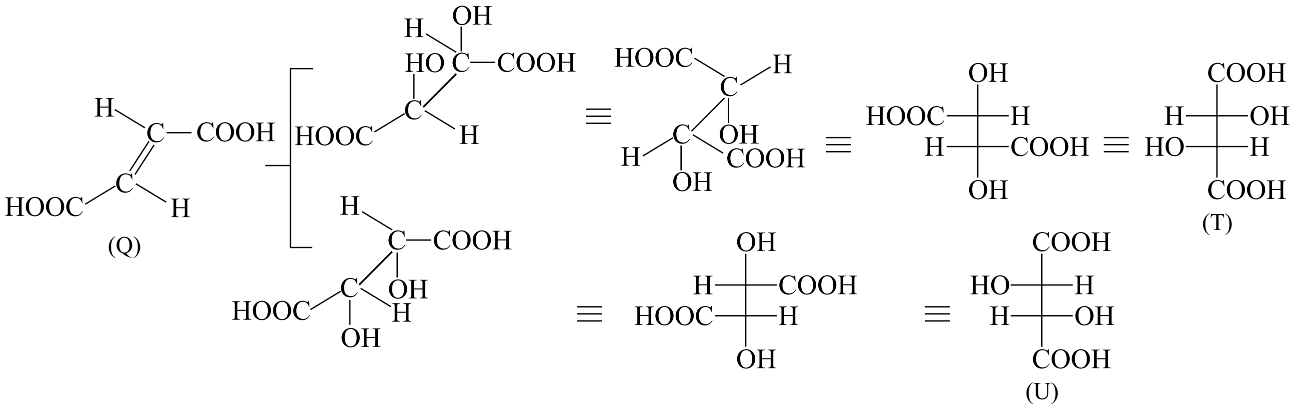

(Q)

The compound P forms cyclic anhydride



The treatment of P and Q with alkaline $KMnO_4$ causes hydroxylation across the double bond via syn mode.

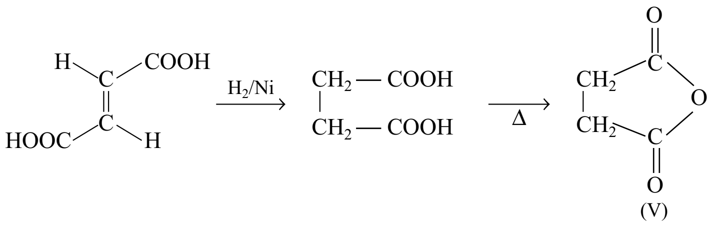


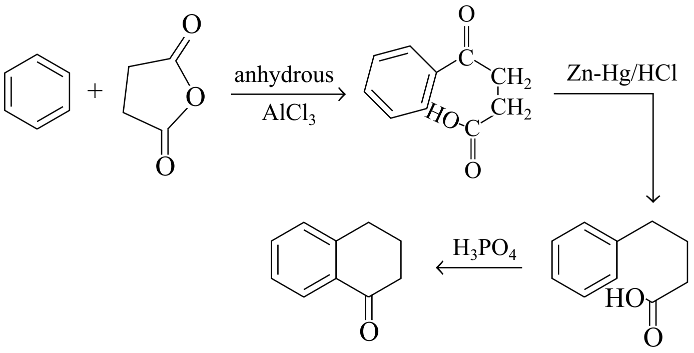


Hydroxylation P gives rise to optically inactive *meso* compound S while that of Q produces optically inactive pair (T, U) of racemic mixture.

Therefore, the **choice (b)** of Q.11 is correct.

Q.12 The reactions involved in Q.12 are as follows.

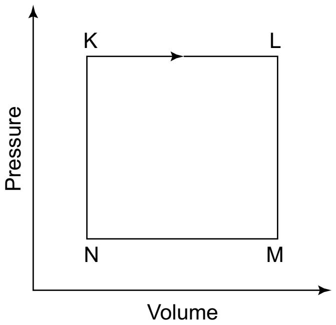




Therefore, the **choice (a)** of Q. 12 is correct.

Using the following paragraph, solve Q. No. 13 and 14

A fixed mass *m* of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



13. The succeeding operations that enable this transformation of states are

(a) Heating, cooling, heating, cooling (b) Cooling, heating, cooling, heating

(c) Heating, cooling, cooling, heating (d) Cooling, heating, heating, cooling

14. The pair of isochoric processes among the transformation of states is

(a) K to L and L to M (b) L to M and N to K

(c) L to M and M to N (d) M to N and N to K

Solutions :

Q. 13 The operation K to L involves constant pressure and increase in volume. The increase in volume is accompanied with increase of temperature (Charles law), thus heating is observed.

The operation L to M involves constant volume and decrease in pressure. The decrease in pressure is accompanied with decrease in temperature, thus cooling is observed. Similarly, M to N is accompanied with cooling and that N to K is accompanied with heating.

Therefore, the **choice (c)** is correct.

Q. 14 The processes L to M and N to K involves constant volume and thus are isochoric processes.

Therefore, the **choice (b)** is correct.

Using the following paragraph, solve Q. No. 15 and 16

The reaction of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The Cl_2 gas reacts with SO_2 gas in presence of charcoal to give a product R. The product R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorous, T.

15. P and Q, respectively, are the sodium slats of

(a) hypochlorus and chloric acids (b) hypochlorus and chlorus acids

(c) chloric and perchloric acids (d) chloric and hypochlorus acids

16. R, S and T, respectively, are

(a) SO_2Cl_2, PCl_5 and H_3PO_4 (b) SO_2Cl_2, PCl_3 and H_3PO_3

(c) $SOCl_2$, PCl_3 and H_3PO_2 (d) $SOCl_2$, PCl_5 and H_3PO_4

Solutions :

Q. 15 The reaction are :

$$2\text{ NaOH} + Cl_2 \xrightarrow{\text{cold}} \text{NaCl} + \underset{(P)}{\text{NaOCl}} + H_2O$$

$$6\text{ NaOH} + Cl_2 \xrightarrow{\text{hot}} 5\text{ NaCl} + \underset{(Q)}{NaClO_3} + 3H_2O$$

Therefore, the **choice (a)** is correct.

Q.16 The reaction are :

$$SO_2 + Cl_2 \rightarrow \underset{(R)}{SO_2Cl_2}$$

$$P_4 + 10\ SO_2Cl_2 \rightarrow 4\ \underset{(S)}{PCl_5} + 10\ SO_2$$

$$\underset{(S)}{PCl_5} + 4\ H_2O \rightarrow \underset{(T)}{H_3PO_4} + 5HCl$$

Therefore, the **choice (a)** is correct.

SECTION–III

(Matching List Types)

This section contains **4 Multiple choice questions**. Each question has matching list. The codes for the lists have choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

17. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists.

	List I		**List II**
P	$\underset{(X)}{(C_2H_5)_3N} + \underset{(Y)}{CH_3COOH}$	1.	Conductivity decreases and then increases
Q	$\underset{(X)}{KI(0.1\ M)} + \underset{(Y)}{AgNO_3\ (0.1\ M)}$	2	Conductivity decreases and then does not change much
R	$\underset{(X)}{CH_3COOH} + \underset{(Y)}{KOH}$	3	Conductivity increases and then does not change much
S	$\underset{(X)}{NaOH} + \underset{(Y)}{HI}$	4.	Conductivity does not change much and then increases

Codes:

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

Solution :

In the choice P of List I, a weak base is added to a weak acid. There will be salt formation till whole of acid is neutralized. This will cause an increase in conductivity. Beyond this point, the conductivity will not change much as the compound X is a weak base. The behaviour is given by the choice 3 of List II.

In the choice of Q of List I, we have

$$\underset{(X)}{KI} + \underset{(Y)}{AgNO_3} \rightarrow AgI\downarrow + KNO_3$$

Effectively, Ag^+ ions are replaced by K^+ ions. Since their conductivities are more of less same, the conductivity of the solution does not change much. After the complete precipitation of AgI, the solution will contain an increasing concentration of KI, hence, its conductivity will increase. This behaviour is given by the choice 4 of List II.

In the choice R of List I , we have

$$\underset{(X)}{CH_3COOH} + \underset{(Y)}{KOH} \rightarrow CH_3COOK + H_2O$$

Effectively KOH is replaced by CH_3COOK. Since conductivity of OH^- ions is much larger than that of CH_3COO^-, the conductivity of the solution will decrease. After the complete neutralization of KOH, the solution will contain a fixed amount of CH_3COOK and increasing amount of CH_3COOH, a weak acid. Thus, it conductivity will not change much. This behaviour is given by the choice 2 of List II.

In the choice S of List I, we have

$$\underset{(X)}{NaOH} + \underset{(Y)}{HI} \rightarrow NaI + H_2O$$

Effectively, H^+ is replaced by Na^+. This will cause a decrease in conductivity after the complete neutralization of HI, the solution will contain fixed amount of NaI and increasing amount of NaOH. This will cause an increase in conductivity. This behaviour is given by the choice 1 of List II.

Hence, the correct matching (choice a) are as follows

(P) ↔3; (Q) ↔ 4; (R) ↔ 2 and (S) ↔ 1.

18. The standard reduction potential data at 25 °C is given below.

$E°(Fe^{3+}, Fe^{2+}) = +0.77\ V$; $E°(Fe^{2+}, Fe) = -0.44\ V$

$E°(Cu^{2+}, Cu) = +0.34\ V$; $E°(Cu^{+}, Cu) = +0.52\ V$

$E°(O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O) = +1.23\ V$

$E°(O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-) = +0.40\ V$

$E°(Cr^{3+}, Cr) = -0.74\ V$; $E°(Cr^{2+}, Cr) = -0.91\ V$

Match E^o of the redox pair in List I with the values given in List II and select the correct answer using the code given below the list:

	List I		**List II**
P	$E°(Fe^{3+}, Fe)$	1.	−0.18 V
Q	$E°(4\ H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2	−0.4 V
R	$E°(Cu^{2+} + Cu \rightarrow 2Cu^+)$	3	−0.04 V
S	$E°(Cr^{3+}, Cr^{2+})$	4	−0.83 V

Codes:

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

Solution :

For the choice P of List I, we have

$$\begin{array}{ll} \mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} & \Delta G^\circ_1 = -(1)F\,(+\,0.77\ \mathrm{V}) \\ \mathrm{Fe^{2+} + 2e^- \rightarrow Fe} & \Delta G^\circ_2 = -(2)\,F\,(-\,0.44\ \mathrm{V}) \\ \hline \mathrm{Fe^{3+} + 3e^- \rightarrow Fe} & \Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2 = (-\,0.77\ \mathrm{V} + 0.88\ \mathrm{V})\,F \\ & \qquad = (0.11\ \mathrm{V})\,F \end{array}$$

$$E^\circ_3 = \Delta G^\circ_3/(-3F) = -0.04\ \mathrm{V}$$

Since this value appears in the choice 3 of List II, we will have the matching (P) ↔ 3. With this matching alone, one can say that the choice (d) of the given codes is correct.

However, we may proceed to prove the remaining matching of the choice (d).

For the choice Q of List I, we have

$$\begin{array}{lll} & \mathrm{O_2(g) + 2\,H_2O(g) + 4e^- \rightarrow 4OH^-} & E^\circ_1 = 0.40\ \mathrm{V} \\ & \mathrm{O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O} & E^\circ_2 = 1.23\ \mathrm{V} \\ \hline \text{Subtract} & \mathrm{4H_2O \rightarrow 4H^+ + 4OH^-} & E^\circ = E^\circ_1 - E^\circ_2 = (0.40 - 1.23)\mathrm{V} = -0.83\ \mathrm{V} \end{array}$$

Thus, correct matching is Q → 4.

For the choice R of List I, we have

$$\begin{array}{lll} & \mathrm{Cu^{2+} + 2e^- \rightarrow Cu} & E^\circ_1 = 0.34\ \mathrm{V} \\ & \mathrm{2Cu^+ + 2e^- \rightarrow 2\,Cu} & E^\circ_2 = 0.52\ \mathrm{V} \\ \hline \text{Subtract} & \mathrm{Cu^{2+} + Cu \rightarrow 2Cu^+} & E^\circ = E^\circ_1 - E^\circ_2 = (0.34 - 0.52)\ \mathrm{V} = -\,0.18. \end{array}$$

The correct matching is (R) ↔ 1.

For the choice S of List I, we have

$$\begin{array}{lll} & \mathrm{Cr^{3+} + 3e^- \rightarrow Cr} & \Delta G^\circ_1 = -3F\,(-\,0.74\ \mathrm{V}) \\ & \mathrm{Cr^{2+} + 2e^- \rightarrow Cr} & \Delta G^\circ_2 = -\,2F\,(-\,0.91\ \mathrm{V}) \\ \hline \text{Subtract} & \mathrm{Cr^{3+} + e^- \rightarrow Cr^{2+}} & \Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2 \\ & & \qquad = (2.22\ \mathrm{V} - 1.82\ \mathrm{V})\ \mathrm{F} = (0.40\ \mathrm{V})\,F \end{array}$$

$$E^\circ_3 = -\Delta G^\circ_3/nF = -(0.40\ \mathrm{V})\ F/\ (1 \times F) = -\ 0.40\ \mathrm{V}$$

The correct matching is S ↔ 2.

Therefore, the **choice (d)** of the given code is correct.

19. The unbalanced chemical reactions given in List I show missing reagent or condition(?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists:

	List I		**List II**
P	$\mathrm{PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2}$ + other product	1	NO
Q	$\mathrm{Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4}$ + other product	2	I_2
R	$\mathrm{N_2H_4 \xrightarrow{?} N_2}$ + other product	3	warm
S	$\mathrm{XeF_2 \xrightarrow{?} Xe}$ + other product	4	Cl_2

Codes

	P	Q	R	S
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

Solution :

For the choice P in List I, we write the complete reaction as

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + O_2 + 2H_2O$$

The reaction will proceeds on warming the solution. This is given by the choice 3 in the List II.

For the choice Q in List I, we need a suitable oxidizing agent. This is accomplished by using Cl_2 which is the choice 4 in List II. The complete reaction is

$$Na_2S_2O_3 + 5H_2O \xrightarrow{4\,Cl_2} 2NaHSO_4 + 8HCl$$

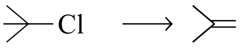
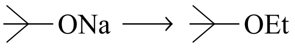
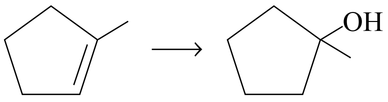
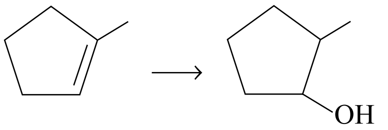
With the two cases considered above, it seems that the choice (d) of the given codes is the correct answer. We can complete the choices R and S in List I as follows.

$$N_2H_4 \xrightarrow[\text{(choice 2)}]{2I_2} N_2 + 4HI$$

$$XeF_2 \xrightarrow[\left(\text{choice 1}\right)]{2NO} Xe + 2NOF$$

Therefore, the **choice (d)** of the given codes is correct

20. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the Lists.

	List I		**List II**
P		1	(i) $Hg(OAc)_2$; (ii) $NaBH_4$
Q		2	NaOEt
R		3	Et – Br
S		4	(i) BH_3; (ii) H_2O_2/NaOH

Codes

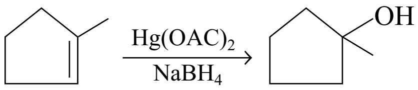
	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

Solution:

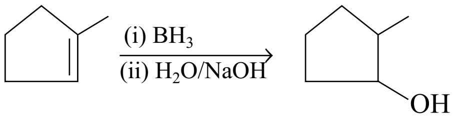
For the choice P in List I, a strong base such as RO^- is required. This is given by the choice 2 in List II. Hence

For the reaction Q, the reagent Et-Br (choice 3 of List II) can be used.

For the choice R in List I, it may be achieved by oxymercuration – demercuration process. The reagent used in this process is mercury acetate in water followed by reduction with sodium borohydride. The net result is the addition of H_2O across the double bond in accordance with Markovnikv's rule (—OH is attached to the more substituted carbon). The choice 1 of List II provides these reagents



For the choice S in List I, it may be achieved by hydroboration-oxidation process The reagent used in this process is diborane followed by oxidation with alkaline H_2O_2. The net result is the addition of H_2O across the double bond in accordance with anti-Markovnikov's rule (—OH is attached to the less substituted carbon). The choice 4 of List II provides these reagents.



Therefore, the **choice (a)** of the given codes is the correct answer.

CHEMISTRY JEE ADVANCED—2014 PAPER-I—MODEL SOLUTIONS

SECTION–I

(One or More than One Options Correct Type)

This section contains **10 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONE** or **MORE THAN ONE** are correct.

1. For the reaction:

$$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$$

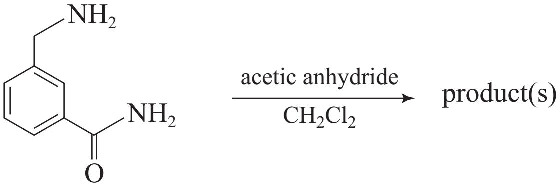
the correct statement(s) in the balanced equation is/are

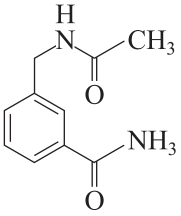
(a) Stoichiometric coefficient of HSO_4^- is 6.
(b) Iodide is oxidised
(c) Sulphur is reduced
(d) H_2O is one of the products.

2. The pair(s) of reagents that yield paramagnetic species is/are

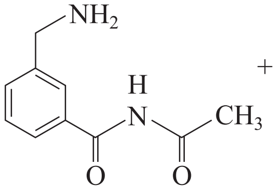
(a) Na and excess of NH_3
(b) K and excess of O_2
(c) Cu and dilute HNO_3
(d) O_2 and 2-ethylanthraquinol

3. In the reaction shown below, the major product(s) formed is/are

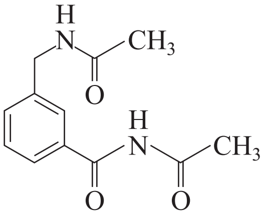


(a)


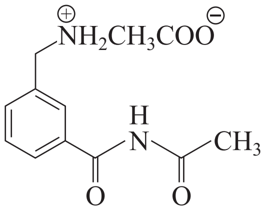
+ CH_3COOH

(b)


+ CH_3COOH

(c)


+ H_2O

(d)


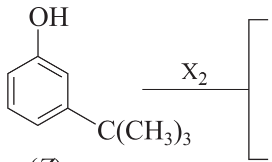
4. In a galvanic cell, the salt bridge

(a) does not participate chemically in the cell reaction
(b) stops the diffusion of ions from one electrode to another
(c) is necessary for the occurrence of the cell reaction
(d) ensures mixing of the two electrolytic solutions

5. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are
(a) $CuFeS_2$ (b) CuO (c) Cu_2O (d) $CuSO_4$

6. Hydrogen bonding plays a central role in the following phenomena:
(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerization of acetic acid in benzene.

7. The reactivity of compound *Z* with different halogens under appropriate conditions is given below.



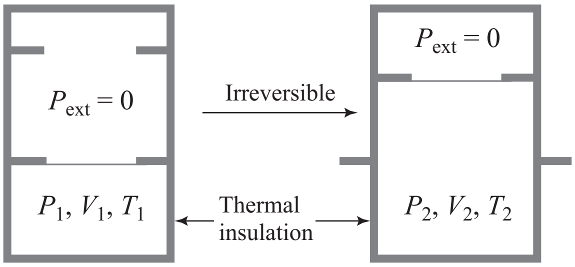
(*Z*)

mono halo substituted derivative when $X_2 = I_2$
di halo substituted derivative when $X_2 = Br_2$
tri halo substituted derivative when $X_2 = Cl_2$

The obsered pattern of electrophilic substitution can be explained by
(a) the steric effect of the halogen (b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group (d) the electronic effect of the *tert*-butyl group.

8. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are
(a) *tert*-butanol and 2-methylpropan-2-ol (b) *tert*-butanol and 1, 1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol (d) isobutyl alcohol and 2-methylpropan-1-ol

9. An ideal gas in a thermally insulated vessel at internal pressure P_1, volume V_1 and absolute temperature T_1 expands irreversibly against zero external pressure as shown in the diagram.



The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion
(a) $q = 0$ (b) $T_2 = T_1$ (c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^\gamma = P_1V_1^\gamma$

10. The correct statement(s) for orthoboric acid is/are
(a) It behaves as a weak acid in water due to self ionization.
(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.
(c) It has a three-dimensional structure due to hydrogen bonding.
(d) It is a weak electrolyte in water.

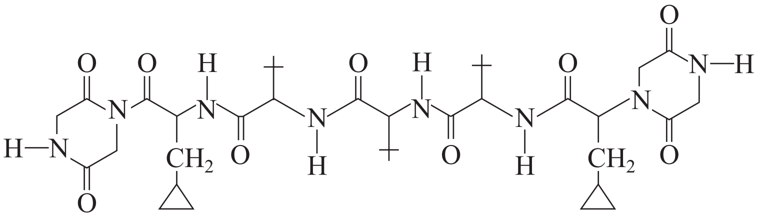
SECTION–II

(One Integer Value Correct Type)

This section contains **10 questions**. Each question when worked out will result in one integer from 0 to 9 (both inclusive)

11. In an atom, the total number of electrons having quantum number $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is ________.

12. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown as follows is ________.



13. If the value of Avogadro constant is 6.023×10^{23} mol^{-1} and the value of Boltzmann constant is 1.380×10^{-23} J K^{-1}, then the number of significant digits in the calculated value of the universal gas constant is________.

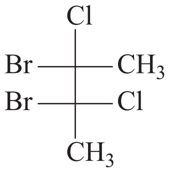
14. A compound H_2X with molar mass of 80 g mol^{-1} is dissolved in a solvent having density 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is________mol kg^{-1}.

15. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) is 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociaton is________.

16. Consider the following list of reagents.

Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is ________.

17. The total number(s) of **stable** conformers with non-zero dipole moment for the following compound is/are



18. Among PbS, CuS, HgS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of **BLACK**-coloured sulphides is ________.

19. Consider all possible isomeric ketones including stereo isomers of relative molar mass of 100. All these isomers are independently reacted with $NaBH_4$ (**Note:** stereo isomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are ________.

20. A list of species having the formula XZ_4 is given below.

XeF_4, SF_4, SiF_4, BrF_4^-, BF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is ________.

ANSWERS

1. (a), (b), (d)	**2.** (a), (b), (c)	**3.** (a)	**4.** (a), (c)	**5.** (b), (c), (d)
6. (a), (b), (d)	**7.** (a), (b), (c)	**8.** (a), (c), (d)	**9.** (a), (b), (c)	**10.** (b), (d)
11. (6)	**12.** (1)	**13.** (4)	**14.** (8)	**15.** (2)
16. (7)	**17.** (3)	**18.** (7)	**19.** (5)	**20.** (4)

Solutions

1. The balanced chemical equation is

$$6\overset{-1}{I^-} + \overset{+5}{Cl}O_3^- + 6H_2SO_4 \rightarrow \overset{-1}{Cl^-} + 6HSO_4^- + 3\overset{0}{I_2} + 3H_2O$$

The species undergoing change in oxidation number are:

Iodine from –1 to 0

Chlorine from +5 to –1

Hence, iodine is oxidised and chlorine is reduced.

2. Na in excess of NH_3 produces deep blue solution and contains solvated electrons. Due to the latter, solution shows paramagnetic behaviour.

   K in excess of O_2 produces potassium superoxide KO_2. The species O_2^- contains one unpaired electron and thus is paramagnetic

   The reaction of Cu with dilute HNO_3 is

   $$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

   Nitric oxide has 11 valence electrons. The presence of an odd electron makes the molecule paramagnetic.

   The oxidation of 2-ethylanthraquinol produces 2-ethylanthraquinone and H_2O_2. None of the two species are paramagnetic.

3. Only the group — CH_2NH_2 is acetylated.

4. The salt bridge is used to connect the two half-cells of a galvanic cells. It does not participate chemically in the cell reaction.

   The two half-cells are not in direct touch with each other. Thus, salt bridge does not stop the diffusion of ions from one electrode to another.

   There are many galvanic cells which do not require the use of salt bridge. One of the examples is lead accumulator. However, a galvanic cell which requires the use of a salt bridge, the cell reaction will not ocur without the salt bridge.

5. The reagents CuO, Cu_2O and $CuSO_4$ give the metal Cu on heating with Cu_2S.

   $$Cu_2S + 2\,CuO \rightarrow 4\,Cu + SO_2$$

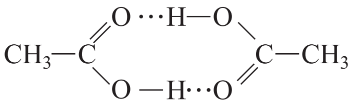
   $$Cu_2S + 2\,Cu_2O \rightarrow 6\,Cu + SO_2$$

   $$Cu_2S + CuSO_4 \rightarrow 3\,Cu + 2\,SO_2$$

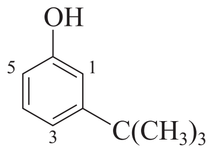
6. Ice floats in water because it is less dense than the liquid water due to its open crystal structure because of hydrogen bondings.

   Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. Thus, primary amines are more basic than tertiary amines in aqueous solution.

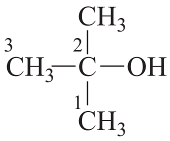
   Acetic acid dimerise in benzene due to hydrogen bonding.



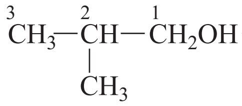
7. Halogen can be introduced at the positions 1, 3 and 5 as shown in the figure. This is due to *ortho*- and *para* directing phenolic group



   Because of steric effect of iodine and —$C(CH)_3$, the former can be inserted in position 5 only. Bromine, being less bulky, can be inserted at 3 and 5 positions. Chlonine can be inserted in all the three positions.

8. Tertiary butanol is  $\overset{3}{\mathrm{CH_3}}-\underset{\substack{1| \\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3} \\ 2|}}{\mathrm{C}}}-\mathrm{OH}$. Its IUPAC name is 2-methylpropan–2–ol

   n-Butanol is $CH_3CH_2CH_2CH_2OH$. Its IUPAC name is butan-1-ol.

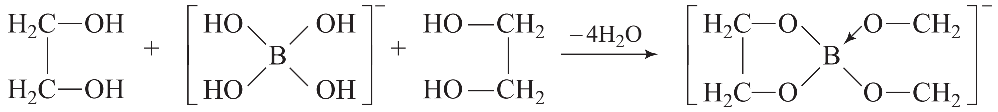
   Isobutyl alcohol is  $\overset{3}{\mathrm{CH_3}}-\underset{\substack{| \\ \mathrm{CH_3}}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CH_2OH}}$. Its IUPAC name is 2-methylproan-1-ol.

9. The expression of work is $w = -p_{\text{ext}}\mathrm{d}V$. Since $p_{\text{ext}} = 0$, we have $w = 0$
Since the gas is thermally insulated, $q = 0$
Since $\Delta U = q + w$, we have $\Delta U = 0$
Since $\Delta U = 0$, the temperature of the gas remains constant. Hence, $T_2 = T_1$
From Boyle's law $P_2V_2 = P_1V_1$ at constant temperature.
The choice (d) is not applicable as the expansion is not reversible.

10. Boric acid, also known as orthoboric acid, is H_3BO_3, i.e. $B(OH)_3$. It is a weak acid not due to self ionization but due to acceptance of OH^- ions. Thus, it behaves as a Lewis acid.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O + [B(OH)_4]^-$$

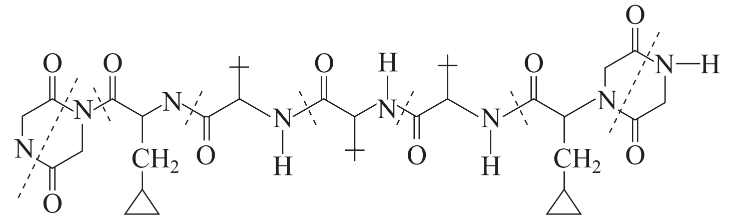
In the presence of ethylene glycol, boric acid acts as a strong acid (i.e. its acid strength is increased). This is due to the formation of very stable complex with $[B(OH)_4]^-$.



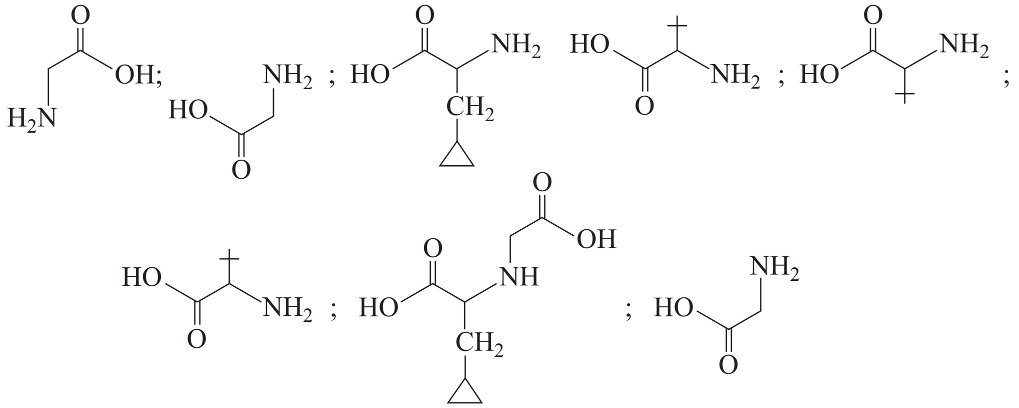
Because of this complex formation, the equilibrium shown above between $B(OH)_3$ and H_2O is displaced to the right causing complete ionization of H_3BO_3.
In boric acid, B is sp^2 hybridised forming planar structure. In the solid, the boric acid units are hydrogen bonded together into two-dimensional sheets.
Boric acid acts as a weak electrolyte.

