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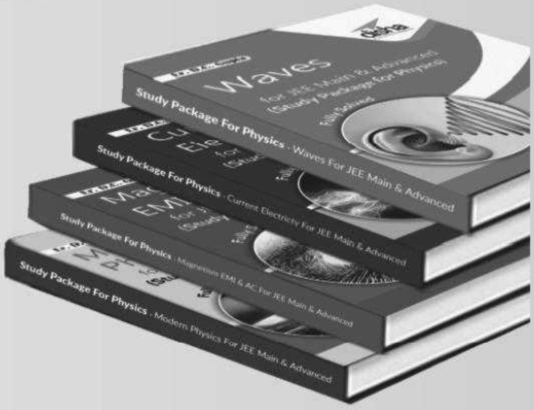

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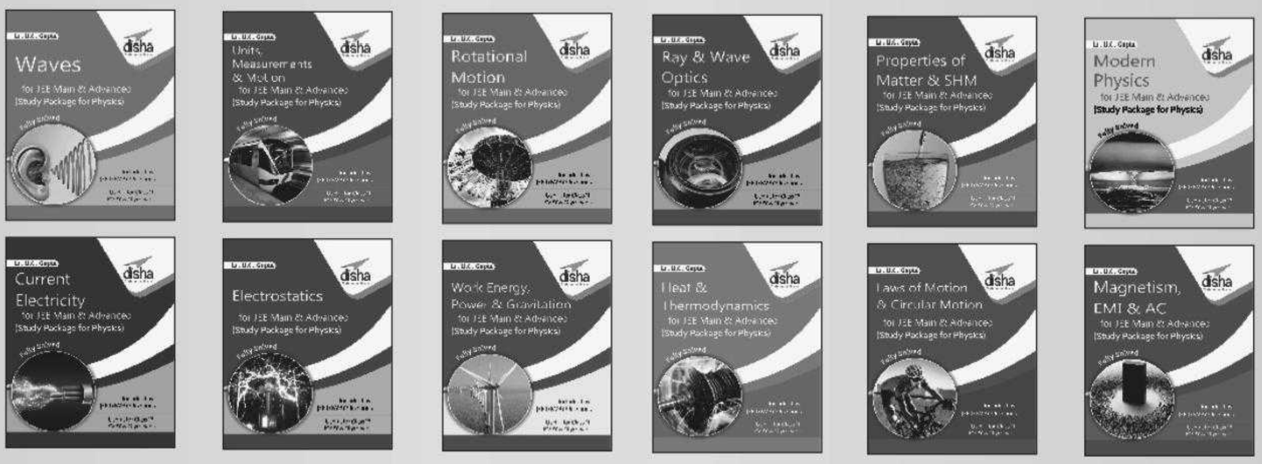


1

Chapter

Some Basic Concepts of Chemistry

INTRODUCTION

Chemistry is the science which involves the study of composition and properties of matter or we can say, chemistry is the science of matter - what matter is like, what makes up matter, what changes occur in matter, what causes those changes. It is key to all the other sciences and a part of every aspect of our world. Chemistry also studies the reactions between different chemicals, known as chemical reactions. Basic chemical reactions are always going on around us as well as a more complex system of reactions, even just within our bodies. With the knowledge of chemistry we understand

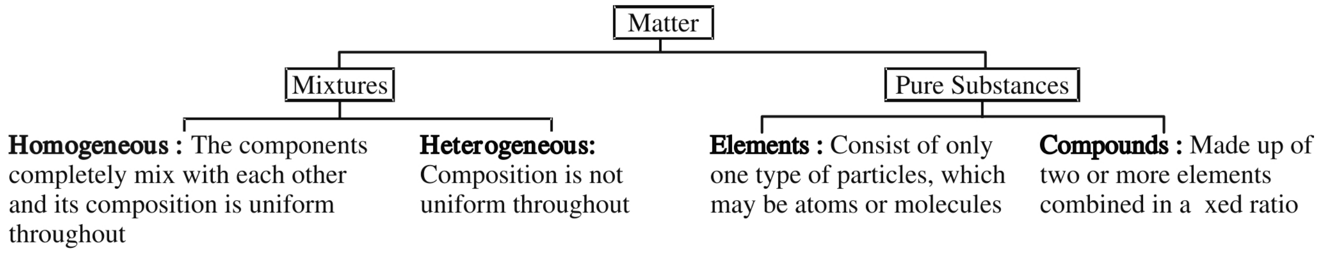
- How the composition of substances affect its properties.
- When and how substances change within chemical reactions.
- Why the properties that we observe with our senses occur in matter.

Chemistry plays an important role in every aspect of our lives, It has allowed other sciences to blossom and has expanded our collective knowledge.

MATTER AND ITS NATURE

Anything which has mass and occupies space is called matter. Everything around us is composed of matter. Matter is classified at microscopic and macroscopic levels.

At macroscopic or bulk level, it is classified as :



Homogeneous : The components completely mix with each other and its composition is uniform throughout

Heterogeneous: Composition is not uniform throughout

Elements : Consist of only one type of particles, which may be atoms or molecules

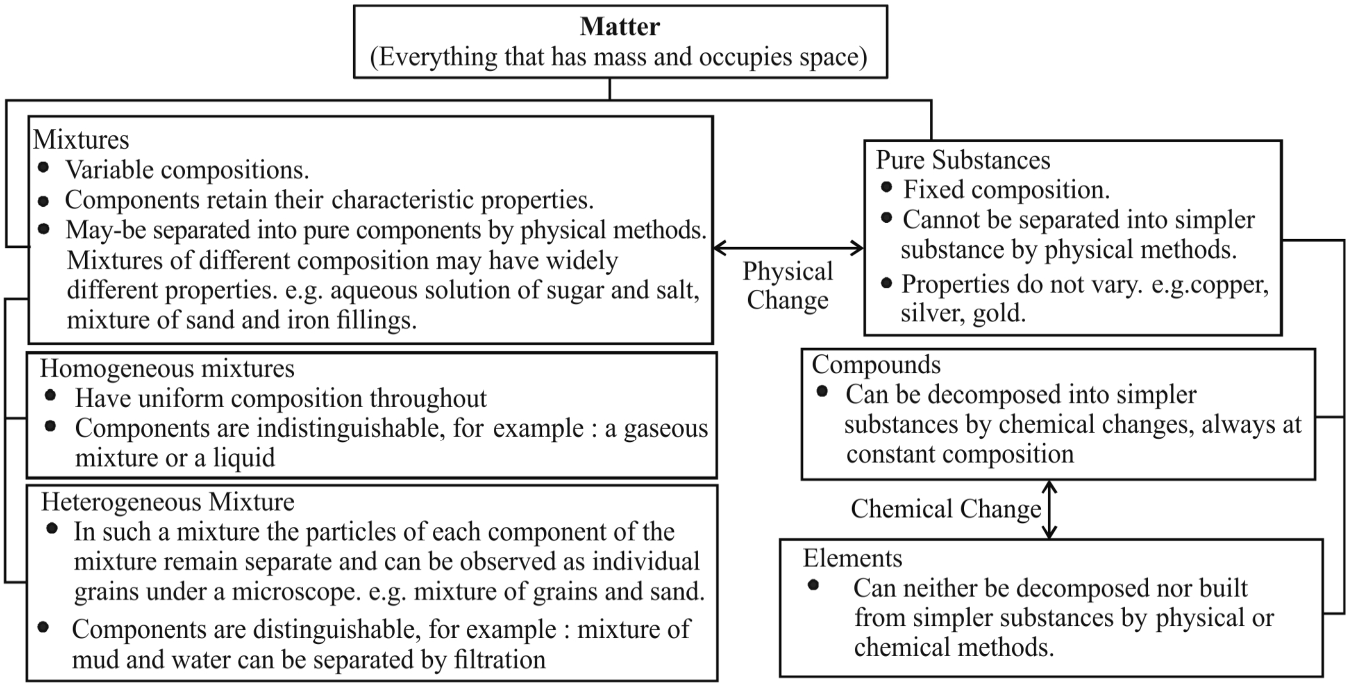
Compounds : Made up of two or more elements combined in a fixed ratio

At microscopic level, it can exist in three physical states, namely, solid, liquid and gas.

- Solids are matter having fixed shape, fixed volume and are almost impossible to compress.
- Liquids are matter having a fixed volume but no fixed shape - they take the shape of the container in which they are kept. Liquids are in compressable.
- Gases are matter having neither a fixed shape nor a fixed volume. They are easy to compress.

These three states of matter are interconvertible by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Gas}$$



Matter
(Everything that has mass and occupies space)

Mixtures
- Variable compositions.
- Components retain their characteristic properties.
- May-be separated into pure components by physical methods. Mixtures of different composition may have widely different properties. e.g. aqueous solution of sugar and salt, mixture of sand and iron fillings.

Physical Change

Pure Substances
- Fixed composition.
- Cannot be separated into simpler substance by physical methods.
- Properties do not vary. e.g.copper, silver, gold.

Homogeneous mixtures
- Have uniform composition throughout
- Components are indistinguishable, for example : a gaseous mixture or a liquid

Compounds
- Can be decomposed into simpler substances by chemical changes, always at constant composition

Chemical Change

Heterogeneous Mixture
- In such a mixture the particles of each component of the mixture remain separate and can be observed as individual grains under a microscope. e.g. mixture of grains and sand.
- Components are distinguishable, for example : mixture of mud and water can be separated by filtration

Elements
- Can neither be decomposed nor built from simpler substances by physical or chemical methods.

PHYSICAL AND CHEMICAL PROPERTIES

Physical properties are those which can be measured or observed without changing the identity or composition of the substance, For example, mass, volume, density, etc.

Chemical properties are those in which a chemical change occurs in the substance.

Many physical properties of the substance are quantitative in nature. Such properties are, therefore, called *physical quantities*.

All such quantities which we come across during our scientific studies are called *physical quantities*.

The measurement of any physical quantity consists of two parts :

(a) the number (b) the unit

- The accuracy of the number is expressed using the concept of significant figures.
- The units of measurement are expressed in S.I. units.
- The unit of any physical quantity derived using the concept of dimensional analysis.

UNIT AND MEASUREMENT

Out of many systems of measurements SI system (International System of Units) is commonly used.

S.I.unit :

The international system of units (abbreviated as SI) was established by the 11th General conference on weights and measures. The SI system has seven base units which pertain to seven fundamental scientific quantities. The other physical quantities such as speed, volume, density, etc. can be derived from these quantities.

The SI system has seven base units which are listed as

Physical Quantity	Symbol for quantity	Name of Unit	Symbol for unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Temperature	T	kelvin	K
Electric current	I	ampere	A
Luminous intensity	I_v	candela	cd
Amount of substance	n	mole	mol

Some Commonly Used Physical Quantities and Their Derived Units

Physical quantity	Definition	Unit	Symbol
Area	length square	square metre	m^2
Volume	length cube	cubic metre	m^3
Density	mass/unit volume	kilogram per cubic metre	$kg\ m^{-3}$
Velocity	distance/unit time	metre per second	ms^{-1}
Acceleration	speed change/ unit time	metre per second square	ms^{-2}
Force	mass × acceleration	Newton	$N = kg\ m\ s^{-2}$
Pressure	force/unit area	pascal	$P = Nm^{-2} = kg\ m^{-1}s^{-2}$
Work, energy	force × distance	joule	$J = Nm = kg\ m^2s^{-2}$

Uncertainty in measurement

Uncertainty of measurement is the doubt that exists about the result of any measurement. In any circumstances, a single measurement of a quantity is often sufficient for the purposes of the measurement being taken. The uncertainty of a single measurement is limited by the precision and accuracy of the measuring instrument, along with any other factors that might affect the ability of the experimenter to make the measurement and it is up to the experimenter to estimate the uncertainty

Scientific Notation

Scientific notation is exponential notation in which any number can be represented in the form $N \times 10^n$ where n is an exponent having positive or negative values. N is a number and can vary between 1 to 10.

Here are some examples of numbers written in scientific notation:

$34{,}000 = 3.47 \times 10^7$

$0.0000613 = 6.13 \times 10^{-5}$

Precision and Accuracy

Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result. For example let the true value for a result be 2.00 g. A student '*A*' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise but not accurate. Another student repeats the experiment and obtains 1.94 g and 2.05 g as result. These observations are neither precise nor accurate. A third student repeats the measurements and reports 2.01 g and 1.99 g as result. These values are both precise and accurate.

Significant Figures

Significant figures in a number are all certain digits plus one doubtful digit. For example, a figure 10.52 has four significant figures, the last digit (2) having a greater uncertainty than other digits. Note that the decimal point does not determine the number of significant figures. There are several general rules governing the significance of zeros: a) Final zeros after a decimal points are significant figures; b) Final zeros before a decimal point may or may not be significant .c) If a number is less than one, zeros following the decimal point are not significant but those following the digits would be, for example , $\underline{0.00}12300$, the zeros underlined are not significant but the zeros after 123 are significant.

Rules for determining significant figures :

(a) All non-zero digits are significant. For example, 768 cm has three significant figures and 0.768 also has three significant figures.

(b) Zeros to the left of the first non-zero digit in the number are not significant. For example, 0.008 gram has only one significant figure; 0.036 has two significant figures.

(c) Zeros between non-zero digits are significant. For example, 3.05 has three significant figures.

(d) Zeros to the right of the decimal point are significant. For example, 6.00,0.060, 0.6000 have three, two and four significant figures respectively.

(e) If a number ends in zeros that are not to right of a decimal, the zeros may or may not be significant. For example, 3800 cm may be have two, three or four significant figures.

Calculations with Significant Figures

Carrying out calculations with these numbers, the rule used is that the accuracy of the final result is limited to the least accurate measurement.

Rounding off : The rules employed for rounding off a number to the required number of significant digits are as follows –

(a) If the digit to be retained is less than five, the last digit is left unchanged. For example, 1.35083, here 3 is less than 5 so round off number is 1.3508.

(b) If the digit following the last digit to be retained is more than five, the last digit retained is increased by one. For example, 82.87 is to be round off to three significant digits. Since 7 is more than five, therefore, 8 would be increased by one to 9. The result in terms of significant figures would be expressed as 82.9.

(c) If the digit following the last digit to be retained is equal to five, the last digit is left unchanged, if it is even and is increased by one if it is odd. For example, 1.85, significant figure is 1.8; 1.75, significant figure is 1.8.

(i) Addition and subtraction :

In addition and subtraction the final result should be reported to the same number of decimal places as the number with the minimum number of decimal places.

Example 1 :

$$\begin{array}{r} 2.345 \\ +1.23 \\ \hline 3.575 \\ \hline \end{array} \quad \text{(Rounded off to 3.58)}$$

Example 2 :

$$\begin{array}{r} 44.341 \\ -\ \ 1.4432 \\ \hline 42.8978 \\ \hline \end{array} \quad \text{(Rounded off to 42.898)}$$

(ii) Multiplication and division :

In multiplication and division, the final result should be reported as having the same number of significant digits as the number with least number of significant digits.

Example 1 : $3.9898 \times 0.23 = 0.917654$ (Rounded off to 0.92)

Example 2 : $\frac{4.25417\text{ cm}}{627\text{ cm}} = 0.00678496$ (Rounded off to 0.00678)

Dimensional Analysis

Often while calculating, there is a need to convert units from one system to other. The method used to accomplish this is called factor label method or unit factor method or dimensional analysis.

Some Useful Conversion Factors

(i) From given unit to another unit :

Units of length	Units of mass	Units of volume
1 mile = 1760 yards	1 metric ton = 1000 kg	1 $m^3 = 10^3$L
1 yard = 3 feet	1 kg = 1000 g	1 dm^3 = 1 L
1 foot = 12 inches	1 g = 1000 mg	1 $cm^3 = 10^{-3}$L
1 inch = 2.54 cm	1 *l*b = 453.6 g	1 quart = 0.9464 L
1 metre = 100 cm	1 Oz = 28.35 g	1 L = 1.056 quarts
1 km = 1000 m	1 g = 15.4 grains	1 US gallon = 4.55 L
	1 carat = 3.168 grains	= 0.83 British gallon

(ii) From given unit to S.I. unit :

1Å = 10^{-10} m

1 a.m.u. = 1.66053×10^{-27} kg

t°C = t + 273.15 K $\simeq$ t + 273 K

1 litre = $10^{-3}m^3$ = 1dm^3

1 dyne = 10^{-5} N

1 atm = 760 mm or torr = 101, 325 Pa or Nm^{-2}

= 1.013×10^6 dynes/cm^2

1 bar = 10^5 Nm^{-2} = 10^5 Pa

1 mm or 1 torr = 133.322 Pa or Nm^{-2}

1 calorie = 4.184 J

1 erg = 10^{-7} J

1 electron volt (ev) = 1.6022×10^{-19}J

LAWS OF CHEMICAL COMBINATION

Law of Conservation of Mass

(i) This law was given by "**Lavoisier**" in 1744.

(ii) This law states that "matter can neither be created nor destroyed, or in a chemical reaction, the total mass of the reactants is equal to the total mass of the products".

Example 1:

$2Mg + O_2 \longrightarrow 2MgO$

2 × 24 32 2(24 + 16)

48 32 2(40) = 80

Total mass of reactants = Total mass of product = 80

Example 2 :

$C + O_2 \longrightarrow CO_2$

12 32 12 + 32 = 44

Total mass of reactants = Total mass of product = 44

(iii) The exception to this law is nuclear reactions where **Einstein's equation** ($E = mc^2$) is applicable.

Law of Constant Composition or Definite Proportions

(i) This law was given by "**Proust**" in 1799.

(ii) This law states that "All pure samples of the same chemical compound contain the same elements combined in the same proportion by weight".

Example : Different samples of carbon dioxide contain carbon and oxygen in the ratio of 12 : 32 or 3 : 8 by weight. Similarly in H_2O ratio of weight of hydrogen to oxygen is 1 : 8.

Law of Multiple Proportions

(i) This law was given by **John Dalton** in 1804.

(ii) This law states that *"When two elements A and B combine together to form more than one compound, then masses of A which separately combine with a fixed mass of B, are in a simple ratio."*

Example : CO and CO_2

12 : 16 12 : 32

Ratio of masses of oxygen in CO and CO_2 = 16 : 32 = 1 : 2

Similarly, H_2O and H_2O_2

2 : 16 2 : 32

Ratio of masses of oxygen in H_2O and H_2O_2 = 16 : 32 = 1 : 2

Law of Reciprocal Proportions

(i) This law was given by "**Richer**" in 1792–94.

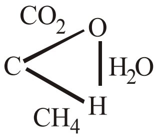
(ii) This law states that *"When two elements combines separately with third element and form different types of molecules their combining ratio is directly reciprocated if they combine directly"*.

Example 1:

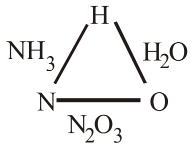
$C + O_2 \longrightarrow CO_2$, $C + 2H_2 \longrightarrow CH_4$

12 32 12 4

C combines with O to form CO_2 and with H to form CH_4. In CO_2, 12 gm of C reacts with 32 gm of O, where as in CH_4, 12 gm of C reacts with 4 gm of H. Therefore when O combines with H, they should combine in the ratio of 32 : 4 (i.e. 8 : 1) or in simple multiple of it. The same ratio is found to be true in H_2O molecule, the ratio of weight of H and O in H_2O is 1 : 8.



Example 2: NH_3, H_2O and N_2O_3



Law of Gaseous Volume

(i) This law was given by "**Gay lussac**" in 1808.

(ii) This law states that *"Whenever gases react together, the volumes of the reacting gases as well as the products if they are gases, bear a simple whole number ratio, provided all the volumes are measured under similar conditions of temperature and pressure.*

Example 1 :

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

1 unit vol. 1 unit vol . 2 unit vol.

ratio = 1 : 1 : 2

Example 2 :

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

1 unit vol . 3 unit vol. 2 unit vol.

ratio = 1 : 3 : 2

Avogadro Hypothesis

(a) *"Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules"*

Example : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

2 unit vol. 1 unit vol. 2 unit vol.

Ratio of number of molecules = 2 : 1 : 2

(b) This law helped to remove anomaly between **Dalton's atomic theory** and **Gaylussac's law** of volume by making a clear distinction between atoms and molecules.

(c) It reveals that common elementary gases like hydrogen, nitrogen, oxygen etc. are diatomic.

(d) It provides a method to determine the molecular weights of gaseous elements.

(e) It provides a relationship between vapour density and molecular weight of substances.

molecular weight of gas = 2 × vapour density.

DALTON'S ATOMIC THEORY

In 1808, **Dalton** published '*A new system of chemical philosophy*' in which he proposed the following :

(a) Matter consists of indivisible atoms.

(b) All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.

(c) Compounds are formed when atoms of different elements combine in a fixed ratio.

(d) Atoms are neither created nor destroyed in a chemical reaction. **Dalton's theory** could explain the laws of chemical combination.

ATOMIC MASSES

Atomic mass of an element may be defined as a number which indicates that average mass of an atom is how many times heavier as compared with 1/12th of the mass of an atom of carbon 12(C^{12}).

$$\text{At. mass of an element} = \frac{\text{Average mass of an atom}}{\frac{1}{12}\times\text{Mass of an atom of } C^{12}}$$

Thus, the atomic masses of elements are average relative masses.

Units of atomic mass:

The modern definition of atomic mass is $\frac{1}{12}^{\text{th}}$ of the mass of the atom of C-12. Thus, atomic mass of an element is a simple ratio and has no unit but expressed in amu (or u, unified mass).

$$1\text{amu} = \frac{1}{12}\times \text{ mass of C-12 atom}$$

The real mass of one atom of C-12 has been determined as 1.9924×10^{-23} g.

$$\therefore \quad 1 \text{ a.m.u.} = \frac{1.9924 \times 10^{-23}}{12} \text{g} = 1.66 \times 10^{-24} \text{g}$$

1.66×10^{-24} g is referred to as the gram equivalent of a.m.u.

Average Atomic Mass

Atomic masses of many elements are not whole number due to the presence eof stable isotopes. For example, natural chlorine is a mixture of two isotopes, *viz.,* Cl-35 (75% abundance) and Cl-37 (25% abundance). Thus, atomic mass of chlorine is

$$\frac{75 \times 35 + 25 \times 37}{100} = 35.5 \text{ amu}$$

Thus, the average atomic mass of an element depends upon (i) the mass numbers of isotopes and (ii) relative abundance of these isotopes.

Average mass of one atom of an element = At. mass × 1.66×10^{-24} g

Thus, average mass of 1 atom of hydrogen = $1.008 \times 1.66 \times 10^{-24}$ g = 1.673×10^{-24} g

Gram Atomic Mass (GAM)

Atomic mass of an element when expressed in grams is called its gram atomic mass or gram atom or mole atom.

(a) No. of gram atom or mole atoms = $\dfrac{\text{Mass of an element}}{\text{GAM}}$

(b) $\therefore$ Mass of an element in g = No. of g atoms × GAM

(c) No. of atoms in 1 GAM = 6.022×10^{23}

$\therefore$ No. of atoms in given substance = No. of GAM × 6.022×10^{23} = $\dfrac{\text{Mass of an element}}{\text{GAM}} \times 6.02 \times 10^{23}$

for example, No. of atoms in 5.4 g of Ag = $\dfrac{5.4}{108} \times 6.022 \times 10^{23} = 3.01 \times 10^{23}$

(d) No. of atoms in 1 g of an element = $\dfrac{6.022 \times 10^{23}}{\text{At. Mass}}$

(e) Mass of one atom of the element (in g) = $\dfrac{\text{GAM}}{6.022 \times 10^{23}}$

for example, Mass of 1 atom of S = $\dfrac{32}{6.022 \times 10^{23}} = 5.33 \times 10^{-23}$ g

Illustration 1 :

A signature written in carbon pencil weighs 1 mg. Determine the number of carbon atoms present in the signature.

Solution: Amount of carbon in the signature = 1 mg = 0.001 g

$\therefore$ No. of atoms of carbon in 0.001 g = $\dfrac{0.001}{12}$

No. of carbon atoms in 0.001 / 12 g atom of C = $\dfrac{0.001 \times 6.02 \times 10^{23}}{12} = 5.02 \times 10^{19} = 0.502 \times 10^{20}$

MOLECULAR MASS

It is the relative mass of a molecule of an element or a compound as compared to 1/12 of the mass of one atom of C-12.

Thus, **molecular mass is also a ratio and hence, has no units.** It is expressed in amu (u).

$$\text{Mol. mass} = \frac{\text{Mass of one molecule of the substance}}{(1/12) \times \text{ Mass of one atom of C-12}}$$

Actual mass of one molecule = Mol. mass × 1.66×10^{-24}g

Molecular mass of a substance is the additive property and can be calculated by adding the atomic masses of the elements present in one molecule.