11. For $n = 4$, we will have
$l = 0, 1, 2, 3$
$m_l = 0, \pm 1, \pm 2, \ldots, \pm l$
The number of orbitals with $n = 4$ and $|m_l| = 1$ will be
1. $l = 1$, $m_l = \pm 1$ 2. $l = 2$, $m_l = \pm 1$ and 3. $l = 3$, $m_l = \pm 1$
Hence, there will be 6 orbitals. Each orbital can accommodate one electron with $m_s = -1/2$.
Thus, the answer is **six**.

12. The site of hydrolysis is shown by the broken lines in the following figures.



The products at each hydrolysis step are as follows.



Only naturally occurring amino acid is glycine ($H_2N — CH_2 – COOH$).

13. Both the numbers 6.023×10^{23} and 1.380×10^{-23} have four significant digits, the universal gas constant $R(=N_A k)$ will have four significant digits.

14. In 3.2 molar solution, we have

Amount of solute = 3.2 mol
Volume of solution = 1.0 L

Since there occurs no change in volume on dissolving solute, we will have

$$\begin{aligned}\text{Volume of solvent} &= 1.0\ \text{L}\\ \text{Mass of solvent} &= (1.0\ \text{L})\ (0.4\ \text{g mL}^{-1})\\ &= (10^3\ \text{mL})\ (0.4\ \text{g mL}^{-1})\\ &= 400\ \text{g} \equiv 0.4\ \text{kg.}\end{aligned}$$

$$\text{Molality of the solution} = \frac{3.2\ \text{mol}}{0.4\ \text{kg}} = 8\ \text{mol kg}^{-1}$$

15. $$\underset{m_0(1-\alpha)}{MX_2(aq)} \rightleftharpoons \underset{m_0\alpha}{M^{2+}(aq)} + \underset{m_0(2\alpha)}{2X^-(aq)}$$

$$\begin{aligned}\text{Total molality of solution} &= m_0(1 + 2\alpha)\\ &= m_0(1 + 2 \times 0.5) = 2m_0\end{aligned}$$

Hence $$\frac{(-\Delta T_f)_{\text{observed}}}{(-\Delta T_f)_{\text{undissociated}}} = \frac{2m_0}{m_0} = 2$$

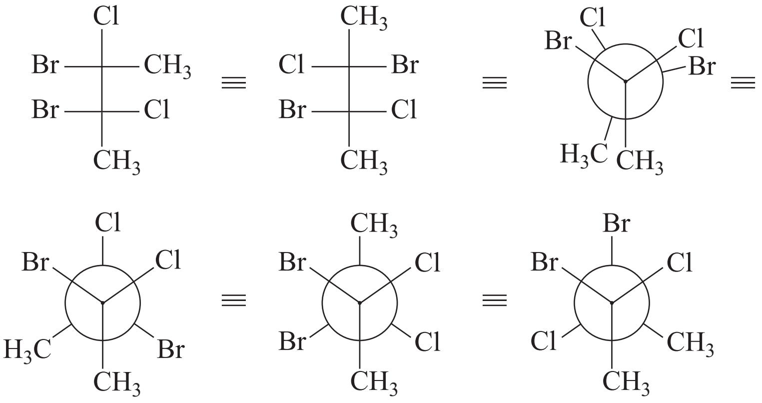
16. The reagents $K_2Cr_2O_7$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$ and HNO_3 can oxidize I^- to I_2. The reactions are:

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$
$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$
$H_2O_2 + 2I^- \rightarrow 2OH^- + I_2$
$Cl_2 + 2I^- \rightarrow 2\ Cl^- + I_2$
$O_3 + H_2O + 2I^- \rightarrow 2OH^- + O_2 + I_2$
$FeCl_3 + 2I^- \rightarrow FeCl_2 + I_2 + 2Cl^-$
$8HNO_3 + 6I^- \rightarrow 6NO_3^- + 3I_2 + 2NO + 4H_2O$

The total number of reagents are **seven**.

Alkaline $KMnO_4$ (undergoing reaction $MnO_4^- + e^- \rightarrow MnO_4^{2-}$) cannot oxidise I^- to I_2 because E^o (MnO_4^-, MnO_4^{2-}, OH^- |Pt) < E^o(I^-, I_2 |Pt).

17.



$\mu \neq 0$ $\mu \neq 0$ $\mu \neq 0$

There are three stable conformers.

18. The black-coloured sulphides are : PbS, CuS, HgS, Ag_2S, NiS, CoS and Bi_2S_3.

The yellow-coloured sulphide is SnS_2.

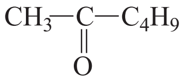
There are **seven** black-coloured sulphides.

19. The general formula of ketons is $C_nH_{2n}O$. The given relative molar mass is 100. Thus

$$12 \times n + 2n \times 1 + 16 = 100$$

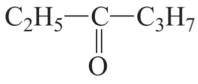
This gives $14n = 84 \quad \Rightarrow \quad n = 6$

The ketone is $C_6H_{12}O$. The possible ketones are:



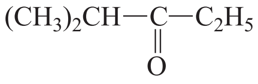
$CH_3-\underset{\underset{O}{\|}}{C}-C_4H_9$

(I)



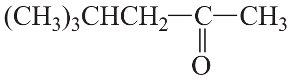
$C_2H_5-\underset{\underset{O}{\|}}{C}-C_3H_7$

(II)



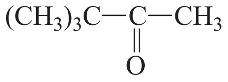
$(CH_3)_2CH-\underset{\underset{O}{\|}}{C}-C_2H_5$

(III)



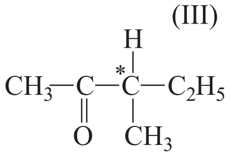
$(CH_3)_3CHCH_2-\underset{\underset{O}{\|}}{C}-CH_3$

(IV)



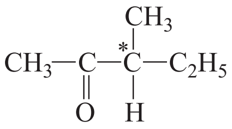
$(CH_3)_3C-\underset{\underset{O}{\|}}{C}-CH_3$

(V)



$CH_3-\underset{\underset{O}{\|}}{C}-\overset{H}{\underset{CH_3}{\overset{*}{C}}}-C_2H_5$

(VI)



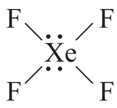
$CH_3-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\underset{H}{\overset{*}{C}}}-C_2H_5$

(VII)

The isomers (VI) and (VII) are optically active enantiomers.

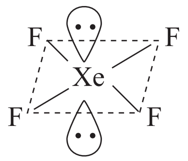
All ketones except (VI) and (VII) (which are optically active) give racemic mixture of alcohols as on reduction carbon bearing—OH group becomes chiral carbon. Thus, the number of ketones that give racemic products are **Five**.

20. XeF_4; valence electrons = 8 + 4 × 7 = 36. Electronic distribution around XeF_4 is



There are six pairs of electrons around Xe. The hybridization is sp^3d^2 of Xe orbitals

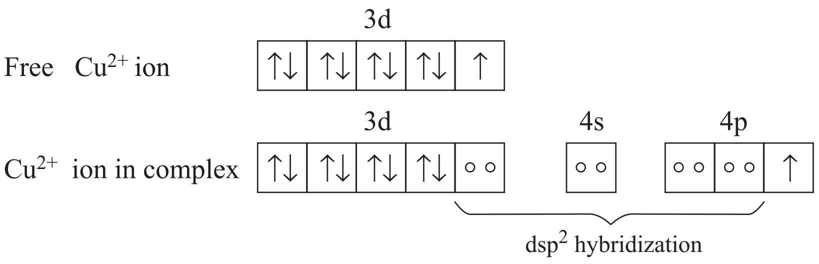
The actual shape is



The shape of XeF_4 is square planar.

Working similarly, we find that BrF_4^-, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ are also square planar. The explanations of the later two complexes are given in the following.

In $Cu(NH_3)_4^{2+}$, we have



The shape of $Cu(NH_3)_4^{2+}$ is square planar.

In $[Pt\,Cl_4]^{2-}$, the electronic configuration of free Pt^{2+} ion is $5d^8$. The orbitals of Pt will undergo dsp^2 hybridization to accommodate four Cl^- ligands and thus the shape of $[Pt\,Cl_4]^{2-}$ is also square planar.

$[FeCl_4]^{2-}$ and $[CoCl_4]^{2-}$ involve sp^3 hybridization as there is no empty d orbital in the electronic configurations of free Fe^{2+} and Co^{2+} ions and the ligand Cl^-, being a weak ligand, is not able to pair the 3d electrons.

SiF_4 and BF_4^- (no d orbitals available in B) involve sp^3 hybridization.

SF_4 has five pair of electrons around sulphur and thus involve dsp^3 hybridization.

Chemistry JEE Advanced—2014 Paper-II—Model Solutions

SECTION–I

(Only one Option Correct Type)

This section contains **10 multiple choice questions**. Each question has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

1. Assuming 2s-2p mixing is **NOT** operative, the paramagnetic species among the following is

(a) Be_2 (b) B_2 (c) C_2 (d) N_2

2. For the process $H_2O(l) \rightarrow H_2O(g)$ at $T = 100$ °C and 1 atm pressure, the correct choice is

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$ (b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$

(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$ (d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

3. For the reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the cencentration of M. The order of the reaction with respect to M is

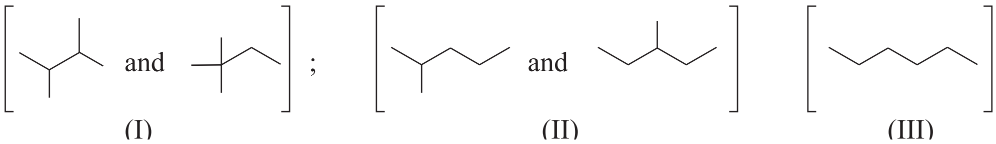
(a) 4 (b) 3 (c) 2 (d) 1

4. For the identification of β-naphthol using dye test, it is necessary to use

(a) dichloromethane solution of β-naphthol (b) acidic solution of β-naphthol

(c) neutral solution of β-naphthol (d) alkaline solution of β-naphthol

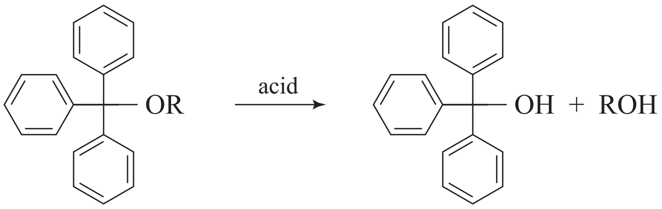
5. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



The correct order of their boiling points is

(a) I > II > III (b) III > II > I (c) II > III > I (d) III > I > II

6. The acidic hydrolysis of ether (X) shown below is fastest when:



(a) One phenyl group is replaced by a methyl group

(b) One phenyl group is replaced by a *para*-methoxyphenyl group.

(c) two phenyl groups are replaced by two *para*-methoxyphenyl groups

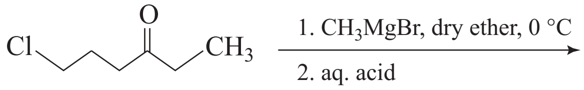
(d) no structural change is made to X.

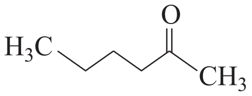
7. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH, respectively, is acting as a

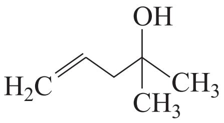
(a) reducing agent, oxidising agent (b) reducing agent, reducing agent

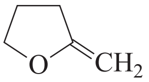
(c) oxidising agent, oxidising agent (d) oxidising agent, reducing agent

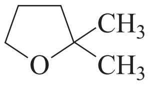
8. The major product in the following reaction is



(a) 

(b) 

(c) 

(d) 

9. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

$$XeF_6 \xrightarrow[\text{hydrolysis}]{\text{complete}} P + \text{other product} \xrightarrow{OH^-/H_2O} Q \xrightarrow[OH^-/H_2O]{\text{slow disproportionation in}} \text{Products}$$

(a) 0 (b) 1 (c) 2 (d) 3

10. The product formed in the reaction of $SOCl_2$ with white phosphorus is

(a) PCl_3 (b) SO_2Cl_2 (c) SCl_2 (d) $POCl_3$

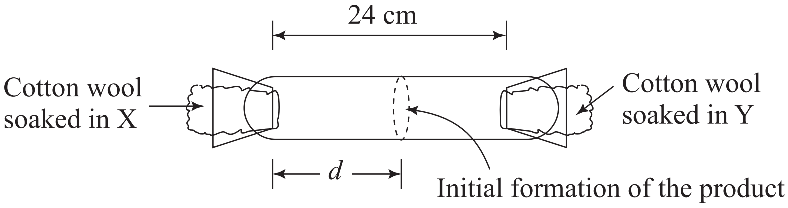
SECTION – II

Comprehension Type (Only One Option Correct)

This section contains 3 paragraphs each describing theory, experiment, data, etc. Six questions relate to three paragraphs with two questions on each paragraph. Each question has only one correct answer among the four given options (a), (b), (c) and (d).

Paragraph for Questions 11 and 12

X and **Y** are two volatile liquids with molar mass of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in **X** and the other soaked in **Y**, are simultaneous placed at the ends of a tube of length L = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atm pressure and a temperature of 300 K. Vapours of **X** and **Y** react to form a product which is first observed at a distance d from the plug soaked in **X**. Take **X** and **Y** to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



11. The value of d in cm (shown in the figure), as estimated from Graham's law, is

(a) 8 (b) 12 (c) 16 (d) 20

12. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to

(a) larger mean free path for **X** as compared to that of **Y**

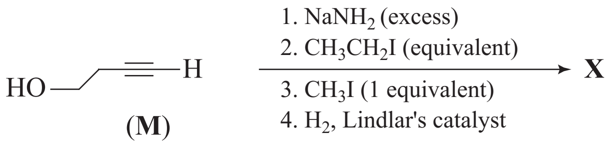
(b) larger mean free path for **Y** as compared to that of **X**

(c) increased collision frequency of **Y** with the inert gas as compared to that of **X** with the inert gas.

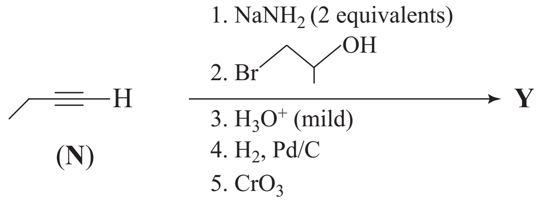
(d) increased collision frequency of **X** with the inert gas as compared to that of **Y** with the inert gas.

Paragraph for Questions 13 and 14

Schemes **1** and **2** describe sequential transformation of alkynes **M** and **N**. Consider only the **major products** formed in each step for both the schemes.



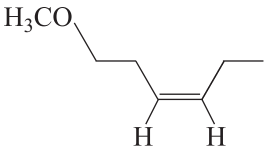
Scheme-1



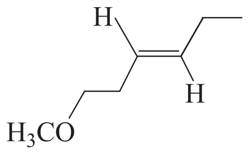
Scheme-2

13. The product **X** is

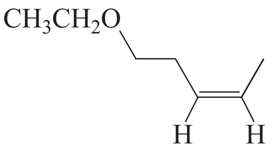
(a)



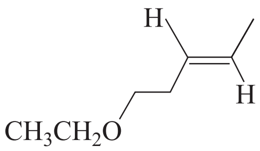
(b)



(c)



(d)



14. The correct statement with respect to product **Y** is:

(a) It gives a positive Tollens test and is a functional isomer of **X**
(b) It gives a positive Tollens test and is a geometrical isomer of **X**
(c) It gives a positive iodoform test and is a functional isomer of **X**
(d) It gives a positive iodoform test and is a geometrical isomer of **X**

Paragraph for Questions 15 and 16

An aqueous solution of metal ion **M1** reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion **M2** always forms tetrahedral complexes with these reagents. Aqueous solution of **M2** on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below.

SCHEME

$$\begin{tikzcd}
\text{Tetrahedral} & \text{M1} \arrow[l, "\text{Q}", "\text{excess}"'] \arrow[r, "\text{R}", "\text{excess}"'] & \text{Square planar} \\
\text{Tetrahedral} & \text{M2} \arrow[l, "\text{Q}", "\text{excess}"'] \arrow[r, "\text{R}", "\text{excess}"'] \arrow[d, "\text{S, stoichiometric amount}"] & \text{Tetrahedral} \\
 & \text{White precipitate} \arrow[r, "\text{S}", "\text{excess}"'] & \text{Precipitate dissolves}
\end{tikzcd}$$

15. M1, Q, R, respectively, are

(a) Zn^{2+}, KCN and HCl
(b) Ni^{2+}, HCl, HCN
(c) Cd^{2+}, KCN and HCl
(d) Co^{2+}, HCl, HCN

16. The reagent S is:

(a) $K_4Fe(CN)_6$
(b) Na_2HPO_4
(c) K_2CrO_4
(d) KOH

SECTION – III

Matching List Type (One Option Correct)

This section contains four questions, each having two matching lists. Choices for the correct combination of elements from **List-I** and **List-II** are given as option (a), (b), (c) and (d) out of which one is correct.

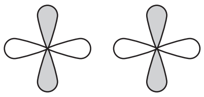
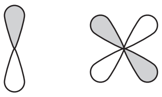
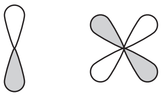
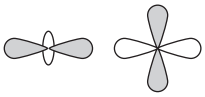
17. Match each coordination compound in **List-I** with an appropriate pair of characteristics from **List-II** and select the correct answer using the code given below the lists.
(en = $H_2NCH_2CH_2NH_2$; atomic numbers: Ti = 22, Cr = 24, Co = 27, Pt = 78)

List-I	**List-II**
P. $[Cr(NH_3)_4Cl_2]\ Cl$	1. Paramagnetic and exhibits ionisation isomerism
Q. $[Ti(H_2O)_5Cl]\ (NO_3)_2$	2. Diamagnetic and exhibits *cis-trans* isomerism
R. $[Pt(en)(NH_3)Cl]\ NO_3$	3. Paramagnetic and exhibits *cis-trans* isomerism
S. $[Co(NH_3)_4(NO_3)_2]\ NO_3$	4. Diamagnetic and exhibits ionisation isomerism

Code:

	P	Q	R	S
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

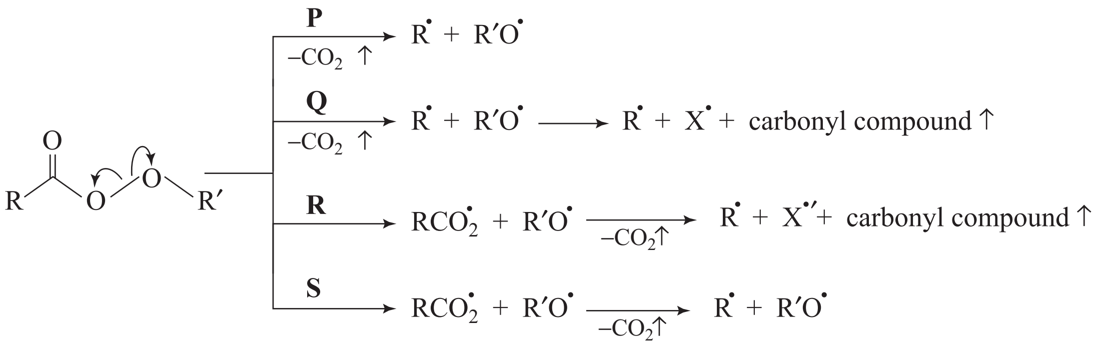
18. Match the orbital overlap figures shown in **List-I** with the description given in **List-II** and select the correct answer using the code given below the lists.

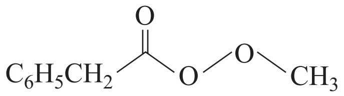
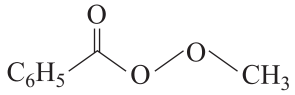
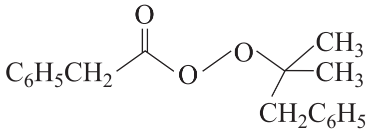
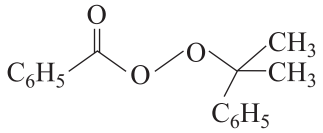
List-I	**List-II**
P. 	1. p – d π antibonding
Q. 	2. d – d σ bonding
R. 	3. p – d π bonding
S. 	4. d – d σ antibonding

Code:

	P	Q	R	S
(a)	2	1	3	4
(b)	4	3	1	2
(c)	2	3	1	4
(d)	4	1	3	2

19. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List-I** with an appropriate structure from **List-II** and select the correct answer using the code given below the lists.



List-I	**List-II**
P. Pathway **P**	1. 
Q. Pathway **Q**	2. 
R. Pathway **R**	3. 
S. Pathway **S**	4. 

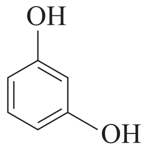
Code:

	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

20. Match the four starting materials (**P**, **Q**, **R**, **S**) given in **List-I** with the corresponding reaction schemes (I, II, III, IV) provided in **List-II** and select the correct answer using the code given below the lists.

List-I

P. H—≡—H

Q. 

List-II

1. **Scheme I**

(i) $KMnO_4$, $H\overset{\ominus}{O}$, heat
(ii) H^+, H_2O
(iii) $SOCl_2$, (iv) NH_3

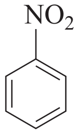
$$? \xrightarrow{\qquad\qquad\qquad} C_7H_6N_2O_3$$

2. **Scheme II**

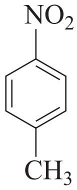
(i) Sn/HCl (ii) CH_3COCl
(iii) conc. H_2SO_4, (iv) HNO_3
(v) dil. H_2SO_4, heat
(vi) $H\overset{\ominus}{O}$

$$? \xrightarrow{\qquad\qquad\qquad} C_6H_6N_2O_2$$

R.



S.



Code:

	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

3. **Scheme III**

(i) red hot iron, 873 K
(ii) fuming HNO_3, H_2SO_4, heat
(iii) H_2S, NH_3, (iv) $NaNO_2$, H_2SO_4
(v) hydrolysis

$$? \xrightarrow{\hspace{4cm}} C_6H_5NO_3$$

4. **Scheme IV**

(i) conc. H_2SO_4, 60 °C
(ii) conc. HNO_3, conc. H_2SO_4
(iii) dil. H_2SO_4, heat

$$? \xrightarrow{\hspace{4cm}} C_6H_5NO_4$$

ANSWERS

1. (c) **2.** (b) **3.** (b) **4.** (d) **5.** (b)
6. (c) **7.** (a) **8.** (d) **9.** (c) **10.** (a)
11. (c) **12.** (d) **13.** (a) **14.** (c) **15.** (b)
16. (d) **17.** (b) **18.** (c) **19.** (a) **20.** (c)

Solutions

1. If 2s – 2p mixing is not operative, the increasing order of energies of molecular orbitals for a diatomic molecule is

$$(\sigma\, 2s) < (\sigma^*\, 2s) < \sigma\, 2p_z < \pi\, 2p_x = \pi\, 2p_y < \pi^*\, 2p_x = \pi^*\, 2p_y < (\sigma\, 2p_z)$$

The electronic configurations of the given molecules are

Be_2	$(\sigma 2s)^2\, (\sigma^* 2s)^2$
B_2	$(\sigma 2s)^2\, (\sigma^* 2s)^2\, (\sigma\, 2p_z)^2$
C_2	$(\sigma 2s)^2\, (\sigma^* 2s)^2\, (\sigma\, 2p_z)^2\, (\pi\, 2p_x)^1\, (\pi\, 2p_y)^1$
N_2	$(\sigma 2s)^2\, (\sigma^* 2s)^2\, (\sigma\, 2p_z)^2\, (\pi\, 2p_x)^2\, (\pi\, 2p_y)^2$

The species C_2 has two unpaired electrons and thus it is paramagnetic.

2. For the conversion of $H_2O(l) \rightarrow H_2O(g)$, the system absorbs heat from the surroundings.

Thus $q_{\text{system}} = +\text{ve}$ and $q_{\text{surroundings}} < 0$

The transformation $H_2O(l) \rightarrow H_2O(g)$ at 1 atm and 100 °C is reversible. Hence

$$\Delta S_{\text{system}} = \frac{q_{\text{system}}}{T} > 0$$

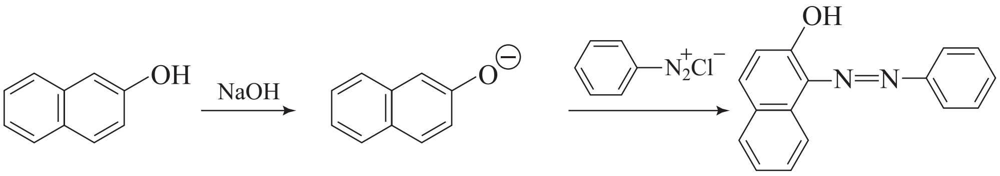
$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} < 0$$

3. For the given reaction, we write

$$r = k\,[\mathrm{M}]^n$$

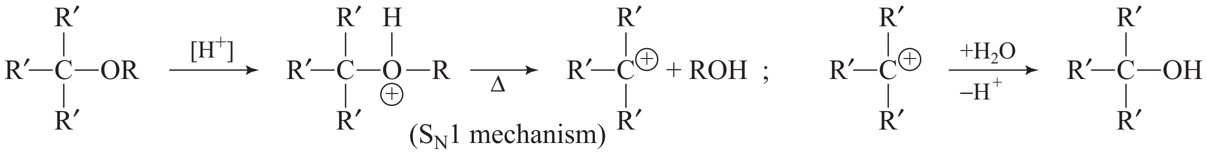
where n is the order of the reaction. Since on doubling the concentration of M, the rate of reaction becomes 8 times, it is obvious that $n = 3$.

4. An alkaline solution is used for the dye test of β-naphthol.



5. Greater the extent of branching, lesser the boiling point of hydrocarbon.

6. The reaction proceeds via the formation of oxonium salt. Ether linkage is cleaved by heating to form a corbocation which combines with water to give the given product.



The stability of the intermediate carbocation decides the rate of reaction. The larger the stability of carbocation, larger the rate of reaction.

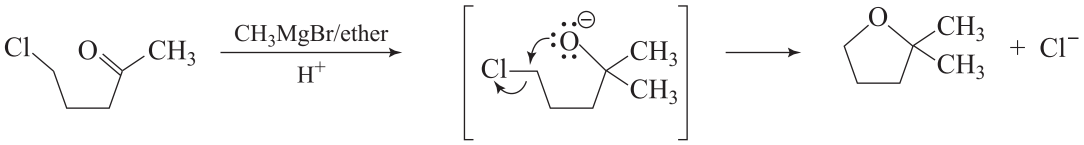
p-Methoxyphenyl is the electron releasing group and thus helps stabilising the carbocation. The replacement of two phenyl groups by two *p*-methoxy groups stabilises the carbocation better than any other choice given in (a), (b) and (d).

7. Hydrogen peroxide is an oxidising as well as a reducing agent. In the presence of very strong oxidising agent such as $\mathrm{KIO_3}$, it behaves as a reducing agent. The reactions of $\mathrm{H_2O_2}$ with $\mathrm{KIO_4}$ and $\mathrm{NH_2OH}$ are as follows.

$$\underset{\substack{\text{oxidising}\\ \text{agent}}}{\mathrm{KIO_4}} + \underset{\substack{\text{reducing}\\ \text{agent}}}{\mathrm{H_2O_2}} \rightarrow \mathrm{KIO_3} + \mathrm{H_2O} + \mathrm{O_2}$$

$$\underset{\substack{\text{oxidising}\\ \text{agent}}}{\mathrm{H_2O_2}} + \underset{\substack{\text{reducing}\\ \text{agent}}}{2\,\mathrm{NH_2OH}} \rightarrow \mathrm{N_2} + 4\,\mathrm{H_2O}$$

8. The given reaction may be formulated as follows.



9. The reactions are:

$$\left.\begin{array}{lll} \mathrm{XeF_6 + H_2O} & \rightarrow & \mathrm{XeOF_4 + 2\,HF} \\ \mathrm{XeOF_4 + H_2O} & \rightarrow & \mathrm{XeO_2F_2 + 2\,HF} \\ \mathrm{XeO_2F_2 + H_2O} & \rightarrow & \mathrm{XeO_3 + 2\,HF} \end{array}\right]\text{Complete hydrolysis}$$

$$\mathrm{XeO_3 + OH^-} \rightarrow \mathrm{HXeO_4^-(aq)}$$

$$2\,\mathrm{HXeO_4^-} + 2\,\mathrm{OH^-} \xrightarrow[\text{disproportionation}]{\text{slow}} \mathrm{XeO_6^{4-}} + \mathrm{Xe(g)} + \mathrm{O_2(g)} + 2\,\mathrm{H_2O}$$

10. The reaction is $P_4 + 8\,SOCl_2 \rightarrow 4\,PCl_3 + 4\,SO_2 + 2\,S_2Cl_2$

11. According to Graham's law, the rates of diffusion of the two gases is related to each other through the expression

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{d/t}{(24\text{ cm} - d)/t} = \sqrt{\frac{40}{10}}$$

or $$\frac{d}{24\text{ cm} - d} = 2.\ \text{This gives } d = 16\text{ cm.}$$

12. The expression of collision frequency between the molecules of Gas 1 and Gas 2 is

$$Z_{12} = \pi\,\sigma_{12}^2\,\bar{u}\,N_1^*\,N_2^* = \pi\,\sigma_{12}^2\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_1^*\,N_2^*$$

where $\sigma_{12}\,(= (\sigma_1 + \sigma_2)/2)$ is the molecular collision diameter, N_1^* and N_2^* are the respective number of molecules per unit volume and μ is the reduced mass. The latter is gives as

$$\mu = \frac{m_1\,m_2}{(m_1 + m_2)} = \frac{M_1 M_2}{(M_1 + M_2)}\frac{1}{N_A}$$

For the gases X and inert gas (molar mass M), the reduced mass is

$$\mu_X = \frac{M_X M}{(M_X + M)}\frac{1}{N_A}$$

For the gases Y and inert gas, we have

$$\mu_Y = \frac{M_Y M}{(M_Y + M)}\frac{1}{N_A}$$

It can be shown that $\mu_X < \mu_Y$. Thus the collision frequency of X with inert gas will be larger than that between Y and inert gas.

The mean free path $\lambda(= \bar{u}/Z_{12})$ is

$$\lambda = \frac{1}{\pi\,\sigma_{12}^2\,N_1^*\,N_2^*}$$

It follows that the mean free path is independent of molar masses.

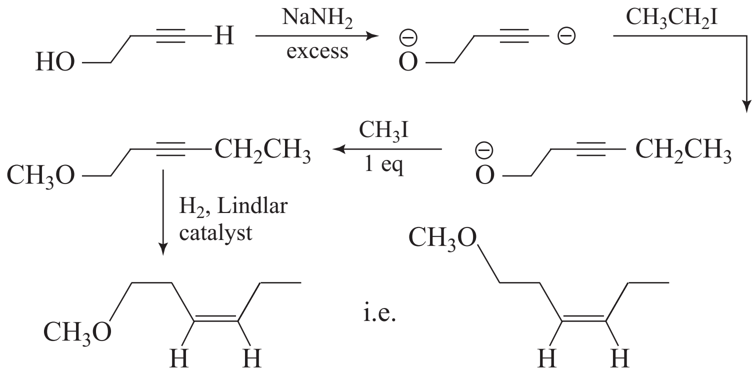
13. $NaNH_2$ (excess) removes acetylinic hydrogen and hydroxyl hydrogen.

CH_3CH_2I causes substitution of CH_3CH_2– towards acetylinic end.

CH_3I causes the formation of ether.

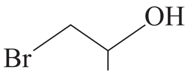
H_2, Lindlar's catalyst causes *syn* addition of hydrogen in the triple bond.

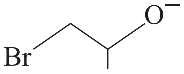
The reactions are



(X)

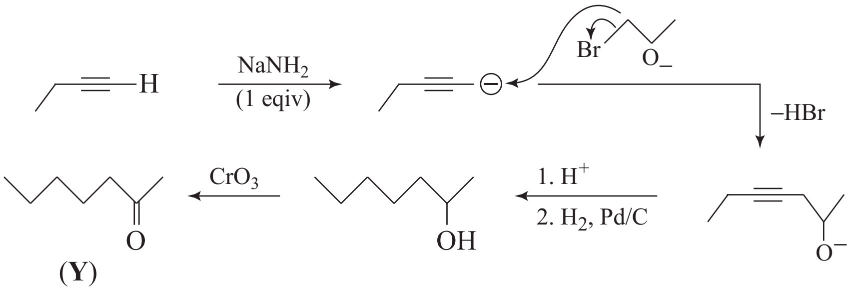
14. $NaNH_2$ (1 eqiv.) removes acetylinic hydrogen



forms


in the presence of $NaNH_2$ and adds up towards acetylinic end with the elimination of Br^-.

The treatment of the resultant compound with H_3O^+ converts it into alcohol.
H_2, Pd/C causes hydrogenation of triple bond upto the fully saturation.
CrO_3 causes oxidation of hydroxyl group. The reactions are as follows.



(Y)

The compound Y will show iodoform test as this contains $CH_3CO—$ group.
The compound Y is a functional isomer of X, same molecular formula (X contains ether group and Y contains keto group).

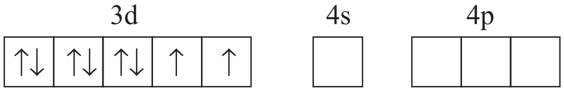
15. The electronic configurations of the given ions in the choices of Q.15 are:

${}_{30}Zn^{2+}$; $(3d^{10})$ ${}_{28}Ni^{2+}$; $(3d^8)$ ${}_{48}Cd^{2+}$; $(4d^{10})$ ${}_{27}Co^{2+}$; $(3d^7)$

From these choices, the metal ion **M1** cannot be Zn^{2+} and Cd^{2+} as their d orbitals are completely filled and thus cannot form square planar complexes which require dsp^2 hybridization of orbitals.

The ion Co^{2+} generally forms 6-coordinated complexes.

The ion Ni^{2+} does form 4-coordinated complexes. Its electronic configuration is



It can form tetrahedral complex (involving sp^3 hybridization) with weak ligand such as Cl^- (from HCl)

It can form square planar complex (involving dsp^2 hybridization) with strong ligand such CN^- (from HCN). The latter is able to pair 3d electrons making a vacant 3d orbital for dsp^2 hybridization.

Hence, the **choice (b)** is correct.

16. The reaction of **M2** with S indicates the amphoteric nature of metal ion.
This ion may be Zn^{2+} ions as it form only tetrahedral complexes. The reagent S seems to be KOH. Its reaction with metal ion M2 are as follows.

$$Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(OH)_2\,(s)$$

$$Zn(OH)_2(s) + 2\,OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}$$

Hence, the choice (d) is correct.

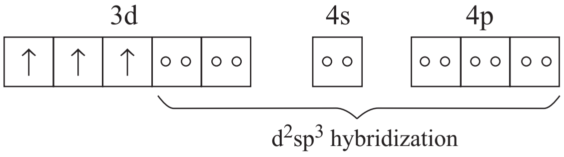
17. In the choices (a) to (d) of the given code, none of the choices (1) to (4) of List II is repeated for the compound P. Therefore, it is sufficient to pick up the correct choice from the List II for the compound P in the List I. Rest of matchings follow automatically. (However, these may be checked for the correctness.)

The coordination compound P is $[Cr(NH_3)_4Cl_2]$ Cl.

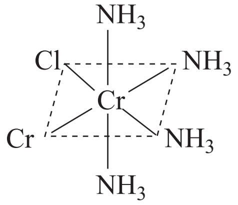
The chromium ion in the complex is ${}_{24}Cr^{3+}$.

Its electronic configuration is $3d^3$.

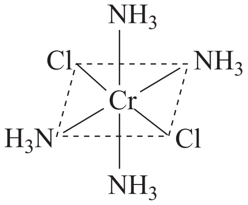
Free ions as well as in the complex compound



Cr^{3+} involves d^2sp^3 hybridization to give six equivalent orbitals for the accommodation of ligands. Since Cr^{3+} involves 3 unpaired electrons, the complex will be paramagnetic. The complex $[Cr(NH_3)_4Cl_2]^+$ will exhibit *cis-trans* isomerisation as depicted in the following.

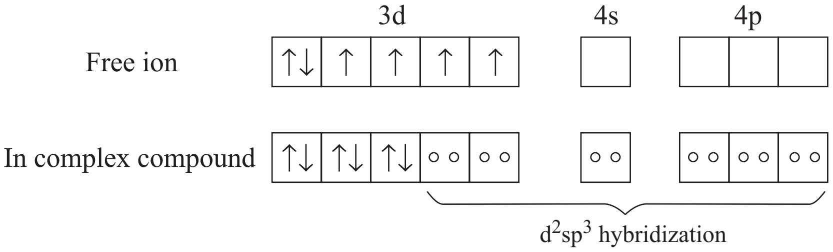


cis-isomer



trans-isomer

Thus, the item P of List-I matches with item 3 of List-II. This match is given by the choice (b) of the given code. Rest of matching follows automatically. For example, the complex $[Co(NH_3)_4(NO_3)_2]\ NO_3$ involves the following electronic configuration of $_{24}Co^{3+}$ ($3d^6$)



The complex will be diamagnetic and also exhibits *cis-trans* isomerism. Thus, the item S in List-I matches with item 2 in the List-II. This is exactly the same in the **choice (b)** in the given code.

18. Identification of the items P and Q of **List-I** with the correct choice in the **List-II** is sufficient to choose the correct answer in the code.

The item P involves two d orbitals. There is end to end overlap between two identical types of lobes which leads to σ bonding orbital. Hence, P involves d – d σ bonding, which is the item 2 of the List-II.

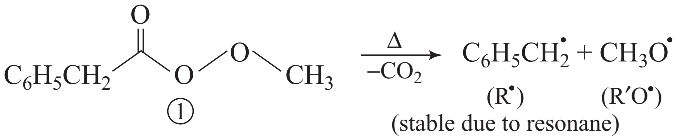
The item Q of List-I involves p and d orbitals. There is side ways overlap between the same type of lobes, which leads to π bonding orbital. Hence, Q involves p – d π bonding, which is the item 3 of List-II.

Hence, the **choice (c)** of the given code is correct.

Rest of matchings follow automatically. The item R involves p and d orbitals. There is side ways overlap between different types of lobes, which leads to p – d π antibonding. Thus R in the List-I matches with the item 1 of the List-II.

The item S involves d – d σ antibonding.

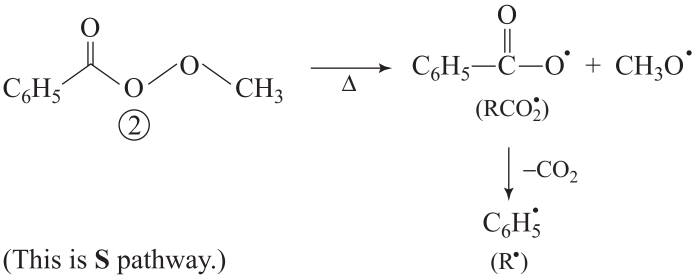
19.



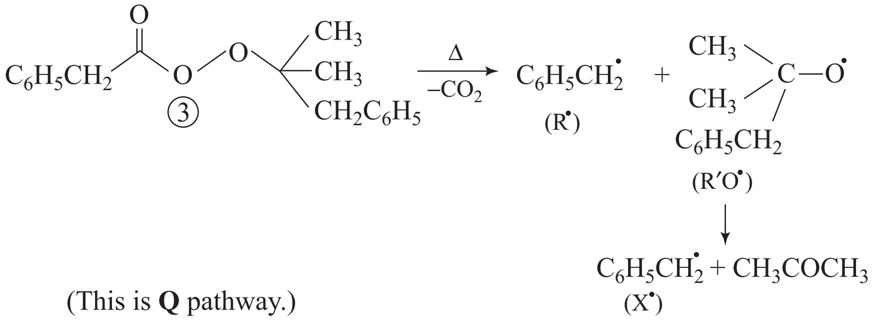
(This is **P** pathway.)

This fixing of pathway P for the compound (1) indicates the **choice (a)** of the given code is correct. This follows from the fact that the choices (b), (c) and (d) do not involve the structure (1) with the pathway P.

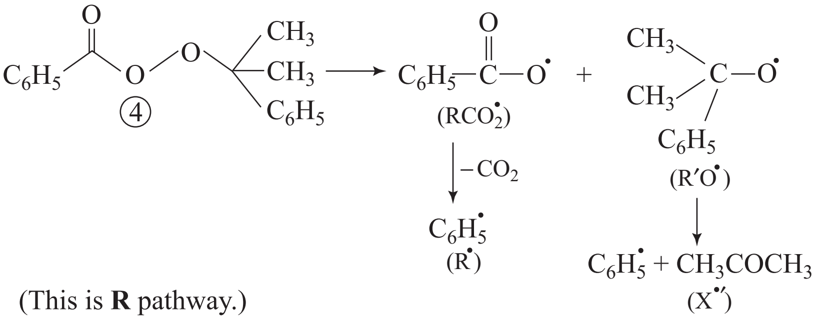
However, the remaining matchings in the **choice (a)** may be carried out to verify the correctness of choice (a)



(This is **S** pathway.)



(This is **Q** pathway.)



(This is **R** pathway.)

20. This question deals with the organic conversions of a compound into another compound via series of steps. The correct answer, however, can be arrived at by the following observations.

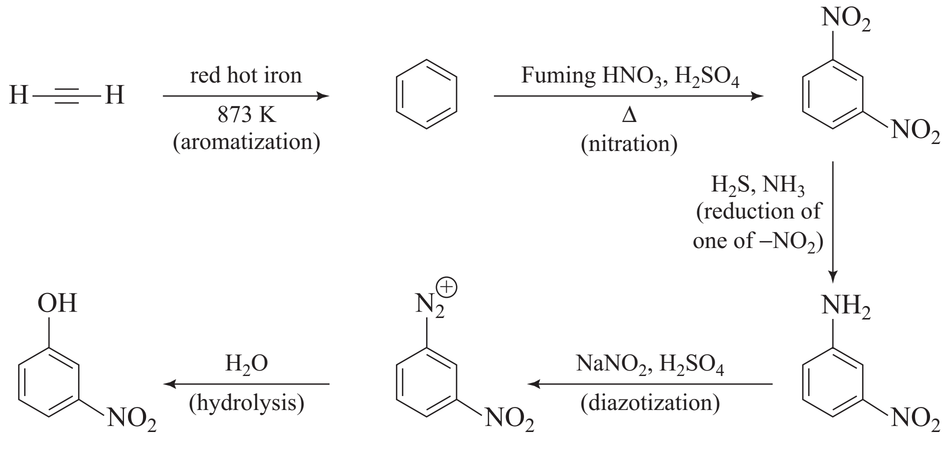
(1) All the products given in the schemes 1, 2, 3 and 4 are probably aromatic. Only the compound P is aliphatic which can be converted into aromatic by the use of red hot iron at 873 K, which is given as the first step in Scheme III. Thus, the compound **P** is fixed with the Scheme III.

(2) The first step in Scheme I uses Baeyer's reagent (alkaline $KMnO_4$) This will oxidize the side group—CH_3 of the compound **S** into—COOH group. Thus, the compound **S** is fixed with the Scheme I.

Based on the above informations, the **choice (c)** of the given code seems to be the correct choice. This choice, fixes the compound R with the scheme (2) and Q with the scheme (4).

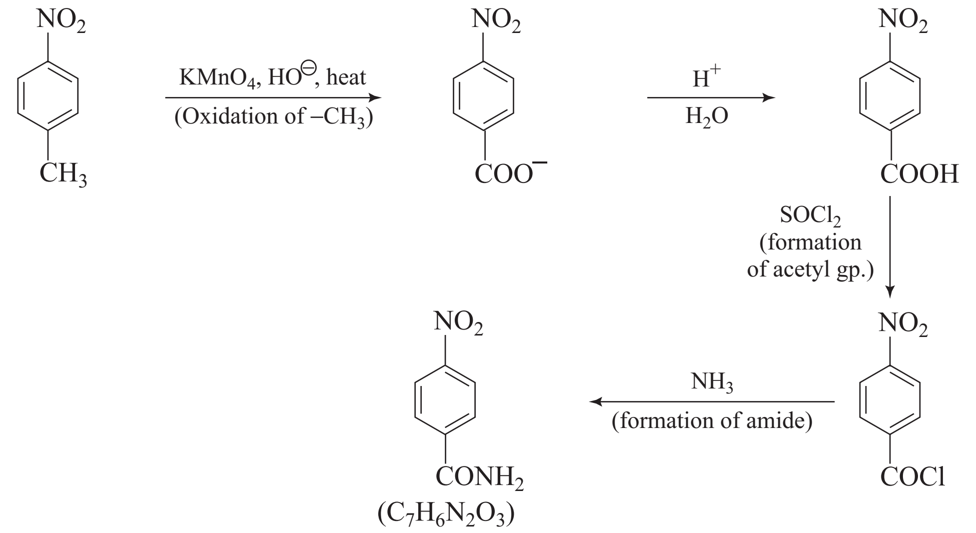
The correctness of the choice (c) may be ascertained by carrying out the actual conversions, which are given in the following.

Compound P ↔ Scheme (3)

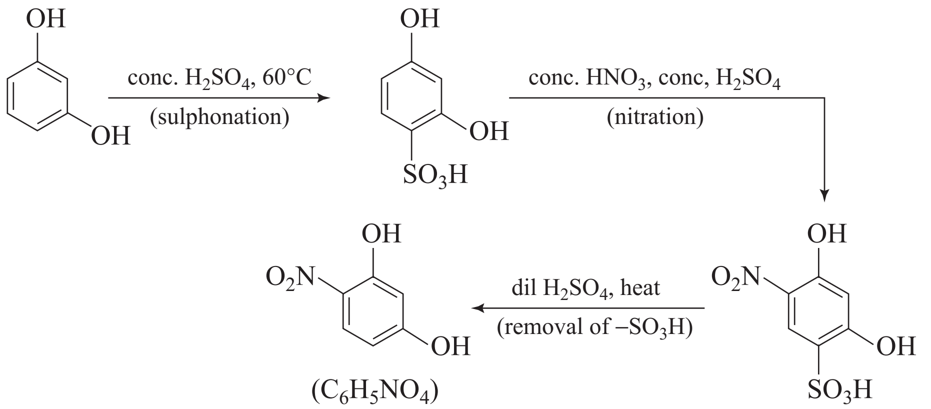


($C_6H_5NO_3$)

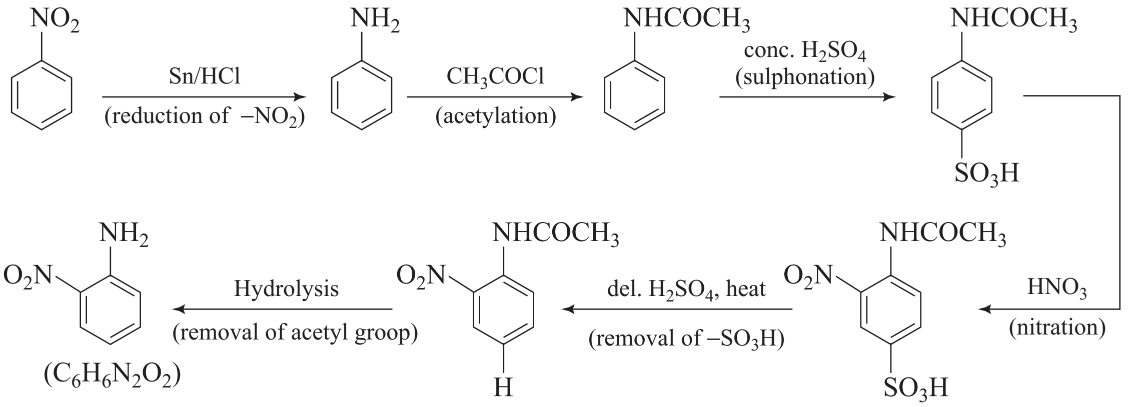
Compound S ↔ Scheme (1)



Compound Q ↔ Scheme (4)



Compound R ↔ Scheme (2)



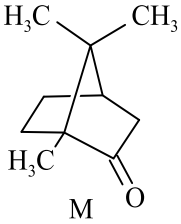
JEE ADVANCED 2015: PAPER–I
(MODEL SOLUTIONS)

SECTION I

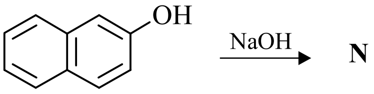
(Single Digit Integer Type)

This section contains **EIGHT** questions.
This answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive

1. The total number of stereoisomers that can exist for **M** is ______.



2. The number of resonance structures for **N** is



3. The total number of lone pairs of electrons in N_2O_3 is _________ .
4. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is ________.

   [Atomic number of Fe = 26]
5. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is _____.

   [Atomic number: S = 16, Cl = 17, I = 53 and Xe = 54]
6. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H atom is 9, while the degeneracy of the second excited state of H^- is _________ .
7. All the energy released from the reaction $X \rightarrow Y$, $\Delta G^o = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E^o = -0.25V$.

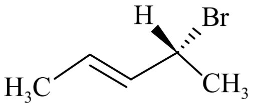
   Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is __________ . [$1F = 96500$ C mol^{-1}]
8. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558 ºC, the number of chloride(s) in the coordination sphere of the complex is ________.

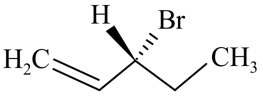
   [K_f of water = 1.86 K kg mol^{-1}]

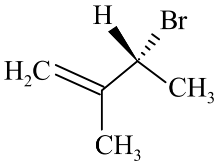
SECTION II
(One or More than One Options Correct Type)

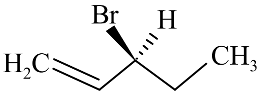
This section contains **TEN** questions
Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options(s) is (are) correct

9. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are)

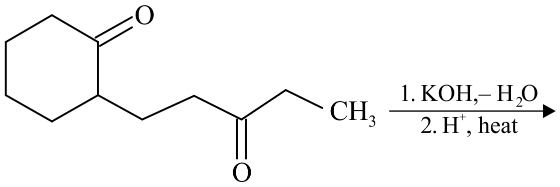
(a)


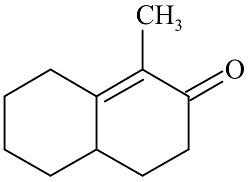
(b)


(c)


(d)


10. The major product of the following reaction is



(a)


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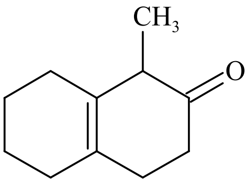

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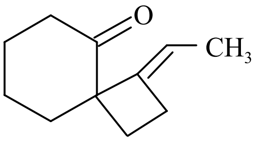

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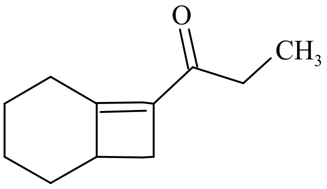
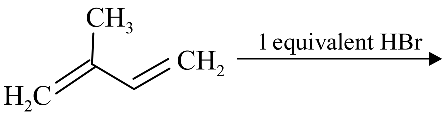
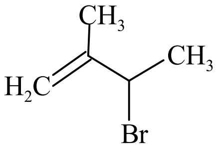


11. In the following reaction, the major product is



(a)


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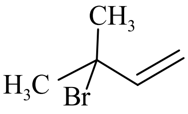
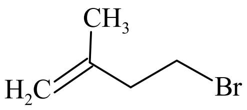
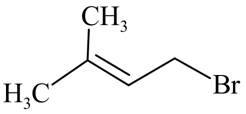
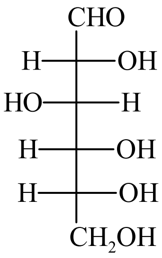


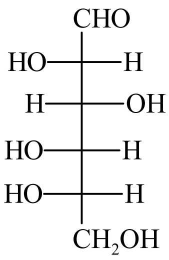
(c)


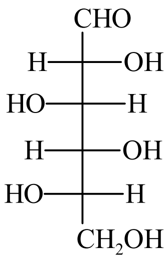
(d)


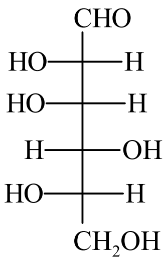
12. The structure of D-(+)-glucose is

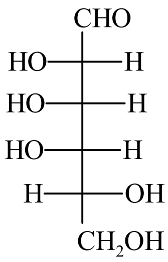


The structure of L-(–)-glucose is

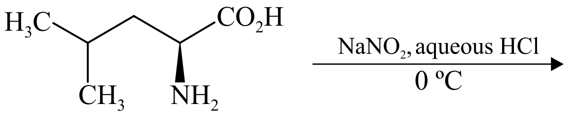
(a) 

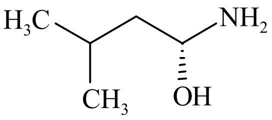
(b) 

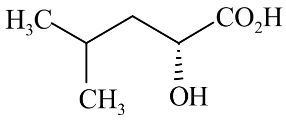
(c) 

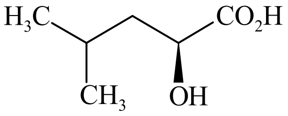
(d) 

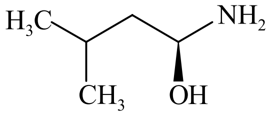
13. The major product of the reaction is



(a) 

(b) 

(c) 

(d) 

14. The correct statement(s) about Cr^{2+} and Mn^{3+} is(are)
[Atomic numbers of Cr = 24 and Mn = 25]

(a) Cr^{2+} is a reducing agent
(b) Mn^{3+} is an oxidizing agent
(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

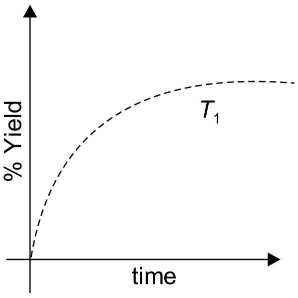
15. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is(are)

(a) Impure Cu strip is used as cathode
(b) Acidified aqueous $CuSO_4$ is used as electrolyte
(c) Pure Cu deposits at cathode
(d) Impurities settle as anode–mud

16. Fe^{3+} is reduced to Fe^{2+} by using

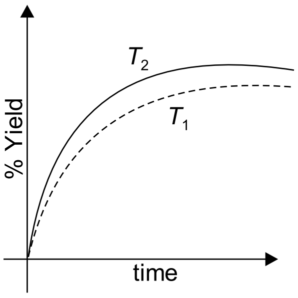
(a) H_2O_2 in presence of NaOH
(b) Na_2O_2 in water
(c) H_2O_2 in presence of H_2SO_4
(d) Na_2O_2 in presence of H_2SO_4

17. The % yield of ammonia as a function of time in the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H < 0$ at (P, T_1) is given as follows:

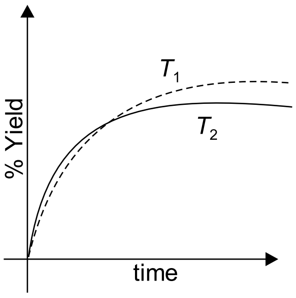


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by

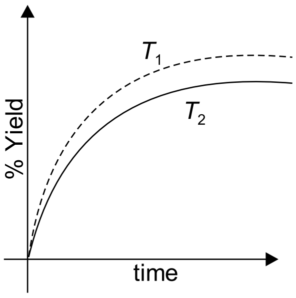
(a)



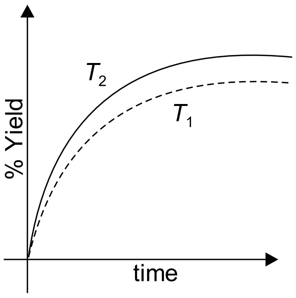
(b)



(c)



(d)



18. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n, respectively, are

(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

SECTION III

This section contains **TWO** questions

19. Match the anionic species given in Column I with that are present in the ore(s) given in Column II

Column I

(a) Carbonate
(b) Sulphide
(c) Hydroxide
(d) Oxide

Column II

(p) Siderite
(q) Malachite
(r) Bauxite
(s) Calamine
(t) Argentite

20. Match the thermodynamic processes given under Column I with the expressions given under Column II:

Column I	**Column II**
(a) Freezing of water at 273 K and 1 atm	(p) $q = 0$
(b) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(q) $w = 0$
(c) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(r) $\Delta S_{sys} < 0$
(d) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$
	(t) $\Delta G = 0$

ANSWERS

1. (2) **2.** (9) **3.** (8) **4.** (4) **5.** (4)
6. (3) **7.** (4) **8.** (1) **9.** (b), (d) **10.** (a)
11. (d) **12.** (a) **13.** (c) **14.** (a), (b), (c) **15.** (b), (c), (d)
16. (a), (b) **17.** (c) **18.** (a)

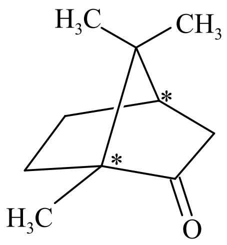
19. The correct-bubbled diagram is as follows.

A	**p**	**q**	r	**s**	t
B	p	q	r	s	**t**
C	p	**q**	**r**	s	t
D	p	q	**r**	s	t

20. (a) ↔ (r), (t); (b) ↔ (p), (q), (s); (c) ↔ (p), (q), (s); (d) ↔ (p), (q), (s), (t)

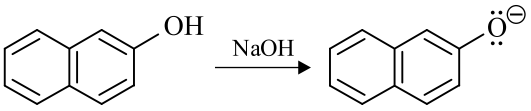
Solutions

1. There are two asymmetric carbon atoms in the molecule.



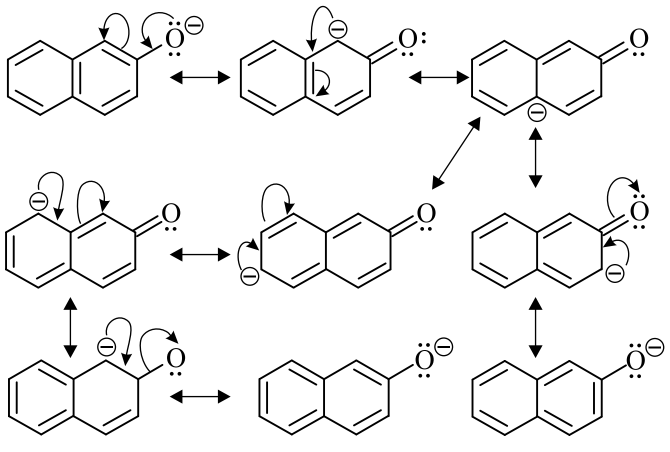
Due to rigid bridged-bicyclic compound, the number of isomers observed is 2 instead of four.