Gram Molecular Mass (GMM)

Molecular mass of an element or compound when expressed in gram is called its gram molecular mass, gram molecule or mole molecule.

$$\text{No. of gram molecules or mole molecules} = \frac{\text{Mass of substance}}{\text{GMM}}$$

$\therefore$ Mass of substance in g = No. of g molecules × GMM

Formula Mass

The formula mass of a compound is the amount of that compound that has the same mass in grams as the formula mass in atomic mass unit. An atom of each element has a characteristic mass and in the same manner each molecule of a compound has a characteristic formula mass.

When the formula mass of an ionic compound is determined by the addition of its component is atomic masses and expressed in grams, it is called the **Gram Formula Mass**.

MOLE CONCEPT

Molecules and atoms are extremely small objects - both in size and mass and their numbers in even a very small amount of any substance is really very large. Consequently, working with them in the laboratory requires a large collection of them. To handle such large numbers a standard needs to be introduced. This standard is the "mole". The mole is based upon the carbon-12 isotope.

In the SI system the **mole** is measure of quantity of a "chemical entity", which can be an atom, molecule, formula unit, electron or photon.

One mole is the amount of substance which contains as many elementary particles or entities as there are atoms in 0.012 kilogram of carbon-12.

Avagadro's number $N_A = 6.022 \times 10^{23}$, like any pure number, is dimensionless. It is commonly known as **Avogadro's constant.**

1 mole of an atom means 1 GAM of it and 1 mole of a compound means 1 GMM of it

Thus, 1 mole of N_A weighs 23 g

1 mole of H_2O weighs 18 g

1 mole of H_2 weighs 2 g

1 mole of any substance contains 6.022×10^{23} particles.

1 mole molecule of NaOH = 6.022×10^{23} molecules of NaOH = 40 g of NaOH

Thus, 1 mole = 1 g molecule = 1 g molecular mass = molecular mass in g

= 22.4 litres at NTP (only for gases) = 6.022×10^{23} molecules = 1 g atomic mass

= Atomic mass in g = 6.022×10^{23} atoms

$$\text{Number of moles} = \frac{\text{Mass of substance in g}}{\text{g mol. mass}} = \frac{\text{No. of unitary particles}}{\text{Avogadro's number}} = \frac{\text{Volume in litre at NTP}}{22.4\text{ litre}}$$

Gram Molar Volume (GMV)

Volume occupied by one mole of any gas at STP is called gram molar volume. The value of gram molar volume is 22.4 litres. Volume of 1 mole of any gas at STP is 22.4 litres.

Thus, Volume of 1 mole of H_2 or 2 g of H_2 at STP = 22.4 lit

$$\text{Volume of 16 g}\left(\frac{1}{2}\text{ mole}\right)\text{ of }O_2 = 11.2\text{ lit}$$

$$\text{Volume of 7 g}\left(\frac{1}{4}\text{ mole}\right)\text{ of }N_2 = 5.6\text{ lit}$$

$$\text{Volume of 0.5 g}\left(\frac{1}{4}\text{ mole}\right)\text{ of }H_2 = 5.6\text{ lit}$$

$$\text{Volume of 16 g (1 mole) of }CH_4 = 22.4\text{ lit}$$

Points to Remember : (a) Mass of 11.2 L of any gas at STP = VD of that gas in gram

(b) Density of a gas at NTP = $\frac{\text{Mol. mass in g}}{\text{22400 mL}}$

Important generalizations :

(a) No. of molecules of a substance = No. of GMM × $6.022 \times 10^{23} = \frac{\text{Mass}}{\text{GMM}} \times 6.022 \times 10^{23}$

For example, No. of molecules in 1.8 g $H_2O = \frac{1.8}{18} \times 6.022 \times 10^{23} = 6.022 \times 10^{22}$

(b) Mass of 1 molecule of a substance (in g) = $\frac{\text{GMM}}{6.022 \times 10^{23}}$

For example, Mass of 1 molecule of $SO_2 = \frac{64}{6.022 \times 10^{23}}$

(c) No. of molecules in 1 g of a compound = $\frac{6.022 \times 10^{23}}{\text{Mol. mass}}$

(d) No. of atoms in a substance = No. of GMM × 6.022×10^{23} × Atomicity

For example, No. of atoms in 32 g of $CH_4 = \frac{32}{16} \times 6.022 \times 10^{23} \times 5 = 6.022 \times 10^{24}$

(e) No. of electrons in a given substance = No. of GMM × 6.022×10^{23} × No. of electrons

For example, No. of electrons in 4 g of $CH_4 = \frac{4}{16} \times 6.022 \times 10^{23} \times 10 = 1.5 \times 10^{24}$

No. of neutrons in 1.8 g of $H_2O = \frac{1.8}{18} \times 6.022 \times 10^{23} \times 8 = 4.82 \times 10^{23}$

PERCENTAGE COMPOSITION

The percent composition of a compound is an expression of the elemental composition of that compound. The percent composition of each element (actually the mass percent) is equal to the mass of that element divided by the total mass present (the formula mass) multiplied by 100%.

$$\%\ \text{Composition A} = \frac{\text{mass of A}}{\text{total mass}} \times 100\%$$

The sum of the percent (by mass) of each element in a compound equal to 100%.

Illustration 2 :

Find the present composition of calcium (Ca), oxygen (O) and hydrogen (H) in calcium hydroxide $Ca(OH)_2$?

Solution: The formula mass of calcium hydroxide can be calculated as

1. Ca (amu = 40) = 40

2. O (amu = 16) = 2 × 16 = 32

3. H (amu = 1) = 2 × 1 = 2

Formula mass $Ca(OH)_2$ = 74 amu

Therefore percent composition for Ca = 40 amu/74 amu × 100% = 54% calcium

Percent composition of O = 32 amu/74 amu × 100% = 43% Oxygen

Percent composition of H = 2 amu/74 amu × 100% = 2.7% Hydrogen

CHEMICAL FORMULA

A chemical formula is the combination of atoms of all elements which make up a compound. It represents the relative ratio of atoms of its constituent elements. Chemical formula of a compound represents one molecule, one mole, one gram molecular mass of that compound.

Empirical Formula

The relative number of atoms of each element in one molecule of that compound is indicated by its empirical formula (simplest formula)

Determination of empirical formula:

(a) Divide present composition of each element by, its atomic weight.

(b) Divide all the numbers by the smallest of them.

(c) Multiply these numbers with a suitable number to make them whole numbers (if they are not whole numbers).

(d) Write the empirical formula in the ratio of atoms of each element as obtained above.

Illustration 3 :

2.2 g of a compound of phosphorus and sulphur has 1.24 g of P in it. Determine its empirical formula.

Sol. $P : S = \frac{1.24}{31} : \frac{0.96}{32} = 0.04 : 0.03 = 4 : 3$

$\therefore$ Empirical formula = P_4S_3

Illustration 4 :

A sample of pure compound is found to have Na = 0.0887 mole, O = 0.132 mole, C = 2.65 × 10^{22} atoms. What is the empirical formula of the compound?

Sol. Calculation of number of moles in 2.65 × 10^{22} atoms of carbon

6.022 × 10^{23} atoms of C = 1 mole of C

$$2.65 \times 10^{22} \text{ atoms of C} = \frac{1 \times 2.65 \times 10^{22}}{6.022 \times 10^{23}} \text{ mole} = \frac{2.65}{6.022 \times 10} = 0.044 \text{ mole}$$

Determination of empirical formula

Element	Relative No. of moles	Simple ratio of mole
Na	0.0887	$\frac{0.0887}{0.044} = 2$
O	0.132	$\frac{0.0132}{0.044} = 3$
C	0.044	$\frac{0.044}{0.044} = 1$

Thus, the empirical formula of the compound is Na_2CO_3.

Molecular Formula

The actual number of atoms of each element present in the molecule of a substance is called its molecular formula.

Molecular formula = Empirical formula × n

$$\text{where, } n = \frac{\text{Mol. mass}}{\text{Empirical formula mass}}$$

Illustration 5 :

1 volume of a gaseous compound requires 2 volumes of O_2 for combustion and gives 2 volumes of CO_2 and 1 volume of N_2. Determine the molecular formula of the compound.

Sol. According to problem,

$$S_xCl_y \rightarrow xSO_4^{2-} + yCl^- \rightarrow xBaSO_4 + \frac{y}{2}PbCl_2$$

$$0.1 \text{ mole of } S_xCl_y = 0.1 \times \text{mole of } BaSO_4 + \frac{0.1}{2} \text{ mole of } PbCl_2$$

or $0.1x = 0.2$ $\quad x = 2$

$\frac{0.1y}{2} = 0.1$ $\quad y = 2$

$\therefore$ Molecular formula = S_2Cl_2

STOICHIOMETRY AND STOICHIOMETRIC CALCULATION

Calculation based on chemical equations are known as stiochiometry. A chemical equation is the symbolic representation of a chemical change. it supplied following information used in solving problem based on a chemical equation:

(a) It indicates the number of moles of the reactants involved and number of moles of the products formed.

(b) It gives the relative weight of the reactants and products.

(c) It gives the volume of the gaseous reactants and products.

For example, the equation $CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$
indicates that

(i) 1 mole of $CaCO_3$ gives 1 mole of CaO and 1 mole of CO_2.

(ii) 100 g (mol. wt. of $CaCO_3$) of $CaCO_3$ gives 56 g of CaO and 44 g (or 22.4 litres) of carbon dioxide.

Limiting Reagent

It may be defined as the reactant which is completely consumed during the reaction. A reactant that is not completely consumed is often referred to as an excess reactant. Once one of the reactant is used up, the reaction stop. The moles of product are always determined by the starting moles of limiting reactant.

Illustration 6 :

Calculate the mass of oxygen required to burn 14g of C_2H_4 completely :

Sol.

$$\begin{array}{lcccc} & C_2H_4 + & 3O_2 \longrightarrow & 2CO_2 + & 2H_2O \\ \text{Mole ratio} & 1 & 3 & 2 & 2 \end{array}$$

Moles of C_2H_4 to be burnt $= \frac{14}{28} = \frac{1}{2}$ mole.

$\because$ 1 mole C_2H_4 requires = 3 moles of O_2 for combustion

$\therefore \frac{1}{2}$ mole C_2H_4 requires $= 3 \times \frac{1}{2}$ mole $O_2 = \frac{3}{2}$ mol O_2

Mass of oxygen = 3/2 × 32 = 48 gm.

Illustration 7 :

10 ml of liquid carbon disulphide (sp. gravity 2.63) is burnt in oxygen. Find the volume of the resulting gases measured at STP.

Sol. 1 ml of CS_2 weighs 2.63 g

10 ml of CS_2 weighs 26.3 g

$$\underset{\substack{12+(2\times32)\\ \\76\text{ gm}}}{CS_2} + 3O_2 \longrightarrow \underbrace{\underset{22.4\text{ lit}}{CO_2} \quad + \quad \underset{44.8\text{ lit}}{2SO_2}}_{67.2\text{ lit}}$$

$\because$ 76 g of CS_2 will yield 67.2 lit of a mixture of CO_2 and SO_2 at STP.

$\therefore$ 26.3 g of CS_2 would yield $= \frac{67.2}{76} \times 26.3 = 23.26$ lit.

Expression of Strength/Concentration of Solution

"The amount of solute which dissolves in unit volume of solution is called concentration of solution".

$$\text{Concentration} = \frac{\text{Amount of solute}}{\text{Volume of solution}}$$

(i) Weight-weight percent (w/W) :

Weight of solute in grams present in 100 gm of the solution.

$$\text{Weight percent} = \frac{\text{Weight of solute (gm)}}{\text{Weight of solution (gm)}} \times 100$$

$$\text{\% by weight} = \frac{w}{W} \times 100$$

Illustration 8 :

What is the weight percentage of urea solution in which 10gm urea is dissolved in 90gm of water.

Sol. Weight % of urea $= \frac{\text{Weight of urea}}{\text{Weight of solution}} \times 100 = \frac{10}{90+10} \times 100 = 10\%$ urea solution (w/W)

(ii) Normality : The number of gram equivalents of the solute dissolved per litre of the solution. It is denoted by 'N'

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{volume of solution (lit.)}}$$

$$\because \text{ Gram equivalents of solute} = \frac{\text{weight of solute (gm)}}{\text{Equivalent weight of solute}}$$

$$\therefore \text{ Normality} = \frac{\text{weight of solute (gm)}}{\text{Equivalent weight of solute}} \times \frac{1}{\text{volume of solution (lit.)}}$$

Illustration 9 :

4 gm NaOH is present in 100 ml of the solution. What is the normality ?

Sol. Normality $= \frac{w}{E} \times \frac{1000}{V\text{ (ml)}} = \frac{4}{40} \times \frac{1000}{100} = 1\text{ N}$

(iii) Molarity : It is the number of moles of solute present in one litre of solution.

$$\text{M} = \frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$$

$$= \frac{\text{Weight of solute}}{\text{GMM of solute} \times \text{Volume of solution (L)}}$$

$\Rightarrow$ Moles $= \text{M} \times \text{V}_{(\text{in litre})}$ and millimoles $= \text{M} \times \text{V}_{(\text{in ml})}$.

Molarity and mass percentage have the relation M

$$= \frac{\text{mass percentage} \times 10 \times \text{d}}{\text{GMM of solute}}, \qquad \text{where d = density}$$

If a solution of molarity M_1 and volume V_1 adds up with a solvent to a final volume V_2, then molarity M_2 is given by

$$\text{M}_2 = \frac{\text{M}_1\text{V}_1}{\text{V}_2}$$

If two different solutions (M_1, V_1) and (M_2, V_2) are mixed then molarity of resulting solution is

$$\text{M} = \frac{\text{M}_1\text{V}_1 + \text{M}_2\text{V}_2}{\text{V}_1 + \text{V}_2}$$

Also, Molarity × GMM of solute = Normality × GEM of solute

Illustration 10 :

3.65 gm HCl gas is present in 100 ml of its aqueous solution. What is the molarity of solution ?

Sol. Molarity $= \frac{w}{M'} \times \frac{1000}{\text{volume(ml.)}} = \frac{3.65}{36.5} \times \frac{1000}{100} = 1\text{ M}$

$\therefore$ we have, 1M solution of HCl.

(iv) Molality : The number of gram moles of solute dissolved in 1000 gm or 1 kg of the solvent. It is denoted by 'm'

$$\text{molality} = \frac{\text{Gram moles of solute}}{\text{weight of solvent (kg)}}$$

$$\therefore \text{ Gram moles of solute} = \frac{\text{weight of solute (gm)}}{\text{Molecular weight of solute}}$$

$$\text{Molality} = \frac{\text{weight of solute (gm)}}{\text{Molecular weight of solute}} \times \frac{1}{\text{weight of solvent (kg)}}$$

Formula :

$$m = \frac{w}{M'} \times \frac{1}{W(\text{kg})} \qquad \text{............. (i)}$$

$$m = \frac{w}{M'} \times \frac{1000}{W(\text{gm})} \qquad \text{.............. (ii)}$$

$$m = n_M \times \frac{1}{W(\text{kg})} \qquad \text{........... (iii)}$$

where w = weight of solute, M' = molecular weight of solute, W = weight of solvent, n_M = no. of moles of solute.

Illustration 11 :

8 gm of NaOH dissolved in water to form 500 ml of its aqueous solution. If density of the solution is 1.2 gm/ml, then find the molality of the solution.

Sol. Weight of solute = 8 gm

Volume of solution = 500 ml

Density of solution = 1.2 gm/cm^3

∴ Weight of solution = 500 × 1.2 = 600 gm.

∴ Weight of solvent = weight of solution – weight of solute = 600 – 8 = 592 gm

$$\therefore\ m = \frac{w}{M'} \times \frac{1000}{W} = \frac{8}{40} \times \frac{1000}{592} = 0.34$$

(v) Mole fraction : The mole fraction of a component in a solution is the ratio of the number of moles of that component to the total number of moles present in the solution.

$$\text{Suppose : } \left.\begin{matrix} A - \text{Solute} \\ B - \text{Solvent} \end{matrix}\right\} \text{Solution}$$

n_A = No. of moles of solute,

n_B = No. of moles of solvent

Then, mole fraction of solute $= x_A = \dfrac{n_A}{n_A + n_B}$

Mole fraction of solvent $= x_B = \dfrac{n_B}{n_A + n_B}$

$$x_A + x_B = 1$$

EQUIVALENT WEIGHT

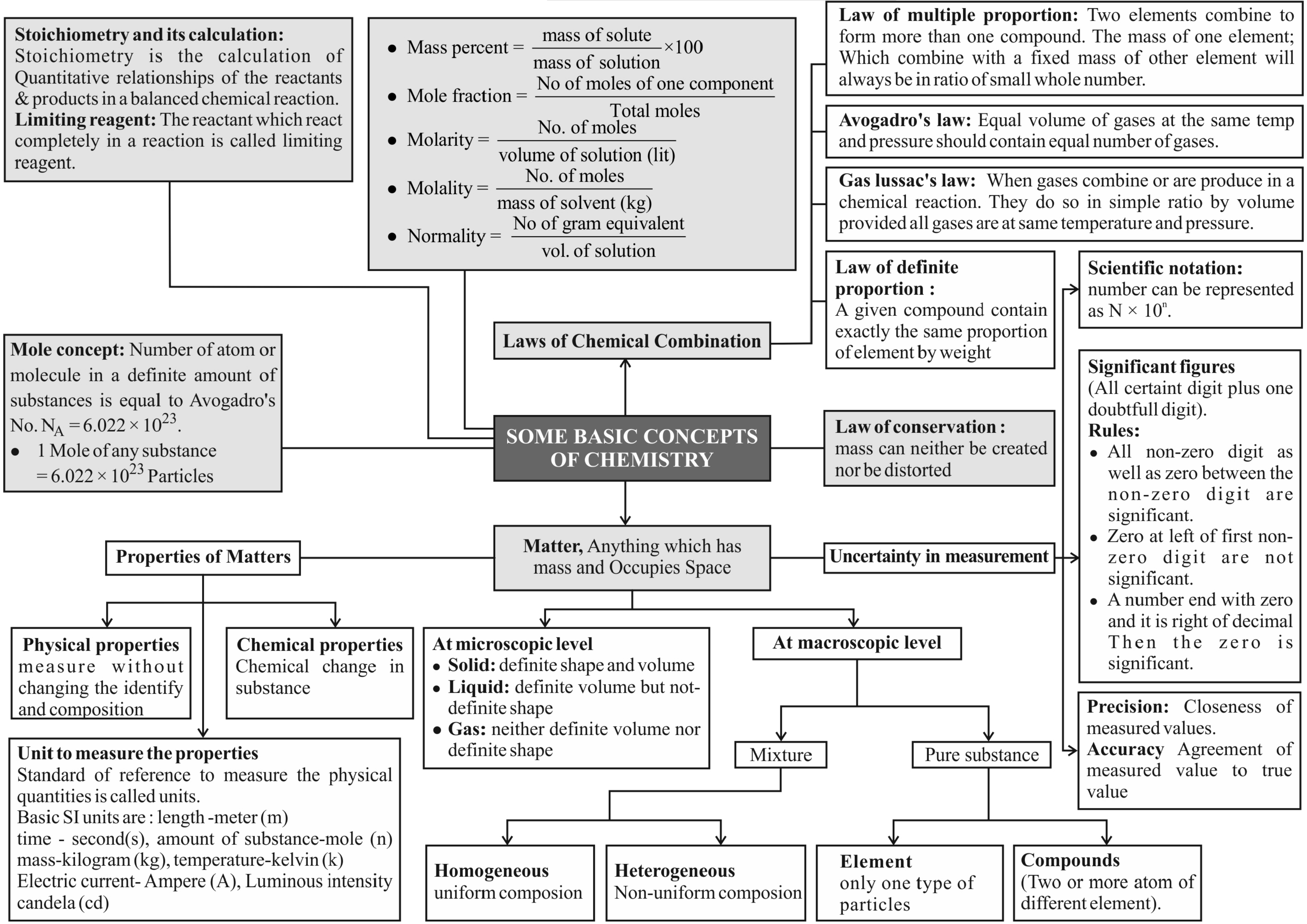
Equivalent weight of a substance (element or compound) is defined as *"The number of parts by weight of it, that will combine with or displace directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen, 35.5 parts by weight of chlorine or the equivalent parts by weight of another element".*

Equivalent weight of a substance depends on the reaction in which it take part.

Equivalent weight is a relative quantity so it is unit less. When equivalent weight of a substance is expressed in grams, it is called *Gram equivalent weight (GEW).*

- Equivalent mass of elements = At. mass/ valency
- Eq. wt of an acid $= \dfrac{\text{Molecular mass}}{\text{Basicity of acid}}$
- Eq. wt of a base $= \dfrac{\text{Molecular mass}}{\text{Acidity of base}}$
- Equivalent mass for salts $= \dfrac{\text{Formula mass}}{\text{(Valency of cation) (No. of cations)}}$
- Equivalent mass for oxidising agents $= \dfrac{\text{Formula mass}}{\text{No. of electrons gained per molecule}}$
- Equivalent mass for reducing agents $= \dfrac{\text{Formula mass}}{\text{No. of electrons lost per molecule}}$

CONCEPT MAP



SOME BASIC CONCEPTS OF CHEMISTRY

Stoichiometry and its calculation: Stoichiometry is the calculation of Quantitative relationships of the reactants & products in a balanced chemical reaction. **Limiting reagent:** The reactant which react completely in a reaction is called limiting reagent.

- Mass percent = $\frac{\text{mass of solute}}{\text{mass of solution}} \times 100$
- Mole fraction = $\frac{\text{No of moles of one component}}{\text{Total moles}}$
- Molarity = $\frac{\text{No. of moles}}{\text{volume of solution (lit)}}$
- Molality = $\frac{\text{No. of moles}}{\text{mass of solvent (kg)}}$
- Normality = $\frac{\text{No of gram equivalent}}{\text{vol. of solution}}$

Mole concept: Number of atom or molecule in a definite amount of substances is equal to Avogadro's No. $N_A = 6.022 \times 10^{23}$.

- 1 Mole of any substance $= 6.022 \times 10^{23}$ Particles

Laws of Chemical Combination

Law of multiple proportion: Two elements combine to form more than one compound. The mass of one element; Which combine with a fixed mass of other element will always be in ratio of small whole number.

Avogadro's law: Equal volume of gases at the same temp and pressure should contain equal number of gases.

Gas lussac's law: When gases combine or are produce in a chemical reaction. They do so in simple ratio by volume provided all gases are at same temperature and pressure.

Law of definite proportion : A given compound contain exactly the same proportion of element by weight

Law of conservation : mass can neither be created nor be distorted

Matter, Anything which has mass and Occupies Space

Uncertainty in measurement

Scientific notation: number can be represented as $N \times 10^n$.

Significant figures (All certaint digit plus one doubtfull digit).

Rules:

- All non-zero digit as well as zero between the non-zero digit are significant.
- Zero at left of first non-zero digit are not significant.
- A number end with zero and it is right of decimal Then the zero is significant.

Precision: Closeness of measured values. **Accuracy** Agreement of measured value to true value

Properties of Matters

Physical properties measure without changing the identify and composition

Chemical properties Chemical change in substance

Unit to measure the properties Standard of reference to measure the physical quantities is called units.
Basic SI units are : length -meter (m)
time - second(s), amount of substance-mole (n) mass-kilogram (kg), temperature-kelvin (k)
Electric current- Ampere (A), Luminous intensity candela (cd)

At microscopic level

- **Solid:** definite shape and volume
- **Liquid:** definite volume but not-definite shape
- **Gas:** neither definite volume nor definite shape

At macroscopic level

Mixture

Pure substance

Homogeneous uniform composion

Heterogeneous Non-uniform composion

Element only one type of particles

Compounds (Two or more atom of different element).

Textbook Exercises

1.1 Calculate the molecular mass of the following :
(i) H_2O (ii) CO_2 (iii) CH_4

Ans. (i) Molecular mass of H_2O = 2 (1 .008 amu) + 16 .00 amu = 18.016 amu.

(ii) Molecular mass of CO_2 = 12.01 amu + 2×16.00 amu = 44.01 amu.

(iii) Molecular mass of CH_4 = 12.01 amu + 4 (1.008 amu) = 16.042 amu.

1.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

Ans. Mass % of an element

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

Now, molar mass of

$Na_2SO_4 = 2\,(23.0) + 32\,.0 + 4 \times 16\,.0 = 142\ \text{g mol}^{-1}$

Mass percent of sodium, Na $= \frac{46}{142} \times 100 = 32.39\%$

Mass percent of sulphur, S $= \frac{32}{142} \times 100 = 22.54\%$

Mass percent of oxygen, O $= \frac{64}{142} \times 100 = 45.07\%$

1.3 Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass.

Ans.

Element	Symbol	%by mass	Atomic mass	Moles of the element	Simplest molar ratio	Simplest whole number molar ratio
Iron	Fe	69.9	55.85	$\frac{69.9}{55.85} = 1.25$	$\frac{1.25}{1.25} = 1$	2
Oxygen	O	30.1	16.0	$\frac{30.1}{16.0} = 1.88$	$\frac{1.88}{1.25} = 1.5$	3

∴ Empirical formula = Fe_2O_3.

1.4 Calculate the amount of carbon dioxide that could be produced when
(i) 1 mole of carbon is burnt in air.
(ii) 1 mole of carbon is burnt in 16 g of dioxygen.
(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

Ans. The balanced equation for the combustion of carbon in dioxygen/air is

$$\begin{array}{lll} C(s) \; + & O_2(g) \longrightarrow & CO_2(g) \\ 1\text{ mole} & 1\text{ mole} & 1\text{ mole} \\ (12\text{ g}) & (32\text{ g}) & (44\text{ g}) \end{array}$$

(i) In air, combustion is complete. Therefore, CO_2 produced from the combustion of 1 mole of carbon = 44g.

(ii) Since only 16 g of dioxygen is available, hence it can combine only with 0.5 mole of carbon, i.e., dioxygen is the limiting reactant. Hence, CO_2 produced = 22 g.

(iii) In this case dioxygen again is the limiting reactant. 16 g of dioxygen can combine only with 0.5 mole of carbon. CO_2 produced again is equal to 22 g.

1.5 Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

Ans. 0.375 M aqueous solution means that sodium acetate is present in 1000 mL of solution.

∴ Moles of sodium acetate present in solution = 0.375/2

Molar mass of sodium acetate = 82.0245 g mol^{-1}

Mass of sodium acetate required

= 0.375/2 mole × 82.0245 g mol^{-1} = 15.380 g.

1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

Ans. Mass percent of 69% means that 100 g of nitric acid solution contain 69 g of nitric acid by mass.

Molar mass of nitric acid (HNO_3) = 1 + 14 + 48 = 63 g mol^{-1}

Moles in 69g of HNO_3 = 69/63 = 1.095 mole

Volume of 100 g nitric acid solution = 100/1.41 = 70.92 mL = 0.07092 L

Conc. of HNO_3 in moles per litre = 1.095 / 0.0792 L = 13.83 M

1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$) ?

Ans. One mole of $CuSO_4$ contains 1 mole (1 g atom) of Cu

Molar mass of $CuSO_4$ = 63.5 + 32 + 4×16 = 159.5 g mol^{-1}.

Thus, amount of Cu that can be obtained from 159.5 g of $CuSO_4$ = 63.5 g

Cu that can be obtained from 100 g of $CuSO_4$

$$= \frac{63.5}{159.5} \times 100\text{ g} = 39\,.81\text{ g}$$

1.8 Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively.

Ans. Calculation of Empirical Formula. Refer Q. 1.3

Empirical formula mass of Fe_2O_3

$= 2 \times 55.85 + 3 \times 16.00 = 159\,.7\ \text{g mol}^{-1}$

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{159.8}{159.7} = 1$$

Hence, molecular formula are empirical formula, viz., Fe_2O_3.

1.9 Calculate the atomic mass (average) of chlorine using the following data :

	% Natural Abundance	**Molar Mass**
^{35}Cl	**75.77**	**34.9689**
^{37}Cl	**24.23**	**36.9659**

Ans. Fractional abundance of ^{35}Cl = 0.7577,

Molar mass = 34 .9689

Fractional abundance of ^{37}Cl = 0.2423,

Molar mass = 36 .9659

Average atomic mass

= (0 .7577) (34.9689 amu) + (0.2423) (36.9659 amu)

= 26.4959 + 8.9568 = 35.4527

1.10 In three moles of ethane (C_2H_6), calculate the following :
(i) Number of moles of carbon atoms.
(ii) Number of moles of hydrogen atoms.
(iii) Number of molecules of ethane.

Ans. (i) 1 mole of C_2H_6 contains 2 moles of carbon atoms. Hence 3 moles of C_2H_6 will contain C–atoms = 6 moles.

(ii) 1 mole of C_2H_6 contains 6 moles of hydrogen atoms. Hence 3 moles of C_2H_6 will contain H–atoms = 18 moles.

(iii) 1 mole of C_2H_6 contains $6.\,02 \times 10^{23}$ molecules. Hence 3 moles of C_2H_6 will contain ethane molecules = $3 \times 6.02 \times 10^{23} = 18.06 \times 10^{23}$ molecules.

1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

Ans. Molar mass of sugar ($C_{12}H_{22}O_{11}$)

$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342\ g\ mol^{-1}$

No. of moles in 20 g of sugar $= \dfrac{20g}{342 g\ mol^{-1}} = 0.0585$ mole

Molar concentration

$$= \frac{\text{Moles of solute}}{\text{Volume of solution}} = \frac{0.0585}{2} = 0.0293\ M$$

1.12 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

Ans. Molar mass of methanol (CH_3OH) = 32 g mol^{-1}

$= 0.032\ kg\ mol^{-1}$

$$\text{As Molarity} = \frac{\text{mass of solute}}{\text{molar mass of solute} \times \text{volume of solution}}$$

$$\text{We can write molarity} = \frac{\text{density of solution}}{\text{molar mass of solute}}$$

Thus the molarity of the given solution will be

$$\frac{0.793\ kg\ L^{-1}}{0.032\ kg\ mol^{-1}} = 24.78\ mol\ L^{-1}$$

$$\text{Applying} \quad \underset{\text{(Given solution)}}{M_1} \times V_1 = \underset{\text{(Solution to be prepared)}}{M_2} \times V_2$$

$24.78 \times V_1 = 0.25 \times 2.5\ L$

or $V_1 = 0.02522\ L = 25.22 mL$

1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below :

1Pa = 1N m^{-2}

If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

Ans. Pressure is the force (i.e., weight) acting per unit area

But weight = mg

Pressure = Weight per unit area

$= 1034\ g \times 9.8\ ms^{-2}/cm^2$

$$= \frac{1034 g \times 9.8 ms^{-2}}{cm^2} \times \frac{1kg \times 100cm \times 100cm}{1000g}$$

$$\times \frac{1N}{1m \times 1m} \times \frac{1Pa}{kg\ m\ s^{-2}} = 1.01332 \times 10^5\ Nm^{-2}$$

$= 1.01332 \times 10^5$ Pa

1.14 What is the SI unit of mass? How is it defined?

Ans. S.I. unit of mass is kilogram (kg). It is equal to the mass of the international prototype of the kilogram. It is defined as the mass of platinum–iridium cylinder that is stored in air–tight jar at International Bureau of Weights and Measures in France.

1.15 Match the following prefixes with their multiples:

	Prefixes	**Multiples**
(i)	**micro**	**10^6**
(ii)	**deca**	**10^9**
(iii)	**mega**	**10^{-6}**
(iv)	**giga**	**10^{-15}**
(v)	**femto**	**10**

Ans. micro = 10^{-6}, deca = 10, mega = 10^6, giga = 10^9, femto = 10^{-15}.

1.16 What do you mean by significant figures?

Ans. The total number of digits in a number including the last digit whose value is uncertain is called the number of significant figures.

1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in percent by mass.

(ii) Determine the molality of chloroform in the water sample.

Ans. (i) 15 ppm means 15 parts in million (10^6) parts,.

$$\% \text{ by mass } \frac{15}{10^6} \times 100 = 15 \times 10^{-4} = 1.5 \times 10^{-3}\ \%$$

(ii) Molar mass of chloroform

($CHCl_3$) = $12 + 1 + 3 \times 35.5 = 119.5\ g\ mol^{-1}$

100 g of the sample contain chloroform

$= 1.5 \times 10^{-3}$ g

$\therefore$ 1000 g (1 kg) of the sample will contain chloroform

$= 1.5 \times 10^{-2}$ g

$$\text{Now molality} = \frac{1.5 \times 10^{-2}}{119.5} = 1.255 \times 10^{-4}\ m$$

$\therefore$ Molality = 1.255×10^{-4} m.

1.18 Express the following in the scientific notation:

(i) 0.0048 **(ii) 234,000**

(iii) 8008 **(iv) 500.0**

(v) 6.0012

Ans. (i) 4.8×10^{-3} (ii) 2.34×10^5

(iii) 8.008×10^3 (iv) 5.000×10^2

(v) 6.0012×10^0

1.19 How many significant figures are present in the following?

(i) 0.0025 **(ii) 208**

(iii) 5005 **(iv) 126,000**

(v) 500.0 **(vi) 2.0034**

Ans. (i) 2 (ii) 3

(iiii) 4 (iv) 3

(v) 4 (vi) 5

1.20 Round up the following upto three significant figures:

(i) 34.216 **(ii) 10.4107**

(iii) 0.04597 **(iv) 2808**

Ans. (i) 34.2 (ii) 10.4

(iii) 0.0460 (iv) 2.80

1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds :

	Mass of dinitrogen	**Mass of dioxygen**
(i)	**14 g**	**16 g**
(ii)	**14 g**	**32 g**
(iii)	**28 g**	**32 g**
(iv)	**28 g**	**80 g**

(a) Which law of chemical combination is obeyed by the above experimental data?

Give its statement.

(b) Fill in the blanks in the following conversions:

(i) 1 km = ... mm = ... pm

(ii) 1 mg = ... kg = ... ng

(iii) 1 mL = ... L = ... dm^3

Ans. (a) Fixing the mass of dinitrogen as 28g, masses of dioxygen combined will be 32,64,32 and 80 g in the given four oxides. These are in the ratio 1: 2:1: 2.5 or 2 : 4 : 2 : 5 which is a simple whole number ratio.

Hence, the given data obey the law of multiple proportions.

Definition – When two elements combine to form two or more chemical compounds, then the masses of one of the elements which combine with a fixed mass of the other, bear a simple ratio to one another.

(b) (i) $1\,\text{km} = 1\,\text{km} \times \dfrac{1000\text{ m}}{1\text{ km}} \times \dfrac{100\text{ cm}}{1\text{ m}} \times \dfrac{10\text{ mm}}{1\text{ cm}} = 10^6\text{mm}$

$$1\text{ km} = 1\text{ km} \times \frac{1000\text{ m}}{1\text{ km}} \times \frac{1\text{ pm}}{10^{-12}\text{m}} = 10^{15}\text{ pm}$$

(ii) $1\text{ mg} = 1\text{ mg} \times \dfrac{1\text{ g}}{1000\,\text{mg}} \times \dfrac{1\text{kg}}{1000\text{g}} = 10^{-6}\text{ kg}$

$$1\text{ mg} = 1\text{ mg} \times \frac{1\text{ g}}{1000\,\text{mg}} \times \frac{1\text{ng}}{10^{-9}\text{g}} = 10^{6}\text{ ng}$$

(iii) $1\text{ mL} = 1\text{ mL} \times \dfrac{1\text{L}}{1000\,\text{mL}} = 10^{-3}\text{ L}$

$$1\text{ mL} = 1\text{ cm}^3 = \frac{1\text{cm}^3 \times 1\text{dm} \times 1\text{dm} \times 1\text{dm}}{10\text{cm} \times 10\text{cm} \times 10\text{cm}}$$

$$= 10^{-3}\text{ dm}^3$$

1.22 If the speed of light is $3.0 \times 10^8\text{ m s}^{-1}$, calculate the distance covered by light in 2.00 ns.

Ans. Distance covered = Speed × Time

$= 3.0 \times 10^8\,\text{ms}^{-1} \times 2.00\text{ ns}$

$$= 3.0 \times 10^8\,\text{ms}^{-1} \times 2.00\text{ns} \times \frac{10^{-9}\text{s}}{1\text{ns}} = 6.00 \times 10^{-1}\text{ m} = 0.600\text{ m}$$

1.23 In a reaction

$$\mathbf{A + B_2 \longrightarrow AB_2}$$

Identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B
(ii) 2 mol A + 3 mol B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 mol A + 2.5 mol B
(v) 2.5 mol A + 5 mol B

Ans. (i) According to the given reaction, 1 atom of A reacts with 1 molecule of B. Therefore 200 molecules of B will react with 200 atoms of A and 100 atoms of A will be left unreacted. Hence, B is the limiting reagent while A is the excess reagent.

(ii) According to the given reaction, 1 mol of A reacts with 1 mol of B. Therefore 2 mol of A will react with 2 mol of B. Hence, A is the limiting reactant.

(iii) No limiting reagent

(iv) 2.5 mol of B will react with 2.5 mol of A. Hence B is the limiting reagent.

(v) 2.5 mol of A will react with 2.5 mol of B . Hence A is the limiting reagent.

1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$$\mathbf{N_2(g) + H_2(g) \longrightarrow 2NH_3(g)}$$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?

Ans. (i) Balanced equation for preparation of ammonia is

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

1 mol of N_2, i.e., 28 g react with 3 mol of H_2, i.e., 6g of H_2. 2000 g of N_2 will react with $H_2 = \dfrac{6}{28} \times 2000$ g = 428. 6 g but the amount of H_2 actually present is 1000g, thus H_2 is in excess and remain unreacted. Thus, N_2 is the limiting reagent while H_2 is the excess reagent.

1 mol of N_2, i.e., 28 g of N_2 produce NH_3 = 2 mol = 34 g
2000g of N_2 will produce NH_3

$$= \frac{34}{28} \times 2000\text{g} = 2428.57\text{g}$$

(ii) H_2 will remain unreacted.

(iii) Mass left unreacted = 1000g – 428.6 g = 571.4 g

1.25 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

Ans. Molar mass of Na_2CO_3 = 2 ×23 + 12 + 3×16 = 106 g mol^{-1}
0.50 mol Na_2CO_3 means = 0.50 × 106 g = 53 g
0.50 M Na_2CO_3 means 0.50 mol i.e, 53 g Na_2CO_3 are present in 1 litre of the solution .

1.26 If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

Ans. H_2 and O_2 react according to the equation

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Therefore, 2 volumes of H_2 react with 1 volume of O_2 to produce 2 volumes of water. Hence, 10 volumes of H_2 will react completely with 5 volumes of O_2 to produce 10 volumes of water vapour.

1.27 Convert the following into basic units:
(i) 28.7 pm (ii) 15.15 pm (iii) 25365 mg

Ans. (i) $28.7\,\text{pm} = 28.7\,\text{pm} \times \dfrac{10^{-12}\text{m}}{1\text{pm}} = 2.87 \times 10^{-11}\text{ m}$

(ii) $15.15\,\text{pm} = 15.15\,\text{pm.} \times \dfrac{10^{-12}\text{m}}{1\text{pm}} = 1.515 \times 10^{-5}\text{ m}$

(iii) $25365\text{ mg} = 25365\text{ mg} \times \dfrac{1\text{g}}{1000\,\text{mg}} \times \dfrac{1\text{kg}}{1000\text{g}}$
$= 2.5365 \times 10^{-2}\text{ kg}$

1.28 Which one of the following will have largest number of atoms?
(i) 1 g of Au (s) (ii) 1 g of Na (s)
(iii) 1 g of Li (s) (iv) 1 g of Cl_2(g)

Ans. (i) $1\text{ g Au} = \dfrac{1}{197}\text{ mol} = \dfrac{1}{197} \times 6.022 \times 10^{23}\text{ atoms}$

$$= 0.030 \times 10^{23}\text{ atoms} = 3.0 \times 10^{21}\text{ atoms}$$

(ii) $1\text{ g Na} = \dfrac{1}{23}\text{ mol} = \dfrac{1}{23} \times 6.022 \times 10^{23}\text{atoms } 2$

$$= 0.261 \times 10^{23}\text{ atoms} = 2.61 \times 10^{22}\text{ atoms}$$

(iii) $1\text{ g Li} = \dfrac{1}{7}\text{mol} = \dfrac{1}{7} \times 6.022 \times 10^{23}\text{ atoms}$

$$= 0.86 \times 10^{23}\text{ atoms} = 8.6 \times 10^{22}\text{ atoms}$$

(iv) 1 g Cl_2

$$= \frac{1}{71}\text{mol} = \frac{1}{71} \times 6.022 \times 10^{23}\text{ molecules}$$

$$= \frac{2}{71} \times 6.022 \times 10^{23}\text{ atoms} = 1.69 \times 10^{22}\text{atoms}$$

Thus 1 g of Li has the largest number of atoms.

1.29 Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040.

Ans. Given mole fraction of ethanol = 0.040

$$\text{i.e., } X_{C_2H_5OH} = \frac{n_{(C_2H_5OH)}}{n_{(C_2H_5OH)} + n_{(H_2O)}} = 0.040 \quad \ldots\text{(i)}$$

Now we have to find number of moles of ethanol in 1 L of the solution which is nearly = 1 L of water (because solution is dilute)

No. of moles in 1L water $= \dfrac{1000\text{g}}{18\,\text{g mol}^{-1}} = 55.55$ moles

Substituting $n(H_2O) = 55.55$ in eqn (i), we get

$$\frac{n_{(C_2H_5OH)}}{n_{(C_2H_5OH)} + 55.55} = 0.040$$

$$0.040\, n_{(C_2H_5OH)} + 55.55 \times 0.040 = n_{(C_2H_5OH)}$$

or $\quad 0.96\, n_{(C_2H_5OH)} = 55.55 \times 0.040$

or $\quad n_{(C_2H_5OH)} = 2.31\text{mol}$

Hence, molarity of the solution = 2.31M

1.30 What will be the mass of one ^{12}C atom in g?

Ans. 1 mol of ^{12}C atoms $= 6.022 \times 10^{23}$ atoms = 12g

thus, 6.022×10^{23} atoms of ^{12}C have mass = 12g

$\therefore$ 1 atom of ^{12}C will have mass

$$= \frac{12}{6.022 \times 10^{23}}\,\text{g} = 1.9927 \times 10^{-23}\,\text{g}$$

1.31 How many significant figures should be present in the answer of the following calculations?

(i) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5 × 5.364

(iii) 0.0125 + 0.7864 + 0.0215

Ans. (i) The least precise term has 3 significant figures (in 0.112). Hence , the answer should have 3 significant figures.

(ii) Leaving the exact number (5), the second term has 4 significant figures. Hence, the answer should be 4 significant figures.

(iii) In the given addition the least number of decimal places in the term is 4. Hence the answer should have the 4 significant figures.

1.32 Use the data given in the following table to calculate the molar mass of naturally occuring *argon* isotopes:

Isotope	**Isotopic molar mass**	**Abundance**
^{36}Ar	**35.96755 g mol^{-1}**	**0.337%**
^{38}Ar	**37.96272 g mol^{-1}**	**0.063%**
^{40}Ar	**39.9624 g mol^{-1}**	**99.600%**

Ans. Molar mass of Ar

$= 35.96755 \times 0.00337 + 37.96272 \times 0.00063 + 39.96924 \times 0.99600$

$= 39.948\ \text{g mol}^{-1}$

1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

Ans. (i) 1 mol of Ar $= 6.022 \times 10^{23}$ atoms

52 mol of Ar $= 52 \times 6.022 \times 10^{23}$ atom $= 3.131 \times 10^{25}$ atoms

(ii) 4 u of He = 1atom of He

52 u of He = ¼ × 52 atoms = 13 atoms

(iii) 1 mole of He = 4g of He $= 6.022 \times 10^{23}$ atoms

$$52\text{ g of He} = \frac{6.022 \times 10^{23}}{4} \times 52 \text{ atoms}$$

$= 7.8286 \times 10^{24}$ atoms

1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

Ans. Amount of carbon in 3.38 g of

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

Amount of hydrogen in 0.690 g of

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

As compound contains only C and H, therefore, total mass of the compound = 0.9218 + 0.0767 = 0.9985 g

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

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

Element	**% by mass**	**Atomic mass**	**Moles of the element**	**Simplest molar ratio**	**Simplest whole number molar ratio**
C	92.32	12	$\frac{92.32}{12} = 7.69$	1	1
H	7.68	1	$\frac{7.68}{1} = 7.68$	1	1

$\therefore$ Empirical Formula = CH

$\therefore$ 10.0 L of the gas at STP weigh = 11.6 g

22.4 L of the gas at STP will weigh

$= \dfrac{11.6}{10.0} \times 22.4 = 25.984\text{g}$ or 26 approx

Molar mass = 26 g mol^{-1}

Empirical formula mass of CH = 12 + 1 = 13

$$\therefore\ n = \frac{\text{Molecular mass}}{\text{E.F.mass}} = \frac{26}{13} = 2$$

$\therefore$ Molecular formula = 2 × CH = C_2H_2

1.35 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction.

$CaCO_3(s) + 2HC1(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(\ell)$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

Ans. Step 1.

Calculate mass of HCl in 25mL of 0.75M HCl

1000 mL of 0.75 M HCl contain HCl = 0.75 mol

= 0.75 × 36.5 g = 27.375g

25 mL of 0.75 M HCl will contain HCl

$$= \frac{27.375}{1000} \times 25\,\text{g} = 0.6844\,\text{g.}$$

Step 2. Calculate mass of $CaCO_3$ reacting completely with 0.6844 g of HCl

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(\ell)$

2 mol of HCl, i.e., 2 × 36.5g = 73g of

HCl react completely with $CaCO_3$ = 1 mol = 100 g

$\therefore$ 0.6844 g of HCl will react completely with

$$CaCO_3 = \frac{100 \times 0.6844}{73}\,\text{g} = 0.938\,\text{g}$$

1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction

$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(\ell) + MnCl_2(aq) + Cl_2(g)$

How many grams of HCl react with 5.0 g of manganese dioxide?

Ans. 1 mol of MnO_2, i.e., 55 + 32 = 87 g of MnO_2 react with 4 moles of HCl, i.e., 4 × 36.5 g = 146 g of HC1.

Hence 5.0 g of MnO_2 will react with HCl

$$= \frac{146}{87} \times 5.0\text{g} = 8.40\text{g}$$

Practice Questions

Very Short Answer Questions [1 Mark]

1. Calculate the mass of one atom of carbon?

2. Calculate the total number of electrons present in 1.4 g of nitrogen gas?

3. A colourless liquid used in rocket engines, whose empirical formula is NO_2, has a molar mass of 92. What is its molecular formula?

4. What is the mass of 2 atoms of oxygen?

5. How many significant figures are present in 6.023×10^{23}?

6. Write the formulae and names of three compounds containing same percentage composition of C, H and O.

7. Why are the atomic masses of most of the elements fractional?

8. Is the law of constant composition true for all types of compounds? Explain why or why not.

9. Volume of a solution changes with change in temperature, then, will the molality of the solution be affected by temperature? Give reason for your answer.

10. In what smallest whole-number ratio must N and O atoms combine to make dinitrogen to tetroxide N_2O_4 ? What is the mole ratio of the elements in this compound ?

11. How many grams of silver are in 0.263 mol of Ag ?

12. Calculate the mass of 6.022×10^{22} atoms of He.

13. Write 0.0005729 in scientific notation.

14. Nitrogen and Oxygen form N_2O, NO, NO_2, N_2O_4, N_2O_5. Which Law of chemical combination is followed?

15. Which element is used as a standard for comparing atomic and molecular masses?

16. Q is an impure substance, is it an element, compound or a mixture?

17. Express the following results to the proper number of significant figures.

$$\frac{\left(1.38\times10^{-4}\right)(0.8)}{3.9}$$

18. Boron occurs in nature in the form of two isotopes $^{11}_{5}B$ and $^{10}_{5}B$ in ratio of 81% and 19% respectively. Calculate its average atomic mass.

19. Alkaline solution of $KMnO_4$ reacts as follows:

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Calculate the equivalent weight of $KMnO_4$ in basic medium.

20. Calculate the mass of ferric oxide that will be obtained by complete oxidation of 2 g of Fe.
[Atomic weights of Fe = 56 u, O = 16 u]

21. Why air is not always regarded as homogeneous mixture?

22. Balance the equation

$$C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(1)$$

23. What is the law called which deals with the ratios of volumes of the gaseous reactants and products?

24. Vanadium metal is added to steel to impart strength. The density of vanadium is 5.96 g/cm^3. Express this in SI unit.

25. What is the difference between 2H and H_2?

26. What are basic properties used to identify a substance?

27. Dinitrogen combines with dihydrogen to form ammonia according to the following reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What is the ratio of their volumes under similar conditions of temperature and pressure?