2. The reaction is



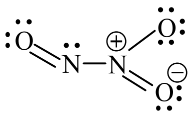
(N)

The resonating structures of N are as follows:



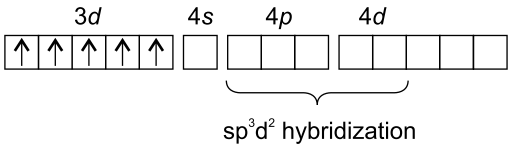
There are 9 resonating structures.

3. The structure of N_2O_3 is



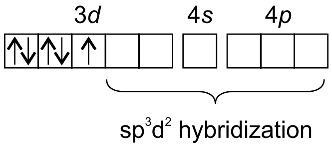
There are 8 pairs of lone electrons in N_2O_3.

4. SCN^- being a weak ligand, it will form high-spin complex with Fe^{3+} ($3d^5$) ion.
   Fe^{3+} *in* $[Fe(SCN)_6]^{3-}$



Its spin only magnetic moment will be $\mu = \sqrt{n(n+2)}\,\mu_B = \sqrt{5(7)}\,\mu_B = 5.92\,\mu_B$

CN^- being a strong ligand, it will form low-spin complex with Fe^{3+} ion.
Fe^{3+} in $[Fe(CN)_6]^{3-}$



Its spin-only magnetic moment will be $\mu = \sqrt{n(n+2)}\,\mu_B = \sqrt{1(3)}\,\mu_B = 1.73\,\mu_B$

The difference between the two magnetic moment is $\Delta\mu = (5.92 - 1.73)\ \mu_B = 4.19\ \mu_B \simeq 4\ \mu_B$ (nearest integer)

5. The valence electrons, their distributions, involved hybridization of the central atom in the given molecules/ions are as follows.

$BeCl_2$	2+2×7=16	$:\overset{..}{\underset{..}{Cl}}—Be—\overset{..}{\underset{..}{Cl}}:$	sp linear
N_3^-	3×5+1=16	$:\overset{..}{\underset{..}{N}}—N—\overset{..}{\underset{..}{N}}:$	sp linear
NO_2	2×5+6=16	$:\overset{..}{\underset{..}{N}}—N—\overset{..}{\underset{..}{O}}:$	sp linear

NO_2^+	5+2×6–1=16	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}-\mathrm{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:$	sp linear
O_3	3×6=18	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}-\overset{\cdot\cdot}{\mathrm{O}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:$	sp^2 Nonlinear
SCl_2	6+2×7=20	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{S}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$	sp^3 Nonlinear
ICl_2^-	7+2×7+1=22	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{I}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$	dsp^3 Nonlinear
I_3^-	3×7+1=22	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{I}}}-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{I}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{I}}}:$	dsp^3 Nonlinear
XeF_2	8+2×7=22	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}-\underset{\cdot\cdot\,\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Xe}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:$	dsp^3 Nonlinear

There are **four** molecules/ion(s) which are linear without involving d orbitals in hybridization.

6. For one-electron species, the energy of electron is governed by the principal quantum number n while for the multi-electron species, the energy is governed by the sum of principal and azimuthal quantum numbers (i.e. $n + l$)

In H atom, for $n = 3$, the degeneracy is 9 involving 3s, three 3p orbitals and five 3d orbitals.

In H^- ion, the second excited state is 2p orbitals and their degeneracy is **three**.

7. The free energy change involved in the reaction $M^{3+} \rightarrow M^{3+} + 2e^-$ is

$$\begin{aligned}\Delta G^\circ &= -\,nFE^\circ = -\,(2)\ (96500\ \mathrm{C\ mol^{-1}})\ (-0.25\ \mathrm{V})\\ &= 48250\ \mathrm{J\ mol^{-1}}\end{aligned}$$

The number of moles of M^+ oxidized is

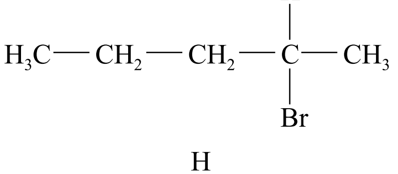
$$n = \frac{-\text{Ä}G^o(\mathrm{X} \rightarrow \mathrm{Y})}{\text{Ä}G^o(\mathrm{M^+} \rightarrow \mathrm{M^{3+}})} = \frac{193 \times 10^3\ \mathrm{J\ mol^{-1}}}{48250\ \mathrm{J\ mol^{-1}}} = 4$$

8. For an electrolyte, the van't Hoff factor is defined as

$$i = i - \frac{\Delta T_\mathrm{f}}{K_\mathrm{f} m} = \frac{0.0558\,\mathrm{K}}{(1.86\,\mathrm{K\ kg\ mol^{-1}})\ (0.01\ \mathrm{mol\ kg^{-1}})} = 3$$

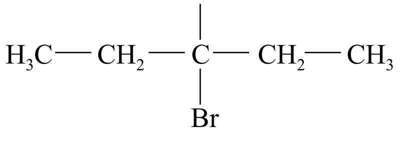
From this, it follows that the complex is $[Co(NH_3)_5Cl]Cl_2$ as it gives three species in the solution. Hence, the number of chloride within the coordination sphere is 1.

9. The hydrogenated products are:

(a) 

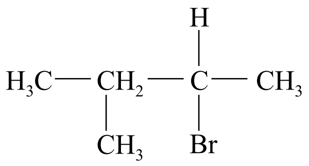
$$H_3C-CH_2-CH_2-\underset{\mathrm{Br}}{\overset{\mathrm{H}}{\mathrm{C}}}-CH_3$$

Optically active

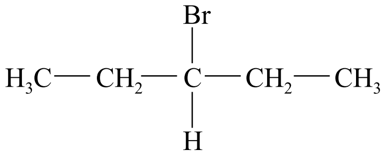
(b) 

$$H_3C-CH_2-\underset{\mathrm{Br}}{\overset{\mathrm{H}}{\mathrm{C}}}-CH_2-CH_3$$

Optically inactive

(c) 

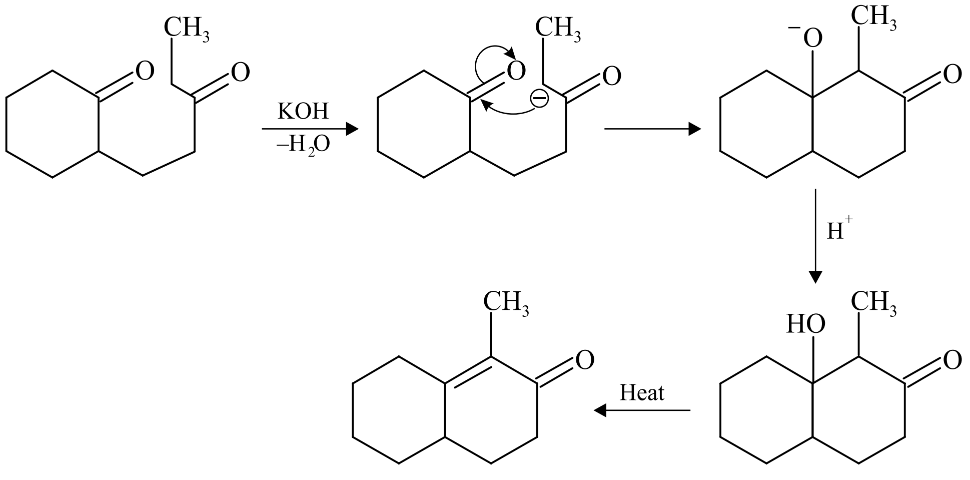
$H_3C-\underset{CH_3}{CH_2}-\overset{H}{\underset{Br}{C}}-CH_3$ Optically active

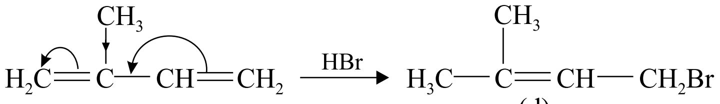
(d) 

$H_3C-CH_2-\overset{Br}{\underset{H}{C}}-CH_2-CH_3$ Optically inactive

Therefore choice (b) and (d) are correct.

10. The molecule undergoes intramolecular aldol condensation.



11. 

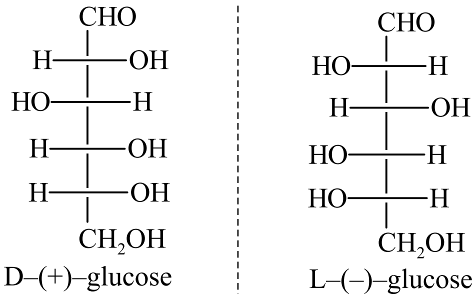
$H_2C=\overset{CH_3}{C}-CH=CH_2 \xrightarrow{HBr} H_3C-\overset{CH_3}{C}=CH-CH_2Br$

(d)

12. If the –OH group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right, the molecule is said to have D absolute configuration and if it lies on left, the molecule is said to have L configuration.

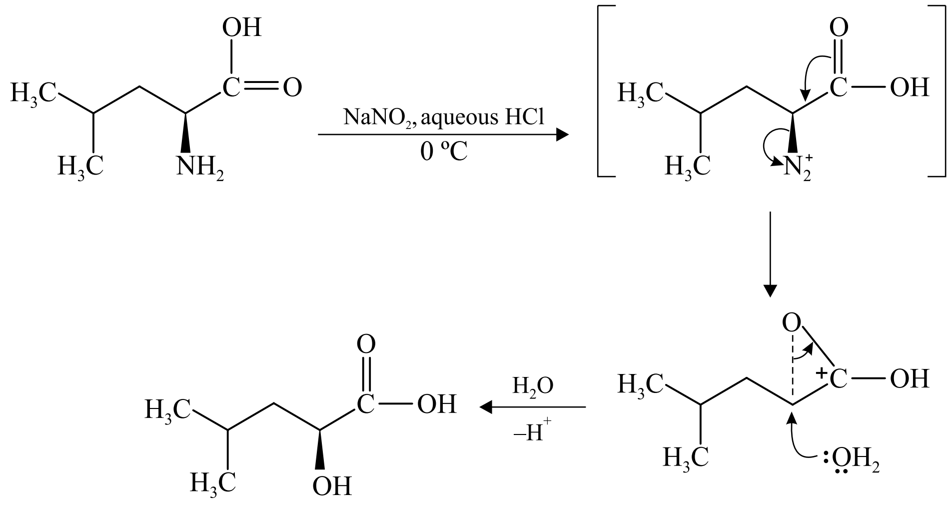
The dextrorotatory (rotating the light to right) and levorotatory (rotating the light to left) are indicated by plus and minus signs written within the parenthesis and inserted immediately after the symbol D and L

Guided by these, we have



D–(+)–glucose L–(–)–glucose

13. The reaction involves neighbouring group participation in the S_N2 substitution of —NH_2 by —OH. The reaction proceeds through a new reaction intermediate by a substituent that bonds to the reaction centre involving intramolecular nucleophilic attack followed by intermolecular substitution. This results into the retention of configuration.



14. The electronic configurations of Cr and Mn are $(3d)^5(4s)^1$ and $(3d)^5(4s)^2$, respectively, and those of Cr^{2+} and Mn^{3+} are $(3d)^4$ and $(3d)^4$, respectively (Choice c).

Cr^{2+} acts as a reducing agent and its electronic configuration changes from $(3d)^4$ to $(3d)^3$.

Mn^{3+} is an oxidizing agent and its electronic configuration changes from $(3d)^4$ to $(3d)^5$ – a more stable electronic configuration.

Thus, the choices (a), (b) and (c) are correct.

15. In the electrolytic refining of blister copper, the electrodic reactions are:

Cathode: $Cu^{2} + (ap) + 2e^- \longrightarrow \underset{\text{(Pure)}}{Cu}$

Anode: $\underset{\text{(Impure)}}{Cu} \longrightarrow Cu^{2+}\,(ap) + 2e^-$

Impurities settle as anode-mud.

The choice (b), (c) and (d) are correct.

16. The reduction of Fe^{3+} to Fe^{2+} is possible provided reduction potential of Fe^{3+} to Fe^{2+} is larger than the reduction potential of H_2O_2. The standard reduction potentials are :

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $E^\circ = 0.77$ V

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ $E^\circ = 1.77$ V

$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^-$ $E^\circ = -\ 0.15$ V

It follows that H_2O_2 is more powerful reducing agent in alkaline medium as compared to acidic medium. Fe^{3+} is reduced to Fe^{2+} by alkaline H_2O_2. Na_2O_2 in water is equivalent to $2NaOH + H_2O_2$.

Hence, the choice (a) and (b) are correct.

The net reaction is

$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ $E^\circ = 0.77$ V

$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^-$ $E^\circ = 0.15$ V

$2Fe^{3+} + H_2O_2 + 2OH^- \longrightarrow 2Fe^{2+} + O_2 + 2H_2O$ $E^\circ = 0.92$ V

17. The given reaction is exothermic in nature. As per Le-Chatelier principle, the yield of NH_3 will decrease with increase in temperature. Therefore, the choice (c) is correct.

18. Let there be x ions of Al^{3+} and y ions of Mg^{2+}. Since there are 4 oxide ions per unit cell of cubical-closest packed structure, the balancing of positive and negative charges gives

$$x\,(+3) + y\,(+2) = -4\,(-2)$$

This equation is satisfied if $x = 2$ and $y = 1$. Since there are 4 octahedral holes per unit cell, the fraction of holes occupied by Al^{3+} ions is 2/4 i.e. 1/2.

Since there are 8 tetrahedral holes per unit cell, the fraction of holes occupied by Mg^{2+} ions is 1/8.

Therefore, the choice (a) is correct.

19. (p) Siderite is $FeCO_3$

(q) Malachite is $CuCO_3.Cu(OH)_2$

(r) Bauxite is $Al_2O_3.2H_2O$

(s) Calamine is $ZnCO_3$

(t) Argentite is Ag_2S

Thus, matchings go as follows:

(a) → (p), (q), (s); (b) → (t); (c) → (q), (r); (d) → (r)

20. (a)Freezing of water of 273 K and 1 atm is accompanied with decrease in entropy (i.e. $\Delta S_{sys} < 0$) and $\Delta G = 0$ (as the process is at equilibrium.)

(b)Expansion of an ideal gas against vacuum is accompanied with $q = 0$, $w = 0$, and $\Delta U = 0$

(c)Mixing of ideal gases is accompained with $q = 0$, $\Delta U = 0$ and $w = 0$.

(d)Reversible heating of a gas followed by cooling to the *same state* is accompained with $q = 0$, $w = 0$, $\Delta U = 0$ and $\Delta G = 0$

Hence, the matching goes as follows:

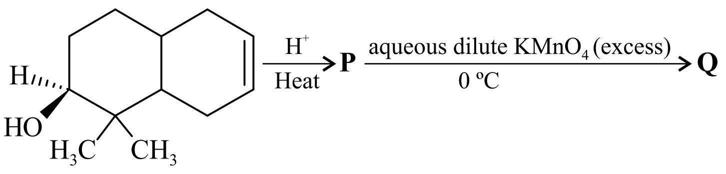
(a) → (r), (t); (b) → (p), (q), (s); (c) → (p), (q), (s); (d) → (p), (q), (s), (t)\

JEE ADVANCED 2015: PAPER–II
(MODEL SOLUTIONS)

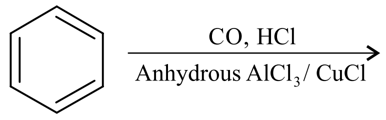
SECTION I
(Single Digit Integer Type)

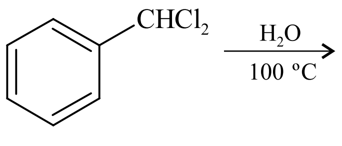
This section contains **EIGHT** questions.
This answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive

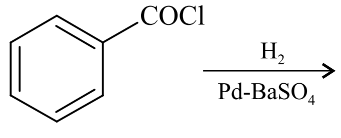
1. The number of hydroxyl group(s) in **Q** is

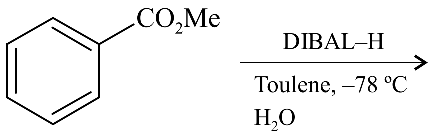


2. Among the following, the number of reaction(s) that produce(s) benzaldehyde is

I.


II.


III.


IV.


3. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is ________.

4. Among the complex ions, $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2CH_2CH_2NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is ________.

5. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing products formed is __________.

6. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^{\infty}_{X^-} \approx \lambda^{\infty}_{Y^-}$, the difference in their pK_a values, pK_a (HX) – pK_a (HY), is ________ . (Consider degree of ionization of both acids to be << 1)

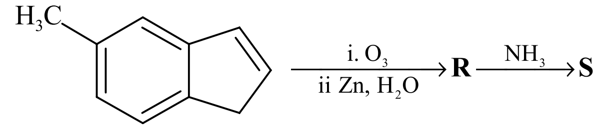
7. A closed vessel with rigid walls contains 1 mol of $^{238}_{92}U$ and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}U$ to $^{206}_{82}Pb$, the ratio of the final pressure to the initial pressure of the system at 298 K is _______ .

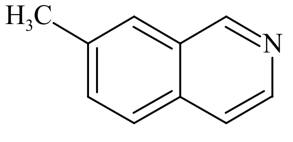
8. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is _______.

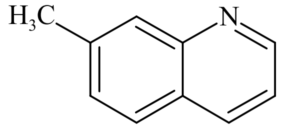
SECTION II
(One or More than One Options Correct Type)

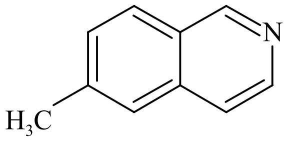
This section contains **EIGHT** questions
Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options(s) is (are) correct

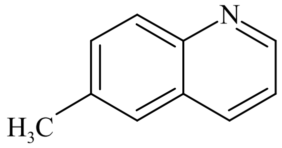
9. In the following reactions, the product **S** is



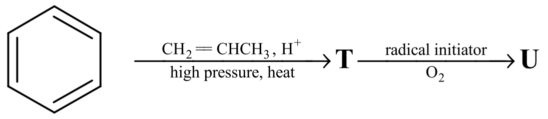
(a)


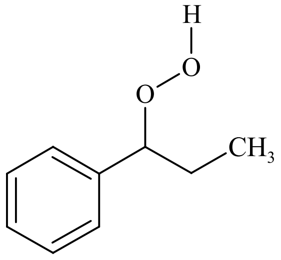
(b)


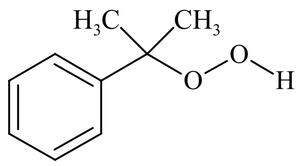
(c)


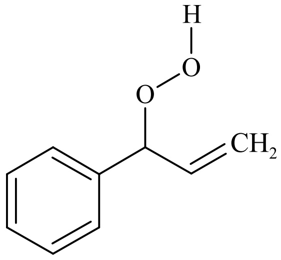
(d)


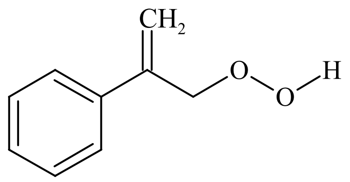
10. The major product **U** in the following reactions is



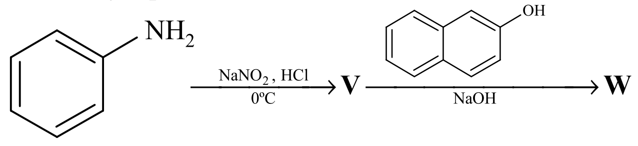
(a)


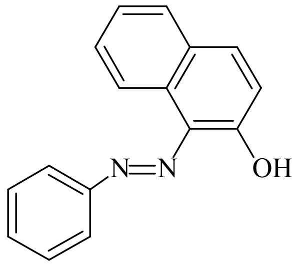
(b)


(c)


(d)


11. In the following reactions, the major product **W** is



(a)


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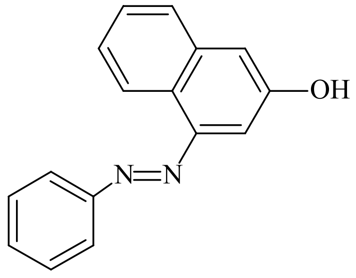
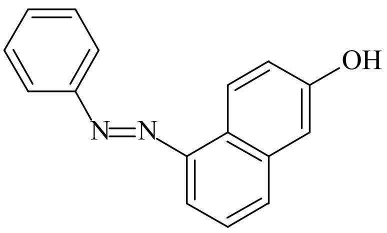
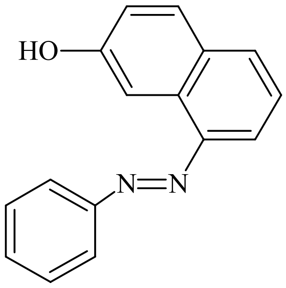


(c)


(d)


12. The correct statement(s) regarding, (i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is (are)

(a) The number of Cl=O bonds in (ii) and (iii) together is two

(b) The number of lone pairs of electrons in Cl in (ii) and (iii) together is three

(c) The hybridization of Cl in (iv) is sp^3

(d) Amongst (i) to (iv), the strongest acid is (i)

13. The pair(s) of ions where **BOTH** the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are)

(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+} (c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

14. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are

(a) CH_3SiCl_3 and $Si(CH_3)_4$ (b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

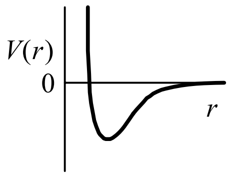
(c) $(CH_3)_2SiCl_2$ and CH_3SiCl_3 (d) $SiCl_4$ and $(CH_3)_3SiCl$

15. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The **TRUE** statement(s) regarding this adsorption is(are)

(a) O_2 is physisorbed (b) Heat is released

(c) Occupancy of π^*2p of O_2 is increased (d) Bond length of O_2 is increased

16. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by

(a)


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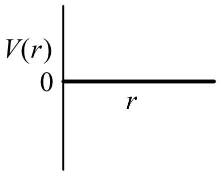

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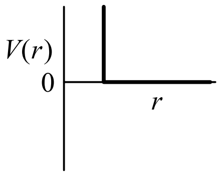

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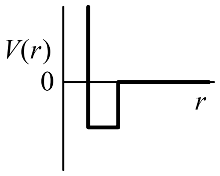


SECTION III

This section contains **TWO** Paragraphs

Based on each paragraph, there will be **TWO** questions

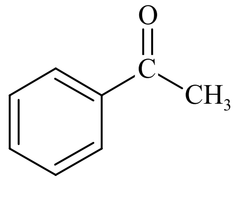
Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is(are) correct

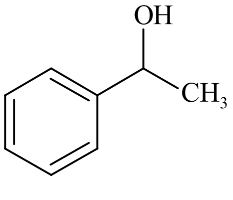
Passage-1

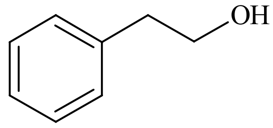
In the following reactions

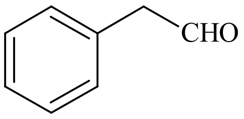
$$\begin{tikzcd}
C_8H_6 \arrow[r, "Pd{-}BaSO_4", "H_2"'] \arrow[d, "H_2O \\ HgSO_4,\ H_2SO_4"] & C_8H_8 \arrow[r, "i.\ B_2H_6", "ii.\ H_2O_2,\ NaOH, H_2O"'] & X \\
C_8H_8O \arrow[r, "i.\ EtMgBr,\ H_2O", "ii.\ H^+,\ heat"'] & Y &
\end{tikzcd}$$

17. Compound **X** is

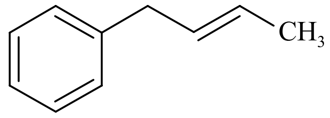
(a) 

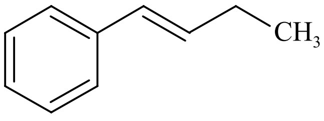
(b) 

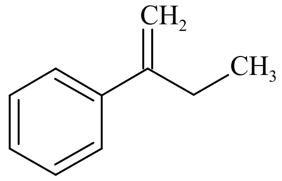
(c) 

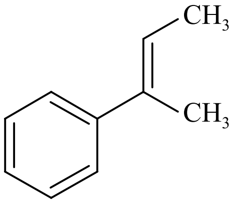
(d) 

18. The major compound **Y** is

(a) 

(b) 

(c) 

(d) 

Passage-2

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents **(Expt. 1).** Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant.

In a second experiment **(Expt. 2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1)** where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

19. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is

(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4

20. The pH of the solution after **Expt. 2** is

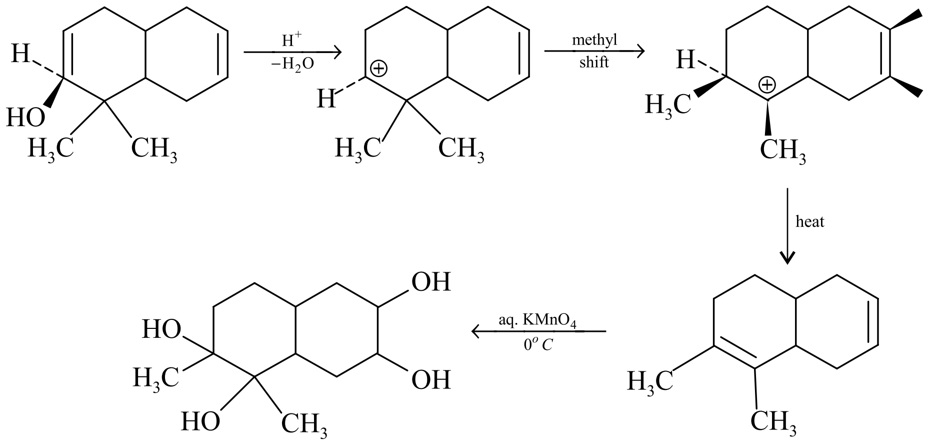
(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

ANSWERS

1.	(4)	**2.**	(4)	**3.**	(3)	**4.**	(6)	**5.**	(6)
6.	(3)	**7.**	(9)	**8.**	(8)	**9.**	(a)	**10.**	(b)
11.	(a)	**12.**	(b), (c)	**13.**	(c), (d)	**14.**	(b)	**15.**	(b), (c), (d)
16.	(c)	**17.**	(c)	**18.**	(d)	**19.**	(a)	**20.**	(b)

Solutions

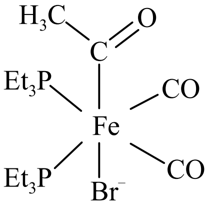
1.



There are **4** hydroxyl groups.

2. In all the **four** reactions, benzaldehyde is produced.

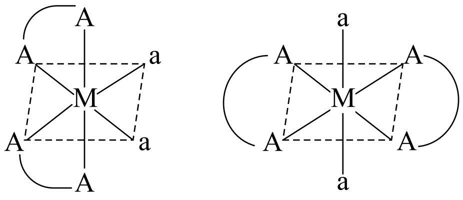
3. The given complex is



The number of Fe—C bonds is **three.**

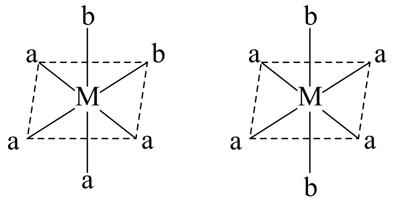
4.

Complex	Type	*cis-trans* Isomerism
$[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$	$M(A–A)_2a_2$	Yes
$[CrCl_2(C_2O_4)_2]^{3-}$	$M(A–A)_2a_2$	Yes
$[Fe(H_2O)_4(OH)_2]^+$	Ma_4b_2	Yes
$[Fe(NH_3)_2(CN)_4]^-$	Ma_4b_2	Yes
$[Co(NH_2CH_2CH_2NH_2)_2[NH_3]Cl]^{2+}$	$M(A–A)_2ab$	Yes
$[Co(NH_3)_4(H_2O)Cl]^{2+}$	Ma_4bc	Yes



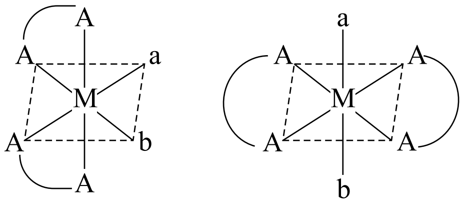
cis- *trans-*

$M(A–A)_2a_2$



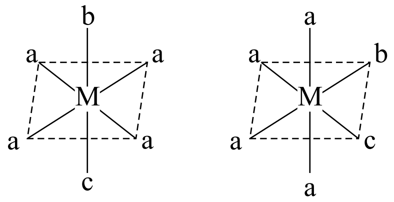
cis- *trans-*

Ma_4b_2



cis- *trans-*

$M(A–A)_2ab_2$



cis- *trans-*

Ma_4bc

The number of complex ions is **6.**

5. The reaction of B_2H_6 with methanol is

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

One mole of B_2H_6 gives two moles of $B(OCH_3)_3$. Hence, three moles of B_2H_6 will give **6** mol of $B(OCH_3)_3$. The answer is **6.**

6. For a weak acid HA, we have

$$\underset{c(1-\alpha)}{\text{HA}} \rightleftharpoons \underset{c\alpha}{\text{H}^+} + \underset{c\alpha}{\text{A}^-}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[c\alpha]\,[c\alpha]}{c(1-\alpha)} \simeq c\alpha^2 \qquad \text{(Since } \alpha \ll 1\text{)}$$

Also, $\alpha = \Lambda_{\text{HA}} / \Lambda^{\infty}_{\text{HA}} = \Lambda_{\text{HA}} / \left(\lambda^{\infty}_{\text{H}^+} + \lambda^{\infty}_{\text{A}^-}\right)$

Hence, $K_{\text{a}} = c\ \Lambda^2_{\text{HA}} / \left(\lambda^{\infty}_{\text{H}^+} + \lambda^{\infty}_{\text{A}^-}\right)^2$

Since $\lambda^{\infty}_{\text{X}^-} \simeq \lambda^{\infty}_{\text{Y}^-}$, for the given two acids, we have

$$\frac{K_{\text{a}}(\text{HX})}{K_{\text{a}}(\text{HY})} = \frac{c_{\text{HX}}}{c_{\text{HY}}}\left(\frac{\Lambda_{\text{HX}}}{\Lambda_{\text{HY}}}\right)^2 = \left(\frac{0.01\text{M}}{0.1\text{ M}}\right)\left(\frac{1}{10}\right)^2 = 10^{-3}$$

Hence $\text{p}K_{\text{a}}(\text{HX}) - \text{p}K_{\text{a}}(\text{HY}) = 3$

7. Since mass number in a radioactive decay changes due to emission of α-particles (i.e. He^{2+}), the amount of α-particles emitted when ^{238}U changes to ^{206}Pb, is

$$n_\alpha = \frac{238-206}{4} = 8$$

The total amount of gases at the final stage will be 9 (=8 mol He + 1 mol air). Thus,

$$\frac{p_{\text{final}}}{p_{\text{initial}}} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{9\text{ mol}}{1\text{ mol}} = 9$$

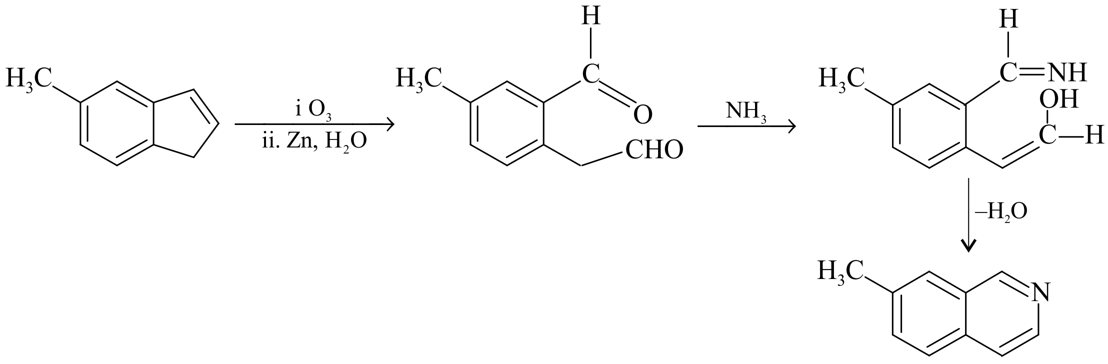
8. The changes in $[\text{H}^+]$ and $[\text{MnO}_4^-]$ are due to the reaction.

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$

Hence,

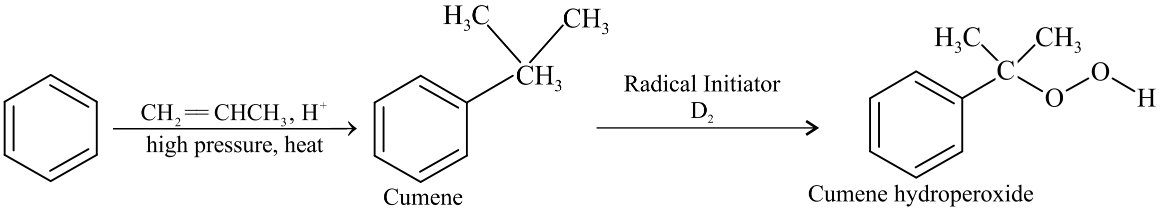
$$\frac{\text{Rate of change of }[\text{H}^+]}{\text{Rate of change of }[\text{MnO}_4^-]} = 8$$

9.

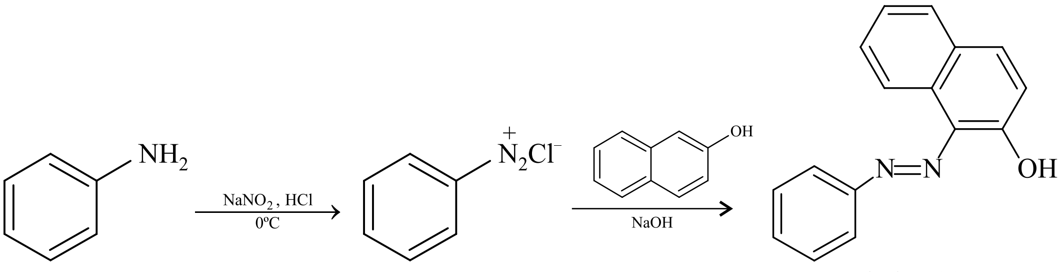


Choice (a)

10.



11. The reaction is

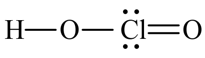


Choice (a)

12.

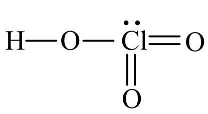
$H-O-Cl$

(i)



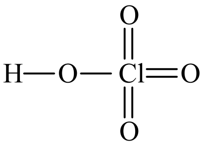
$H-O-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}=O$

(ii)



$H-O-\underset{\underset{O}{\|}}{\overset{\cdot\cdot}{Cl}}=O$

(iii)



$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cl}}=O$

(iv)

sp^3 hybrid orbitals of Cl are involved in the bonding with oxygen atoms. Larger the number of oxygen atoms attached to Cl, stronger the acid. From the structures, it is obvious that the choice (b) and (c) are correct.

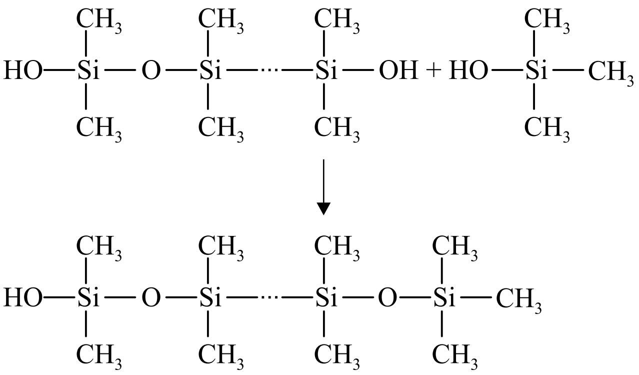
13. Cu^{2+} and Pb^{2+} (Choice c) and also Hg^{2+} and Bi^{3+} belong to the same group of salt analysis. These are precipitated as sulphides when H_2S is passed in acidic medium.

14. Linear polymer is produced from $(CH_3)_2SiCl_2$

$$(CH_3)_2SiCl_2 + H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$n(CH_3)_2\,Si(OH)_2 \xrightarrow[-H_2O]{} (O - Si(CH_3)_2—O)_n$$

The chain termination is brought about by the use of $(CH_3)_3SiCl$



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-\cdots-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

$$\downarrow$$

$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-\cdots-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

15. O_2 is **not** physisorbed as electron is transferred from the metal to O_2. During adsorption, heat is released due to the interaction beween the adsorbent and adsorbate (Choice b)

The electronic configuration of O_2 is

KK $(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)\,(\pi^* 2p_y)$

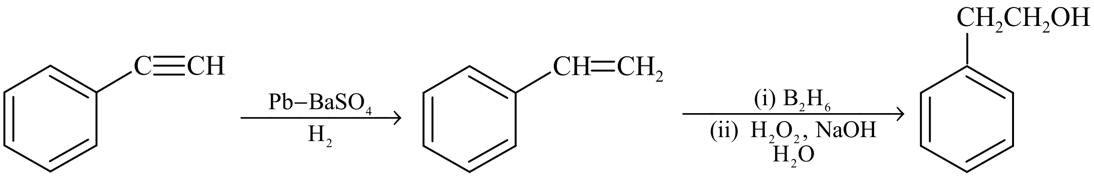
The electron transfer from the metal to O_2 enters π^*2p orbital (Choice c)

The bond length of O_2 is increased due to decrease in bond order from 2 to 1.5 (Choice d)

16. From the given equation of state, it follows that there exists no interatomic attractions. Thus, the potential energy remains zero till the two atoms touch each other, thereafter the potential energy will increase steeply as the distance between the two atoms cannot be decreased further.

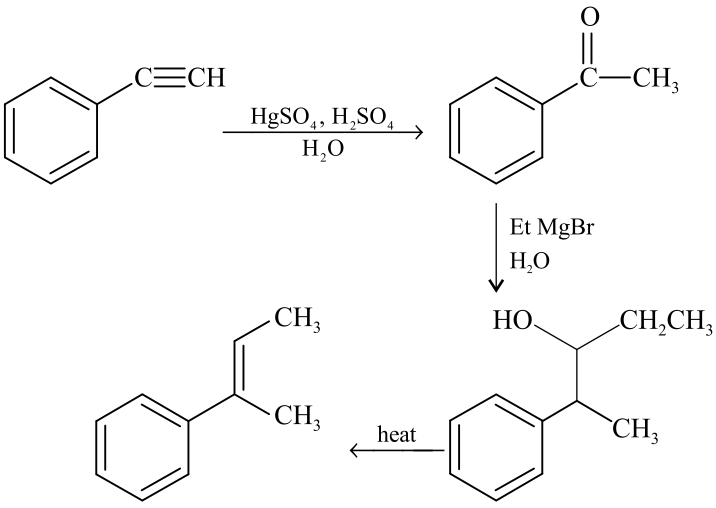
Passage-1

17.



The first step is partial hydrogenation and the second step is hydroboration–oxidation process where H_2O is added to double bond in accordance with anti-Markovnikov's rule.

18.



(d)

Passage-2

19. The calorimeter constant will be

$$C = \frac{\text{Ä}_{\text{new}}H}{\text{Ä}T} = \frac{57.6 \text{ kJ mol}^{-1}}{5.7 \text{K}} \simeq 10 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

The enthalpy of dissociation of acetic acid will be

$$\text{Ä}_{\text{dis}}H = C(5.7\text{K} - 5.6\text{K}) = (10 \text{ kJ K}^{-1} \text{ mol}^{-1})\ (0.1 \text{ K}) = 1 \text{ kJ mol}^{-1}$$

20. After Expt 2, the solution (after taking into account the dilution) will contain 0.5 M each in acetic acid and sodium acetate. Its pH will be

$$\text{pH} \quad = \text{p}K_\text{a} + \log \left\{\frac{[\text{salt}]}{[\text{Acid}]}\right\} = -\log (2.0 \times 10^{-5}) + \log \left(\frac{0.5\text{M}}{0.5\text{M}}\right) = 4.7$$

JEE ADVANCED 2016: PAPER-I
(MODEL SOLUTIONS)

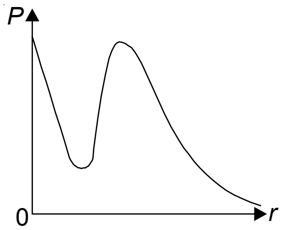
SECTION I
(Single Correct Answer Type)

This section contains **FIVE** questions.

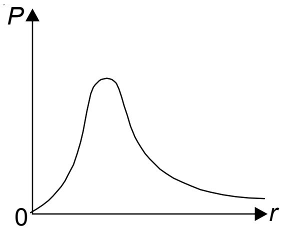
Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is correct.

1. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is

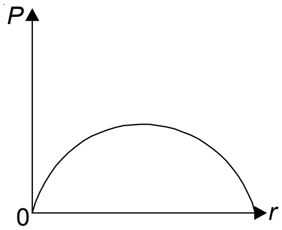
(a)



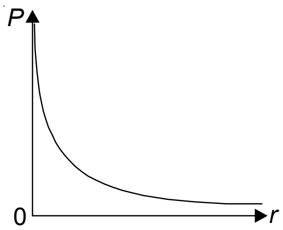
(b)



(c)



(d)



2. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings $(\Delta_{\text{surr}} S)$ in J K^{-1} is (1 L atm = 101.3 J)

(a) 5.763 (b) 1.013 (c) –1.013 (d) –5.763

3. The increasing order of atomic radii of the following Group-13 elements is

(a) Al < Ga < In < Tl
(b) Ga < Al < In < Tl
(c) Al < In < Ga < Tl
(d) Al < Ga < Tl < In

4. On complete hydrogenation, natural rubber produces

(a) ethylene – propylene copolymer
(b) vulcanised rubber
(c) polypropylene
(d) polybutylene

5. Among $[\text{Ni(CO)}_4]$, $[\text{NiCl}_4]^{2-}$, $[\text{Co(NH}_3)_4\text{Cl}_2]\text{Cl}$, $\text{Na}_3[\text{CoF}_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is

(a) 2 (b) 3 (c) 4 (d) 5

SECTION II
(One or More than One Options Correct Type)

This section contains **EIGHT** questions.

Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct.

6. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upward deviation from linearity for atomic number, $Z > 20$. For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are)

(a) β^- decay (β emission)

(b) orbital or K–electron capture

(c) Neutron emission

(d) β^+ decay (positron emission)

7. The correct statement(s) about the following reaction sequence is(are)–

$$\text{Cumene } (C_9H_{12}) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2} P \xrightarrow{CHCl_3/NaOH} Q \text{ (major)} + R\text{(minor)}$$

$$Q \xrightarrow[PhCH_2Br]{NaOH} S$$

(a) R is steam volatile

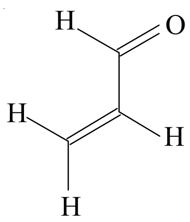
(b) Q gives dark violet coloration with 1% aqueous $FeCl_3$ solution.

(c) S gives yellow precipitate with 2, 4–dinitrophenylhydrazine.

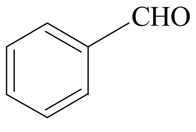
(d) S gives dark violet coloration with 1% aqueous $FeCl_3$ solution.

8. Positive Tollens test is observed for

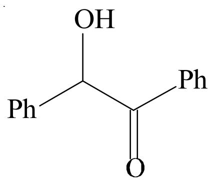
(a)



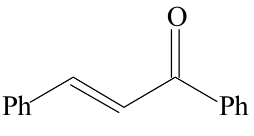
(b)



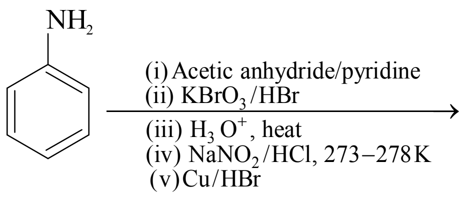
(c)



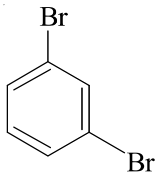
(d)



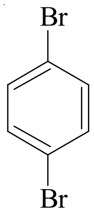
9. The product(s) of the following reaction sequence is(are)



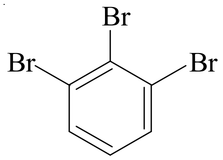
(a)



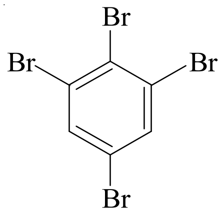
(b)



(c)



(d)



10. The compounds with **TWO** lone pairs of electrons on the central atom is(are)

(a) BrF_5 (b) ClF_3 (c) XeF_4 (d) SF_4

11. The crystalline form of borax has

(a) Tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit

(b) All boron atoms in the same plane

(c) Equal number of sp^2 and sp^3 hybridized boron atoms

(d) One terminal hydroxide per boron atom

12. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is(are)

(a) $CuCl_2$ (b) $BaCl_2$ (c) $Pb(OOCCH_3)_2$ (d) $Na_2[Fe(CN)_5NO]$

13. According to Arrhenius equation,

(a) A high activation energy usually implies a fast reaction.

(b) Rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.

(c) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.

(d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energies.

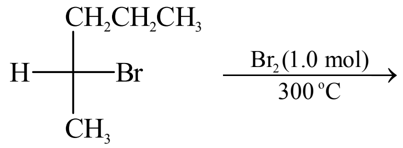
SECTION II
(Single Digit Integer Type)

This section contains **FIVE** questions.

This answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive

14. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3}. The ratio of the molecular weights of the solute and solvent, $(M_{\text{solute}} / M_{\text{solvent}})$, is ___________ .

15. In the following monobromination reaction, the number of possible chiral products is ________ .



(1.0 mol)
(enantiomerically pure)

16. The diffusion coefficient of an ideal gas is proportional to mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ________ .

17. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$, where L= $H_2NCH_2CH_2O^-$), is ________ .

18. The neutral or faintly alkaline solution, 8 mol of permanaganate anions quantitatively oxidize thiosulphate anions to produce X mol of sulphur containing product. The magnitude of X is ________ .

ANSWERS

1. (b)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (b)
6. (b), (d)	**7.** (b), (c)	**8.** (a), (b), (c)	**9.** (b)	**10.** (b), (c)
11. (a), (c), (d)	**12.** (a)	**13.** (b), (c), (d)	**14.** 9	**15.** 5
16. 4	**17.** 5	**18.** 6		

Solutions

1. The r-dependent part of the wave function of 1s orbital of hydrogen atom is

$$R_{1,0} = 2\left(\frac{1}{a_0}\right)^{3/2} \mathrm{e}^{-r/a_0}$$

where a_0 is the Bohr radius (= 52.9 pm). The probability of finding the 1s electron in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus is

$$P = 4\pi r^2 R_{1,0}^2 \mathrm{d}r = 4\pi r^2 \left[4\left(\frac{1}{a_0}\right)^3 \mathrm{e}^{-2r/a_0}\right]\mathrm{d}r$$

For shorter distances, the variation of r^2 is larger than that of e^{-2r/a_0}, with the result that P increases with increase in the value of r. For larger distance, the reverse is true, consequently, P decreases exponentially with increase in the value of r. These characteristics are displayed in the Choice (b).

2. From the first law of thermodynamics, we have $\Delta U = q + w$

Since temperature of the ideal gas remains constant, $\Delta U = 0$. Hence

$$\begin{aligned} q &= -w = -(-p_{\text{ext}}\Delta V) = p_{\text{ext}}\Delta V \\ &= 3.0 \text{ atm } (2.0 \text{ L} - 1.0 \text{ L}) \\ &= 3.0 \text{ atm L} \equiv 3.0 \times 101.3 \text{ J} \\ &= 303.9 \text{ J} \end{aligned}$$

Now $$q_{\text{surr}} = -q = -303.9 \text{ J}$$

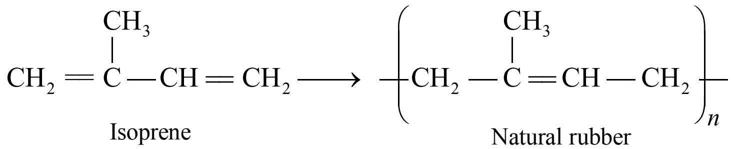
$$\Delta_{\text{surr}} S = \frac{q_{\text{surr}}}{T} = \frac{-303.9\,\text{J}}{300\,\text{K}} = -1.013 \text{ J K}^{-1}$$

3. The descending order of elements is $_{13}$Al, $_{31}$Ga, $_{49}$In, $_{81}$Tl

In general, the radius of atom increases on descending a group. This is due to outmost shell of higher principal quantum number. However, due to the poor shielding of nucleus by 3d electrons, the size of Ga is smaller than that of Al.

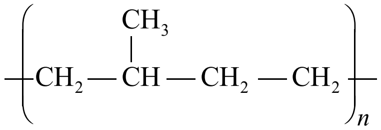
The size of Tl is a little larger than In due to lanthanide contraction.

4. The natural rubber results from the polymerization of isoprene:



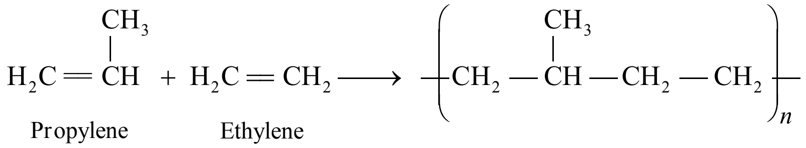
$$\underset{\text{Isoprene}}{\mathrm{CH_2{=}C(CH_3){-}CH{=}CH_2}} \longrightarrow \underset{\text{Natural rubber}}{\left(\mathrm{{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}}\right)_n}$$

The complete hydrogenation of natural rubber gives



$$\left(-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-\right)_n$$

This may be obtained by the copolymerization of ethylene and propylene:

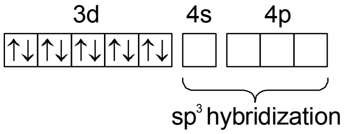


$$H_2C=\overset{\displaystyle CH_3}{\overset{|}{CH}}+H_2C=CH_2\longrightarrow\left(-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-\right)_n$$

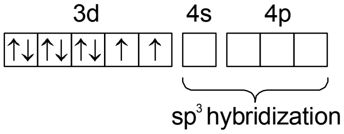
Propylene Ethylene

5. We have the following facts.

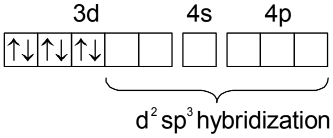
$_{28}$Ni($3d^8 4s^2$) Ni in $Ni(CO)_4$

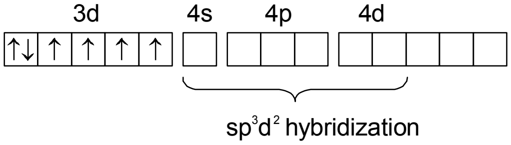


Ni in $[NiCl_4]^{2-}$



$_{27}$Co($3d^7 4s^2$) Co in $[Co(NH_3)_4Cl_2]Cl$





Co in $[CoF_6]^{3-}$

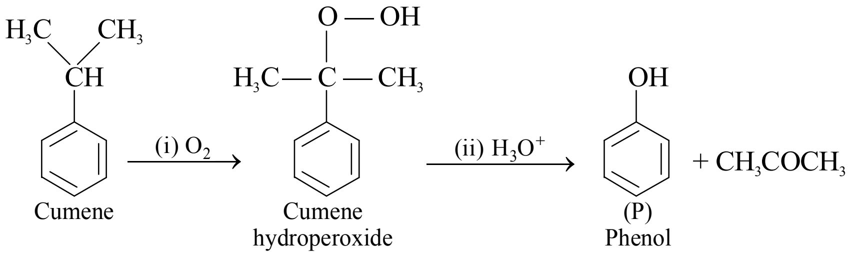
O_2^{2-} in Na_2O_2 $KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^2$

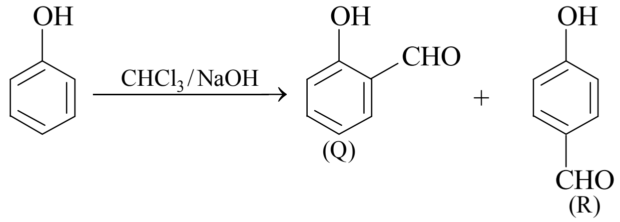
O_2^{-} in CsO_2 $KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^1$

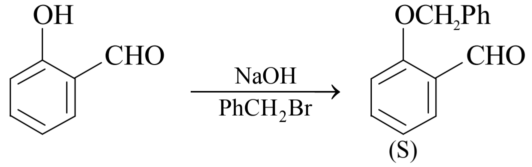
The species $[NiCl_4]^{2-}$, $Na_3[CoF_6]$ and CsO_2 have unpaired electrons and thus are paramagnetic.

6. To attain stability, the ratio N/P has to be increased. From the given choices, the Choice b (K-electron capture) and the Choice d (positron emission) will decrease the number of protons and hence increase in the ratio N/P.

7. The given reactions are as follows:





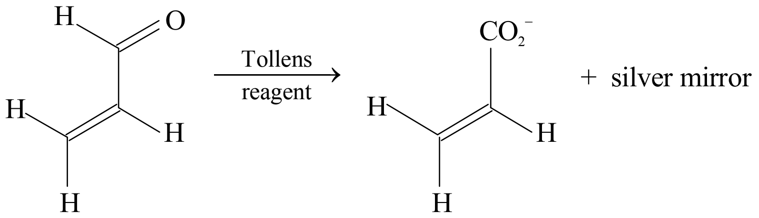


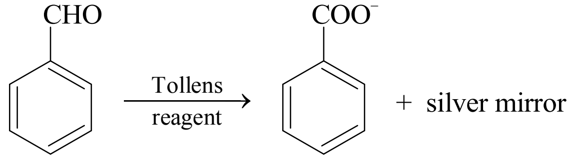
Q is steam volatile as it involves intramolecular hydrogen bonding. R is *not* steam volatile as it involves intermolecular hydrogen bonding.

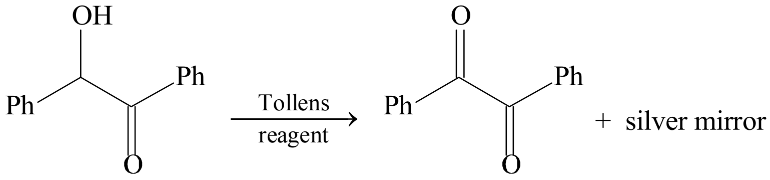
Q gives dark violet coloration with 1% aqueous $FeCl_3$ soluton due to phenolic group.

S gives yellow precipitate with 2, 4-dinitrophenylhydrazine due to —CHO group. It will not give dark violet coloration with 1% aqueous $FeCl_3$ solution as there is no free phenolic group.

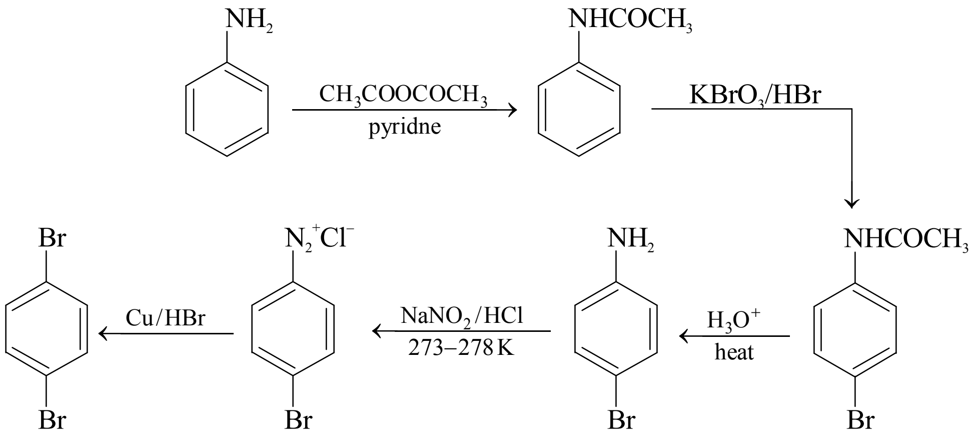
8. The Tollens reagent is an ammoniacal solution of silver nitrate. Aldehydes (Choices a and b) reduce Tollens reagent to a bright silver mirror. Also, α-hydroxy carbonyl compound (Choice c) is oxidised by Tollens reagent. The reactions are:



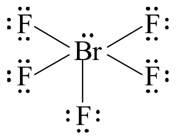
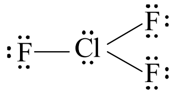
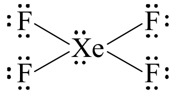
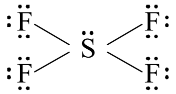




9. The given reactions are: (i) acetylation of —NH_2, (ii) monobromination due to liberated bromine ($BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$), (iii) deactylation of —NH_2, (iv) diazotisation of —NH_2 and (v) its replacement with Br.

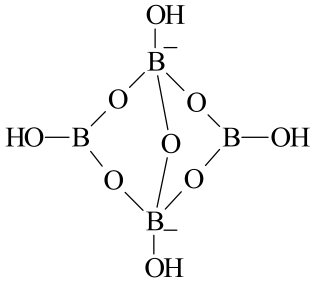


10.

Molecule	**Valence electrons**	**Lewis structure**
BrF_5	$7 + 5 \times 7 = 42$	
ClF_3	$7 + 3 \times 7 = 28$	
XeF_4	$8 + 4 \times 7 = 36$	
SF_4	$6 + 4 \times 7 = 34$	

The molecule ClF_3 (Choice b) and XeF_4 (Choice c) have two lone pairs of electrons on the central atom.

11. The borax is $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$. The structure of $[B_4O_5(OH)_4]^{2-}$ is



This structure has a tetranuclear (boron) unit. Two boron atoms are sp^2 hydridized while the other two are sp^3 hybridized. There is one terminal hydroxide per boron atom. The entire unit is **not** planar due to sp^3 hybride orbitals.

12. We have the following facts.

$$\begin{aligned}
\text{CuCl}_2 + \text{S}^{2-} &\longrightarrow \text{CuS}\downarrow + 2\text{Cl}^- \\
\text{CuCl}_2 + \text{SO}_4^{2-} &\longrightarrow \text{No precipitation} \\
\text{BaCl}_2 + \text{S}^{2-} &\longrightarrow \text{No precipitation} \\
\text{BaCl}_2 + \text{SO}_4^{2-} &\longrightarrow \text{BaSO}_4\downarrow + 2\text{Cl}^- \\
\text{Pb(OOCCH}_3)_2 + \text{S}^{2-} &\longrightarrow \text{PbS}\downarrow\ + 2\text{CH}_3\text{COO}^- \\
\text{Pb(OOCCH}_3)_2 + \text{SO}_4^{2-} &\longrightarrow \text{PbSO}_4\downarrow\ + 2\text{CH}_3\text{COO}^- \\
\text{Na}_2[\text{Fe(CN)}_5\text{NO}] + \text{S}^{2-} &\longrightarrow \text{Purpule colour due to } [\text{Fe(CN)}_5\text{NOS}]^{4-} \\
\text{Na}_2[\text{Fe(CN)}_5\text{NO}] + \text{SO}_4^{2-} &\longrightarrow \text{No precipitation}
\end{aligned}$$

Only CuCl_2 (Choice a) can cause selective precipitation of S^{2-} ions.