28. Balance the equation

$$P_4(s) + O_2(g) \longrightarrow P_4O_{10}(s)$$

29. What is the S.I. unit of energy?

30. State the number of significant figures in each of the following numbers.
(i) 0.05031 (ii) 2.563×10^{10}

Short Answer Questions [2 & 3 Marks]

1. Express the following numbers upto three significant figures:
(i) 5.607883 (ii) 32.394800
(iii) six thousand (iv) 0.007838

2. What is derived unit? Derive the unit for density in SI unit?

3. The population of India based on 1981 census figure was 684 million. Express the results in scientific notation and calculate the number of significant figures.

4. How many molecules of water of hydration are present in 39.2 mg of Mohr's salt ? $[FeSO_4 . (NH_4)_2SO_4 . 6H_2O]$

5. Naphthalene contains 93.7% carbon and 6.29% hydrogen, if its molecular mass is 128 g/mol. Calculate its molecular formula.

6. How many moles of hydrogen, phosphorous and oxygen are present in 0.213 moles of H_3PO_4 (Phosphoric acid)?

7. Calculate the molality of 1M NaOH solution which has a density of 1.2 g/mL?

8. When 36g of H_2O reacted with Fe it gave 90.0g of Fe_3O_4. what is the % yield of the reaction?

$$3\,Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

9. Calculate the weight of CaO obtained by heating 200g of 95% pure limestone, $CaCO_3$?

10. A glass of juice contains 9 gm of glucose ($C_6H_{12}O_6$). How many atoms of each element (C, H and O) are there in the juice.

11. $BaCl_2$ solution has a density of 1.279 g/mL and the percent of solute is 26%. Calculate the molality of the solution? (Mol. Weight of $BaCl_2$ = 208)

12. Calculate the molality of a sulphuric acid solution in which mole fraction of water is 0.85.

13. Calculate the number of atoms of the constituent elements in 53 g of Na_2CO_3.

14. Is the Law of constant composition true for all types of compounds? If not so, then why?

15. (a) When 4.2 g of $NaHCO_3$ (sodium hydrogen carbonate) is added to a solution of CH_3COOH (acetic acid) weighing 10.0 g, it is observed that 2.2 g CO_2 is released into atmosphere. The residue is found to weigh 12.0 g. Show that three observations are in agreement with the law of conservation of mass.

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

16. (a) Classify the following as pure substances or mixtures

(b) Separate the pure substance into elements and compounds and divide the mixtures into homogeneous and heterogenous categories:
(i) graphite (ii) milk (iii) air (iv) diamond (v) petrol (vi) tap water (vii) distilled water (viii) oxygen (ix) 22 carat gold (x) steel (xi) iron (xii) iodized table salt (xiii) wood (xiv) cloud.

17. What information is conveyed by the following chemical equation?
$Mg + 2HCl \rightarrow MgCl_2 + H_2$.

18. 4 g of copper chloride on analysis was founded to contain 1.890 g of copper (Cu) and 2.110 g of chlorine (Cl). What is the empirical formula of copper chloride? [Atomic mass of Cu = 63.5 u, Cl = 35.5 u]

19. If 20 g of $CaCO_3$ is treated with 20 gram of HCl, how many grams of CO_2 can be generated according to given equation :
$CaCO_3(s) + 2HCl\,(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

20. (a) What is limiting reactant?
(b) Oxygen is prepared by catalytic de-composition of potassium chlorate ($KClO_3$). Decomposition of potassium chlorate gives potassium chloride (KCl) and oxygen (O_2). If 2.4 mole of oxygen is needed for an experiment, how many grams of potassium chlorate must be decomposed? (At mass K = 39, Cl = 35.5, O = 16)

21. Calculate the moles of NaOH required to neutralize the solution produced by dissolving 1.1 g P_4O_6 in water. Use the following reactions:
$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$
(Atomic mass/g mol^{-1} ; P = 31, O = 16

22. Calculate the weight of FeO formed from 2g of VO and 5.75 g of Fe_2O_3. Also report the limiting reagent.
$2VO + 3Fe_2O_3 \rightarrow 6FeO + V_2O_5$
(Atomic mass V = 51.4, O = 16, Fe = 55.9 g)

23. The cost of table salt (NaCl) and table sugar ($C_{12}H_{22}O_{11}$) are Rs. 2 per kg and Rs. 6 per kg respectively calculate their cost per mole.

24. The vapour density of a mixture of NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the number of moles of NO_2 in 100 g of the mixture.

25. Give at least four points of difference between a compound and a mixture.

26. What do you mean by the term 'Formality' ? To what type of compounds it is applied?

27. Calculate the number of moles in each of the following.
(i) 392 g of sulphuric acid
(ii) 44.8 litres of sulphur dioxide at N.T.P.
(iii) 8g of calcium

28. The density of water at room temperature is 1.0 g/mL. How many molecules are there in a drop of water if its volume is 0.05 mL?

29. Explain how compounds differ from elements?

30. Explain how mixture differs from pure substance?

31. What volume of 6M HCl and 2M HCl should be mixed to get two litres of 3M HCl?

32. (a) How many significant figures are there in 1.00×10^6?
(b) One mole of sugar contains ....oxygen atoms.
(c) Give an example of molecule in which the empirical formula is CH_2O and the ratio of molecular formula weight and empirical formula weight is 6.

33. What are various types of mixtures? Give at least one example in each case?

34. Calculate the number of electrons present in 21g of nitride ions.

Long Answer Questions [5 Marks]

1. (i) 0.9031g of mixture of NaCl and KCl on treatment with conc. H_2SO_4 yields 1.0784g of a mixture of Na_2SO_4 and K_2SO_4. Calculate the % composition of the mixture.
(ii) Calculate the percentage of the naturally occurring isotopes ^{35}Cl and ^{37}Cl that accounts for the mass of chlorine taken as 35.45.

2. (i) Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.84 g mL^{-1}. What volume of the concentrated acid is required to make 5.0L of 0.50 M H_2SO_4 solution? (Mol. weight of sulphuric acid = 98)
(ii) You are given a solution of 14.8M NH_3. How many milliliters of this solution do you require to give 100 ml of 1MNH_3? How much of water will you add?

3. (i) Calculate the volume at STP occupied by (a) 14 g of nitrogen, (b) 1.5 moles of carbon dioxide and (c) 10^{21} molecules of oxygen.
(ii) Ammonia contains 82.35% of nitrogen and 17.65% of hydrogen. Water contains 88.90% of oxygen and 11.10% of hydrogen. Nitrogen trioxide contains 63.15% of oxygen and 36.85% of nitrogen. Show that these data illustrate the law of reciprocal proportions.

4. What are the limitations of a chemical equation? How could these limitations be removed?

5. A compound on analysis gave the following percentage composition:
Na = 14.31%, S = 9.97%, H = 6.22% O = 69.50%
Calculate the molecular formula of the compound on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallization. Molecular mass of the compound is 322.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Reaction, $2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$, is used for commercial preparation of bromine from its salts. Suppose we have 50.0 ml of a 0.060M solution of NaBr. What volume of a 0.050 M solution of Cl_2 is needed to react completely with Br^-? **[HOTS]**

2. 0.5 mole each of H_2S and SO_2 mixed together in a reaction flask, react according to equation :
$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$
Calculate the number of moles of 'S' formed. **[HOTS]**

3. Describe the difference between the mass of a mole of oxygen atoms (O) and the mass of a mole of oxygen molecules (O_2). **[HOTS]**

4. 45.4L of dinitrogen reacted with 22.7 L of dioxygen and 45.4 L of nitrous oxide was formed. The reaction is given below:
$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$
Which law is being obeyed in this experiment? Write the statement of the law. **[Exemplar]**

Short Answer Questions [2 & 3 Marks]

1. One second is required to count two wheat grain, then calculate the time (in years) required to count one mole of wheat grains. **[HOTS]**

2. Zinc and hydrochloric acid react according to the equation
$Zn(s) + 2HCl\,(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$
If 0.30 mole of Zn are added to hydrochloric acid containing 0.52 mole of HCl. Which of the two reactant is limiting reagent and how many moles of H_2 are produced? **[HOTS]**

3. From 6.02×10^{22} molecules of N_2 present in a container, 700 mg of N_2 are removed. What is the amount of H_2 in grams required to convert the remaining N_2 into NH_3? **[HOTS]**

4. A 0.1g sample of a compound when burnt completely in oxygen produced 0.191g of CO_2 and 0.1172g of H_2O. What is the empirical formula of the compound? **[HOTS]**

5. Two bulbs B_1 and B_2 of equal capacity contain 10g oxygen (O_2) and ozone (O_3) respectively. Which bulb will have greater number of O-atoms and which will have greater number of molecules? **[HOTS]**

6. $Fe_2(SO_4)_3$ is empirical formula of a crystalline compound of iron. It is used in water and sewage treatment to aid in the removal of suspended impurities. Calculate the mass percentage of iron, sulphur and oxygen in this compound. **[HOTS]**

7. If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in whole number ratio.
- (a) Is this statement true?
- (b) If yes, according to which law?
- (c) Give one example related to this law. **[Exemplar]**

8. The reactant which is entirely consumed in reaction is known as limiting reagent. In the reaction $2A + 4B \rightarrow 3C + 4D$, when 5 moles of A react with 6 moles of B, then
- (i) which is the limiting reagent?
- (ii) calculate the amount of C formed? **[Exemplar]**

Long Answer Questions [5 Marks]

1. (i) Copper oxide was prepared by the following methods:
- (a) In one case, 1.75 g of the metal were dissolved in nitric acid and igniting the residual copper nitrate yielded 2.19 g of copper oxide.
- (b) In the second case, 1.14 g of metal dissolved in nitric acid were precipitated as copper hydroxide by adding caustic alkali solution. The precipitated copper hydroxide after washing, drying and heating yielded 1.43g of copper oxide.
- (c) In the third case, 1.45 g of copper when strongly heated in a current of air yielded 1.83 g of copper oxide.

Show that the given data illustrate the law of constant composition.

(ii) Elements A and B form two different compounds. In first case 0.52 grams of A combines with 0.72 grams of B and in second case 0.15 grams of A combines with 0.65 grams of B. Show that these data illustrate the Law of multiple proportion. **[HOTS]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
- ***(i) Attempt all questions***
- ***(ii) Questions 1 to 3 carry 1 mark each.***
- ***(iii) Questions 4 and 5 carry 2 marks each.***
- ***(iv) Question 6 carry 3 marks***
- ***(v) Question 7 carry 5 marks***

1. What are the SI units of molarity?

2. Which is more concentrated 1 molal or 1molar ?

3. A commercially available sample of H_2SO_4 is 15% H_2SO_4 by weight (density = 1.10g/ml). Calculate molarity of the solution.

4. In the reaction $2A + B + 3C \rightarrow P + 2Q$. Starting with 3 mol of A, 2 mol of B and 6 mol of C, calculate the number of moles of the products P and Q.

5. Find out the volume of Cl_2 at STP produced by action of 100 cc of 0.2M HCl on excess of MnO_2.

6. 500 cc of 0.250 M Na_2SO_4 solution added to an aqueous solution of 15.00 g of $BaCl_2$. How many moles and how many grams of $BaSO_4$ are formed? (Mol. wt. Of $BaSO_4$ = 233, and $BaCl_2$ = 208)

7. (i) Two oxides of metal contain 27.6% and 30% of oxygen respectively. If the formula of first oxide is M_3O_4, find that of second.

(ii) Gastric juice contains about 3.0 g of HCl per liter. If a person produces about 2.5 liter of gastric juice per day, how many antacid tablets each containing 400 mg of $Al(OH)_3$ are needed to neutralise all the HCl produced in one day? Atomic mass of Cl = 35.5 ; Al = 27; O =16; H =1.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. We know that at wt. of carbon
= 12 and 6.022×10^{23} atoms of carbon weighs = 12 g
Therefore, 1 atom of carbon weighs
$= 12 / 6.022 \times 10^{23} = 1.99 \times 10^{-23}$ g

2. Number of moles of nitrogen gas $= \frac{1.4}{28} = 0.05$ mole
Number of molecules of N_2 gas
$= 0.05 \times 6.022 \times 10^{23} = 3.01 \times 10^{22}$ molecules
$= 3.01 \times 10^{22} \times 14$ electrons $= 4.214 \times 10^{23}$ electrons.

3. The formula mass is 46.
The number of times the empirical formula NO_2, occurs in the compound is = 92/46 = 2.
The molecular formula is N_2O_4

4. We know 6.022×10^{23} atoms of oxygen weighs = 16 g
Therefore, 2 atoms of oxygen weighs
$$= \frac{16 \times 2}{6.02 \times 10^{23}} = 5.33 \times 10^{-23} \text{ g}$$

5. Four

6. Compounds with the same percentage composition of C, H and O will have the same emperical formula. The compounds with the emperical formula CH_2O can be

HCHO	CH_3COOH	$C_6H_{12}O_6$
Formaldehyde	Acetic acid	Glucose

7. This is because atomic masses are the relative masses of atoms as compared with an atom of C-12 isotope taken as 12.

8. No, law of constant composition is not true for all types of compounds. It is true only for the compounds obtained from one isotope. For example, carbon exists in two common isotopes, ^{12}C and ^{14}C. When it forms CO_2 from ^{12}C, the ratio of masses is 12 : 32 = 3 : 8 but from ^{14}C, the ratio will be 14 : 32 = 7 : 16 which is not same as in the first case.

9. No, molality of solution does not change with temperature since mass remains unaffected with temperature.

10. 1 : 2

11. No. of grams of Ag = (0.263 mol of Ag)
$$\frac{107.9 \text{g of Ag}}{1 \text{ mol of Ag}} = 28.4 \text{ g of Ag}$$

12. 6.022×10^{23} atom of He weights 4 g
$\therefore$ 6.022×10^{22} atoms of He will weighs
$$= \frac{4 \times 6.022 \times 10^{22}}{6.022 \times 10^{23}} = 0.4 \text{ g}$$

13. 0.0005729 could be written in scientific notations as 5.729×10^{-4}.

14. The Law of multiple proportions.

15. Carbon, C^{12} isotope is used as a standard for comparing the atomic as well as molecular masses.

16. Q is a mixture.

17. $$\frac{\left(1.38 \times 10^{-4}\right)(0.8)}{3.9} = 28.3 \times 10^{-6}$$

18. Average atomic weight $= \frac{11 \times 81 + 10 \times 19}{100} = 10.81$

19. Equivalent weight $= \frac{\text{Molecular Weight}}{\text{Number of Electrons gained}}$
$$= \frac{158}{1} = 158 \text{ g} \quad \boxed{Mn^{7+} + e^- \rightarrow Mn^{6+}}$$

20. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
4 × 56g of Fe gives 2 × 160 g of Fe_2O_3
2 g of Fe gives $\frac{2 \times 160}{4 \times 56} \times 2 = 2.857$ g of Fe_2O_3.

21. This is due to the presence of dust particles.

22. $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

23. Gay Lussac's law of combining volumes.

24. 5960 kg/m^3.

25. 2H represents two atoms of hydrogen and H_2 represents one molecule of hydrogen.

26. These are colour, density, solubility, melting point, boiling point, etc.

27. The ratio of their volumes is 1 : 3 : 2.

28. $P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s)$

29. Joule

30. (i) 4 (ii) 4

Short Answer Questions

1. (i) 5.61 (ii) 32.4
(iii) 6.00×10^3 (iv) 0.00784

2. The units for physical quantities such as area, volume , density etc which are derived from the SI units of basic physical quantities are called derived units.
Density = Mass / Volume
The SI unit of mass is kg and volume is m^3, hence unit of density is kg m^{-3}.

3. 1 million = 10^6 hence 684 million = 684×10^6
The value in terms of scientific notation may be expressed as 6.84×10^8. It has three significant figures.

4. Molecular mass of Mohr's salt = 392 gm
392 gm of $FeSO_4.(NH_4)_2SO_4.6H_2O$ has $6 \times 6.023 \times 10^{23}$ molecules of water of crystallization hence, 39.2×10^{-3}gm of Mohr's salt contains $= \frac{6 \times 6.023 \times 10^{23} \times 39.2 \times 10^{-3}}{392}$
$= 3.61 \times 10^{20}$ molecules of water of crystallization.

5. (i) Calculate the empirical formula.

Element	% by mass	Atomic mass	Atomic Ratio	Simplest molar ratio	Simplest whole number molar ratio
Carbon (C)	93.7	12	$\frac{93.7}{12} = 7.81$	$\frac{7.81}{6.29} = 1.24$	$1.24 \times 4 = 5$
Hydrogen(H)	6.29	1	$\frac{6.29}{1} = 6.29$	$\frac{6.29}{6.29} = 1$	$1 \times 4 = 4$

Hence empirical formula = C_5H_4

(ii) Calculate molecular formula:

Empirical formula mass = 5 × 12 + 4 × 1 = 64

Molecular mass = 128

n = Molecular mass / empirical formula mass = 128 / 64 = 2

Thus molecular formula = n × empirical formula mass

$= 2 \times C_5H_4 = C_{10}H_8$

6. In 1 mole of H_3PO_4 there are 1 mole of phosphorus, 3 moles of hydrogen and four moles of oxygen atoms. Thus 0.213 moles of H_3PO_4 consists of 3 × 0.213 = 0.639 moles of hydrogen. Thus 0.213 moles of H_3PO_4 consists of 1× 0.213 = 0.213 moles of phosphorus. Thus 0.213 moles of H_3PO_4 consists of 4 × 0.213 = 0.852 moles of oxygen.

7. The number of moles of NaOH = 1mole

$$\text{Density of solution} = \frac{\text{Mass of solution}}{\text{Volume of solution}},$$

$$1.2\ \text{g/mL} = \frac{\text{Mass of solution}}{1000\text{mL}}$$

1200 g = mass of solution = Mass of solute + Mass of solvent

Mass of solute (NaOH) = 1 × 40 g = 40 g

Mass of solvent = 1200 – 40 = 1160 g or 1.160 kg

We know molality m

$$= \frac{\text{weight of solute} \times 1000}{\text{Mol. weight of solute} \times \text{weight of solvent (in grams)}}$$

$$= \frac{40 \times 1000}{40 \times 1160} = 0.862$$

8. 4 ×18g of H_2O produces = 232g of Fe_3O_4

$$36\text{g of } H_2O \text{ will give } = \frac{232 \times 36}{4 \times 18} = 116\text{g of } Fe_3O_4$$

$$\%\ \text{yield} = \frac{\text{Mass of product obtained experimentally}}{\text{Mass of product obtained theoretically}} \times 100$$

= 90 × 100 / 116 = 77.6%

9. $CaCO_3 \longrightarrow CaO + CO_2$

Amount of $CaCO_3$ in the sample

= 200 × 95/100 = 190g of $CaCO_3$

According to the equation; 100g of $CaCO_3$ gives = 56g of CaO

190g of $CaCO_3$ will give = 56 × 190/100 = 106.4g of CaO

10. Molecular mass of glucose ($C_6H_{12}O_6$) = 180 gm.

180 gm of glucose has 'C' atoms = $6 \times 6.02 \times 10^{23}$

$$\text{Hence 9 gm of glucose has} = \frac{6 \times 6.02 \times 10^{23} \times 9}{180}$$

= 1.806×10^{23} ‘C’ atoms

Also 180 gm of glucose has 'H' atoms = $12 \times 6.02 \times 10^{23}$

$$\text{Hence 9 gm of glucose has } = \frac{12 \times 6.02 \times 10^{23} \times 9}{180}$$

= 36.12×10^{22} ‘H’ atoms.

Number of 'O' atoms will be similar to 'C' atoms as per the molecular formula of glucose.

11. Determine mass of $BaCl_2$ and mass of water in the solution From the given data, density of solution

$$= \frac{\text{Mass of solution}}{\text{Volume of solution}}$$

Since the data of density is in g/ mL and percentage of solute is given, thus volume of solution is = 100 mL

$$1.279\ \text{g/ml} = \frac{\text{Mass of solution in gram}}{100\ \text{mL}}$$

127.9 g = Mass of solution in gram

We know that mass of solution

= mass of solute + mass of solvent

Now the mass of solute in given 26% of the solution

$$= \frac{26}{100} \times 127.9 = 33.254\,\text{g}$$

Hence, mass of solvent will be = 127.9 – 33.254 = 94.646 g

We know molality (m)

$$= \frac{\text{Weight of solute} \times 1000}{\text{Mol. weight} \times \text{Weight of solvent in (grams)}}$$

$$= \frac{33.254 \times 1000}{208 \times 94.646} = 1.689\text{m}$$

12. $x_{(H_2O)} = 0.85$

$x_{(H_2SO_4)} = 1 - 0.85 = 0.15$

$$\text{i.e.} \quad \frac{n_{(H_2SO_4)}}{n_{(H_2SO_4)} + n_{(H_2O)}} = 0.15 \qquad \ldots(1)$$

$$\text{Similarly} \quad \frac{n_{(H_2O)}}{n_{(H_2SO_4)} + n_{(H_2O)}} = 0.85 \qquad \ldots(2)$$

Divide eqn (1) by (2),

$$\frac{n_{(H_2SO_4)}}{n_{(H_2O)}} = \frac{0.15}{0.85} = 0.176 \qquad \ldots(3)$$

$$\frac{n_{(H_2SO_4)}}{\text{weight}\,(H_2O)} \times \text{Mol.Mass}\,(H_2O) \times 1000$$

= 0.176 × 1000 or molality × 18 = 0.176×1000

$$\text{molality} = \frac{0.176 \times 1000}{18} = 9.8$$

13. By mole concept,

1 mole of Na_2CO_3 = Gram formula mass of Na_2CO_3

= 2 × 23 + 12 + 16 × 3 = 106 g

Now, 106 g of Na_2CO_3 = 1 mole

$$53\text{ g of } Na_2CO_3 = \frac{1 \times 53}{106} = 0.5 \text{ mole of } Na_2CO_3$$

But 1 mole of Na_2CO_3 contains 2 moles of Na^+ ion or 2 × 6.022×10^{23} Na^+ ions.

0.5 mole of Na_2CO_3 will contain 2 × 6.022 × 10^{23} × 0.5 Na^+ ions = 6.022 × 10^{23} Na^+ ions

Again, 1 mole of Na_2CO_3 contains 1 mole of carbon atoms = 6.022 × 10^{23} carbon atoms

0.5 mole of Na_2CO_3 will contain = 6.022 × 10^{23} × 0.5 carbon atoms = 3.011 × 10^{23} carbon atoms

Further, 1 mole of Na_2CO_3 contains 3 moles of oxygen atoms or 3 × 6.022 × 10^{23} oxygen atoms

0.5 mole of Na_2CO_3 will contain

3 × 6.022 × 10^{23} × 0.5 oxygen atoms = 9.033 × 10^{23} oxygen atoms.

14. The Law of constant composition is not always true because same compound when formed using different isotopes of an element does not have the same ratio of masses. For example

In ordinary water O : H ratio is 16 : 2 or 8 : 1 while in heavy water D_2O the ratio between O : Deuterium is 16 : 4 i.e. 4 : 1.

15. (a)
$$\underset{4.2\text{ g}}{NaHCO_3} + \underset{10.0\text{ g}}{CH_3COOH} \longrightarrow \underset{12.0\text{ g}}{CH_3COONa} + H_2O + \underset{2.2\text{ g}}{CO_2} \uparrow$$

$\therefore$ Total mass of the reactants = Total mass of the products
Hence, the law of conservation of mass is followed.

(b) $NaHCO_3 + CH_3COOH \longrightarrow$

$$\underset{6.3\text{ g}}{NaHCO_3} + \underset{15.0\text{ g}}{CH_3COOH} \longrightarrow \underbrace{CH_3COONa + H_2O + CO_2}_{18.0\text{ g}}$$

According to the Law of conservation of mass, The mass of reactants = The mass of the products

$6.3 + 15.0 \rightarrow 18.0 + x$

$21.3 \rightarrow 18.0 + x$

$\therefore$ x (The mass of CO_2 formed)
$= 21.3 - 18 = 3.3$ g.

16. (a) **Pure substances :** Graphite, diamond, distilled water, oxygen, iron.
Mixtures : Milk, air, petrol, tap water, 22 carat gold, steel, iodized table salt, wood, cloud.

(b) **Elements :** Graphite, diamond, iron,
Compunds : Distilled water, oxygen,
Homogeneous mixtures : Milk, air, wood, petrol, tap water, 22 carat gold. steel
Heterogeneous mixtures : Iodized table salt, cloud.

17. $Mg + 2HCl \rightarrow MgCl_2 + H_2$

(i) Qualitatively this equation conveys that magnesium metal reacts with hydrochloric acid forming magnesium chloride, liberating hydrogen gas.