Note: The solubility products of PbS and PbSO_4 are:

$K_{\text{sp}}^{\circ}(\text{PbS}) = 3 \times 10^{-28}$ and $K_{\text{sp}}^{\circ}(\text{PbSO}_4) = 2.53 \times 10^{-8}$. Since $K_{\text{sp}}^{\circ}(\text{PbS}) << K_{\text{sp}}^{\circ}(\text{PbSO}_4)$, S^{2-} ions can be preferentially precipitated out from a solution containing both these ions.

13. The Arrhenius equation is $k = A\text{e}^{-E_\text{a}/RT}$

(a) High activation energy leads to a slower reaction because the rate constant, k has a lower value.

(b) With increase in temperature, the number of molecules having energies more than activation energy is increased.

(c) We have

$$\frac{\text{d}k}{\text{d}T} = A\left(\frac{E_\text{a}}{RT^2}\right)\text{e}^{-E_\text{a}/RT}$$

Since $\text{d}k/\text{d}t \propto E_\text{a}$, there will be large change in the value of k for a larges value of E_a

(d) If all collisions between molecules lead to the reaction, the rate of reaction or the rate constant will have a maximum value. According to the Arrhenius equation, the maximum value of k is A (where $E_\text{a} = 0$). Thus, the pre-exponential factor is a measure of the rate at which collision occur, irrespect of their energies.

14. Let the subscripts 1 and 2 represent solvent and solute, respectively. It is given that

$$x_2 = \frac{n_2}{n_1 + n_2} = 0.1$$

Let $n_2 = 0.1$ mol and thus $n_1 = 0.9$ mol

$$\begin{aligned}
\text{Mass of solute, } m_2 &= n_2 M_2 \\
\text{Mass of solvent, } m_1 &= n_1 M_1
\end{aligned}$$

$$\text{Volume of solution, } V = \frac{m_1 + m_2}{\rho}$$

$$\text{Molarity of solution, } M = \frac{n_2}{V} = \frac{n_2}{(m_1 + m_2)/\rho};\ (V \text{ expressed in dm}^3)$$

$$\text{Molality of solution, } b = \frac{n_2}{m_1};\ (m_1 \text{ expressed in kg})$$

Since the numerical values of molarity and molality are identical, we write

$$\frac{n_2/\text{mol}}{m_1/\text{kg}} = \frac{n_2/\text{mol}}{\{(m_1 + m_2)/\rho\}/\text{dm}^3}$$

This gives $$\frac{m_1}{\text{kg}} = \frac{(m_1 + m_2)}{\rho}\frac{1}{\text{dm}^3}$$

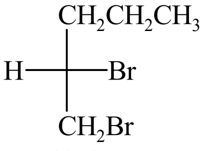
or $$\{(\text{kg}^{-1}\ \text{dm}^3)\ \rho - 1\}\ m_1 = m_2$$

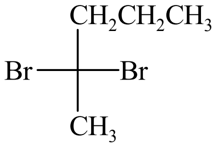
Since 1 $\text{kg}^{-1}\ \text{dm}^3 \equiv 1\ \text{g}^{-1}\ \text{cm}^3$, we have

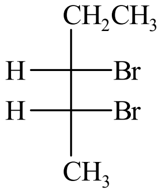
$$\frac{m_2}{m_1} = \{(\text{g}^{-1}\ \text{cm}^3)\ \rho - 1\} = (\text{g}^{-1}\ \text{cm}^3)\ (2\ \text{g cm}^{-3}) - 1 = 1$$

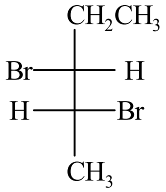
i.e. $$\frac{n_2 M_2}{n_1 M_1} = 1 \quad \text{or} \quad \frac{M_2}{M_1} = \frac{n_1}{n_2} = \frac{0.9\ \text{mol}}{0.1\ \text{mol}} = 9$$

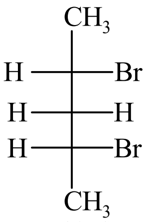
15. The possible products are:

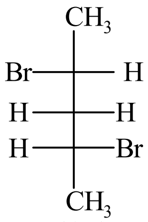

(Chiral) ;

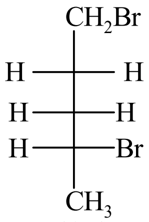

(Achiral) ;


(Chiral) ;


(Chiral) ;


(Achiral) ;


(Chiral) ;


(Chiral) ;

There are 5 chiral products.

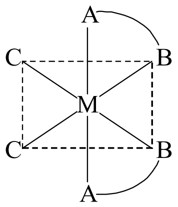
16. It is given that $D \propto \lambda u_{\text{av}}$

Now $$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 (p/kT)} \quad \text{and} \quad u_{\text{av}} = \sqrt{\frac{8kT}{\pi m}}$$

Hence, $$\lambda \propto \frac{T^{3/2}}{p}.$$

Thus, $$\frac{\lambda_2}{\lambda_1} = \frac{(4T)^{3/2}/2p}{T^{3/2}/p} = \frac{4^{3/2}}{2} = \frac{4 \times 2}{2} = 4$$

17. The given complex is of the type $[\text{M(AB)}_2\,\text{C}_2]$. Its possible geometrical isomers are:



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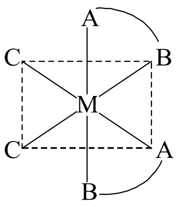

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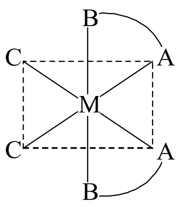

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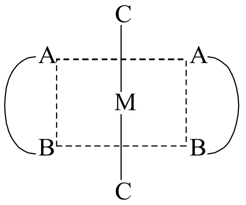

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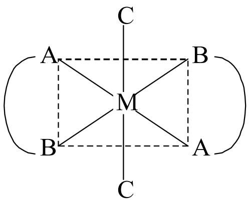
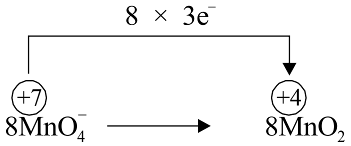
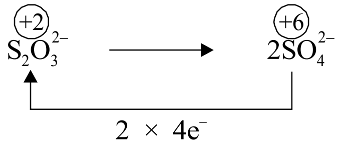


There are 5 geometrical isomers.

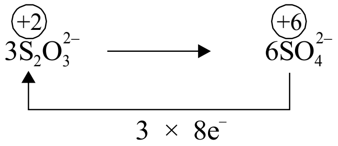
18. The basic reactions are:



and



To make electrons equal, the oxidation reaction of $S_2O_3^{2-}$ will have to multiplied by 3, i.e.



The value of X is 6. The complete reaction is

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 8 \\ S_2O_3^{2-} + 10\,OH^- \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^-] \times 3 \\ \hline 8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^- \\ \hline \end{array}$$

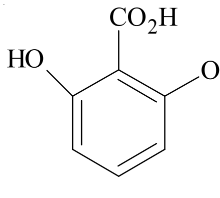
■■

JEE ADVANCED 2016: PAPER-II
(MODEL SOLUTIONS)

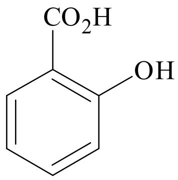
SECTION I
(Single Correct Answer Type)

This section contains **FIVE** questions.
Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is correct.

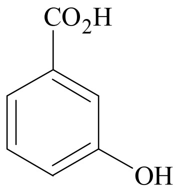
1. The correct order of acidity for the following compounds is



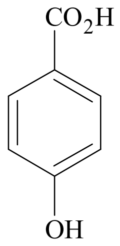
I



II



III



IV

(a) I > II > III > IV (b) III > I > II > IV (c) III > IV > II > I (d) I > III > IV > II

2. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively, are

(a) octahedral, square planar and tetrahedral
(b) square planar, octahedral and tetrahedral
(c) tetrahedral, square planar and octahedral
(d) octahedral, tetrahedral and square planar

3. For the following electrochemical cell at 298 K,

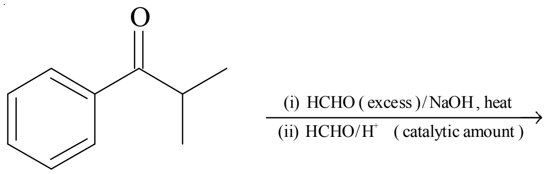
$$\mathrm{Pt(s)\mid H_2(g,\ 1\ bar)\mid H^+\ (aq,\ 1M)\mid\mid M^{4+}(aq),\ M^{2+}(aq)\mid Pt}$$

$$E_{\text{cell}} = 0.092\ \text{V when } \frac{[\mathrm{M^{2+}(aq)}]}{[\mathrm{M^{4+}(aq)}]} = 10^x.$$

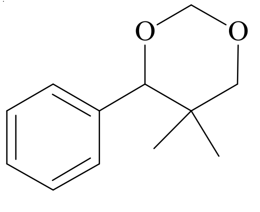
Given : $E^{\circ}_{\mathrm{M^{4+}|M^{2+}}} = 0.151\,\mathrm{V};\ 2.303\,\dfrac{RT}{F} = 0.059\ \mathrm{V}$. The value of x is

(a) –2 (b) –1 (c) 1 (d) 2

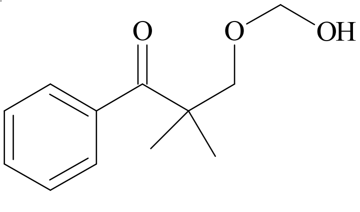
4. The major product of the following reaction sequence is



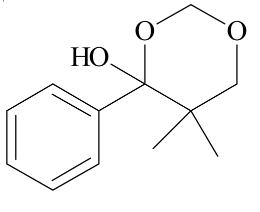
(a)



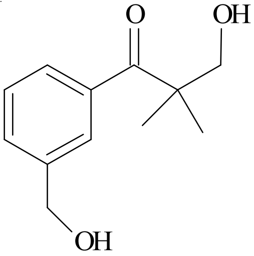
(b)



(c)



(d)



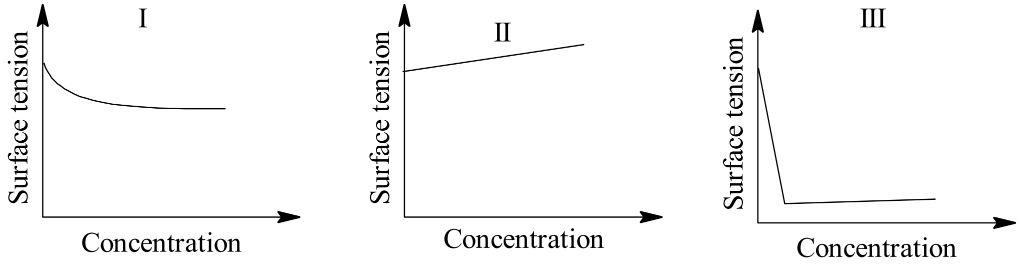
5. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\text{clear solution}}{X} \xrightarrow{Ag^+} \underset{\text{white precipitate}}{Y} \xrightarrow{\text{with time}} \underset{\text{black precipitate}}{Z}$$

(a) $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S (b) $[Ag(S_2O_3)_2]^{3-}$, Ag_2SO_3, Ag_2S

(c) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag (d) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4, Ag

6. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^- Na^+$ at room temperature. The correct assignment of the sketches is



(a) I : KCl II : CH_3OH III : $CH_3(CH_2)_{11}OSO_3^-Na^+$

(b) I : $CH_3(CH_2)_{11}OSO_3^-Na^+$ II : CH_3OH III : KCl

(c) I : KCl II : $CH_3(CH_2)_{11}OSO_3^-Na^+$ III : CH_3OH

SECTION II
(One or More than One Options Correct Type)

This section contains **EIGHT** questions.

Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct.

7. For 'invert sugar', the correct statement(s) is(are):

Given: specific rotations of (+)–sucrose, (+)–maltose, L–(–)–glucose and L–(+)–fructose in aqueous solution are +66°, +140°, –52° and +92°, respectively.

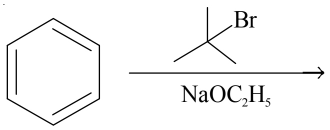
(a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose

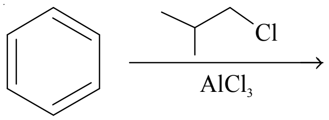
(b) 'invert sugar' is an equimolar mixture of D–(+)–glucose and D–(–)–fructose

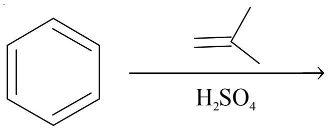
(c) specific rotation of 'invert sugar' is –20°

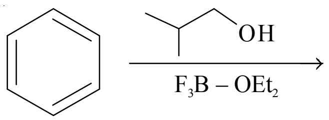
(d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products.

8. Among the following reaction(s) which gives(give) *tert*-butylbenzene as the major product is(are):

(a)


(b)


(c)


(d)


9. Extraction of copper from copper pyrite ($CuFeS_2$) involves

(a) crushing followed by concentration of the ore by froth-flotation

(b) removal of iron as slag

(c) self-reduction step to produce 'blister copper' following evolution of SO_2

(d) refining of 'blister copper' by carbon reduction

10. The **correct** statement(s) for cubic-close packed (ccp) three dimensional structure is(are):

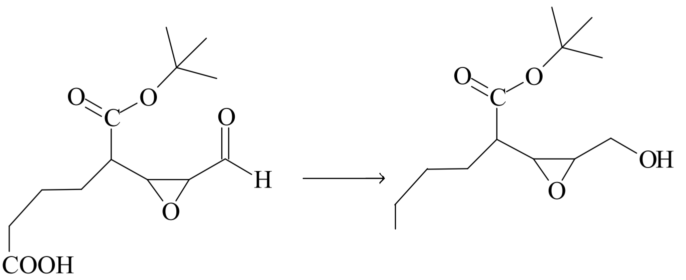
(a) The number of the nearest neighbours of an atom present in the topmost layer is 12.

(b) The efficiency of atom packing is 74%.

(c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively.

(d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom.

11. Reagent(s) which can be used to bring about the following transformation is(are)



(a) $LiAlH_4$ in $(C_2H_5)_2O$

(b) BH_3 in THF

(c) $NaBH_4$ in C_2H_5OH

(d) Raney Ni/H_2 in THF

12. Mixture(s) showing positive deviation from Raoult's law at 35 °C is(are)
(a) carbon tetrachloride + methanol
(b) carbon disulphide + acetone
(c) benzene + toluene
(d) phenol + aniline

13. The nitrogen containing compound produced in the reaction of HNO_3 and P_4O_{10}
(a) can also be prepared by reaction of P_4 and HNO_3
(b) is diamagnetic
(c) contains one N—N bond
(d) reacts with Na metal producing a brown gas.

14. According to molecular orbital theory,
(a) C_2^{2-} is expected to be diamagnetic
(b) O_2^{2+} expected to have a longer bond length than O_2
(c) N_2^+ and N_2^- have the same bond order
(d) He_2^+ has the same energy as two isolated He atoms

SECTION II
(Single Digit Integer Type)

This section contains **FIVE** questions.
This answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive

PARAGRAPH-1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2\,(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^o$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, β_{eq} is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given : $R = 0.083$ L bar K^{-1} mol^{-1}.)

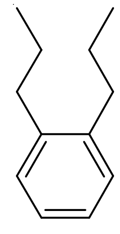
15. The standard equilibrium constant K_p^o for this reaction at 298 K, in terms of β'_{eq} (= β_{eq} / mol), is

(a) $\dfrac{8\beta'^2_{eq}}{2-\beta'_{eq}}$
(b) $\dfrac{8\beta'^2_{eq}}{4-\beta'^2_{eq}}$
(c) $\dfrac{4\beta'^2_{eq}}{2-\beta'_{eq}}$
(d) $\dfrac{4\beta'^2}{4-\beta'^2_{eq}}$

16. The **incorrect** statement among the following, for this reaction, is
(a) Decrease in the total pressure will result in formation of more moles of gaseous X.
(b) At the start of the reaction, dissociation of gaseous X_2, takes place spontaneously.
(c) $\beta_{eq} = 0.7$ mol.
(d) $K_c < 1$.

PARAGRAPH-2

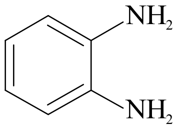
Treatment of compound **O** with $KMnO_4/H^+$ gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with Br_2/NaOH produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl-2-bromopropanoate in the presence of KOH followed by acidification, gave a compound **T**.



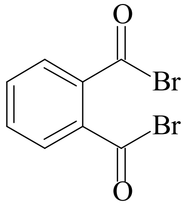
(O)

17. The compound **R** is

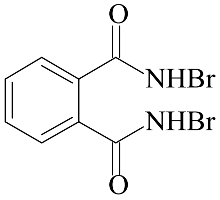
(a)



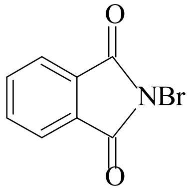
(b)



(c)



(d)



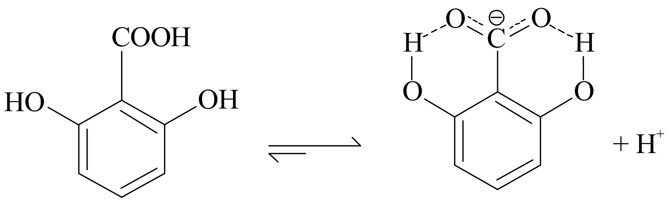
18. The compound **T** is
(a) Glycine (b) Alanine (c) Valine (d) Serine

ANSWERS

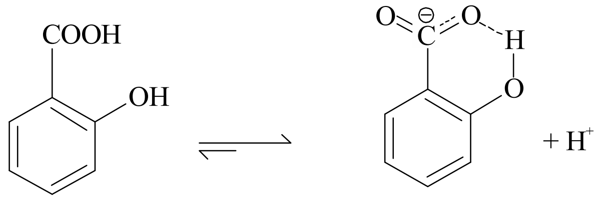
1.	(a)	**2.**	(a)	**3.**	(d)	**4.**	(a)	**5.**	(a)
6.	(d)	**7.**	(b), (c)	**8.**	(b), (c), (d)	**9.**	(a), (b), (c)	**10.**	(b), (c), (d)
11.	(c)	**12.**	(a), (b)	**13.**	(b), (d)	**14.**	(a), (c)	**15.**	(b)
16.	(c)	**17.**	(a)	**18.**	(b)				

Solutions

1. Structure I involves strogest ortho effect due to the chelation of two —OH groups with the —COO$^-$ group. This makes structure I a strongest acid.



Structure II also involves ortho effect due to the chelation of one —OH group with the —COO$^-$ group. This makes structure II a stronger acid as compared to structures III and IV but a weaker acid than the structure I.



Structure III is a stronger acid than structure IV as the latter involves more effective +R effect. The —OH group is electron-donating group which makes ionization of H$^+$ less effective. Therefore, the correct order of acidity is I > II > III > IV (Choice a).

2. The complexes are $[Ni(NH_3)_6]^{2+}$, $[Pt(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$.
The six ammonia in $[Ni(NH_3)_6]^{2+}$ are accommodated in octahedral geometry. Zinc in $[Zn(NH_3)_4]^{2+}$ has $(3d)^{10}$ configuration, and involves sp^3 hybridization to accommodate four ammonia in tetrahedral geometry.
Platinum complexes have square planar geometry.

3. The cell reaction is

Anode $\quad H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Cathode $\quad M^{4+}(aq) + 2e^- \longrightarrow M^{2+}(aq)$

Cell reaction $\quad H_2(g) + M^{4+}(aq) \longrightarrow 2H^+(aq) + M^{2+}(aq)$

The cell potential is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303\,RT}{2F}\log\left\{\frac{[H^+/M]^2}{(p_{H_2}/\text{bar})}\frac{[M^{2+}]}{[M^{4+}]}\right\}$$

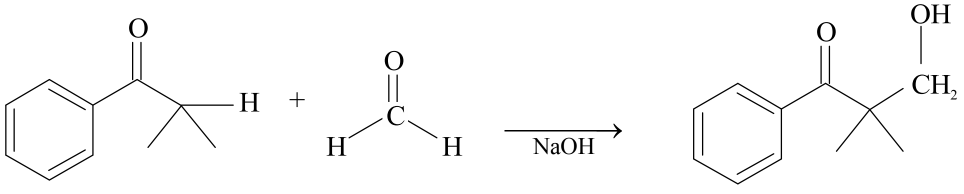
where $\quad E^{\circ}_{\text{cell}} = E^{\circ}_{R} - E^{\circ}_{L} = 0.151\text{ V} - 0\text{ V} = 0.151\text{ V}.$

Substituting the given values in the above expression, we get

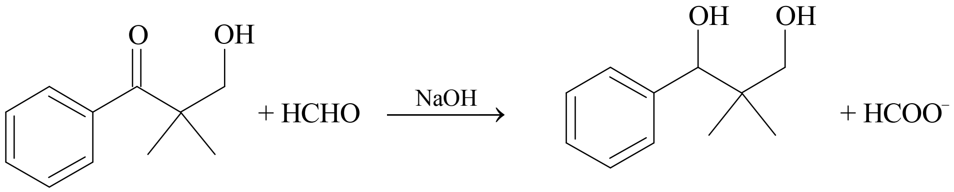
$$0.092\text{ V} = 0.151\text{ V} - \left(\frac{0.059\text{ V}}{2}\right)\log\left\{\frac{(1)^2}{(1)}(10^x)\right\} = 0.151\text{ V} - \left(\frac{0.059\text{ V}}{2}\right)x$$

This gives $\quad x = \dfrac{0.151\text{V} - 0.092\text{V}}{(0.059\text{V}/2)} = 2$

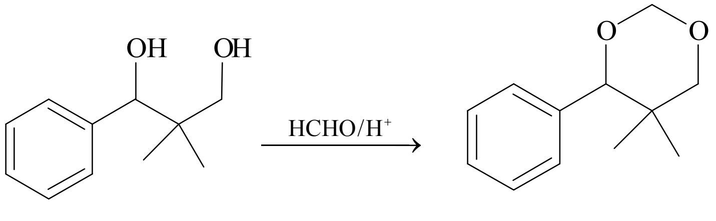
4. The given compound contains α-hydrogen adjacent to CO group. With HCHO/NaOH, it undergoes cross aldol condensation.



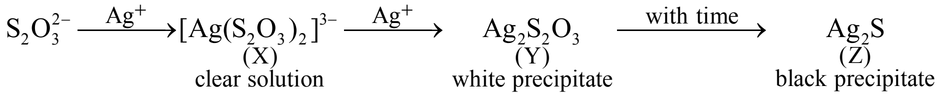
The resultant compound does not contain α-hydrogen. It undergoes cross Cannizzaro reaction with HCHO/NaOH.



The resultant compound forms a cyclic acetal with $HCHO/H^+$ (catalytic amount).



5. The reaction sequence is as follows:



$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\substack{(X)\\ \text{clear solution}}}{[Ag(S_2O_3)_2]^{3-}} \xrightarrow{Ag^+} \underset{\substack{(Y)\\ \text{white precipitate}}}{Ag_2S_2O_3} \xrightarrow{\text{with time}} \underset{\substack{(Z)\\ \text{black precipitate}}}{Ag_2S}$$

6. CH_3OH has more concentration at the surface than in the bulk of aqueous solution. Its effect is to decrease the surface tension as more and more CH_3OH is added (Choice a).

KCl has more concentration in the bulk than at the surface of aqueous solution. Its effect is to increase the surface tension as more and more KCl is added (Choice b).

$CH_3(CH_2)_{11}OSO_3^-Na^+$ is a surface active substance. It is mostly concentrated at the surface with specific orientation (—OSO_3^- group pointing to the surface and $CH_3(CH_2)_{11}$—group pointing away from the surface) and thus causes steep decrease in the surface tension of aqueous solution.

This is continued till the surface is completely covered. Thereafter, the surface tension remains constant.

7. The hydrolysis of sucrose produces 'invert sugar' which is equimolar mixture of D–(+)–glucose and D–(–)–fructose (Choice b).

Specific rotation of D+(+)–glucose = – specific rotation of L–(–)–glucose = 52°

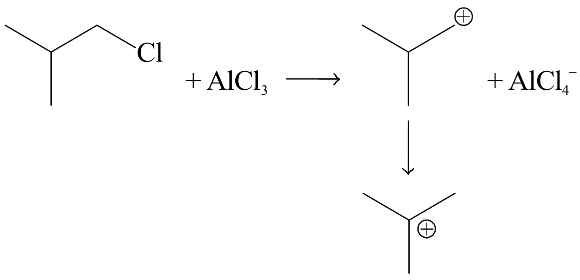
Specific rotation of D–(–)–fructose = – specific rotation of L–(+)–fructose = –92°

Specific rotation of 'invert sugar' is $\dfrac{+52^\circ - 92^\circ}{2} = -20^\circ$ (Choice c)

With Br_2 water, D–glucose forms D–gluconic acid whereas D–fructose shows no reaction.

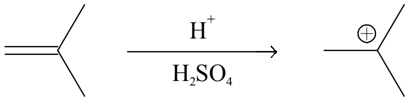
8. Choice (b), (c) and (d) produce *tert*-butyl carbocation which can be substituted in the benzene ring to form *tert*-butylbenzene. This is shown in the following:

Choice (b)

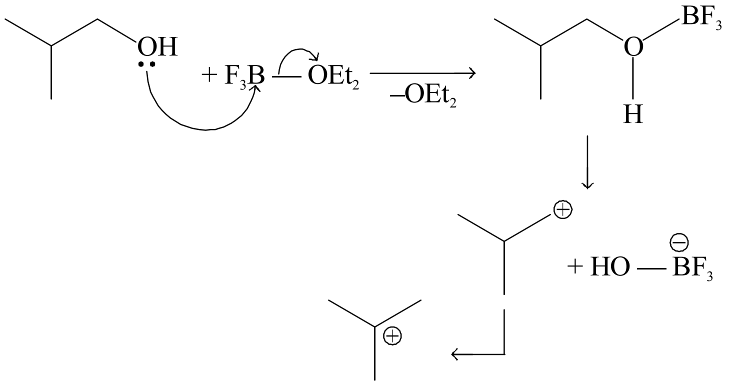


(More stable carbocation)

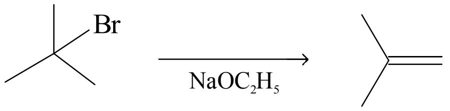
Choice (c)



Choice (d)



Choice a does not produce *tert*-butyl carbocation.



9. The Choice (a), (b) and (c) are correct. The Choice (d) is not correct as the refining is carried out electrolytically.

10. The unit cell of cubic-close packed structure is face-centred cube. In this unit cell, atoms touch each other along the face diagonal (which has a length of $\sqrt{2}a$). If r is the radius of atom, then

$$4r = \sqrt{2}a \quad \text{i.e.} \quad a = \left(\frac{4}{\sqrt{2}}\right)r = \left(2\sqrt{2}\right)r \quad \text{(Choice d)}$$

There are 4 atoms per unit cell. Thus, packing efficiency is

$$\frac{4\left(\frac{4}{3}\pi r^3\right)}{a^3}\times 100 = \frac{4\left(\frac{4}{3}\pi r^3\right)}{\left(2\sqrt{2}r\right)^3}\times 100 = \frac{\pi}{3\sqrt{2}}\times 100 = 74\% \quad \text{(Choice b)}$$

A face-centred cubic unit cell can be divided into 8 smaller cubes of edge length $a/2$. The centre of each smaller cube is the tetrahedral void.

The octahedral void lies at the centre of unit cell and at the mid point of edges. The former belongs exclusively to the unit cell. Each of the octahedral void at the edge is shared by four unit cells. Thus, the total number of ochahedral voids is

$$\underset{\text{(from the centre)}}{1} + \underset{\text{(from the edges)}}{\frac{12\,\text{edges}}{4}} = 4$$

Since there are 4 atoms (one from the corners (= 8 × 1/8 = 1) and three from the centre of faces (= 6 × 1/2 = 3). Hence the number of tetrahedral and octahedral voids per atom will be 2 (= 8/4) and 1 (= 4/4), respectively (Choice c).

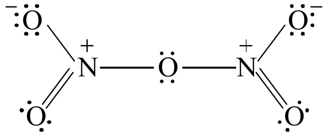
In the top most layer, the coordination of number of atom is 9 (six surrounding the atom and three in the layer just below it). Therefore, the Choice (a) is incorrect.

11. In the given transformation, —CHO group is reduced to —CH_2OH. The reagent in Choice (c), i.e. $NaBH_4$ in C_2H_5OH, can be used for this purpose.

12. If the interaction A ··· B are weaker than those existing in A ··· A and B ··· B, the system displays positive deviation from Raoult's law. The Choices (a) and (b) are the examples. The Choice (c) exhibits ideal behaviour and the Choice (d) exhibits negative deviation.

13. P_4O_{10} is a strong dehydrating agent. It converts HNO_3 into the corresponding anhydride (N_2O_5). The reaction is $P_4O_{10} + 4HNO_3 \longrightarrow 4HPO_3 + 2N_2O_5$

The structure of N_2O_5 is



There is no unpaired electron, and, hence it is diamagnetic (Choice b)

N_2O_5 on reacting with Na produces brown gas NO_2 (Choice d)

$$N_2O_5 + Na \longrightarrow NaNO_3 + \underset{\text{(brown gas)}}{NO_2\uparrow}$$

The reaction of P_4 with HNO_3 produces NO_2.

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

14. The electronic configuration of C_2^{2-} (valence electron = 10), O_2 (valence electrons = 12), N_2^+ (valence electron = 9), N_2^- (valence electrons = 11) and He_2^+ (valence electrons = 3) are as follows:

C_2^{2-} $(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2$

O_2 $(\sigma 2s)^2\,(\sigma^* 2p)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^1\,(\pi^* 2p_y)^1$

N_2^+ $(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^1$

N_2^- $(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2\,(\pi^* 2p_x)^1$

He_2^+ $(\sigma 1s)^2\,(\sigma^* 1s)^1$

C_2^{2-} does not have unpaired electrons. It is diamagnetic (Choice a).

By definition,

$$\text{Bond order} = \frac{\text{(bonding – antibonding) electrons}}{2}$$

$$\text{Bond order of } O_2 = \frac{6-2}{2} = 2 \qquad \text{and} \qquad \text{Bond order of } O_2^{2+} = \frac{6-0}{2} = 3$$

Since bond length is inversely proportional to bond order, bond length of O_2^{2+} is expected to be smaller than O_2.

$$\text{Bond order of } N_2^+ = \frac{5-0}{2} = 2.5 \qquad \text{and} \qquad \text{Bond order of } N_2^- = \frac{6-1}{2} = 2.5$$

He_2^+ will have smaller energy than the two isolated He atom as there is a net one electron in bonding orbital.

15. We have $\underset{1\text{ mol} - \beta_{eq}/2}{X_2(g)} \rightleftharpoons \underset{\beta_{eq}}{2X(g)}$

Total amount of gases = $1 + \beta_{eq}/2$

$$\text{Partial pressure of } X_2 = \left(\frac{1\text{mol} - \beta_{eq}/2}{1\text{mol} + \beta_{eq}/2}\right)p \qquad \text{and} \qquad \text{Partial pressure of } X = \left(\frac{\beta_{eq}}{1\text{mol} + \beta_{eq}/2}\right)p$$

$$K_p = \frac{p_x^2}{p_{x_2}} = \frac{\{\beta_{eq}/(1\,\text{mol} + \beta_{eq}/2)\}^2\, p^2}{\{(1\,\text{mol} - \beta_{eq}/2)/(1\,\text{mol} + \beta_{eq}/2)\}\, p}$$

$$= \left(\frac{\beta_{eq}^2}{(1\,\text{mol})^2 - (\beta_{eq}/2)^2}\right) p = \left(\frac{4\beta_{eq}^2}{4\,\text{mol}^2 - \beta_{eq}^2}\right)(2\ \text{bar})$$

$$K_p^{\circ} = \frac{K_p}{1\ \text{bar}} = \frac{8\beta_{eq}^2}{4\ \text{mol}^2 - \beta_{eq}^2} = \frac{8\beta_{eq}'^2}{4 - \beta_{eq}'^2}\ ;\quad (\text{where } \beta' = \beta/\text{mol})\ \ (\text{Choice b})$$

16. (a) If the total pressure is decreased, the reaction will shift in a direction which tends to increase pressure. This is achieved if more of gaseous species is formed. This is achieved by shifting the reaction in the forward direction.

(b) At the start of reaction, the reaction quotient, $Q^{\circ} = 0$. Since

$$\Delta_r G = \Delta_r G^{\circ} + RT \ln Q^{\circ}$$

we have $\Delta_r G$ = negative. Thus, dissociation of X_2 will take place spontaneously.

(c) For $\beta_{eq} = 0.7$ mol, the value of standard equilibrium constant will be

$$K_p^{\circ} = \frac{8(0.7\ \text{mol})^2}{4\ \text{mol}^2 - (0.7\ \text{mol})^2} = 1.12$$

Since $\Delta_r G^{\circ} = -RT \ln K_p^{\circ}$, we will have

$$\ln K_p^{\circ} = -\frac{\Delta_r G^{\circ}}{RT} = \text{negative}$$

This will give $K_p^{\circ} < 1$.

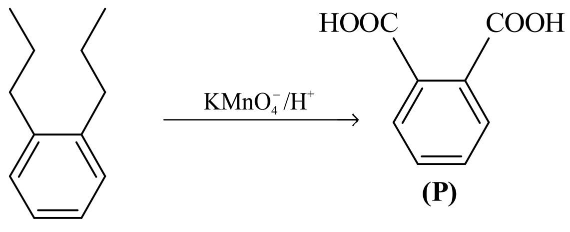
The Choice (b) is incorrect.

(d) $\Delta\nu_g = +1$

We have $K_p = K_c (RT)^{\Delta\nu_g}$ or $K_c = K_p/(RT)^{\Delta\nu_g}$

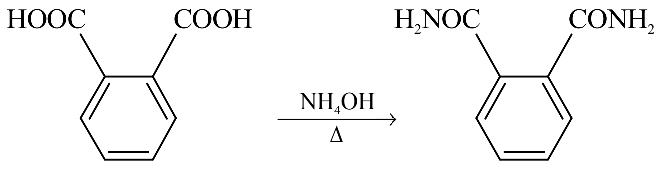
Since $(RT)^{\Delta\nu_g}$ is a positive quantity and has a value more than 1, it is expected that $K_c < K_p$. Since $K_p^{\circ} < 1$, it follows that $K_c^{\circ} < 1$. (correct statement)

17, 18. Treatment with $KMnO_4/H^+$ causes side chain oxidation:



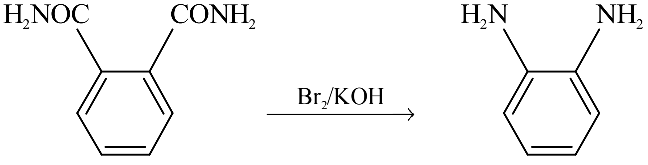
(O) **(P)**

Treatment of the compound **P** with ammonia forms ammonium salt which on heating gives amides.



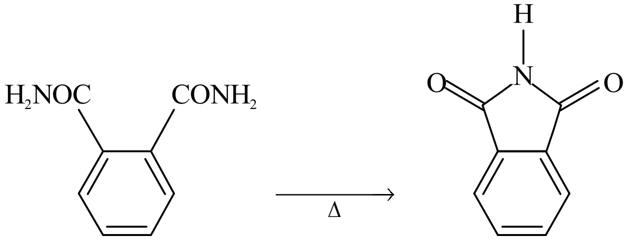
(P) **(Q)**

Treatment of the compound **Q** with Br_2/KOH converts amides into amines. This reaction is Hofmann degradation of amides.



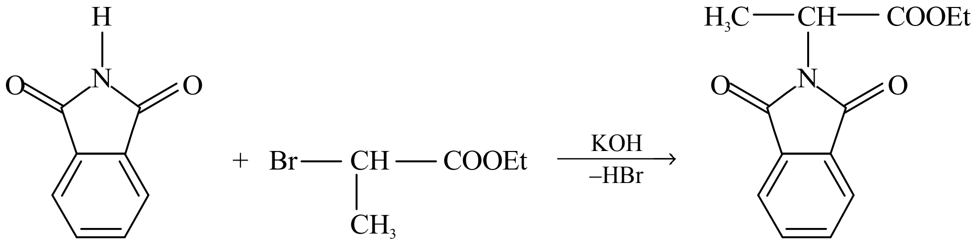
(Q) **(R)**

Streong heating of **Q** causes cyclization of side chains with elimination of NH_3



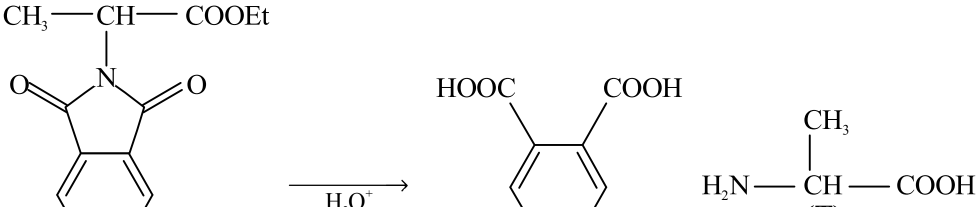
(Q) **(S)**

Treatment S with ethyl-2-bromopropanoate in the presence of KOH causes the following reaction.



(S)

Acidification of the resultant compound causes the following reaction.



(T)
Alanine

The conversion of **S** into **T** is Gabriel's phthalimide synthesis.

The compound **R** is an *ortho*-diamine.

The compount **T** is alanine.

JEE ADVANCED 2017: PAPER–I
(CHEMISTRY)

SECTION – I

This section contains **SEVEN** questions. Each question has **FOUR** options (a), (b), (c) and (d). **ONE** or **More Than One** of these four option(s) is/are correct.

1. The Colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to

(a) The physical state of the X_2 at room temperature changes from gas to solid down the group.

(b) Decrease in HOMO-LUMO gap down the group.

(c) Decrease in $\pi^* - \sigma^*$ gap down the group.

(d) Decrease in ionization energy down the group.

2. Addition of excess ammonia to pink coloured aqueous solution of $MCl_2 \bullet 6H_2O$ (X) and NH_4Cl gives an octahedral complex *Y* in the presence of air. In aqueous solution, complex *Y* behaves as 1 : 3 electrolyte. The reaction of *X* with excess HCl at room temperature results in the formation of a blue coloured complex *Z*. The calculated spin only magnetic moment of *X* and *Z* is 3.87 B.M., where as it is zero for complex *Y*. Among the following options, which statement(s) is (are) correct?

(a) The hybridization of the central metal ion in *Y* is d^2sp^3.

(b) When *X* and *Z* are in equilibrium at 0°C, the colour of the solution is pink

(c) *Z* is a tetrahedral complex

(d) Addition of $AgNO_3$ in *Y* gives only two equivalents of silver chloride.

3. An ideal gas is expanded from (P_1, V_1, T_1) to (P_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are)

(a) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.

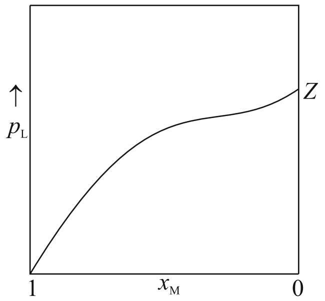
(b) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions

(c) The work done on the gas is maximum when it is compressed irreversibly from (P_2, V_2) to (P_1, V_1) against constant pressure P_1.

(d) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded under adiabatic conditions with $T_1 \neq T_2$.

4. For a solution formed by mixing liquids *L* and *M*, the vapour pressure of *L* plotted against the mole fraction of *M* in solution is shown in the following figure. Here x_L and x_M represent mole fractions of *L* and *M*, respectively, in the solution. The correct statement(s) applicable to this system is (are)

(a) Attractive intermolecular interactions between *L* – *L* in pure liquid *L* and *M* – *M* in pure liquid *M* are stronger than those between *L* – *M* when mixed in solution.

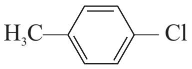


(b) The point *Z* represents vapour pressure of pure liquid *M* and Raoult's law is obeyed when $x_L \to 0$

(c) The point *Z* represents vapour pressure of pure liquid *M* and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

(d) The point *Z* represents vapour pressure of pure liquid *L* and raoult's law is obeyed when $x_L \rightarrow 1$

5. The IUPAC name(s) of the following compound is (are)



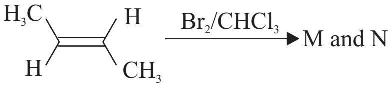
(a) 1 – Chloro – 4 – methylbenzene

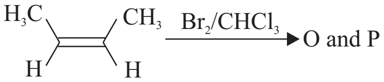
(b) 4 – Chlorotoluene

(c) 1 – Methyl – 4 – Chlorobenzene

(d) 4 – Methylchlorobenzene

6. The correct statement(s) for the following addition reactions is (are)

(i)


(ii)


(a) *O* and *P* are identical molecules

(b) Bromination proceeds through trans-addition in both the reactions

(c) (*M* and *O*) and (*N* and *P*) are two pairs of enantiomers

(d) (*M* and *O*) and (*N* and *P*) are two pairs of diastereomers

7. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is (are)

(a) The conjugate base of HCO_4 is weaker base than H_2O.

(b) The central atom in both $HClO_4$ and HClO is sp^3 hybridized.

(c) $HClO_4$ is formed in the reaction between Cl_2 and H_2O

(d) $HClO_4$ is more acidic than HClO because of the resonance stabilization of its anion

SECTION 2

This section contains **FIVE** questions. The answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive.

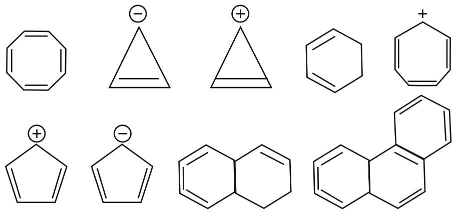
8. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of $1 cm^2$. The conductance of this solution was found to be 5×10^{-7} S. The PH of the solution is 4. The value of limiting molar conductivity (Λ^{∞} m) of this weak monobasic acid in aqueous solution is **Z** $\times 10^2$ S cm^{-1} mol^{-1}. The value of **Z** is _____ .

9. The sum of the number of lone pairs of electrons on each central atom in the following species is _____ .

$[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3 and $[XeF_3]^-$

(Given: Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

10. Among the following, the number of aromatic compound(s) is _____ .



11. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3}, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of *N* is _____ .

Thus, the value of *N* is 2

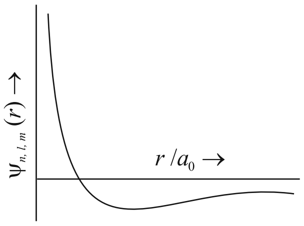
12. Among H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^- and F_2, the number if diamagnetic species is _____ . (Atomic numbers : *H* = 1, *He* = 2, *Li* = 3, *Be* = 4, *B* = 5, *C* = 6, *N* = 7, *O* = 8, *F* = 9).

SECTION 3

- This section contains **SIX** questions of matching type.
- This section contains **TWO** tables (each having 3 columns and 4 rows)
- Based on each table, there are **THREE** questions
- Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is correct.

Answer Q. 13 Q. 14 and Q. 15 by appropriately matching the information given in the three columns of the following table.

The wave function $\psi_{n,\,l,\,m}$ is a mathematical function whose value depends upon spherical polar coordinates ($r,\ \theta,\ \phi$) of the electron and characterized by the quantum numbers $n,\ l$ and m_l. Here r is distance from nucleus, θ is coaltitude and ϕ is azimuth. In the mathematical functions given in the table, Z is atomic number and a_0 is bohr redius.

	Column I	**Column 2**	**Column3**
I.	1s orbital	(i) $\psi_{n,l,m} \propto \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	(P) 
II.	2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto 1/a_0^3$
III.	$2p_z$ orbital	(iii) $\psi_{n,l,m} \propto \left(\frac{Z}{a_0}\right)^{5/2} re^{-(Zr/2a_0)}Cos\theta$	(R) Probability density is maximum at nucleus
IV.	$3d_{z^2}$ orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from n =2 state to n = 4 state is 23/32 times the energy needed to excite electron from n = 2 state to n = 6 state.

13. For He^+ ion, the only **INCORRECT** combination is:

(a) (I), (i), (R) (b) (II), (ii), (Q)

(c) (I), (i), (S) (d) (I), (iii), (R)

14. For the given orbital in column 1, the only **CORRECT** combination for any hydrogen-like species is:

(a) (I), (ii), (S) (b) (IV), (iv), (R)

(c) (III), (iii), (P) (d) (II), (ii), (P)

15. For hydrogen atom, the only **CORRECT** combination is:

(a) (II), (i), (Q) (b) (I), (iv), (R)

(c) (I), (i), (p) (d) (I), (iv), (S)

16. The only **CORRECT** Combination in which the reaction proceeds through radical mechanism is:

(a) (II), (iii), (R) (b) (III), (ii), (P)

(c) (IV), (i), (Q) (d) (I), (ii), (R)

17. For the synthesis of benzoic acid, the only **CORRECT** combination is:

(a) (III), (IV), (R) (b) (IV), (ii), (P)

(c) (II), (i), (S) (d) (I), (iv), (Q)

18. The only **CORRECT** combination that gives two different carboxylic acide is:

(a) (IV), (iii), (Q) (b) (I), (i), (S)

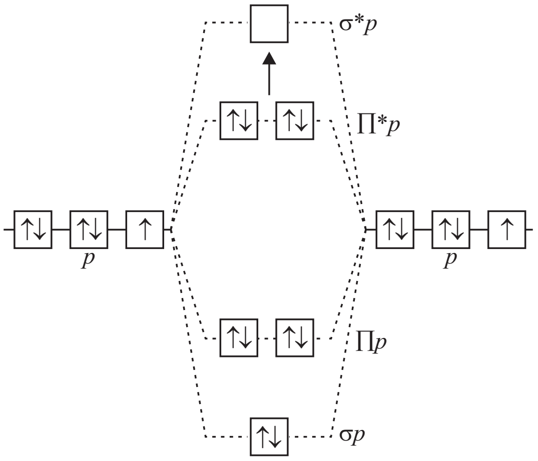
(c) (III), (iii), (P) (d) (II), (iv), (R)

ANSWERS

1. (c) **2.** (a), (b), (c) **3.** (a), (b), (c) **4.** ( ) **5.** ()
6. (b), (d) **7.** ( ) **8.** ( ) **9.** ( ) **10.** ()
11. ( ) **12.** ( ) **13.** ( ) **14.** ( ) **15.** ()
16. ( ) **17.** (c) **18.** (c)

Hints and Solutions

1. The molecular orbitals formed from *p* orbitals of halogens along with the occupancy of 10 electrons are shown in the figure.



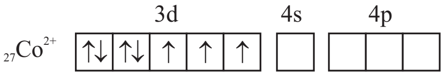
The highest occupied molecular orbital (HOMO) is Π^*p orbitals and the lowest unoccupied orbital (LUMO) is σ^*p. On descending the halogen group, the energy difference between Π^* (i.e. HOMO) and σ^* (i.e. LUMO) is decreased. This is responsible for changing colour from yellow to violet. This is due to the electronic excitation from Π^*p orbital to σ^*p orbital. Thus, the choices (b) and (c) are correct.

2. The compound *X* is MCl_2. $6H_2O$, i.e. $[M(H_2O)_6]Cl_2$. The treatment of *X* with NH_4Cl in the presence of air gives 1 : 3 complex *Y*. This shows that M^{2+} in *X* is oxidised to M^{3+} in *Y*. The metal ion may be that of cobalt since Co(II) complexes are readily oxidised to Co(III) complexes in the presence of air. This is also supported by the spin only magnetic moment of *X*. Given value is 3.87 bohr magneton corresponds to 3 unpaired electrons:

$\sqrt{n(n+2)}$ = 3.8 i.e. $n\ (n + 2) \simeq 15$.

Thus, $n = 3$

The electronic configuration of Co^{2+} confirms this fact.

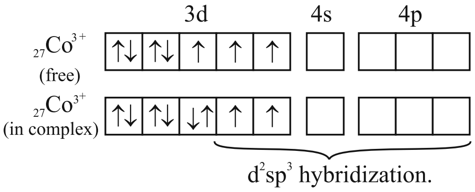


Thus, the compound *X* is $[CO(H_2O)_6]Cl_2$.

The Conversion of *X* into *Y* may be represented by the chemical equation

$$4[Co(H_2O)_6]\ Cl_2 + 4\ NH_4Cl + 20\ NH_3 + O_2 \rightarrow \underset{(Y)}{4\ [Co(NH_3)_6]\ Cl_3} + 26\ H_2O$$

Since NH_3 is a strong ligand, it is able to couple the unpaired electrons in Co^{3+} ion. It is

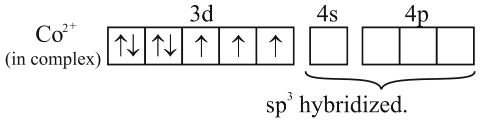


Supported by zero spin magnetic moment. Cobalt, in the complex *Y* is d^2sp^3 hybridized. The reaction of *X* with excess of HCl at room temperature gives blue-coloured complex *Z*. The reaction corresponding to this is:

$$\underset{(x)}{[Co(H_2O)_6]^{2+}} + 4Cl^- \rightleftharpoons \underset{(z)}{[CoCl_4]^{2-}} + 6H_2O$$

The above reaction is an equilibrium reaction and is weakly endothermic, i.e. $\Delta_r H^\circ$ = positive. At room temperature it lies more towards *Z* giving blue-coloured complex. At 0°C, the equilibrium lies more towards complex *X* giving pink colour of the complex.

The compound *Z* involves sp^3 hybridization and is thus tetrahedral in shape. This is due to the fact that Cl is a weak ligand and it is unable to couple the unpaired electrons in Co^{2+} ion.



This is supported by the spin-only magnetic moment of the complex which requires the presence of 3 unpaired electrons.

Addition of $AgNO_3$ to the complex will precipitate three equivalents of silver chloride.

Thus, the choices (a), (b) and (c) are correct.

3. (a) For free expansion, $p_{ext} = 0$

Thus, $w = -p_{ext}\,\Delta V = 0$

For an isothermal expansion, $\Delta T = 0$. Since the internal energy of an ideal gas depends only on temperature, it follows that $\Delta U = 0$ from the first law of thermodynamics ($\Delta U = q + w$), it follows that $q = 0$

Thus, for an isothermal free expansion, we have

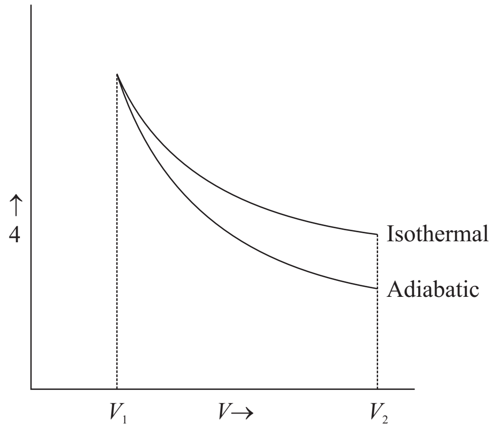
$w = 0$; $q = 0$ and $\Delta U = 0$

For adiabatic free expansion, $q = 0$ as no heat is allowed to enter or leave from the system. Since $w = 0$, it follows that $\Delta U = 0$

Thus, for both isothermal and adiabatic free expansions, $q = 0$, $w = 0$ and $\Delta U = 0$

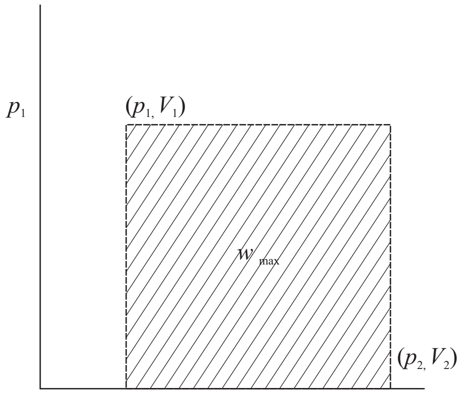
(b) Since in adiabatic expansion, work is done at the expense of internal energy, the temperature T_2 in the final state will be lesser in adiabatic expansion as compared to that in isothermal expansion. Since $p \propto T$, it follows that p_2 in adiabatic expansion will be lesser than that in isothermal expansion.

The variations of P versus V in the two expansions are shown in the figure.



Since work done is represented by the area under $P–V$ curve, it follows that the work done under adiabatic condition will be lesser than that done under isothermal condition

(c) Since the external pressure is equal to pressure of the gas after the gas has gone expansion and it is maximum pressure which the external pressure can have. Thus, work done on the gas will be maximum. It is shown in the figure.



(d) Expansion under isothermal conditions, $T_1 = T_2$,

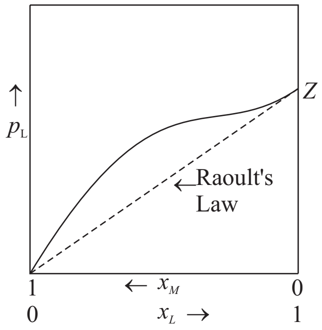
Thus, $\Delta U = 0$

Under adiabatic conditions, $T_2 < T_1$,

Thus, $\Delta U < 0$

Thus, the choices (a), (b) and (c) are correct.

4. (a) Since the pressure P_L is larger than that predicted by Raoult's law (represented by broken line in the figure), larger number of molecules of L are escaping from solution when compared from ideal solution.



This is possible when the molecular attractions L....M are weaker than those existing in L....L and M....M

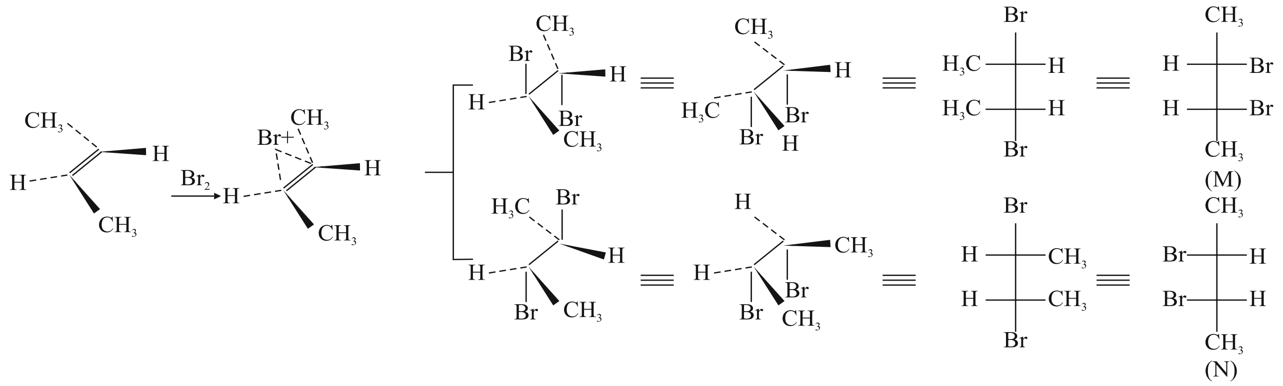
(d) The point Z represents vapour pressure of pure liquid L where $x_L = 1$. The Raoult's law is applicable when $x_L \rightarrow 1$

5. The compound is named either as benzene derivative or by common name. Thus, the IUPAC names are:

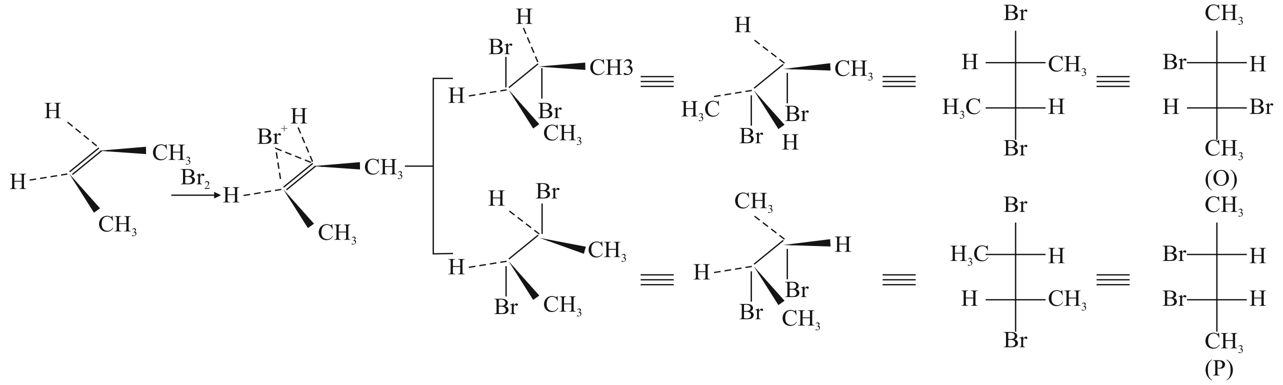
1 – Chloro – 4 – Methylbenzone and 4 – Chlorotoluene

6. Addition of bromine across double bond is anti-addition. The *cis*-alkene yields only racemic mixture whereas *trans*-alkene produces *meso* compound.

(i)



(ii)



The copounds M and N are identical whereas O and P are enantiomers.

The compounds M and O and N and P are diastereomers.

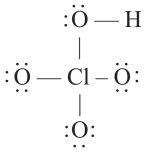
The choices (b) and (d) are correct.