(ii) Quantitatively,

(a) one atom of Mg combines with two molecules of HCl forming one molecule each of $MgCl_2$ and H_2 gas.

(b) one mole of Mg reacts with two moles of HCl to produce one mole each of $MgCl_2$ and H_2 gas.

(c) 24 g of Mg reacts with 73 g of HCl to produce 95 g of $MgCl_2$ and 2 g of H_2 gas.

(d) 24 g of Mg reacts with 73 g of HCl to produce 22.4 lit of H_2 gas at STP.

18. $\%\text{ of Cu} = \frac{1.890}{4.0} \times 100 = 47.25\%$

$\%\text{ of Cl} = \frac{2.11}{4.0} \times 100 = 52.75\%$

Element	%	Atomic weight	Relative no. of atoms	Divide by least %	Simplest ratio
Cu	47.25	63.5	$\frac{47.25}{63.5} = 0.74$	$\frac{0.74}{0.74} = 1$	1
Cl	52.75	35.5	$\frac{52.75}{35.5} = 1.48$	$\frac{1.48}{0.74} = 2$	2

Empirical Formula = $CuCl_2$.

19. $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
Molecular mass of $CaCO_3 = 40 + 12 + 48 = 100$
Molecular mass of $HCl = 1 + 35.5 = 36.5$
100 g of $CaCO_3$ reacts with 2×36.5 g of HCl

20 g of $CaCO_3$ reacts with $\frac{2 \times 36.5}{100} \times 20 = 2 \times 7.3 = 14.6$ g

Since, we have 20 g of HCl
$\therefore$ HCl is excess reactant and $CaCO_3$ is limiting reactant.
100 g of $CaCO_3$ gives 44g of CO_2

20 g of $CaCO_3$ gives $\frac{44}{100} \times 20 = 8.8$ g of CO_2

20. (a) It is the reactant which is entirely consumed when reaction goes to completion.

(b) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
Molecular weight of $KClO_3$
$= 39 + 35.5 + 3 \times 16 = 122.5$
For 3 mole of O_2 we need 2×122.5 g of $KClO_3$
For 2.4 mole of O_2 we need
$= \frac{2 \times 122.5}{3} \times 2.4 = 196$ g of $KClO_3$

21. $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$
Molecular weight of $P_4O_6 = 4 \times 31 + 6 \times 16$
$= 124 + 96 = 220\text{ g mol}^{-1}$

Number of moles of $P_4O_6 = \frac{1.1\text{g}}{220} = \frac{1}{200}$ moles

$\frac{1}{200}$ moles of P_4O_6 produce $4 \times \frac{1}{200}$ moles of H_3PO_3
1 mole of H_3PO_3 requires 2 moles of NaOH

$\frac{1}{50}$ moles of H_3PO_3 requires $2 \times \frac{1}{50} = \frac{1}{25}$
= 0.04 moles of NaOH.

22. $2VO + 3Fe_2O_3 \rightarrow 6FeO + V_2O_5$
Molecular weight of $VO = 51.4 + 16 = 67.4$
Molecular weight of $Fe_2O_3 = 2 \times 55.9 + 3 \times 16$
$= 111.8 + 48 = 159.8$
2×67.4 g of VO reacts with 3×159.8 g of Fe_2O_3

2 g of VO reacts with $\frac{3 \times 159.8}{2 \times 67.4} \times 2 = \frac{479.4}{67.4} = 7.1$g

Since Fe_2O_3 is present in small amount,
$\therefore$ It is limiting reactant.
3×159.8 g of Fe_2O_3 gives $6\,(55.9 + 16)$g of FeO

5.75 g of Fe_2O_3 gives $\frac{6 \times 71.9}{3 \times 159.8} \times 5.75$

$= \frac{143.8}{159.8} \times 5.75 = \frac{826.85}{159.8} = 5.174$ g

23. (a) Cost of table salt (NaCl) per mole
Gram molecular mass of $NaCl = 23 + 35.5 = 58.5$ g
Now, 1000 g of NaCl cost = Rs. 2

$\therefore$ 58.5 g of NaCl will cost $= \frac{2}{(1000g)} \times (58.5g)$
= 0.117 Rupee = 0.117×100 = 12 paise (approx.)

(b) Cost of table sugar ($C_{12}H_{22}O_{11}$) per mole
Gram molecular mass of ($C_{12}H_{22}O_{11}$)
$= 12 \times 12 + 22 \times 1 = 16 \times 11 = 144 + 22 + 176 = 342$ g
Now, 1000 g of sugar cost = Rs. 6

$\therefore$ 342 g of sugar will cost $= \frac{6}{(1000g)} \times (342g)$
= 2.052 = 2.0 Rupees (approx.)

24. Vapour density of the mixture of NO_2 and $N_2O_4 = 38.3$
Molecular mass of the mixture
= 2 × Vapour density = 2 × 38.3 = 76.6 u = 76.6 g
Mass of the mixture = 100g

No. of moles of the mixture $= \frac{100}{76.6}$

Let the mass of NO_2 in the mixture = x g
$\therefore$ Mass of N_2O_4 in the mixture = (100 – x) g
Molar mass of $NO_2 = 14 + 32 = 46$ u = 46 g
Molar mass of $N_2O_4 = 28 + 64 = 92$ u = 92 g

No. of moles of $NO_2 = \dfrac{x}{46}$

No. of moles of $N_2O_4 = \dfrac{(100-x)}{92}$

Total no. of moles in the mixture $= \dfrac{x}{46} + \dfrac{(100-x)}{92}$

Equating (i) and (ii), $\dfrac{x}{46} + \dfrac{(100-x)}{92} = \dfrac{100}{76.6}$

$92x + 46(100-x) = \dfrac{100}{76.6} \times 46 \times 92 = 5524.8$

$92x - 46x = 5524.8 - 4600 = 924.8.$

25.

	Compound	Mixture
1	Elements combine in definite ratio by mass.	1 Constituents may combine in any ratio.
2	They are homogeneous in nature.	2 They may or may not be homogeneous.
3	Components cannot be separated easily.	3 Components could be separated easily.
4	Properties are different from those of constituent elements.	4 Properties resemble with the constituents.

26. Ionic compounds like $\overset{+}{Na}\overset{-}{Cl}$ are not molecular. To express the concentration of their solution the term formality is used in place of molarity. Formality is the number of formula weights present in one litre of a solution.

27. (i) 392 g of sulphuric acid
Molar mass of $H_2SO_4 = 2 \times 1 + 32 + 4 \times 16 = 98$ g
98 g of sulphuric acid = 1 mol
392 g of sulphuric acid
$= 1 \text{ mol} \times \dfrac{392g}{(98g)} = 4 \text{ mol}$

(ii) 44.8 litres of sulphur dioxide at N.T.P.
22.4 litres of sulphur dioxide at N.T.P. = 1 mol
44.8 litres of sulphur dioxide at
N.T.P. $= \dfrac{1 \text{ mol}}{(22.4\text{L})} \times (44.8 \text{ L}) = 2.0 \text{ mol}$

(iii) 8g of calcium
Gram atomic mass of Ca = 40 g
40 g of calcium = 1 mol
8.0 g of calcium $= 1 \text{ mol} \times \dfrac{(8.0g)}{(40g)} = 0.2$ mol.

28. Number of moles in a drop of water
Volume of a drop of water = 0.05 mL
Mass of a drop of water = Volume × density
= (0.05 mL) × (1.0 g/mL) = 0.05 g
Gram molecular mass of water $(H_2O) = 2 \times 1 + 16 = 18$ g
18 g of water = 1 mole
0.05 g of water $= \dfrac{1\text{mol}}{(18\text{ g})} \times (0.05 \text{ g}) = 0.0028$ mol
No. of molecular present
1 mole of water contain molecules $= 6.022 \times 10^{23}$
0.0028 mole of water contain molecules
$= 6.022 \times 10^{23} \times 0.0028 = 1.68 \times 10^{21}$ molecules.

29. Refer text

30. Refer text

31. $M_1V_1 + M_2V_2 = M_3V_3$
$6 \times x + 2(2-x) = 3 \times 2$
$6x + 4 - 2x = 6$
$4x = 2 \Rightarrow x = 0.5$ L
$2 - x = 2 - 0.5 = 1.5$ L

32. (a) 3
(b) One mole of sugar $C_{12}H_{22}O_{11}$ contains $11 \times 6.023 \times 10^{23}$ oxygen atoms
$= 66.253 \times 10^{23} = 6.6253 \times 10^{24}$ atoms of oxygen
(c) $C_6H_{12}O_6$

33. Refer text

34. 14 g of Nitride ion, N^{3-} contains (7 + 3)
= 10 moles of electrons
21 g of $N^{3-} = \dfrac{21}{14} \times 10 \times 6.022 \times 10^{23}$ electrons
$= 9.033 \times 10^{24}$ electrons.

Long Answer Questions

1. (i) $\underset{117g}{2NaCl} + H_2SO_4 \longrightarrow \underset{142g}{Na_2SO_4} + 2HCl$ …(i)

$\underset{149g}{2KCl} + H_2SO_4 \longrightarrow \underset{174g}{K_2SO_4} + 2HCl$ …(ii)

Mass of the mixture = 0.9031g
Let the mass of NaCl = xg
The mass of KCl = (0.9031– x)g
Mass of $Na_2SO_4 + K_2SO_4 = 1.0784$g
From equation (i),
117g NaCl gives = 142g Na_2SO_4
x g of NaCl will give = 142x/117g Na_2SO_4
From equation (ii) 149g KCl gives 174g K_2SO_4
(0.9031–x)g KCl will give = 174(0.9031 – x)/149 g K_2SO_4
Since mass of Na_2SO_4 and K_2SO_4 = 1.0784g
Thus 142x/117+ 174(0.9031 – x)/149 = 1.0784
On solving, x = 0.518g
∴ Mass of NaCl = 0.518g and mass of KCl = 0.9031– 0.518 = 0.3851g
% NaCl = 0.518 × 100/0.9031 = 57.36%
and % of KCl $= \dfrac{0.3851}{0.9031} \times 100 = 42.64\%$

(ii) Suppose ^{35}Cl present is = x%. Then ^{37}Cl present is = (100 – x)%

Average atomic mass $= \dfrac{x \times 35 + (100-x) \times 37}{100} = 35.45$

or 35x + 3700 – 37x = 3545
or 2x = 155 or x = 77.5%.
Hence ^{35}Cl = 77.5 % and ^{37}Cl = 22.5%

2. (i) First let us calculate the molarity using the density of solution

$M = \dfrac{\%\text{ age of solute}}{\text{Mol. Weight of solute}} \times 10 \times \text{density of solution}$

$= \dfrac{98\%}{98} \times 10 \times 1.84 \text{ g/mL} = 18.4\text{M}$

Using $M_1V_1 = M_2V_2$ where $M_1 = 18.4$M;
$V_1 = ?$; $M_2 = 0.50$M; $V_2 = 5.0$L
By substituting the values
$18.4 \times V_1 = 0.50 \times 5$

$V_1 = \dfrac{0.50 \times 5}{18.4} = 0.136\text{L}$

(ii) Using $M_1V_1 = M_2V_2$
where $M_1 = 14.8$ M, $V_1 = ?$,
$M_2 = 1$M, $V_2 = 100$ ml
∴ $14.8\text{M} \times V_1 = 1\text{M} \times 100$ ml

or $V_1 = \frac{1\times100}{14.8}$ ml = 6.76 ml

∴ Volume of water added = 100ml – 6.76ml
= 93.24ml

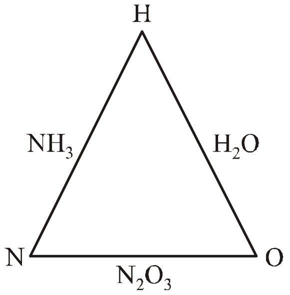
3. (i) (a) Molecular mass of nitrogen = 28 u
1 mole of nitrogen 22.4 litres at STP
i.e., 28 g of nitrogen occupy = 22.4 litres at STP

∴ 14 g of nitrogen occupy = $\frac{22.4}{28}\times14$
= 11.2 litres at STP

(b) 1 mole of carbon dioxide = 22.4 litres at STP
∴ 1.5 moles of carbon dioxide will occupy
$= \frac{22.4}{1}\times 1.5 = 33.6$ litres at STP

(c) 1 mole of O_2 molecules = 6.022×10^{23} molecules = 22.4 litres at STP
i.e., 6.022×10^{23} molecules of oxygen occupy 22.4 litres at STP
10^{21} molecules of oxygen will occupy
$= \frac{22.4}{6.022\times10^{23}}\times10^{21}$ litres at STP
$= 3.72\times10^{-2}$ litres at STP
$= 3.72\times10^{-2}\times10^{3}$ cm^3 at STP
$= 37.2$ cm^3 at STP

(ii) In NH_3, 17.65 g of H combine with N = 82.35 g



∴ 1 g of H combine with N = $\frac{82.35}{17.65}$ g = 4.67 g

In H_2O, 11.10 g of H combine with O = 88.90 g

∴ 1 g of H combine with O = $\frac{88.90}{11.10}$ g = 8.01 g

Ratio of the masses of N and O which combine with fixed mass (=1g) of H = 4.67 : 8.01 = 1 : 1.72
In N_2O_3, ratio of masses of N and O which combine with each other = 36.85 : 63.15 = 1:1.72. Thus, the two ratios are the same. Hence, it illustrates the law of reciprocal proportions.

4. Limitations of chemical equation and their removal is as follows:

(i) Physical states of the reactants and products are not given for example,
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
The suffixes like (s), (l), (g), (aq) are added to remove the drawbacks for example,
$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H2(g)$$

(ii) Reaction conditions are not mentioned, which may be done by writing the conditions on the arrow between the reactants and the products for example,
$$H_2(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} 2HCl(g)$$

(iii) Heat evolved or absorbed is not indicated, which may be done in terms of enthalpy change (ΔH).
$$C(s) + O_2(g) \xrightarrow{\text{Combustion}} CO_2(g)\ ;\ \Delta H = 393.5 kJ$$
$$N_2(g) + O_2(g) \xrightarrow{\text{Combustion}} 2NO(g)\ ;\ \Delta H = 180 kJ.$$

(iv) Concentrations of the reactants and the products are not mentioned. This drawback is removed by writing the prefix dil.(dilute) or conc. (concentrated) to a reactant. For example,
$$Zn(s) + \text{Dil. } HCl \longrightarrow ZnCl_2 + H_2(g)$$

(v) Rate of the reaction is not usually given and the same could be indicated (slow/fast) on the arrow.

(vi) Precipitation or the evolution of gas is normally not given, which may be indicated by the downward arrow (↓) and the upward arrow (↑) respectively.

For example,
$$AgNO_3(aq) + ZnCl(aq) \longrightarrow NaNO_3(aq) + AgCl(s)\downarrow$$
$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)\uparrow$$

5.

Element	**Percentage**	**% age/Atomic mass**	**Simplest atomic ratio**	**Simplest whole number ratio**
Na	14.31	$\frac{14.31}{23} = 0.622$	2	2
S	9.97	$\frac{9.97}{32} = 0.311$	1	1
H	6.22	$\frac{6.22}{1} = 6.22$	20	20
O	69.50	$\frac{69.50}{16} = 4.34$	14	14

Empirical formula = $Na_2S\,H_{20}O_{14}$
Empirical formula mass = (2 × 23) + 32 + 20 + 224 = 322
Molecular mass = 322

$n = \frac{322}{322} = 1$

Molcular formula = 1 × Empirical formula = $Na_2SH_{20}O_{14}$.
Since whole of the hydrogen is present as water molecules. Therefore, molecular formula
= $Na_2\,SO_4.10H_2O$.

HOTS / EXEMPLAR QUESTIONS

Very Short Answer Questions

1. We can do this numerical problem by using

$$M_1V_1(Cl_2) = \frac{M_2V_2(Br^-(aq))}{2}$$

$M_1 = 0.050M$; $V_1 = ?$; $M_2 = 0.060$ M ; $V_2 = 50$ ml

$0.050\times V_1 = \frac{0.060}{2}\times50$

∴ V_1 (Volume of chlorine solution)

$$= \frac{0.060 \times 50}{2 \times 0.050} = 30.00 \text{ ml} = 3.00 \times 10^{-2} \text{ L}$$

2. $2H_2S + SO_2 \rightarrow 2H_2O + 3S$

2 moles of H_2S combine with 1 mole of SO_2 to give 3 moles of S

1 mole of H_2S combines with 0.5 mole of SO_2 to give $\frac{3}{2}$ moles of S

0.5 mole of H_2S combines with 0.25 mole of SO_2 to give $\frac{3}{2} \times 0.5 = 0.75$ moles of S.

3. Because the atomic weight of oxygen is 15.999 amu, a mole of oxygen atoms has a mass of 15.999 grams. Each O_2 molecule has two atoms, however, so the molecular weight of O_2 molecules is twice as large as the atomic weight of the atom.

1 mol O = 15.999 g, 1 mol O_2 = 31.998g

4. According to Gay Lussac's law of gaseous volumes, gases combine or are produced in a chemical reaction in a simple ratio by volume, provided that all gases are at the same temperature and pressure.

Short Answer Questions

1. 1 mole of wheat grains = 6.022×10^{23} grains

Time required to count 2 grains = 1 second

Time required to count 6.022×10^{23} grains

$= 1 \times 6.022 \times 10^{23} / 2 = 3.012 \times 10^{23}$ sec

Convert seconds in years $= \frac{3.012 \times 10^{23}}{60 \times 60 \times 24 \times 365}$

$= 9.55 \times 10^{15}$ years

2. $Zn(s) + 2HCl\,(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

Stoichiometry indicates that 2 mol HCl requires 1 mol Zn.

0.52 mol HCl would require $= \frac{1}{2} \times 0.52$ mol

Zn = 0.26 mol Zn

But moles of Zn actually present = 0.30 mol

Therefore, Zn is in excess and HCl is the limiting reagent.

Now 2 mole of HCl form H_2 = 1 mol

0.52 mol of HCl form $H_2 = \frac{1}{2} \times 0.52 = 0.26$ mol.

3. 6.022×10^{23} molecules of N_2 = 1 mol of N_2

Thus 6.022×10^{22} molecules of N_2 = 0.1 mol

Mol. mass of N_2 = 28 amu

Gram molecular mass of N_2 = 28 g

Now, 28 g of N_2 = 1 mol

Hence, 700 mg of

$N_2 = 700 \times 10^{-3} \times 1/28 = 0.025$ mol

No. of moles of N_2 left = 0.1– 0. 025 = 0.075 mol

The balanced equation for synthesis of NH_3 is

$N_2 + 3H_2 \rightarrow 2NH_3$

1 mol 3 mol 2 mol

Now, 1 mol of N_2 requires 3 mol of H_2

0.075 mol of N_2 would require = 3 × 0.075

= 0.225 mol of H_2 = 0.225 × 2 g of H_2 = 0.45 gm.

4. We know that, 44g CO_2 contains 12g of C

0.191g of CO_2 will contain $= \frac{12 \times 0.191}{44} = 0.05209$g of C

Similarly 18g of water contains = 2g of H

0.1172g of water will contain $= \frac{2 \times 0.1172}{18} = 0.01302$g of H

Sum of the mass of C and H = 0.05209 + 0.01302 = 0.06511g

Mass of O = 0.1– 0.6511 = 0.03489g

Now convert masses into moles of each of the elements. Thus for C

0.05209/12 = 0.00434mol, mol of H = 0.01302/1 = 0.01302, mol of O = 0.03489/16 =0.00218

Simplest ratio in which the elements combine

$C = \frac{0.0043}{0.00218} = 2, \quad H = \frac{0.01302}{0.00218} = 6, \quad O = \frac{0.000218}{0.00218} = 1$

Empirical formula is C_2H_6O

5. 10 g $O_2 = \frac{10}{32}$ mole $= \frac{10}{32} \times 6.02 \times 10^{23}$ molecules $= 1.88 \times 10^{23}$ molecules

$= 2 \times 1.88 \times 10^{23}$ atoms $= 3.76 \times 10^{23}$ atoms

10 g $O_3 = \frac{10}{48}$ mole $= \frac{10}{48} \times 6.02 \times 10^{23}$ molecules

$= 1.254 \times 10^{23}$ molecules

$= 3 \times 1.254 \times 10^{23}$ atoms $= 3.76 \times 10^{23}$ atoms

Thus, both contain the same number of atoms but bulb B_1 contains more number of molecules.

6. Molecular mass of $Fe_2(SO_4)_3$

$= 2 \times 56 + 3 \times 32 + 12 \times 16 = 112 + 96 + 192 = 400$

% age of Fe $= \frac{112}{400} \times 100 = 28$

% age of S $= \frac{96}{400} \times 100 = 24$

% age of O $= \frac{192}{400} \times 100 = 48$

7. (a) Yes

(b) According to the law of multiple proportions

(c) $H_2 + O_2 \rightarrow H_2O$

2g 16g 18 g

$H_2 + O_2 \rightarrow H_2O_2$

2 g 32g 34 g

Here masses of oxygen, (i.e., 16 g in H_2O and 32 g in H_2O_2) which combine with fixed mass of hydrogen (2g) are in the simple ratio i.e., 16 : 32 or 1 : 2

8. $2A + 4B \rightarrow 3C + 4D$

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

Hence, for 5 moles of 'A', the moles of 'B' required = 5 mole of A $\times \frac{4 \text{ mole of B}}{2 \text{ mole of A}} = 10$ mole of B

But we have only 6 moles of 'B', hence, 'B' is the limiting reagent. So amount of 'C' formed is determined by amount of 'B'. Since 4 moles of 'B' give 3 moles of 'C'. Hence 6 moles of 'B' will give

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

Long Answer Questions

1. (i) In the first experiment.

2.19g of copper oxide contained 1.75 g of Cu.

100 g of copper oxide contained

$= \frac{1.75}{2.19} \times 100 = 79.91$ g

In the second experiment.

1.43 g of copper oxide contained 1.14 g of copper

$\therefore$ 100 g of copper oxide contained

$= \frac{1.14}{1.43} \times 100 = 79.72$ g

In the third experiment.

1.83 g of copper oxide contained 1.46 g of copper

$\therefore$ 100 g of copper oxide contained

$= \frac{1.46}{1.83} \times 100 = 79.78$ g

Thus, the percentage of copper in copper oxide derived from all the three experiments is nearly the same. Hence, the above data illustrate the law of constant composition.

(ii) In compound I, 0.52 g of A combines with 0.72 g of B

Thus 1 g of A combines with $\frac{0.72}{0.52}$ g of B

1.4 g of B combines 1 g of A

In compound II, 0.15 g of A combines with 0.65 of B

Thus 1 g of A combines with $\frac{0.65}{0.15}$ of B

4.3 g of B combines 1 g of A

Therefore 4.3 g of B : 1.4 g of B = 3 : 1

Thus the mass of B which combines with 1 g of A in two different compounds bears a simple ratio.

CHAPTER TEST

1. mol/dm^3
2. 1 molar is more concentrated than 1 molal.
3. When % age mass of solute and density of solution is given then molarity is expressed as

$$M = \frac{\%\text{ age of solute} \times 10 \times \text{density of solution}}{\text{Molecular weight of solute}}$$

$$M = \frac{15 \times 10 \times 1.10}{98} = 1.68\text{ M}$$

4. For 3 mol of A : mol of $P = \frac{1}{2} \times 3 = 1.5$; mol of $P = \frac{2}{2} \times 3 = 3$

For 2 mol of B : mol of $P = 2$; mol of $Q = 2 \times 2 = 4$

For 6 mol of C : mol of $P = \frac{1}{3} \times 6 = 2$;

mol of $Q = \frac{2}{3} \times 6 = 4$

A is limiting reactant. Hence, mol of $P = 1.5$ and mol of $Q = 3$

5. $$\underset{}{MnO_2} + \underset{4 \times 36.5}{4HCl} \rightarrow MnCl_2 + 2H_2O + \underset{22400\text{ cc at STP}}{Cl_2}$$

HCl present in 100 cc of 0.2M HCl

$= 0.02$ milimoles $\times 36.5 = 0.73$ g

$\because$ 146 g of HCl produces = 22400 cc of Cl_2 at STP.

$\therefore$ 0.73g of HCl produces $\frac{22400 \times 0.73}{146} = 112$ cc of Cl_2

6. 500 cc of 0.25M $Na_2SO_4 = \frac{0.25}{1000} \times 500 = 0.125$ mole

15 g of $BaCl_2 = 15/208 = 0.072$ mole

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

Evidently, $BaCl_2$ will be limiting reactant.

$BaSO_4$ formed = 0.072 mole

And mass of $BaSO_4$ formed will be

$= 0.072 \times 233 = 16.776$ g

7. (i) In the first oxide, oxygen = 27.6,

metal = 100 – 27.6 = 72.4 parts by mass

As the formula of the oxide is M_3O_4, this means 72.4 parts by mass of metal

= 3 atoms of metal and 4 atoms of oxygen

= 27.6 parts by mass

In the second oxide, oxygen

= 30.0 parts by mass and metal

= 100 – 30 = 70 parts by mass

But 72.4 parts by mass of metal = 3 atoms of metal

$\therefore$ 70 parts by mass of metal

$= \frac{3 \times 70}{72.4} = 2.90$ atoms of metal

Also, 27.6 parts by mass of oxygen = 4 atoms of oxygen

30 parts by mass of oxygen $= \frac{4 \times 30}{27.6}$

= 4.35 atoms of oxygen

Hence, ratio of M : O in the second oxide $= 2.90 : 4.35 = 1 : 1.5 = 2 : 3$

$\therefore$ Formula of the metal oxide is M_2O_3

(ii) HCl is neutralized by $Al(OH)_3$ according to the equation

$$\underset{\substack{27 + 3 \times 17 \\ = 78\text{ g}}}{Al(OH)_3} + \underset{\substack{3 \times 36.5 \\ = 109.5\text{g}}}{3HCl} \rightarrow AlCl_3 + 3H_2O$$

HCl produced from 2.5 litre of gastric juice

$= 3 \times 2.5 = 7.5$ g

$\because$ 109.5 g HCl is neutralized by $Al(OH)_3$ = 78 g

$\therefore$ 7.5 g of HCl will be neutralized by $Al(OH)_3$

$= \frac{78 \times 7.5}{109.5} = 5.342$ g = 5342 mg

$\therefore$ Number of tablets required = 5342 / 400

= 13.35 i.e. , 14 tablets

2

Chapter

Structure of Atom

INTRODUCTION

John Dalton (1767-1844), an english scientist, proposed his famous "Atomic theory" about the structure of matter. According to his concept, Matter is composed of extremely small indivisible particles called atoms.

However the researched done by various scientists like *J.J. Thomson, Rutherford, Goldstein, Chadwick* and *Bohr* have proved that atom is no longer a smallest indivisible particle but have a complex structure. According to these discoveries atom is made up of smaller particles like electrons, protons, neutrons etc.

DISCOVERY OF SUBATOMIC PARTICLES

Discovery of Electron

The discovery of electron came from the experiments of **William crookes** (1879). He performed discharge tube experiments which led to discovery of cathode rays. In this experiment he took a discharge tube which is sealed at both ends and fitted with two metal electrodes. A high voltage is applied across electrodes under reduced pressure. Cathode rays have been found to consist of negatively charged particles, called electrons.

Properties of cathode rays:

The cathode rays have been shown to possess the following properties by the experiments of **J.J. Thomson** and other scientists.

(a) Cathode rays travel in a straight line.

(b) Cathode rays possess particle nature.

(c) Cathode rays contains negatively charged particles called electrons. These particles are deflected towards the positive plate (cathode) on application of electric field.

(d) Cathode rays are deflected by magnetic field.

(e) Cathode rays produce heating effect.

(f) Cathode rays produce X-rays when strikes on the surface of solids such as copper, etc.

(g) Cathode rays produce fluorescence.

(h) Cathode rays ionise the gas through which they pass.

(i) Cathode rays affect the photographic plates.

(j) Cathode rays penetrate through the thin foils of metals.

(k) The nature of these rays does not depend upon the nature of gas and the cathode material used in discharge tube.

In order to determine the exact charge and mass of electrons two experiments were further carried out. These were,

(i) J.J. Thomson's experiment

J. J. Thomson found the ratio of charge to mass (e/m) constant by using different discharge tubes fitted with electrodes of different metals. He also used different gases in the discharge tube. The value of e/m was found to be **1.76×10^8 coulombs/g**. Two important conclusions can be drawn from this experiment.

(i) The electrons are universal constituents of all matter.

(ii) For an electron e/m value is 1.76×10^8 coulomb/g or 1.76×10^{11} C kg^{-1}

(ii) Milikan's oil drop method

The first accurate determination of the charge of an electron (*e*) was made by R.A. Millikan (1909) by his famous **oil drop experiment**.

The charge on the electron is determined to be **1.6×10^{-19} coulombs**. Since this is the smallest charge carried by any charged particle, it is referred to as **one unit charge**.

By knowing the value of $\frac{e}{m}$ ratio and charge on the electron , it is possible to calculate the exact mass of electron.

$$\therefore \text{ Mass of the electron, } m = \frac{e}{e/m} = \frac{1.60\times10^{-19}\text{coulombs}}{1.76\times10^{8}\text{coulombs / g}} = 9.1\times 10^{-28}\text{ g} = 9.1\times10^{-31}\text{ kg}$$

$$\text{Mass of an electron} = \frac{1}{1837}\times\text{mass of one atom of hydrogen}$$

Note: Molar mass of electron is obtained on multiplying mass of electron by Avogadro number (6.023×10^{23}). Therefore, gram molecular mass of electron is = $9.1094 \times 10^{-28} \times 6.023 \times 10^{23} = 5.486 \times 10^{-4}$g

$$\boxed{\text{The mass of } 1.1 \times 10^{27} \text{ electrons is one gram.}}$$

The amount of charge on one mole of electrons is one faraday or 96500 coulomb.

Discovery of Proton

The first proof for the presence of ***proton*** in an atom was provided by the experiment of ***Goldstein in 1886***.

Properties of anode rays:

(a) The anode rays travel in straight line.
(b) Anode rays are made up of material particles which are positively charged.
(c) Anode rays are deflected in the electrical as well as in the magnetic field.
(d) The ratio of charge to mass (i.e. *e/m*) and the value of the charge of the particles in the anode rays depends upon the nature of the gas taken in the discharge tube.
(e) Like cathode rays, they also cause heating effect and affect the photographic plate..

e/m ratio for a proton is determined to be 9.58×10^4 coulombs/g. The charge on proton is equal to electron in magnitude i.e. 1.6×10^{-19} coulombs but opposite in sign. Thus, the mass of each proton is calculated as

$$\text{Mass of proton} = \frac{e}{e/m} = \frac{1.6\times10^{-19}}{9.58\times10^{4}} = 1.67\times10^{-24}\text{ g} = 1.67\times10^{-27}\text{ kg}$$

The value is nearly the same as that of hydrogen atom. Hence proton is 1837 times heavier than electron.

A proton may be defined as a subatomic fundamental particle which carries one unit positive charge (1.6×10^{-19} coulombs) and has mass (1.67×10^{-27} kg) almost equal to that of an atom of hydrogen.

Radio Activity

The phenomenon of radioactivity discovered by **Henri Becqueral** (1896) further supported that atoms are divisible into subatomic particles. Radioactivity is a phenomenon of spontaneous emission of active radiations by a radioactive element.

Rutherford (1902) resolved these radiations into three types by placing uranium mineral in a lead box and passing emitted radiations between two oppositely charged plates.

(a) The radiations bending towards negative plate (cathode) show that these radiations are carrying positive charge and thus named as **alpha rays or alpha particles (alpha ; $_2He^4$).**
(b) The beam of rays which are deflected towards positive electrode (anode) show that these radiations are carrying **negative charge** and are known as **beta rays or beta particles (β).** These rays are deflected to much greater extent in comparison to deflection of α-rays showing that β–rays are lighter than α–rays.
(c) The third type of radiation, which are not deflected even in the strongest electric or magnetic field, are neutral in nature and are termed as **gamma rays.**

Order of penetrating power

α-particles (rays) < β-rays (100 times that of α-particles) < γ-rays (1000 times that of α-particles)

Discovery of Neutron

Penetrating rays are emitted on bombarding α-particles on the elements like beryllium, boron and aluminium. **James Chadwick** in 1932 studied the nature of these radiation and came to the conclusion that these rays are composed of very tiny electrically neutral particles. The mass of these particles is almost equal to that of the hydrogen atom. These particle are called neutrons and are denoted by the symbol, $_0^1n$.

The mass of a neutron is almost equal to that of a proton. Actually it is a little bit heavier than proton. Its mass (*m*) is as follows :

Mass (*m*) of a neutron = 1.6748×10^{-24} gram which is approximately equal to the mass of a proton.

Molar mass of a neutron is obtained by multiplying the mass (*m*) of a neutron with Avogadro number (6.023×10^{23}). Therefore the gram molecular mass of a neutron is

$$1.6748 \times 10^{-24} \times 6.023 \times 10^{23} = 1.00873.$$

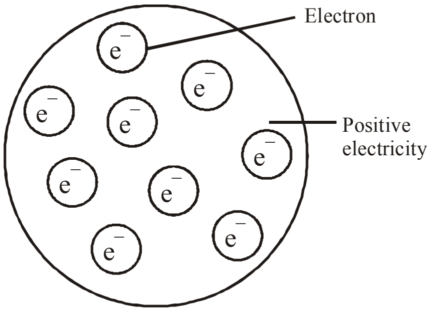
Characteristics of Fundamental Particles

	Electron	Proton	Neutron
1. Symbol	$_{-1}e^{0}$	$_{+1}p^{1}$	$_{-1}n^{0}$
2. Discoverer	J.J. Thomson (1897)	Goldstein (1919)	James Chadwick (1932)
3. Location in the atom	Extra nuclear part	Nucleus	Nucleus
4. Nature	Negatively charged	Positively charged	Neutral (uncharged)
5. Charge			
(i) Relative	–1	1	0
(ii) Absolute	-1.6022×10^{-19}C	1.6022×10^{-19}C	0
6. Mass			
(i) amu	0.0005486	1.00727	1. 00867
(ii) kg	9.10939×10^{-31}kg	1.67262×10^{-27}kg	1.67493×10^{-27}kg
(iii) Relative to hydrogen atom	1/1837	1	1

MODELS OF ATOM

Thomson's Model of Atom

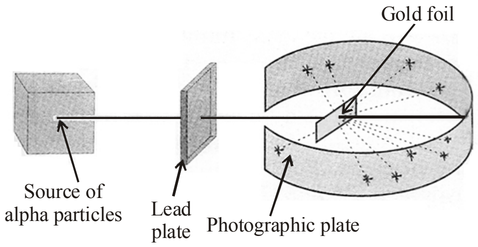
According to **J.J.Thomson** the positive charge is spread over a sphere of the size of the atom (i.e. radius of sphere is of the order 10^{-8} cm). A sufficient number of electron is so as to neutralise the positive charge are embedded over the sphere like the seeds in watermelon. This model of the atom is known as **"Plum pudding model"**.



Limitations of Thomson's Model: Though this model was able to explain the overall neutrality of the atom but it could not explain **Rutherford's** α particle scattering experiment

Rutherford's Model of an Atom

Rutherford (1911) performed scattering experiment by bombarding fast moving α–particles, emitted from a radioactive substance, on thin foil (4×10^{-5} cm thick) of the metals (like silver, gold, copper, platinum, etc).



Rutherford's scattering experiment

In above experiment Rutherford made the following observations

According to Rutherford's model of atom, the atom consists of two parts.

(i) Nucleus

It is a very small positively charged part of the atom. It is situated at the centre and carries almost the entire mass of the atom. The positive charge on the nucleus is due to the presence of protons in the nucleus.

(ii) Extranuclear part

This is the space around the nucleus in which the electrons revolve at a high speed in a fixed path called orbits or shells. This extra nuclear part provides volume to an atom and thus called **atomic volume**.

Rutherford's model of atom is similar to our solar system where the nucleus is like the sun and the electrons, are like the planets thus this model of atom is also called planetary model of atom.

Atomic Number and Mass Number

The number of unit positive charges possessed by the nucleus of an atom is termed as the **atomic number**. Since an atom is electroneutral, the number of positively charged protons in its nucleus is equal to the negatively charged electrons moving around the nucleus in the atom. Thus

Atomic number (Z) = Number of protons = Number of electrons

The total mass of the atom is due to the sum of the protons and neutrons i.e. nucleons, Mass number of an atom is the sum of number of protons and number of neutrons present in that atom. thus,

Mass number (A) = Number of proton + Number of neutrons

Isotopes

Atoms of the same element having same atomic number but different mass number are called *isotopes*. For example, ${}^{1}_{1}H, {}^{2}_{1}H, {}^{3}_{1}H$ have same atomic number i.e. 1, but different mass number 1, 2 and 3. These are named as protium (H), deuterium (D) and tritium (T) respectively. Other examples of isotopes are

(a) ${}^{12}_{6}C, {}^{13}_{6}C, {}^{14}_{6}C$ (b) ${}_{17}Cl^{35}, {}_{17}Cl^{37}$ (c) ${}^{14}_{7}N, {}^{15}_{7}N$ (d) ${}^{16}_{8}O, {}^{17}_{8}O, {}^{18}_{8}O$

Isotopes have same no. of protons but different no. of neutrons.

Isobars

Isobars are atoms of different elements which have same mass number but different atomic number. For example, ${}^{40}_{18}Ar, {}^{40}_{19}K, {}^{40}_{20}Ca$

Other examples of isobars are :

(a) ${}^{130}_{54}Xe, {}^{130}_{56}Ba$ (b) ${}^{14}_{7}N, {}^{14}_{6}C$

Isobars have different number of protons as well as different no. of neutrons.

Isotones

Isotones are atoms of different elements which have different atomic number and mass number but have the same number of neutrons.

For example, ${}^{15}_{7}N, {}^{16}_{8}O$.

Other examples of isotones are

(a) ${}^{14}_{6}C, {}^{15}_{7}N$ (b) ${}^{31}_{15}P, {}^{32}_{16}S$

Isotones have different no. of protons but same no. of neutrons.

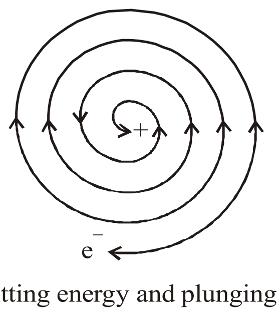
Isoelectronics

The chemical species in which number of electrons is same are called *isoelectronic*. For example

(a)	Li^+	Be^{+2}	B^{+3}		
Electrons	2	2	2		
(b)	Na^+	Mg^{+2}	Al^{+3}	F^-	O^{-2}
Electrons	10	10	10	10	10
(c)	K^+	Ca^{+2}	Ar		
Electrons	18	18	18		

Demerits of Rutherford's model of an atom

(a) According to **Clark Maxwell's theory of electrodynamics**, an electrically charged particle in motion continuously emits energy. This results in regular decrease in the energy of that particle. On the basis of this principle, it can be concluded that an electron moving around the nucleus will continuously emit energy. This will result in decrease in the radius of the electron orbit, due to which the electron would ultimately plunge into the nucleus.



An electron emitting energy and plunging into nucleus

(ii) Plunging of an electron into the nucleus would definitely mean destruction of the atom or end of the existence of the atom. But we know that it never happens. Atom is a stable system. Therefore, Rutherford model failed in explaining the stability of an atomic system.

(iii) If an electron moving around the nucleus continuously emits energy, then the atomic spectrum must be continuous, i.e., the spectrum should not have lines of definite frequency. However, the atomic spectrum is actually not continuous and possesses so many lines of definite frequency. Therefore, Rutherford model failed to explain the line spectrum of an atom.

DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Two very important developments which contributed a major role in the formulation of Bohr's model of atom are following

(a) Dual character of the electromagnetic radiation

(b) Experimental results regarding atomic spectra

Wave Nature of Electromagnetic Radiation

Vames Clark Maxwell Put forward his theory in 1870 which consists of following features

(a) Energy is emitted from any source continuously in the form of radiations and is called the radiant energy.

(b) The electromagnetic waves consist of electric and magnetic fields oscillating perpendicular to each other and both are perpendicular to the direction of propagation of radiation.

(c) These waves do not require any medium for propagation.

(d) All electromagnetic waves travel with the same speed. (i.e. 3.0×10^8 m sec^{-1} or speed of light)

All waves have five characteristics by which they can be recognised, viz. wavelength, frequency, velocity, wave number and amplitude.

(a) Wave length (λ): It is the distance between two neighbouring crests or troughs of the wave. It is denoted by Greek letter Lambda (λ) and is measured in Angstrom (Å) or nanometer (nm).

(b) Frequency (ν) : It is defined as the number of waves which pass through a given point in one second. It is denoted by Greek letter **nu** (ν) and is expressed in units of cycles per second (cps) or Hertz (Hz).

(c) Velocity : The distance travelled by a wave in one second is called velocity of the wave. It is denoted by letter c. It is related to frequency and wavelength of the wave by the expression.

$$c = \nu \times \lambda \text{ or } \nu = c/\lambda$$

(d) Wave number ($\bar{\nu}$) : It is defined as the number of wavelengths per centimeter. It is equal to the inverse of wavelength expressed in centimeters. It is denoted by $\bar{\nu}$ (**nu bar**) and its unit is cm^{-1}. Thus,

$$\text{Wave number } (\bar{\nu}) = \frac{1}{\text{Wavelength } (\lambda)}$$

$$(\bar{\nu}) = \frac{1}{\lambda}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = c\bar{\nu}$$

(e) Amplitude (a): It represent the height of the crest or depth of the trough of a wave. It is denoted by the letter '*a*' and determines the intensity or brightness of radiation.

Relationship between velocity, wave length and frequency of a wave.

$$\text{Velocity} = \text{Wavelength} \times \text{frequency}$$

$$c = \lambda \times \nu$$

Illustration 1 :

The normal human eye responds to visible light of wavelength raging from about 390 to 710 nm. Determine the frequency range of the human eye

Sol. Wavelength λ and frequency υ are related to the velocity by $\upsilon = \frac{c}{\lambda}$

$$\bar{\upsilon} = \frac{3.00 \times 10^8 \text{ms}^{-1}}{390 \times 10^{-9} \text{m}} = 7.7 \times 10^{14} \text{ s}^{-1}$$

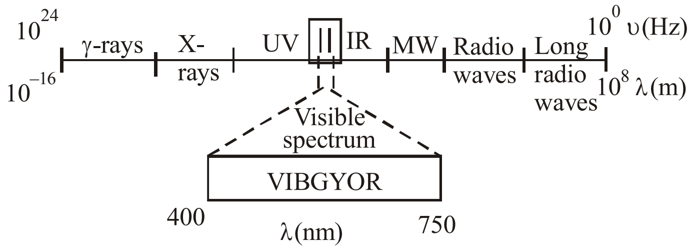
$$\text{and } \upsilon = \frac{3.00 \times 10^8 \text{ms}^{-1}}{710 \times 10^{-9} \text{m}} = 4.2 \times 10^{14} \text{ s}^{-1}$$

The frequency range of the human eye is 4.2×10^{14} to 7.7×10^{14} Hz.

ELECTROMAGNETIC SPECTRUM

It is defined as the arrangement of various types of electromagnetic radiation in terms of increasing (or decreasing) wavelengths (or frequency). The complete range of electromagnetic waves is called electromagnetic spectrum. The wavelength of various waves increases in the following order

Cosmic rays < γ-rays < X-rays < UV rays < Visible < IR rays < Microwaves < Radiowaves



Limitations of electromagnetic wave theory

Electromagnetic wave theory successfully explained the properties of light such as interference and diffraction but it could not explain the phenomenon of photoelectric effect and black body radiations. These phenomenon could be explained only if electromagnetic waves are supposed to have particle nature. It was explained by **Max Planck** and is called the **Planck's Quantum Theory**.

Particle Nature of Electromagnetic Radiation Planck's Quantum Theory

To explain the phenomenon of photoelectric effect and black body radiations. Max Planck postulated quantum theory of radiations, which was further extended by Einstein (1905). Important postulates of this theory are

(a) The radiant energy is not emitted or absorbed continuously but discontinuously in the form of small packets of energy called **quantum**. For light the quantum of energy is termed as **photon**.

(b) The energy associated with each quantum is directly proportional to the frequency of the radiation

i.e. $E \propto \nu$ or $E = h\nu$ ...(i)

Where h is called Planck's constant.

Numerically $h = 6.62 \times 10^{-34}$ Joules sec or 6.62×10^{-27} erg sec.

(c) The total amount of energy emitted or absorbed by a body will be whole number multiple of quantum by an integer n i.e. $E = nh\nu$ where n is an integer e.g., $n = 1, 2, 3$ ....etc. Thus a body can radiate energy in multiples of quantum $h\nu$, $2h\nu$, $3h\nu$ .... $nh\nu$ where n is an integer.

Energy possessed by one mole of photons is called one Einstein of energy

$$\text{One Einstein of energy (E)} = N_o h\nu = N_o h\frac{c}{\lambda}$$

Illustration 2 :

The energy required to remove an electron from the surface of Na metal is 2.3 eV. What is the largest wavelength of radiation which can show the photoelectric effect

Sol. $E = h\upsilon = \dfrac{hc}{\lambda}$

$$2.3 \times 1.6 \times 10^{-19}\ \text{J} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{\lambda}$$

$$\lambda = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{2.3 \times 1.6 \times 10^{-19}} = 5.38 \times 10^{-7}\ \text{m}$$

Photoelectric Effect

Phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it, is called photoelectric effect.

(i) **Threshold frequency (ν_0) :** The minimum frequency of incident radiation to cause the photoelectric effect, is called threshold frequency.

(ii) **Work function :** A part of the photons energy that is absorbed by the metal surface to release the electron is known as work function of the surface denoted by ϕ. The remaining part of the energy of photons goes into the kinetic energy of the electron emitted.

If ν_0 is the threshold frequency and ν the frequency of incident light then $\phi = h\nu_0$ and $E = h\nu$.

$\text{K.E.} = E - \phi = h\nu - h\nu_0 = h(\nu - \nu_0)$

Note: (a) K.E. of the ejected electron is independent of the intensity of light but depends directly on the frequency of the incident radiation.

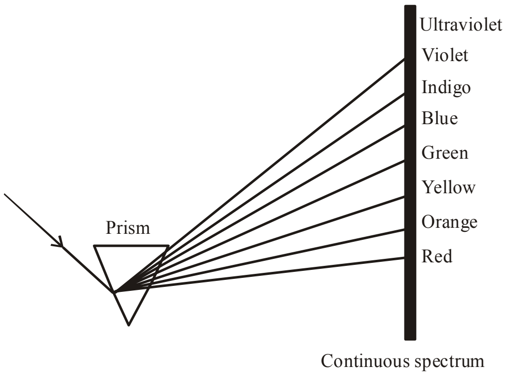
(b) Number of photoelectrons $\propto$ intensity of light

(c) Thus some of properties of light can be explained on the basis of its wave nature and some if we consider light to have particle nature. Hence, light is said to have a dual nature

Atomic Spectra

When energy is provided to any substance, it starts emitting radiations. These radiations are passed through a spectroscope, they get split up into spectral lines producing **emission spectrum**.

When sunlight or a glowing heat fluorescent substance like tungsten wire present in an electric bulb is analysed with the help of a spectroscope, the spectrum obtained on a screen is observed as divided into bands of seven colours, which are in a continuous sequence. Such a spectrum is called a **continuous spectrum**.



Continuous spectrum of white light

Spectrum of radiation emitted by a substance after absorption of energy is called an emission spectrum. Depending upon the source of radiation, the emission spectra are mainly of two types:

(i) **A continuous spectrum** is one in which all wavelengths of radiations are so intermixed that there is no line of separation between two colours. As violet merges into blue, blue into green and so on.

(ii) **A line spectrum** is that spectrum in which only certain wavelengths or bright coloured lines appear on a dark background. Atomic spectra of most elements is line spectrum. Each element has a unique line emission spectra which is used in chemical analysis to identify unknown atoms. For example: neon lamp, sodium vapour lamp, mercury vapour lamp, etc. emit light of different colours and they give specific line spectra.

When a gas, solid or transparent liquid is placed in the path of bright light emitted from any source and then analysed by the spectroscope, dark lines are observed in the spectrum. These dark lines are at the same place where coloured lines are obtained in the emission spectra for the same substance. This show that the wavelength absorbed were same as were emitted in the emission spectra. This type of spectrum is called **absorption spectrum**.

The study of emission or absorption spectra is referred to as **spectroscopy**.

BOHR'S MODEL OF HYDROGEN ATOM

Niels Bohr, in 1913, proposed a theory of hydrogen atom which not only explained the origin of hydrogen spectrum but also led to an entirely new concept of atomic structure. His theory was based upon some postulations of classical physics and some postulations of the newly proposed quantum theory of Planck. The important postulations on which the Bohr model was based are described below :

Postulates of Bohr's Theory

(a) An atom consist of a dense positively charged nucleus situated at the centre surrounded by electrons. The electrons revolves around the nucleus in certain selected circular paths, called orbits without emitting any energy.