7. (a) The strength of oxoacids of chlorine follows the order: $HClO_4 > HClO_3 > HClO_2 > HClO$

The strength of conjugate bases follow the reverse order:

$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$

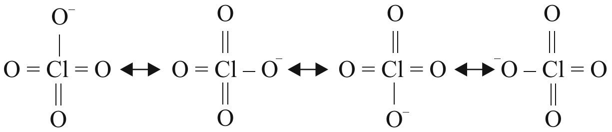
(b)

Molecule	**Valence electrons**	**Lewis structure**	**Prediction**
$HClO_4$	1+7+4×6=32	 $:\ddot{O}-\overset{\overset{:\ddot{O}-H}{|}}{\underset{\underset{:\ddot{O}:}{|}}{Cl}}-\ddot{O}:$	4 pairs of electrons around Cl, sp^3 hybridization
HClO	1 + 7 + 6 = 14	$:\ddot{Cl}-\ddot{O}-H$	4-pairs of electrons around Cl, sp^3 hybridization

(c) The reaction between Cl_2 and H_2O is

$Cl + H_2O \rightarrow HCl + HClO$

(d) ClO^-_4 is stabilized due to resonance structures



$$O=\overset{\overset{O^-}{|}}{\underset{\underset{O}{||}}{Cl}}=O \longleftrightarrow O=\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cl}}-O^- \longleftrightarrow O=\overset{\overset{O}{||}}{\underset{\underset{O^-}{|}}{Cl}}=O \longleftrightarrow {}^-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cl}}=O$$

8. From the expression $G = K\ (a/l)$, we get

$$\kappa = \frac{Gl}{a} = (5 \times 10^{-7} \mathrm{S}) \left(\frac{120\mathrm{cm}}{1\mathrm{cm}^2}\right) = 600 \times 10^{-7} \mathrm{S} \times \mathrm{cm}^{-1}$$

For infinite diluted solution, weak acid is considered to be completed ionized. Hence, weak acid may be considered as strong acid of PH = 4 (i.e. [H] = 10^{-4}M)

$$\text{Now } \Lambda^{\infty}_{\mathrm{m}} = \frac{\kappa}{c} = \frac{600 \times 10^{-7}\,\mathrm{Scm}^{-1}}{10^{-4}\,\mathrm{mol\,dm}^{-3}}$$

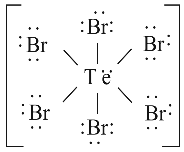
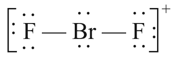
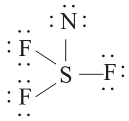
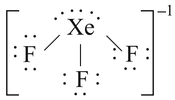
$$= 600 \times 10^{-3}\ \mathrm{S\ cm^{-1}\ dm^{-3}\ mol^{-1}}$$

$$= 600 \times 10^{-3}\ \mathrm{S\ cm^{-1}\ (10\ cm)^3\ mol^{-1}}$$

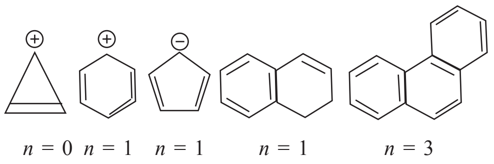
$$= 600\ \mathrm{S\ cm^2\ mol^{-1}} = 6 \times 10^2\ \mathrm{S\ cm^2\ mol^{-1}}$$

Thus, the value of **Z is 6**.

9.

Species	**Valence electrons**	**rewis structure**	**Lone pairs**
$[TeBr_6]^{2-}$	6 + 7 × 6 + 2 = 50		1
$[BrF_2]+$	7 + 2 × 7 – 1 = 20		2
SNF_3	6 + 5 + 3 × 7 = 32		0
$[XeF_3]^-$	8 + 3 × 7 + 1 = 30		3
		Total lone pairs =	6

10. Aromatic compounds have $(4n + 2)\pi$ electrons. The following compounds satisfy this requirement.



The number of aromatic compounds is 5.

11. The expression of density is

$$\rho = \left(\frac{N}{a^3}\right) m$$

where $N = 4$, $a = 400$ pm and m is mass/atom of the solid. From this, use get

$$m = \frac{Pa^3}{N} = \frac{(8g\,\mathrm{cm}^{-3})(400 \times 10^{-10}\,\mathrm{cm})^3}{4}$$

$$= 1.28 \times 10^{-22}\mathrm{g}$$

Number of atoms in 256g is

$$N^1 = \frac{256g}{1.28 \times 10^{-22}\,g} = 2 \times 10^{24}$$

Thus, the value of N is **2**.

12.

Species	**Molecular electronic configuration**	**Conclusion**
H_2	$(\sigma 1s)^2$	Diamagnetic
He^+_2	$(\sigma 1s)^2\ (\sigma^* 1s)^1$	Paramagnetic
Li_2	$KK\ (\sigma 2s)^2$	Diamagnetic
Be_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2$	Diamagnetic
B_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\prod 2p_x)^1\ (\prod 2p_y)^1$	Paramagnetic
C_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\prod 2p_x)^2\ (\prod 2p_y)^2$	Diamagnetic
N_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\prod 2p_x)^2\ (\prod 2p_y)^2\ (\sigma^2 p_y)^2$	Diamagnetic
O^-_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\prod 2p_x)^2\ (\prod 2p_y)^2\ (\prod^* 2p_x)^2\ (\prod^* 2p_y)^2$	Paramagnetic
F_2	$KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\prod 2p_x)^2\ (\prod 2p_y)^2\ (\prod^* 2p_x)^2\ (\prod^* 2p_y)^2$	Diamagnetic

There are 6 diamagnetic species.

13. The choice (d) is incorrect. Is orbital (I in column 1) has no directional characteristics (iii in column 2 contains cos θ)

14. The choice (d) is correct. 2s orbital (II in column 1) has one radial node (= n – l– 1) (ii in column 2) and the plot of $\psi_{n,\,l,\,m}$ (r) has the characteristic of P shown in column 3

15. The choice (d) is correct. Is orbital (I in column 1) has wave function dependence shown in (i) column 2. The option S of column 3 is also correct as shown in the following

Transition from n = 2 to n = 4

$$\Delta E_1 = R_{\infty}hc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= R_{\infty}hc\left(\frac{1}{4}-\frac{1}{16}\right)$$

$$= \frac{3}{16}R_{\infty}hc$$

Transition from n = 2 to n = 6

$$\Delta E_2 = R_{\infty}hc\left(\frac{1}{4}-\frac{1}{36}\right) = \frac{8}{36}R_{\infty}hc$$

$$\frac{\Delta E_1}{\Delta E_2} = \frac{(3/16)\ R\infty he}{(8/36)\ R\infty he} = \frac{27}{32}$$

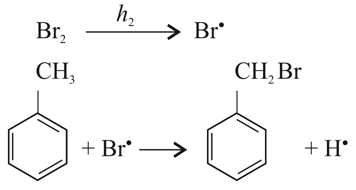
Answer Q 15, Q 17 and Q 18 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2, 3 contain starting materials reaction conditions, and type of reactions respectively.

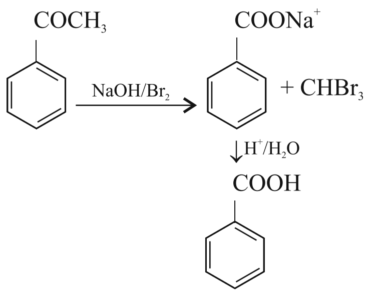
	Column 1		**Column 2**		**Column 3**
(I)	Toluene	(i)	NaOH/Br_2	(P)	Condensation
(II)	Acetophenone	(ii)	Br_2/h_2	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O$/ CH_3COOK	(R)	Substitution
(IV)	Phenol	(iv)	NaOH/CO_2	(S)	Haloform

16. The combination Br_2/h^2 (Choice ii in column 2) produces Br radicals

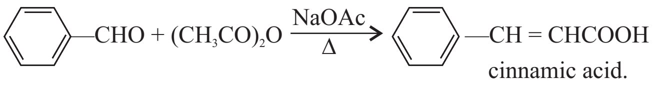
Of the two choices (b) and (d) which include (ii), the choice (d) is correct as bromination of tolune (choice I in column 1) involves substitution (choice S in column 3) in the methyl group as shown in the following.



17. The choice (c) is correct combination as $C_6H_5COCH_3$ (autophenone, choice II in column 1) undergoes haloform reaction (choice S in column 3) with the use of reagents NaOH/Br (choice ii in column 2)



18. The choice (c) is correct. Heating of aromatic aldehyde (choice III in column 1) with acetic anhydride in the presence of sodium acetate (Choice ii in column 2) gives α, β- unsaturated corboxylic acid this is known as perkin reaction.



Cinnamic acid exists in two geometrical isomers due to the presence of a double bond.

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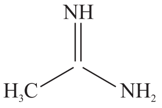
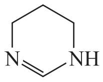
SECTION – I

This section contains **SEVEN** questions. Each question has **FOUR** options (a), (b), (c) and (d). **ONE** or **More Than One** of these four option(s) is/are correct.

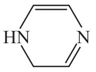
1. The order of basicity among the following compounds is



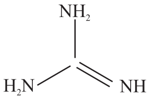
(I)



(II)



(III)



(IV)

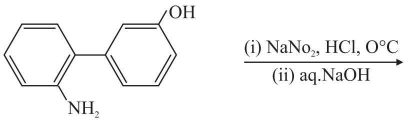
(a) IV > I > II > III

(b) IV > II > III > I

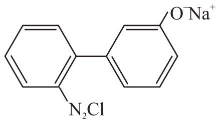
(c) I > IV > III > II

(d) II > I > IV > III

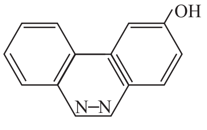
2. The major product of the following reaction is



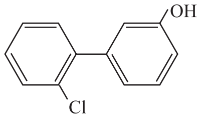
(a)



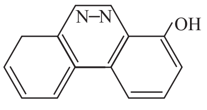
(b)



(c)



(d)



3. Which of the following combination will produce H_2 gas?

(a) Au metal and NaCN [aq] in the presence of air

(b) Zn metal and NaOH [aq]

(c) Fe metal and conc. HNO_3

(d) Cu metal and conc. HNO_3

4. The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at T = 298 K are

$\Delta_f G°$ (C, graphite) = 0 kJ mol^{-1}

$\Delta_f G°$ (C, diamond) = 2.9 kJ mol^{-1}

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of C (graphite) to C (diamond) reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C (graphite) is converted to C (diamond) isothermally at $T = 298$K, the pressure at which C (graphite) is in equilibrium with C (diamond) is

(Useful information: 1 J = 1 kg m^2 s^{-1}, 9pa = 1kg m^{-1} s^{-2}, 1 bar = 10^5 pa)

(a) 14501 bar (b) 29001 bar

(c) 1450 bar (d) 58001 bar

5. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ is

(a) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$

(b) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

(c) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

(d) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$

6. For the following cell.

Zn (s) | $ZnSO_4$ (aq) || $CuSO_4$ (aq) | Cu(s)

when the concentration of Zn^{2+} ions is 10 times the concentration of Cu^{2+} ions, the expression of ΔG of the cell reaction is

(a) 2.303 *RT* – (2.2V) *F*

(b) (1.1V) *F*

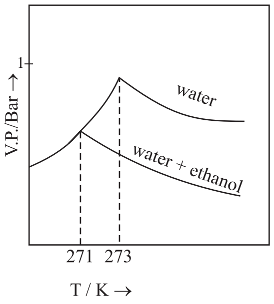
(c) – (2.2V) *F*

(d) 2.303 RT + (1.1V) F

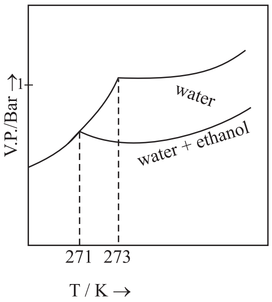
(Where *F* is Faraday constant, *R* is gas constant, *T* is temperature, $E^\circ_{\text{cell}} = 1.1\text{V}$)

7. Pure water freezes at 273 k and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (*T*). (Motor mass of ethanol is 46 g mol^{-1}) Among the following, the option representing changes in the freezing point is

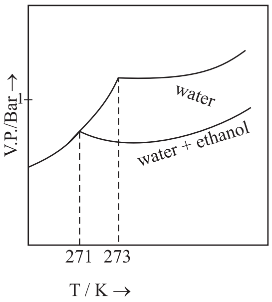
(a)



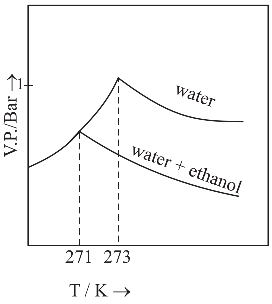
(b)



(c)



(d)



SECTION 2

This section contains **SEVEN** questions. Each question has FOUR options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options is (are) correct.

8. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is (are):

(a) The activation energy of the reaction is unaffected by the value of steric factor

(b) Since P = 4.5, the reaction will not proved unless and effective catalyst is used.

(c) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally.

(d) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by.

(a) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases.

(b) With increases in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive.

(c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.

(d) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases.

10. The correct statement(s) about surface properties is (are):

(a) Adsorption is accompained by decrease in enthalpy and decrease in entropy of the system

(b) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium

(c) The critical temperature of ethane and nitrogen are 563K and 126K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature.

(d) Brownian motion of colloidal particles does not depend on the size of the particle but depends on viscosity of the solution.

11. Among the following the correct statement(s) is (are):

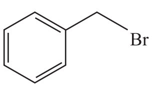
(a) $AlCl_3$ has the three-centre two electron bonds in its dimeric structure.

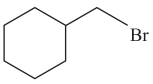
(b) BH_3 has the three-centre two-electron bonds in its dimeric structure.

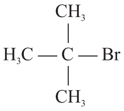
(c) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure.

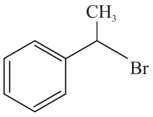
(d) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$.

12. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are)

(I) 

(II) 

(III) 
$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br$

(IV) 

(a) I and III follow S_N1 mechanism

(b) Compound IV undergoes inversion of configuration

(c) The correct order of reactivity for I, III and IV is IV > I > II

(d) I and II follows S_N2 mechanism

13. The option(s) with only amphoteric oxide is (are):

(a) ZnO, Al_2O_3, PbO, PbO_2

(b) Cr_2O_3, CrO, SnO, PbO

(c) Cr_2O_3, BeO, SnO, SnO_2

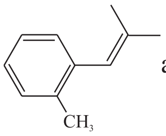
(d) NO, B_2O_3, PbO, SnO_2

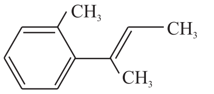
14. Compounds *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is C_8H_8O. *Q* and undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction.

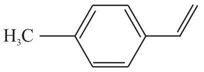
(i) $P \xrightarrow[(ii)\,Z_n/H_2O]{(i)\,O_3/CH_2Cl_2} \underset{(C_8H_8O)}{Q}$

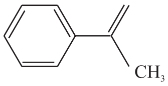
(ii) $R \xrightarrow[(ii)\,Zn/H_2O]{O_3/CH_2Cl_2} \underset{(C_8H_8O)}{S}$

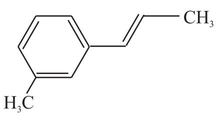
The option(s) with suitable combination of P and R, respectively, is (are)

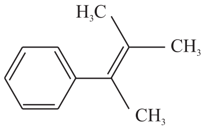
(a) 

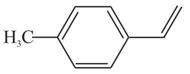
and 

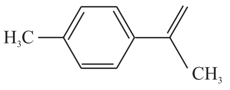
(b) 

and 

(c) 

and 

(d) 

and 

SECTION-3

This section contains **TWO** paragraphs. Based on each paragraph, there are **TWO** questions

Each question has **FOUR** options (a), (b), (c) and (d). **Only ONE** of these options is correct.

Paragraph 1

Upon mixing $KClO_3$ in the presence of catalytic amount of MnO_2, a gas *W* is formed. Excess amount of *W* reacts with phosphorus to give *X*. The reaction of *X* with pure HNO_3 gives *Y* and *Z*.

15. W and X are, respectively.

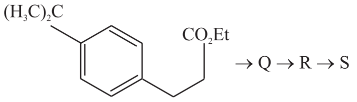
(a) O_3 and P_4O_6
(b) O_2 and P_4O_6
(c) O_2 and P_4O_{10}
(d) O_3 and P_4O_{10}

16. Y and Z are, respectively

(a) N_2O_5 and HPO_3
(b) N_2O_5 and H_3PO_4
(c) N_2O_4 and HPO_3
(d) N_2O_4 and H_3PO_3

Paragraph 2

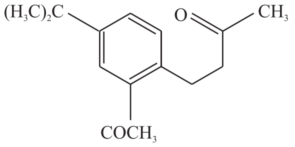
The reaction of compound P with CH_3MqBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives *Q*. The compound *Q* on treatment with H_2SO_4 are 0°C gives *R*. The reaction of *R* with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound S. [Et in compound P is ethyl group]

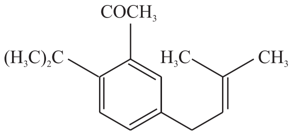


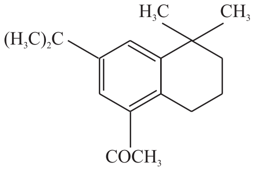
17. The reactions Q to R and R → S are

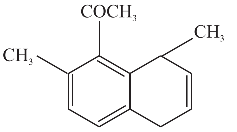
(a) Dehydration and Friedel-Crafts acylation
(b) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
(c) Friedel-Crafts alkylation and Friedel-Crafts acylation
(d) Aromatic sulfonation and Friedel-Crafts acylation

18. The product S is

(a)


(b)


(c)


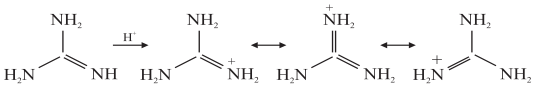
(d)


ANSWERS

1. (a) **2.** (b) **3.** (b) **4.** (a) **5.** (a)
6. (a) **7.** (c) **8.** (a), (b) **9.** (a), (d) **10.** (a), (c)
11. (b), (c), (d) **12.** (a), (b), (d) **13.** (a), (c) **14.** (b), (c) **15.** (c)
16. (a) **17.** (c) **18.** (c)

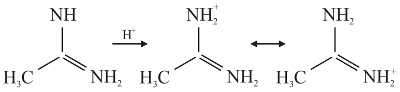
HINTS & SOLUTIONS

1. The molecule IV have maximum basicity. This may be attributed to stability of its conjugate acid due to larger number of resonating structures.



The maximum basicity may be explained on the basis that the basic site = NH is attached to two pi-electrons donors which enhances that electron density on the basic site.

The next lesser basic is the molecule I. This involves lesser number of resonating structures in its conjugate acid.

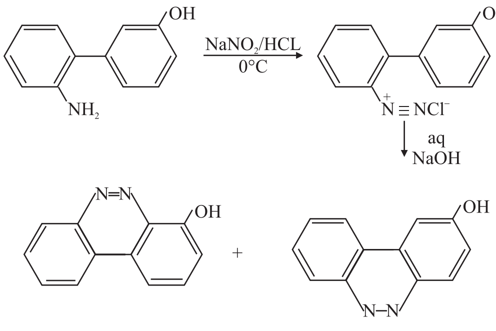


The molecule I has one pi-electrons doner –NH^2 group and one electron-releasing methyl group and thus expected to be lesser basic than molecule IV.

The least basic is the molecule III. The electron pair on nitrogen is delocalised over the whole molecule to make it aromatic. Its lone pair of electrons on nitrogen is not available to make it basic.

Thus, the order of basicity is IV > I > II > III.

2. The reactions are:



(Minor) (Major)

(more steric hindrance)

3. Zn metal produces H_2 gas with NaOH (aq)

$Zn + 2\ NaOH \rightarrow Na_2\ ZnO_2 + H_2$

The other reaction:

$4\ Au + 8\ NaCN + 2H_2O + O_2 \rightarrow 4\ Na\ [Au\ (CN)_2] + 4\ NaOH$

$Fe + 6\ HNO_3 \rightarrow Fe\ (NO_3)_3 + 3NO_2 + 3H_2O$
(Conc.)

$Cu + 4\ HNO_3 \rightarrow Cu\ (NO_3)_2 + 2NO_2 + 2H_2O$
(Conc.)

4. C (graphite) → C (diamond)

$\Delta_f G°$ 0 2.9 kJ mol^{-1}

$\Delta_r G° = \Delta_f G°$ (C, diamond) – $\Delta_f G°$ (C, graphite)

= 2.9 kJ mol^{-1} – D = 2.9 kJ mol^{-1}

= 2900 J mol^{-1}

Since $\Delta G = \Delta H - T\,\Delta S$, we have

$\Delta G = \Delta(U + PV) - T\,\Delta\,S$

$= \Delta U + \Delta\,(PV) - T\,\Delta\,S$

Since $\Delta U = q + w = q - p\Delta V$ and at constant temperature, $\Delta S = q/T$, we get

$\Delta G = (q - p\,\Delta\,V) + (p\,\Delta\,V + V\,\Delta\,p) - q = V\,\Delta\,p$

$$\text{or}\quad \Delta p = \frac{\Delta G}{V} = \frac{2900 J\,mol^{-1}}{2\times10^{-6} m^3\,mol^{-1}} = 1450 \times 10^6\ \text{Pa}$$

= 14500 bar

i.e. $p_2 = p_1 = 14500$ bar

i.e. $p_2 = 14501$ bar ; (Since $p_1 = 1$bar)

5. It x is the oxidation state of phosphorus, then we have

H_3PO_4 $3(+1) + x + 4\,(-2) = 0 \Rightarrow x = +5$

$H_4P_2O_6$ $4\,(+1) + 2x + 6\,(-2) = 0 \Rightarrow x = +4$

H_3PO_3 $3\,(+1) + x + 3(-2) = 0 \Rightarrow x = +3$

H_3PO_2 $3(+1) + x + 2\,(-2) = 0 \Rightarrow x = +1$

Thus, the choice (a) gives the correct order of oxidation state of phosphorus.

6. The cell reaction is

$Cu^{2+}\,(aq) + Zn(s) = Cu(s) = Zn^{2+}\,(aq)$

The cell potential is

$$E_{cell} = E°_{cell} - \frac{RT}{2F}\ln\left(\frac{[Zn\quad]/C°}{[Cu\quad]/C°}\right)$$

$$= 1.1V - \frac{2.303RT}{2F}\log\left(\frac{10}{1}\right)$$

$$= 1.1V - \frac{2.303RT}{2F}$$

Since $\Delta G = -n\ F\ E_{cell}$, we get

$$-\frac{\Delta G}{2F} = 1.1V - \frac{2.303RT}{2F}$$

i.e. $\Delta G = 2.303\ RT - (2.2V)\ F$

Note: It is desireable to write cell reaction to which ΔG stands for.

7. Vapour pressure of solution increases with increase in temperature. Thus, either choice (b) or choice (c) is correct.

Amount of ethanol, $n = \frac{m}{M} = \frac{34.5g}{46g mol^{-1}} = 0.75$ mol

Molality of solution, $n = \frac{n}{m_1} = \frac{0.75mol}{0.5kg} = 1.5$ mol kg^{-1}

Depression in freezing point is

$-\Delta T_f = K_f m$ (2K kg mol^{-1}) (1.5 mol kg^{-1}) = 3K

Freezing point of solution

$T_f = T^*_f - \Delta T_f = 273K - 3K = 270$ K.

The choice (c) satisfies this requirement

Note: It is assumed that ethanol is nonvolatile.

8. The activation energy of the reaction is not affected by steric factor (choice a). Since steric factor is more than one, the frequency factor (i.e. frequency of colliding molecules) determined experimentally will be larger that computed from Arrhenius equation.

In fact $Z_{expt} = PZ^1$

where Z' is frequency factor computed from Arrhenius equation (Choice d)

9. As per Le-Chatelier principle, if the temperature of a reaction at equilibrium is increased, the reaction shifts in a direction so as to decrease the temperature. This decrease in temperature is achieved by releasing less heat in an exothermic reaction and absorbing more heat in an endothermic reaction.

Considering an exothermic reaction

Reactant Product; $\Delta_r H$ = negative

which may be written as

Reactant Product + q

To decrease the value of q_1 reaction moves towards reactant side causing a decrease in equilibrium constant.

$$K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{\text{decrease}}{\text{increase}} = \textbf{decrease}$$

The heat released in an exothermic reaction causes an increase in entropy of the surroundings. Assuming q does not change significantly, the entropy change ($= q/T$) in the surroundings decreases due to increase in temperature. Since the entropy change is positive, this is referred to as favourable change in entropy and its value decreases with increase in temperature (Choice a)

For an endothermic reaction

Reactant Product; $\Delta_r H$ = positive

which may be written as

Reactant + q Product

With the increase in temperature, absorption of q increases thereby equilibrium is shifted towards product side causing an increase in equilibrium constant

$$K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{\text{increase}}{\text{decrease}} = \text{increase.}$$

The absorbed heat is supplied by the surroundings, the entropy change of the surroundings will be negative and is referred to as unfavourable change in entorpy. Its value becomes more negative and thus a decrease in entropy of the surroundings will be observed (choice d)

The change in equilibrium constant with change in temperature is independent of the entropy change of the reaction. It depends only on the enthalpy of reaction through the expression

$$\frac{d\ln k^\circ}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

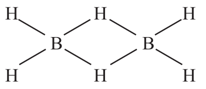
10. Adsorption involves attractions between adsorbent and adsorbate and thus involves a decrease in enthalpy on adsorption. The adsorbate is more ordered after adsorption and is thus accompanied with decrease in entropy. More easily liquefiable gas ethane (which has a higher critical temperature) involves larger intermolecular attractions and thus will exhibit larger adsorption on the same amount of adsorbent.

Cloud belongs to areosol colloid.

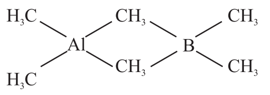
Brownian motion depends on colloidal particle

Thus, the choices (a) and (c) are correct.

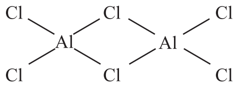
11. The structures of given dimers are:



It has two 3c-2e bonds.



It has two 3c-2e bonds.



No 3c-2e bonds.

BCl_3 is a stronger Lewis acid than $AlCl_3$ due to the presence of more localized *P* orbital in boron.

12. The main characteristics of S_N1 mechanism are:

(i) Steric hindrance for the incoming nucleophile

(ii) Polar solvent accelerates the substitution

(iii) Chiral starting material ends with the racemization of the products

(iv) Intermediate is carbocation more stable the carbocation, the faster the S_n1 mechanism

The main characteristics of S_n2 mechanism are

(i) Lesser steric hindrance for the incoming nucleophile

(ii) Aportic solvent accelerates the substitution

(iii) Involves Walden inversion – stereochemistry around carbon atom is inverted

Primary and secondary halides are likely to undergo S_N2 mechanism

Secondary and tertiary halides are likely to undergo S_N2 mechanism

Choice (a) is correct as intermediate cations are stable

Choice (b) is correct as it can follow S_N2 mechanism

Choice (c) is incorrect as compound (III) is expected to have maximum reactivity.

Choice (d) is also correct as the compounds I and II can follow S_N2 mechanism.

13. The amphoteric oxides in the given oxides are:

ZnO, Al_2O_3, PbO, PbO_2, Cr_2O_3, BeO, SnO and SnO_2

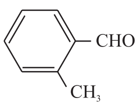
Thus, the choices (a) and (c) are correct.

CrO is a basic oxide

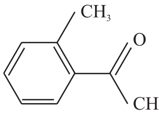
NO is a neutral oxide

B_2O_3 is an acidic oxide

14. The ozonolysis products from P and R of choice (a) are



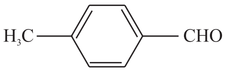
and

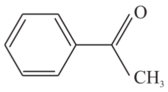


(Q)
Gives Cannizzaro reaction due to CHO group with no α-hydrogen

(S)
The molecular formula of S is not C_8H_8O

The ozonolysis products from *P* and *R* of choice (b) are

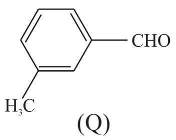


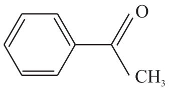


(Q)
Gives Cannizzaro reaction due to –CHO group. with No α-hydrogen

(S)
Gives holoform reaction due to $COCH_3$ Group.

The ozonolysis products from *P* and *R* of choice (c) are

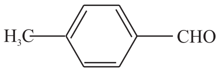


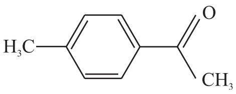


(Q)
Gives Cannizzaro reaction due to –CHO group with no α-hydrogen

(S)
Gives haloform reaction due to $-COCH_3$ group

The ozonolysis products from P and R of choice (d) are





(Q)
Gives Cannizzaro reaction due to –CHO group with no α-hydrogen

(S)
The molecular formula is not C_8H_8O.

Solutions (15 and 16)

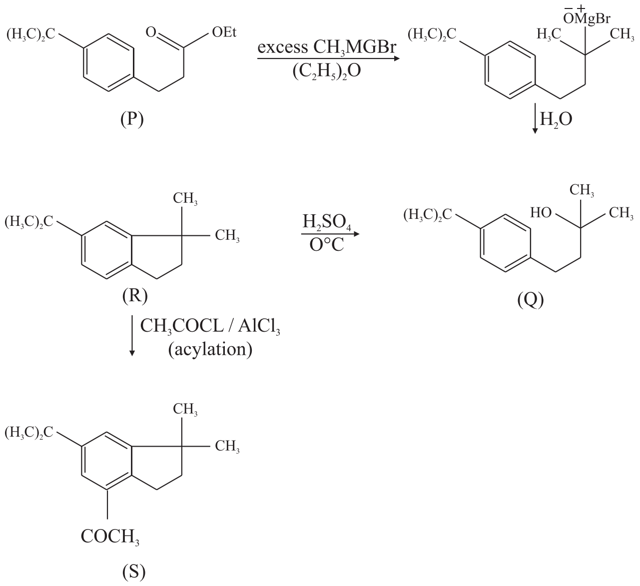
The reactions are

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + \underset{\textbf{(W)}}{3O_2}$$

$$P_4 + 5O_2 \rightarrow \underset{\textbf{(X)}}{P_4O_{10}}$$

$$P_4O_{10} + 4\ HNO_3 \rightarrow \underset{\textbf{(Y)}}{2N_2O_5} + \underset{\textbf{(Z)}}{4\ HPO_3}$$

18. The given reactions are:



17. The conversion of Q to R involves Friedel-Crafts alkylation and dehydration. The conversion of R to S involves Friedel-Crafts acylation.

18. The S is compound of choice (c).

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