(b) The electrons revolve only in those orbits which have fixed value of energy. Hence, these orbits are called energy levels or stationary states.

(i) The expression for energy of an electron in the different stationary states of hydrogen atom

$$E_n = -\frac{2k^2\pi^2 me^4 Z^2}{n^2h^2}$$

where, k = coulomb's law constant m = mass of the electron e = charge on the electron
h = planck's constant Z = atomic number of element

Substituting the values of constants.

$\pi = 3.14$ $m = 9.1\times10^{-31}$ kg $k = 9\times10^9$ Nm^2/c^2
$h = 6.62\times10^{-34}$ J sec^{-1} $e = 1.6\times10^{-19}$ C $Z = 1$(for hydrogen)

$$E_n = -\frac{21.79\times10^{-19}}{n^2}\,\text{J / atom} \qquad = -\frac{1312}{n^2}\,\text{kJ/mole}$$

(ii) For a particular atom the relationship of energy of nth orbit (E_n) with that of first orbit (E_1) is given by the expression.

$$E_n = \frac{E_1}{n^2}$$

$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

$$R_H = 2.18\times10^{-18}\text{ J (Rydberg constant)}$$

Energy of the electron of an atom (say He$^+$ or Li^{2+}) in n^{th} orbit.

$$E_n = -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)J$$

$$E_n(Li^{2+}) = \frac{E_n(H)\times Z^2}{n^2}$$

and radii of different stationary states of hydrogenation

$$r_n = \frac{52.9\left(n^2\right)}{Z}\,pm$$

(iii) The expresion for radius of n^{th} orbit is:

$$r_n = \frac{n^2h^2}{4\pi^2 mZe^2k}$$

where r_n = Radius of the orbit

m = Mass of the electron (9.1×10^{-31} kg)

Now substituting the values of π, h, m, e and k we get

$$r_0 = \frac{(6.62\times10^{-34})^2}{4\times(3.14)^2\times9\times10^{-31}\times(1.6\times10^{-19})\times9\times10^9}$$

$$= 5.290\times10^{-11}\text{ m } = 0.529\text{ Å}$$

Therefore, radius of the n^{th} orbit for the hydrogen atom may be written as

$$r_n = 0.529\times n^2\text{Å}$$

(iv) Velocity of the revolving electron in n^{th} orbit is given by the expression

$$v_n = \frac{2\pi\, k\, Ze^2}{nh}$$

where k = Coloumb's law constant Z = Atomic number of element

e = Charge on the electron h = Plank's constant

(c) The electrons move around the nucleus in only those circular orbits for which their angular momentum (mvr) is an integral multiple of $\frac{h}{2\pi}$. This is called the condition of quantization. The angular momentum (mvr) of an electron is $\frac{nh}{2\pi}$ where m is the mass of electron, r is radius of its circular orbit, v is the velocity of electron, h is Planck's constant; n is called principal quantum number whose value may be 1, 2, 3, 4 etc.

(d) As long as the electron remains in a particular orbit. It neither lose or gain energy. When the electrons in an atom are in their lowest energy state this state is referred as ground state.

(e) When energy is supplied to an electron, it may jump instantaneously from a lower energy level (say K) to a higher energy level (say L,M,N,.......etc) by absorbing one or more quanta of energy.

Amount of energy absorbed or emitted. $\Delta E = E_2 - E_1$

Frequency of radiation absorbed or emitted during transition

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Negative Electronic Energy

When the electron is at distance infinity from the nucleus, there is nor force of attraction on the electron by the nucleus. Hence, the energy of the electron of distance infinity from the nucleus is taken as zero. As the electron moves towards the nucleus, it experiences a force of attraction by the nucleus. As a result, some energy is given out. Since its value was already zero, hence now it becomes negative. Further, as the electron comes more and more close to the nucleus, the attraction increases and more energy is released. Hence, the energy of the electron becomes less and less. This explains why the energy decreases as we move from the outer to the inner levels.

Radiation is abosrbed when electron moves from orbit with lower value of n to orbit with higher vlue of 'n'. On the other hand radition is emitted when electron moves from orbit with higher value of n to orbit with lower value of n. Thus energy gap between two orbits is

$$\Delta E = E_f - E_i,\ \Delta E = \left(\frac{-R_H}{n_f^2}\right) - \left(\frac{-R_H}{n_i^2}\right) = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_t^2}\right)$$

Frequency (v) associated with the absorption and emission of radiation

$$v=\frac{\Delta E}{h}=\frac{R_H}{h}\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right),\quad \bar{v}=\frac{v}{c}=\frac{R_H}{h_c}\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right)$$

In case of absorption $n_f > n_i$
In case of emission $n_i > n_f$

Illustration 3 :

Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of H atom. Also calculate the energy for the corresponding line in the spectra of Li^{2+}

($R_H = 1.09678 \times 10^7\ m^{-1}$, $c = 3 \times 10^8\ ms^{-1}$, $h = 6.625 \times 10^{-34}$ Js)

Sol. $$\frac{1}{\lambda}=R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$=R_H\left[\frac{1}{1^2}-\frac{1}{2^2}\right]=\frac{3}{4}R_H$$

$$\lambda=\frac{4}{3R_H}=\frac{4}{3}\times\frac{1}{1.09678\times10^7\ m^{-1}}=1.216\times10^{-7}\ m$$

$$v=\frac{c}{\lambda}=\frac{3\times10^8\ ms^{-1}}{1.216\times10^{-7}\ m}=2.47\times10^{15}s^{-1}$$

$$E=h\upsilon=6.625\times10^{-34}\ Js\times2.47\times10^{15}s^{-1}=16.36\times10^{-19}\ J$$

$$E_{Li^{2+}}=Z^2\times E_H=3^2\times16.36\times10^{-19}\ J$$

$$=147.24\times10^{-19}\ J$$

Illustration 4 :

Calculate the energy required to remove an electron completely from n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition.

Sol. Electron energy in H - atom

$$E=\frac{2.17\times10^{-11}}{n^2}\ ergs$$

$$E_2=\frac{2.17\times10^{-11}}{4}\ ergs=0.5425\times10^{-11}\ ergs$$

$$\Delta E=E_\infty-E_2=5.425\times10^{-12}\ ergs$$

$$E=\frac{hc}{\lambda}=5.425\times10^{-12}=\frac{6.626\times10^{-27}\times3\times10^{10}}{\lambda}$$

$$\lambda=\frac{6.626\times10^{-27}\times3\times10^{10}}{5.425\times10^{-12}}\ cm=3.66\times10^{-5}\ cm$$

Main Features of Bohr's Model are

(a) It explains the stablity of an atom.
(b) It helps in calculating the energy of an electron in a particular orbit of hydrogen.
(c) It explains the line spectrum of hydrogen.
(d) Simultaneous appearance of a large number of lines in the spectrum of hydrogen. These spectral lines have been grouped into five series namely (i) Lyman series (ii) Balmer series (iii) Paschen series (iv) Brackett series (v) Pfund series.
(e) It helps in calculation of radius of Bohr's orbit.
(f) Calculation of velocity of electron in Bohr's orbit.
(g) Bohr's theory can also be applied to the ions containing only one electron. For example, He^+, Li^{2+}, Be^{3+} and so on.

Limitations of Bohr's Theory

Bohr's theory was unable to explain
(a) line spectra of multielectron atom.
(b) the splitting of spectral lines in magnetic field. (Zeeman effect).

(c) the splitting of lines in electrical field (Stark effect).
(d) the ability of atoms to form molecules by chemical bonds
(e) the three dimensional model of atom.

DEVELOPMENTS LEADING TO QUANTUM MECHANICAL MODEL OF THE ATOM

Due to limitations of the Bohr's model attempts were made to develop a more suitable model of atom.

Dual Nature of Matter and Radiation

Einstein (1905) suggested that light has dual nature i.e. it behaves like a wave as well as like a particle.
In 1924 **De Broglie** suggested that just like light all material objects including electron have dual nature. **DeBroglie's** concept was experimentally verified by **Davisson and Germer** by observing diffraction effect (a property shown by waves) with an electron beam.
De-Broglie derived the following relationship between wavelength (λ) of the wave associated with a particle of mass *m* moving with velocity v i.e.,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}$$

where *h* is Planck's constant and *p* is the momentum of the particle.
Debroglie relationship is significant for microscope objects only Debroglie wavelength of electron accelerated through potential 'v'

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Heisenberg's Uncertainty Principle

The **Heisenberg's Uncertainty Principle** states that it is impossible to determine simultaneously the exact velocity (or momentum) and position of a small moving particle (i.e., electron) with absolute accuracy.
Mathematically, it may be given as

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times m \Delta v \geq \frac{h}{4\pi}$$

$$\therefore \quad \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

where Δx = Uncertainty in determination of position
Δp = Uncertainty in measurement of momentum ($\Delta p = m\,\Delta v$)
h = Planck's constant

This principle is applicable for motion of microscopic objects and not applicable in case of macroscopic objects.
Significance of Heisenberg's uncertainty principle: although Heisenberg's uncertainty principle holds good for all objects but it is of significance only for microscopic particles. The reason for this is quite obvious. The energy of the photon is insufficient to change the position and velocity of bigger bodies when it collides with them. For example, the light from a torch falling on a running rat in a dark room neither changes the speed of the rat nor its direction, i.e., position.

Illustration 5 :

The uncertainity in the position of a bullet weighing 20 g is ± 10^{-4} m. Calculate the uncertainity in its velocity.

Sol. 20 g = 0.02 Kg

$$\pm \Delta x . \Delta p = \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x . m \Delta v = \frac{h}{4\pi}$$

$$\therefore \pm \Delta v = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 0.02 \times 10^{-4}} = 2.63 \times 10^{-29}\ ms^{-1}$$

QUANTUM MECHANICAL MODEL OF ATOM

Newton's law when applied to motion of microscopic particles they were found to be invalid as this does not take dual nature of matter and Heisenberg's principle into consideration. Thus a new branch called quantum mechanics is required.

Schrodinger Wave Equation.

Schrodinger (1927) gave a mathematical expression known as a **Schrodinger wave equation**. His theory is based on quantum mechanical model of atom in which the concept of probability of finding the electron at any position around the nucleus at any instant of time is considered.

Schrondinger regarded electron as having wave nature and put forward the following complex differential equation.

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\phi = 0$$

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

where m = mass of electron, h = Planck's constant,
E = total energy of electron, V = potential energy of electron,
ψ = wave function, ∇ = Laplacian Operator

Significance of ψ : The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function may have positive or negative values depending upon the values of coordinates.

The main aim of Schrodinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space the value of ψ is positive and for some regions the value of ψ is negative. But the probability must be always positive and cannot be negative. It is, thus, proper to use ψ^2 in favour of ψ. ψ^2 provides the information regarding the probability of finding electron at a point in an atom.

An orbital is the three dimensional space around the nucleus within which the probability of finding an electron is maximum (upto 90%).

QUANTUM NUMBERS

Quantum numbers may be defined as set of numbers which display complete information about size, shape and orientation of the orbital. These are designated as **principal quantum number** (*n*), **azimuthal quantum number** (*l*)**, magnetic quantum number** (*m*) and **spin quantum number**(s).

Principal Quantum Number (n)

It refer to the average distance of the electron from the nucleus. It denotes the energy level to which the electron belongs. It gives information about the maximum number of electrons that can be accommodated in any shell. An atom has K, L, M, N, O, P, Q, etc. shells. For $n = 1$, electron is present in first shell K, for $n = 2$ it is present in L shell etc. Number of electrons in any shell is given by expression $2n^2$.

Azimuthal Quantum Number or Angular Momentum Quantum Number (*l*)

It tells about the number of subshells within a given principal energy shell to which the electrons belong. For a given values of principal quantum number, '*n*', the azimuthal quantum number, '*l*', may have all integral values from 0 to (n–1), each of which represent a different subenergy level or subshell.

The value of *l* refer to the shapes of the subshells. For example.

l	Subshell	Shape of subshell
0	*s*	Spherical
1	*p*	Dumbbell
2	*d*	Double dumbbell
3	*f*	complex shape.

The number of orbitals in any sub orbital is determined by the expression $(2\ell + 1)$ and the number of electrons is determined by the expression $2(2\ell + 1)$.

The value of orbital angular momentum, μ_i, of an electron can be determined with the help of azimuthal quantum number

$$\mu_i = \sqrt{\ell(\ell+1)} \times \frac{h}{2\pi}$$

Here, ℓ = Azimuthal quantum number and
h = Planck's constant

Magnetic Quantum Number (*m*)

This quantum number describes the behaviour of electron in a magnetic field. This quantum number provides following information about the electron.

(a) Magnetic quantum number gives the number of permitted orientations of subshells. It gives information about orientation of orbitals. For example, for a given value of '*l*', the possible values of '*m*' range from –*l* through 0 to +*l*. Each value of *m* corresponds to one atomic orbital. For example,

For *s*-subshell,	$l = 0$	$m = 0$	i.e., *s*-subshell has **one** orbital
For *p*-subshell,	$l = 1$	$m = -1, 0, +1$	i.e., *p*-subshell has **three** orbitals
For *d*-subshell,	$l = 2$	$m = -2, -1, 0, +1, +2$	i.e., *d*-subshell has **five** orbitals
For *f*-subshell,	$l = 3$	$m = -3, -2, -1, 0, +1, +2, +3$	i.e., *f*-subshell has **seven** orbitals

(b) It explained successfully the splitting of spectral lines in the magnetic field i.e., Zeeman effect.

The total number of orbitals present in a sublevel is equal to the total values of magnetic quantum number. This can be found by the expression, $m = 2\ell + 1$

The total number of orbitals present in an energy level is determined by the formula n^2 where n is principal quantum number.

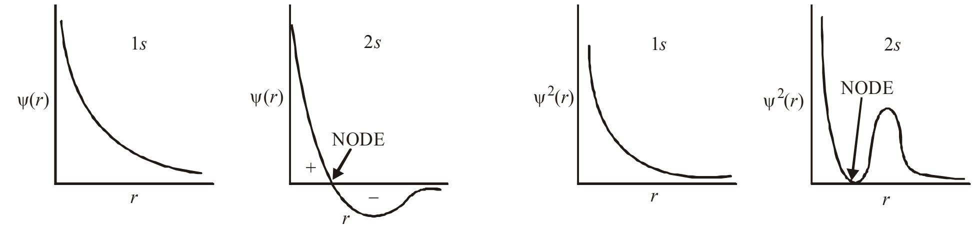
Spin Quantum Number(s)

It accounts for the spinning orientation of the electron. The electron in an orbital can have only two types of spins i.e. in clockwise and anticlockwise direction. Therefore, the spin quantum number can have only two values i.e. $+\frac{1}{2}$ or $-\frac{1}{2}$.

SHAPES OF ORBITALS

Shapes of *s*-orbitals

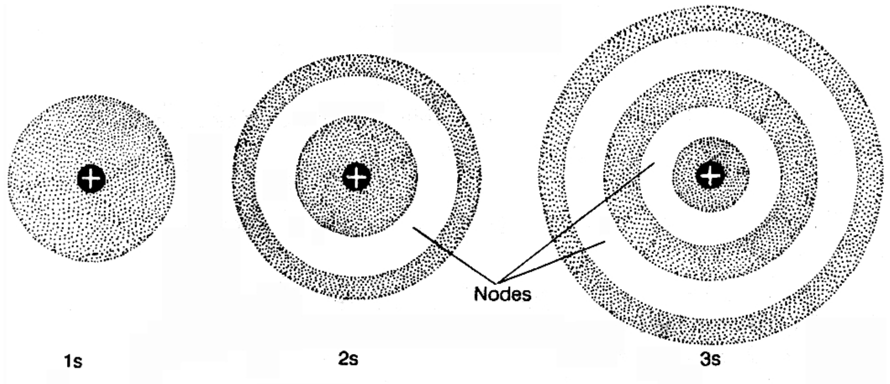
The variation of ψ and $|\psi|^2$ at different distances (r) from the nucleus for 1*s* and 2*s* orbitals are shown in Fig.



(a) (b)

Variation of (a) Orbital wave function ψ (b) Probability density ψ^2 with distance of the electron from the nucleus for 1*s* and 2*s* orbitals

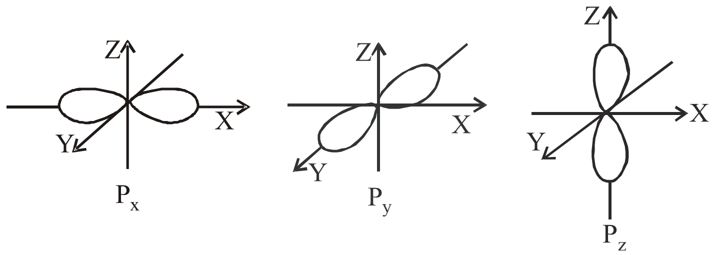
For *s*-orbitials $l = 0$, so there is only one value of m i.e. $m = 0$. Thus, *s*-orbital can have only one orientation i.e. the probability of finding electron is same in all directions at a given distance from the nucleus. Hence *s*-orbital is symmetrical around the nucleus and thus has spherical shape. Between each *s*-orbital there is some region where the probability of finding electrons is minimum or may be considered as zero. This region in called as nodel plane or node. In general, it has been found that *ns*-orbital has (n–1) nodes.



Shapes of 1s, 2s and 3s orbitals

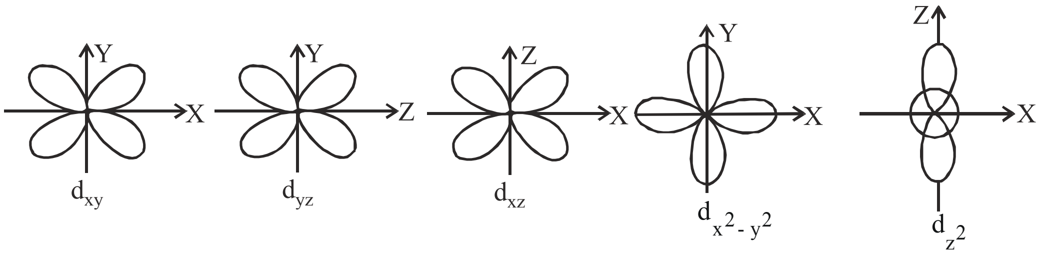
Shapes of *p*-orbitals

For *p*-orbitals $l = 1$, the permissible values of m are +1, 0 and –1. Thus, there are three *p*-orbitals, designated as p_x, p_y and p_z, in each p-subshell. Each p-orbital has two lobes on the opposite side of the nucleus and separated by the nodal plane (probability of finding electron is zero) as depicted in fig. These three orbitals are identical in shape, size and energy but have orientation along x-axis, y-axis and z-axis. Like s orbitals p-orbitals also increase in size and energy with increase in value of 'n'



Shapes of *d*-orbitals

For *d*-orbitals $l = 2$ i.e. the permissible values of m are –2,–1,0, +1, +2. This indicates for the five *d*-orbitals designated as $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ and d_{z}^{2}. Each *d*-orbital is identical in shape, size and energy and looks like double dumbbell in shape shown in fig.



The orbitals having the same energy are called degenerate.

Note: *s*-orbitals have spherical nodes only whereas *p* and *d*-orbitals have spherical as well as planar angular nodes.

Number of spherical/radial nodes in any orbital = $n - \ell - 1$

Number of planer nodes in any orbital = ℓ

$\therefore$ Total number of nodes in any orbital = $n - 1$

FILLING OF ORBITALS

A diagram showing the relative energies of various orbitals in an atom is called energy level diagram. The relative order of energies of various sub-shells in a multielectron atom can be predicted with the help of ***Bohr-Bury's*** rule also known as ***$(n + \ell)$ rule***. The orbital with lower value of $(\mathbf{n} + \boldsymbol{\ell})$ will be filled first

(i) Lower the value of $(\mathbf{n} + \boldsymbol{\ell})$ for an orbital, the lower is its energy. For example 3s orbital has lower energy than 3p orbital.

(ii) If two orbitals have the same value of $(n + \ell)$, the orbital with lower value of n has lower energy. For example, between $2p(n + \ell = 2 + 1 = 3)$ and $3s$ $(n + \ell = 3 + 0 = 3)$, $2p$ orbital has lower energy than $3s$.

The energies of the different subshells present within the same principle shell are in the following order.

$$\xrightarrow[\text{Increasing energy}]{s<p<d<f}$$

The size and energy of *s*-orbital increases with the increase of principal quantum number n i.e.

$$\xrightarrow[\text{size and energy increases}]{1s<2s<3s<4s}$$

Increasing order of energy

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$

The maximum number of electrons that can be accommodated in *s* orbital is 2, in *p* orbital is 6, in d orbital is 10 and in *f* orbital is 14.

Aufbau's Rule

According to this rule the orbitals are filled progressively in order of their increasing energy beginning with the orbital of lowest energy.

Pauli's Exclusion Principle

According to this principle "no two electrons in an atom can have the same set of all the four quantum numbers".

or

Only two electrons can be accomodated in the same orbital because their spin quantum number is different

According to this rule, for any two electrons, a set of maximum three quantum numbers can be same, but the fourth has to be different.

For example, two electrons can have same (*n*, *l* and *m*) or (*l*, *m* or *s*) or (*n*, *m* or *s*)

Example

$1s^1$	and	$1s^2$
$n = 1$		$n = 1$
$\ell = 0$		$\ell = 0$
$m = 0$		$m = 0$
$s = +\dfrac{1}{2}$		$s = -\dfrac{1}{2}$

Hund's Rule of Maximum Multiplicity

This rule governs the arrangement of electrons in the orbitals of indentical energies e.g., within p_x, p_y and p_z or amongst d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. According to this rule, electron pairing in orbitals of same energy (i.e. orbitals of *p*, *d* or *f* subshell) shall take place only when all the orbitals of the subshell contain one electron each.

The orbitals having same energy are called degenerate orbitals. *s*-sub-shell consists of only one orbital. Thus, it cannot have degenerate orbital. Hund's rule is not applicable for H, He, Li and Be, because electrons in them go to s sub-shell, which does not have any degenerate orbital. Hund's rule is not applicable for $_5B$ also, because there is only one electron in p orbital. Therefore, this rule is applicable from $_6C$ onwards.

Electronic Configuration and Stability of Half-filled and Fullyfilled orbitals

The distribution of electrons into different shells, subshells and orbitals of an atom is called its electronic configuration. Alternatively, the electronic configuration of any orbital can be simply represented by the notation, $\boldsymbol{nl^x}$

where n = number of the main or principal shell, l = symbol of the subhsell or orbital (*s, p, d, f*)

x = number of electrons present in that orbital.

Stability of Half-Filled and Fully-Filled Orbitals

The stability of half-filled orbitals (p^3, d^5 and f^7) and fully-filled orbitals (p^6, d^{10} and f^{14}) is higher than that in other states.

(a) When a sub-shell is half–filled or fully-filled, it means that the distribution of electrons is symmetrical in the orbitals of equal energy. Unsymmetrical distribution of electrons results in lower stability.

(b) The electrons present in orbitals of equal energy in an atom can interchange their position, in this process energy is released, resulting in a stable system. The possibility of interchange of positions is highest in half filled and fully-filled states. This provides greater stability to the system.

(c) The exchange energy for half-filled and fully-filled orbitals is maximum. As the number of electrons increases, electrons start pairing resulting in spin coupling. The energy liberated in the process of coupling is called coupling energy.

(d) The spin of electrons in a fully-filled orbital are opposite to each other or antiparallel. The energy of the system decreases due to neutralization of opposite spins. So fully-filled orbitals are more stable.

CONCEPT MAP

STRUCTURE OF ATOM

- Discovery of substomic particles
  - Discovery of Electron (William crookes 1879) cathode rays consist of negatively charged particles called electrons.
    $e/m = 1.76 \times 10^8$ C/g
    $m = 9.1 \times 10^{-31}$ Kg
  - Discovery of Proton (Gold stein 1886) Anode rays are positively charged
  - Discovery of Neutron (Chadwick 1932) Neutral particles with mass highly greater than proton present in the nucleus
- Models of Atom
  - J.J. Thomson's Model also known as Plum-pudding Model
  - Rutherford's Model
    Fast moving α-particles are bombarded on a thin foil of metals like Ag, Au, Cu, Pt etc
    Atom consists of two parts
    (a) Nucleus
    (b) Extranuclear
  - Atomic number (Z)
    = No. of protons
    = no. of electrons
    Mass number (A)
    = No. of protons
    –No. of neutrons
    Isotopes
    = Same at no. but different mass no.
    Isobars
    = Same mass no. but different at no.
- Developments leading to Bohr's Model
  - Wave nature of e.m waves consist of electric and magnetic fields oscillating perpendicular to each other
    $c = v \times \lambda$
    $\upsilon \propto 1/\lambda$
  - Particle nature of e.m. waves
    $E = nhv$
    $K.E = h\,(v - v_o)$
    No. of photoelectrons α intensity of light
- **Bohr's Model of Atom**

  $$E_n = \frac{E_2}{n^2} = -R_H\left(\frac{1}{n^2}\right) = \frac{-1312}{n^2}\ \text{kg/mole}$$

  $$r_n = 0.529 \times n^2 A, mvr = \frac{nh}{2\pi}$$

  $$v = \frac{\Delta E}{h}, \bar{v} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
- **Quantum Mechanical Model of Atom**

  $$\lambda = \frac{h}{mV} = \frac{h}{P} \quad \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

  Principal quantum number (n):
  Denotes the energy level of electron
  No. of electron in any shell = $2n^2$
  Azimuthal quantum number (l) =
  Tell about teh no. of subshells within a given principal energy shell. For n, l = 0 to $n - 1$)
  Magnetic quantum number m)
  (Behaviour of e^- in magnetic field)
  For l, $m = -\ell$ through 0 to $+l$
  Spin quantum number(s)
  (spinning orientation of the electron)

  $$s = +\frac{1}{2} \quad \text{or} \quad -\frac{1}{2}$$
- **Shapes of orbitals**
  S-orbital: l = o, i.e., m = o (Symmertical with spherical shape) p-orbital: l = 1 i.e., m = +1, 0 and Y (there are three dumbell shaped p-orbitals, designated as p_x, p_y and p_z)
- **Fill of orbitals**
  - orbital with lower of (n + l) will be filled first. In case of equal (n + l) values value of n should be low
  - Aufbau's rule; orbitals are filled in order
  - Pauli's exclusion principle: Not we electron can have equal values for al four quantum numbers
  - Hund's rule: Electron pairing in degenerate orbitals take place if each orbital is singly occupied.

Textbook Exercises

2.1 (i) Calculate the number of electrons which will together weigh one gram.

(ii) Calculate the mass and charge of one mole of electrons.

Ans. (i) Mass of one electron = 9.11×10^{-31} kg,

i.e. 9.11×10^{-31} kg = 1 electron

$$\therefore\ 10^{-3}\ \text{kg} = \frac{1}{9.11\times10^{-31}}\times10^{-3}\ \text{electrons}$$

i.e. 10^{-3} kg = 1.098×10^{27} electrons.

(ii) Mass of one electron = 9.11×10^{-31} kg

$\therefore$ Mass of one mole of electrons

$= (9.11\times10^{-31})\times6.022\times10^{23} = 5.486\times10^{-7}$ kg

Charge on one electron

$= 1.602\times10^{-19}$ coulomb

$\therefore$ Charge on one mole of electrons

$= (1.602\times10^{-19})\times(6.022\times10^{23}) = 9.65\times10^{4}$ coulombs.

2.2 (i) Calculate the total number of electrons present in one mole of methane.

(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of ^{14}C.

(Assume that the mass of a neutron = 1.675×10^{-27} kg).

(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at STP. Will the answer change if temperature and pressure are changed?

Ans. (i) 1 molecule of CH_4 contains electrons = 6 + 4 = 10

$\therefore$ 1 mole, i,e., 6.022×10^{23} molecules will contain electrons = 6.022×10^{24}

(ii) (a) 1 g atom of ^{14}C = 14 g = 6.022×10^{23} atoms

$= (6.022\times10^{23})\times8$ neutrons.

(as each ^{14}C atom has 14 – 6 = 8 neutrons)

Thus, 14 g or 14000 mg have $8\times6.022\times10^{23}$ neutrons

$\therefore$ 7 mg will have neutrons

$$= \frac{8\times6.022\times10^{23}}{14000}\times7 = 2.4088\times10^{21}$$

(b) $\because$ Mass of 1 neutron = 1.675×10^{-27}kg

$\therefore$ Mass of 2.4088×10^{21} neutrons

$= (2.4088\times10^{21})(1.675\times10^{-27}\text{kg}) = 4.0347\times10^{-6}$kg

(iii) (a) 1 mol of NH_3 = 17g of NH_3

$= 6.022\times10^{23}$ molecules of NH_3

$= (6.022\times10^{23})\times(7+3)$ protons

$= 6.022\times10^{24}$ protons.

$\therefore$ 34 mg i.e., 0.034g of NH_3

$$= \frac{6.022\times10^{24}}{17}\times0.034\ \text{protons}$$

$= 1.2044\times10^{22}$ protons.

(b) $\because$ Mass of one proton = 1.6726×10^{-27} kg

$\therefore$ Mass of 1.2044×10^{22} protons

$= (1.6726\times10^{-27})\times(1.2044\times10^{22})$ kg

$= 2.0145\times10^{-5}$ kg.

2.3 How many neutrons and protons are there in the following nuclei?

$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

Ans.

Nucleus	Z	A	protons (Z)	Neutrons (A–Z)
$^{13}_{6}C$	6	13	6	13 – 6 = 7
$^{16}_{8}O$	8	16	8	16 – 8 = 8
$^{24}_{12}Mg$	12	24	12	24 – 2 = 12
$^{56}_{26}Fe$	26	56	26	56–26 = 30
$^{88}_{38}Sr$	38	88	38	88–38 = 50

2.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A).

(i) Z = 17, A = 35 (ii) Z = 92, A = 233 (iii) Z = 4, A = 9

Ans. (i) $^{35}_{17}Cl$ (ii) $^{233}_{92}U$ (iii) $^{9}_{4}Be$

2.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (v) and wave number ($\bar{v}$) of the yellow light.

Ans. $\lambda = 580\ \text{nm} = 580\times10^{-9}$m

$$\text{Frequency, } v = \frac{c}{\lambda} = \frac{3.0\times10^{8}\ \text{ms}^{-1}}{580\times10^{-9}\ \text{m}} = 5.17\times10^{14}\ \text{s}^{-1}$$

$$\text{Wave number, } \overline{\nu} = \frac{1}{\lambda} = \frac{1}{580\times10^{-9}\ \text{m}} = 1.72\times10^{6}\ \text{m}^{-1}$$

2.6 Find energy of each of the photons which

(i) correspond to light of frequency 3×10^{15} Hz

(ii) have wavelength of 0.50 Å.

Ans. (i) $v = 3\times10^{15}$ Hz

$E = h\nu = (6.626\times10^{-34}\text{Js})(3\times10^{15}\text{s}^{-1}) = 1.988\times10^{-18}$J

(ii) $\lambda = 0.50\times10^{-10}$m,

$$E = hv = h\frac{c}{\lambda} = \frac{(6.626\times10^{-34}\ \text{Js})(3\times10^{8}\ \text{ms}^{-1})}{0.50\times10^{-10}\ \text{m}}$$

$= 3.98\times10^{-15}$J.

2.7 Calculate the wavelength, frequency and wave number of a light wave whose period is 2.0×10^{-10}s.

Ans. $$\text{Frequency } (v) = \frac{1}{\text{Period}} = \frac{1}{2.0\times10^{-10}\text{s}} = 5\times10^{9}\text{s}^{-1}$$

Wavelength,

$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}\ \text{ms}^{-1}}{5\times10^{9}\ \text{s}^{-1}} = 6.0\times10^{-2}\ \text{m}$$

$$\text{Wave number, } v = \frac{1}{\lambda} = \frac{1}{6\times10^{-2}} = 16.66\ \text{m}^{-1}$$

2.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

Ans. $\lambda = 4000\ \text{pm} = 4000\times10^{-12}\ \text{m} = 4\times10^{-9}$m

$$E = N\,hv = N\,h\frac{c}{\lambda}$$

$$\therefore N = \frac{E\times\lambda}{h\times c} = \frac{(I\,J)\times(4\times10^{-9}\text{m})}{(6.626\times10^{-34}\ \text{Js})(3.0\times10^{8}\ \text{ms}^{-1})}$$

$= 2.012\times10^{16}$ photons

2.9 A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate
(i) the energy of the photon (eV)
(ii) the kinetic energy of the emission and
(iii the velocity of the photoelectron ($1\ \text{eV} = 1.6020 \times 10^{-19}$ J).

Ans. (i) Energy of the photon (E) = hν $= \frac{hc}{\lambda}$

$$= \frac{(6.626 \times 10^{-34}\,\text{Js}) \times (3 \times 10^8\,\text{ms}^{-1})}{4 \times 10^{-7}\,\text{m}}$$

$$= 4.97 \times 10^{-19}\,\text{J} = \frac{4.97 \times 10^{-19}}{1.602 \times 10^{-19}}\,\text{eV} = 3.10\text{eV}$$

(ii) Kinetic energy of emission $\left(\frac{1}{2}mv^2\right)$

$= h\nu - h\nu_0 = 3.10 - 2.13 = 0.97$ eV

(iii) $\frac{1}{2}mv^2 = 0.97\text{eV} = 0.97 \times 1.602 \times 10^{-19}\,\text{J}$

i.e. $\frac{1}{2} \times (9.11 \times 10^{-31}\,\text{kg}) \times v^2 = 0.97 \times 1.602 \times 10^{-19}$ J

or $v^2 = 0.341 \times 10^{12} = 34.\ 1 \times 10^{10}$

or $v = 5.84 \times 10^5\,\text{m s}^{-1}$

2.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Ans. $E = Nh\nu = Nh\frac{c}{\lambda}$

$$= \frac{(6.02 \times 10^{23}\,\text{mol}^{-1}) \times (6.626 \times 10^{-34}\,\text{Js}) \times (3 \times 10^8\,\text{ms}^{-1})}{242 \times 10^{-9}\,\text{m}} = 4.945 \times 10^5\,\text{J mol}^{-1} = 494.5\,\text{kJ mol}^{-1}$$

2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.

Ans. Energy emitted by the bulb = 25 watt = 25 Js^{-1}

($\because$ 1 watt = 1Js^{-1})

Energy of one photon (E) = hν $= h\frac{c}{\lambda}$

Here $\lambda = 0.57\ \mu\text{m} = 0.57 \times 10^{-6}\,\text{m}$

($\because 1\ \mu\text{m} = 10^{-6}\,\text{m}$)

Putting $c = 3 \times 10^{-8}\,\text{ms}^{-1}$

$h = 6.62 \times 10^{-34}$ Js, we get

$$E = \frac{(6.62 \times 10^{-34}\,\text{Js})(3 \times 10^8\,\text{ms}^{-1})}{0.57 \times 10^{-6}\,\text{m}} = 3.48 \times 10^{-19}\,\text{J}$$

$\because$ No. of photons emitted per sec

$$= \frac{25\ \text{Js}^{-1}}{3.48 \times 10^{-19}\,\text{J}} = 7.18 \times 10^{19}$$

2.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

Ans. Threshold wavelength (λ_0) = 6800 Å = 6800×10^{-10}m

As $c = \nu\lambda$,

$$\therefore \quad \nu_0 = \frac{c}{\lambda_0} = \frac{3.0 \times 10^8\,\text{ms}^{-1}}{6800 \times 10^{-10}\,\text{m}} = 4.41 \times 10^{14}\,\text{s}^{-1}$$

Work function (W_0) = hν_0

$= (6.626 \times 10^{-34}\,\text{Js})(4.41 \times 10^{14}\,\text{s}^{-1}) = 2.92 \times 10^{-19}$J

2.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2?

Ans. $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\text{cm}^{-1} = 20564.4\,\text{cm}^{-1}$

$$\nu = \frac{1}{\lambda} = \frac{1}{20564.4\text{cm}^{-1}} = 486 \times 10^{-7}\,\text{cm}$$

$= 486 \times 10^{-9}$ m = 486 nm

2.14 How much energy is required to ionise a H atom if the electron occupies *n* = 5 orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from *n* = 1 orbit).

Ans. $E_n = -\frac{21.8 \times 10^{-19}}{n^2}\,\text{J atoms}^{-1}$

For ionization from 5th orbit, $n_1 = 5$, $n_2 = \infty$

$\therefore \Delta E = E_2 - E_1 = -21.8 \times 10^{-19}$

$$\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 21.8 \times 10^{-19}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 21.8 \times 10^{-19}\left(\frac{1}{5^2} - \frac{1}{\infty}\right) = 8.72 \times 10^{-20}\,\text{J}$$

For ionization from 1st orbit, $n_1 = 1$, $n_2 = \infty$

$$\Delta E = 21.8 \times 10^{-19}\left(\frac{1}{1^2} - \frac{1}{\infty}\right) = 21.8 \times 10^{-19}\,\text{J}$$

2.15 What is the maximum number of emission lines when the excited electron of a H atom in *n* = 6 drops to the ground state?

Ans. No. of lines produced when electron from *n*th shell drops to ground state

$$= \frac{n(n-1)}{2} = \frac{6(6-1)}{2} = 15$$

These are produced due to following transitions:

$6 \longrightarrow 5$	$5 \longrightarrow 4$	$4 \longrightarrow 3$	$3 \longrightarrow 2$	$2 \longrightarrow 1$
$6 \longrightarrow 4$	$5 \longrightarrow 3$	$4 \longrightarrow 2$	$3 \longrightarrow 1$	
$6 \longrightarrow 3$	$5 \longrightarrow 2$	$4 \longrightarrow 1$		
$6 \longrightarrow 2$	$5 \longrightarrow 1$			
$6 \longrightarrow 1$				
(5 lines)	(4 lines)	(3 lines)	(2 lines)	(1 line)

2.16 (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18}J atom^{-1}. What is the energy associated with the fifth orbit?

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Ans. (i) $E_n = -\frac{2.18 \times 10^{-18}}{n^2}$ J.

$$\therefore E_5 = -\frac{2.18 \times 10^{-18}}{5^2} = -8.72 \times 10^{-20}\,\text{J}$$

(ii) For H–atom, $r_n = 0.529 \times n^2$ Å

$\therefore r_5 = 0.529 \times 5^2 = 13.225$ Å $= 1.3225$ nm.

2.17 Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

Ans. For Balmer series, $n_1 = 2$.

Hence, $\bar{\nu} = R\left(\dfrac{1}{2^2} - \dfrac{1}{n_2^2}\right)$

$\bar{\nu} = \dfrac{1}{\lambda}$, For λ to be longest (maximum) $\bar{\nu}$ should be minimum. This can be so when n_2 is minimum, i.e., $n_2 = 3$. Hence,

$$\bar{\nu} = (1.097 \times 10^7\,\text{m}^{-1})\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 1.097 \times 10^7 \times \frac{5}{36}\,\text{m}^{-1} = 1.523 \times 10^6\,\text{m}^{-1}$$

2.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

Ans. As ground state electronic energy is -2.18×10^{-11} ergs, this means that

$$E_n = \frac{-2.18 \times 10^{-11}}{n^2}\ \text{ergs.}$$

$$\Delta E = E_5 - E_1 = 2.18 \times 10^{-11}\left(\frac{1}{1^2} - \frac{1}{5^2}\right)$$

$$= 2.18 \times 10^{-11}\left(\frac{24}{25}\right) = 2.09 \times 10^{-11}\ \text{ergs.}$$

$= 2.09 \times 10^{-18}$ J (1 erg $= 10^{-7}$ J)

When electron returns to ground state (i.e., to n = 1), energy emitted $= 2.09 \times 10^{-18}$ J

As $E = h\nu = h\dfrac{c}{\lambda}$ or

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\,\text{Js})(3 \times 10^{10}\,\text{cm s}^{-1})}{2.09 \times 10^{-18}\,\text{J}}$$

$= 9.51 \times 10^{-6}$ cm $= 951 \times 10^{-8}$ cm $= 951$ Å

2.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

Ans. $\Delta E = E_\infty - E_2 = 0 - \left(-\dfrac{2.18 \times 10^{-18}\,\text{J atom}^{-1}}{2^2}\right)$

$= 5.45 \times 10^{-19}$ J atoms^{-1}

$$\Delta E = h\nu = h\frac{c}{\lambda} \text{ or } \lambda = \frac{hc}{\Delta E}$$

$$= \frac{(6.626 \times 10^{-34}\,\text{Js}) \times (3 \times 10^8\,\text{ms}^{-1})}{5.45 \times 10^{-19}\,\text{J}}$$

$= 3.647 \times 10^{-7}$ m $= 3.647 \times 10^{-5}$cm.

2.20 Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 ms^{-1}.

Ans. By de Broglie equation

$$\lambda = \frac{h}{m\nu} = \frac{6.626 \times 10^{-34}\,\text{Js}}{(9.11 \times 10^{-31}\,\text{kg})(2.05 \times 10^7\,\text{ms}^{-1})}$$

$= 3.55 \times 10^{-11}$m (1 J = 1 kg m^2 s^{-2})

2.21 The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Ans. $\text{K.E.} = \dfrac{1}{2}m\nu^2$

$$\therefore \nu = \sqrt{\frac{2\,\text{K.E}}{m}}. = \sqrt{\frac{2 \times 3.0 \times 10^{-25}\,\text{J}}{9.1 \times 10^{-31}\,\text{kg}}} = 812\,\text{ms}^{-1}$$

(1 J = 1 kg m^2 s^{-2})

By de Broglie equation,

$$\lambda = \frac{h}{m\nu} = \frac{6.626 \times 10^{-34}\,\text{Js}}{(9.1 \times 10^{-31}\,\text{kg})(812\,\text{ms}^{-1})}$$

$= 8.967 \times 10^{-7}$ m $= 8967$ Å

2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons ?
Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

Ans. No. of electrons : $Na^+ = 11 - 1 = 10$, $K^+ = 19 - 1 = 18$, $Mg^{2+} = 12 - 2 = 10$, $Ca^{2+} = 20 - 2 = 18$, $S^{--} = 16 + 2 = 18$, Ar = 18.

Hence, isoelectronic species are (i) Na^+ and Mg^{2+}; (ii) K^+, Ca^{2+}, S^{2-} and Ar.

2.23 (i) Write the electronic configurations of the following ions:

(a) H^- (b) Na^+ (c) O^{2-} (d) F^-

(ii) What are the atomic numbers of elements whose outermost electrons are represented by

(a) $3s^1$ (b) $2p^3$ (c) $3p^5$?

(iii) Which atoms are indicated by the following configurations ?

(a) $|He|\ 2s^1$ (b) $|Ne|\ 3s^2 3p^3$ (c) $|Ar|\ 4s^2 3d^1$.

Ans. (i) (a) $_1H = 1s^1 \therefore H^- = 1s^2$

(b) $_{11}Na = 1s^2\,2s^2 2p^6\,3s^1$

$\therefore Na^+ = 1s^2\,2s^2\,2p^6$

(c) $_8O = 1s^2\,2s^2\,2p^4 \therefore O^{2-} = 1s^2\,2s^2\,2p^6$

(d) $_9F = 1s^2\,2s^2\,2p^5 \therefore F^- = 1s^2\,2s^2\,2p^6$

(ii) (a) $1s^2\,2s^2\,2p^6\,3s^1$ (Z = 11)

(b) $1s^2\,2s^2\,2p^3$ (Z = 7)

(c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ (Z = 17)

(iii) (a) [He] $2s^1$ → Lithium, Li

(b) [Ne] $3s^2\,3p^3$ → Phosphorus, P

(c) [Ar] $4s^2\,3d^1$ → Scandium, Sc

2.24 What is the lowest value of *n* that allows *g* orbitals to exist?

Ans. For *g*–subshell, $\ell = 4$, As for a given value of n, ℓ can have values ranging from $\ell = 0$ to $n - 1$, to have $\ell = 4$, minimum value of $n = 5$

2.25 An electron is in one of the 3*d* orbitals. Give the possible values of *n*, ℓ and m_ℓ for this electron.

Ans. For 3*d* orbital, $n = 3$, $\ell = 2$. For $\ell = 2$, $m = -2\,-1, 0, +1 +2$.

2.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

Ans. For neutral atom, number of protons = number of electrons = 29

Thus, atomic number of the element = 29

Electronic configuration of element with Z = 29 will be

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$ or $[Ar]^{18}\,3d^{10}\,4s^1$, i.e., $_{29}Cu$.

2.27 Give the number of electrons in the species H_2^+, H_2 and O_2^+.

Ans. $H_2 = {}_1H + {}_1H = 2$ electrons.

$\therefore$ H_2^+ has $= 2 - 1 = 1$ electron.

$O_2 = {}_8O + {}_8O = 16$ electrons.

$\therefore$ O_2^+ has $= 16 - 1 = 15$ electrons.

2.28 (i) An atomic orbital has $n = 3$. What are the possible values of l and m_ℓ?

(ii) List the quantum numbers (m_ℓ and ℓ) of electrons for 3*d*– orbital.

(iii) Which of the following orbitals are possible ? 1*p*, 2*s*, 2*p* and 3*f*.

Ans. (i) When $n = 3$, $l = 0, 1, 2$

When $\ell = 0$, $m = 0$. When $\ell = 1$, $m = -1, 0, +1$.

When $\ell = 2$, $m = -2, -1, 0, +1, +2$.

(ii) For 3*d*–orbital, $n = 3$, $\ell = 2$,

For $\ell = 2$, $m = -2, -1, 0, +1, +2$.

(iii) For any value of n ℓ varies from 0 to $(n - 1)$. Therefore 1p is not possible because when $n = 1$, $\ell = 0$ whereas for *p* orbital ℓ should have minimum value of 1.

2*s* is possible because when $n = 2$, $\ell = 0$ (for *s*, $\ell = 0$)

2*p* is possible because when $n = 2$, $\ell = 0$, 1(for *p*, $\ell = 1$)

3*f* is not possible because when $n = 3$, $\ell = 0, 1, 2$ (for *f*, $\ell = 3$)

2.29 Using *s*, *p*, *d* notations, describe the orbital with the following quantum numbers:

(a) $n = 1, \ell = 0$ (b) $n = 3, \ell = 1$

(c) $n = 4, \ell = 2$ (d) $n = 4, \ell = 3$.

Ans. (a) 1*s* (b) 3*p* (c) 4*d* (d) 4*f*.

2.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(a) $n = 0,\ \ell = 0,\ m_l = 0,\ m_s = +1/2$

(b) $n = 1,\ \ell = 0,\ m_l = 0,\ m_s = -1/2$

(c) $n = 1,\ \ell = 1,\ m_l = 0,\ m_s = +1/2$

(d) $n = 2,\ \ell = 1,\ m_l = 0,\ m_s = -1/2$

(e) $n = 3,\ \ell = 3,\ m_l = -3,\ m_s = +1/2$

(f) $n = 3,\ \ell = 1,\ m_l = 0,\ m_s = +1/2$

Ans. (a) Not possible because n can never be equal to zero. (b) Possible (c) Not possible (d) Possible (e) Not possible because when $n = 3$, $l \neq 3$ as value of ℓ varies from 0 to $n - 1$. (*f*) Possible.

2.31 How many electrons in an atom may have the following quantum numbers ?

(a) $n = 4, m_s = -1/2$ (b) $n = 3, \ell = 0$

Ans. (a) Total electrons in $n = 4$ are $2n^2$, i,e., $2 \times 4^2 = 32$ Half of them, i.e., 16 electrons have $m_s = -\frac{1}{2}$.

(b) $n = 3$, $\ell = 0$ means 3*s* orbital which can have maximum 2 electrons.

2.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the De Broglie wavelength associated with the electron revolving around the orbit.

Ans. According to Bohr postulate of angular momentum,

$$mvr = n\frac{h}{2\pi} \quad \text{or} \quad 2\pi r = n\frac{h}{mv} \qquad \ldots(i)$$

According to de Broglie equation, $\lambda = \dfrac{h}{mv}$ ...(ii)

Substituting this value in eqn. (*i*), we get $2\pi r = n\lambda$

Thus, the circumference ($2\pi r$) of the Bohr orbit for hydrogen atom is an integral multiple of de Broglie wavelength.

2.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, $n = 4$ to $n = 2$ of He^+ spectrum?

Ans. For H–like particles in general

$$\bar{\nu} = \frac{2\pi^2 mZ^2 e^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$\therefore$ For He^+ spectrum, for Balmer transition, $n = 4$ to $n = 2$.

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = R \times 4 \times \frac{3}{16} = \frac{3R}{4}$$

For hydrogen spectrum

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{3}{4}R \text{ or } \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

which can be so for $n_1 = 1$ and $n_2 = 2$, i.e., the transition is from $n = 2$ to $n = 1$

2.34 Calculate the energy required for the process

$$\mathbf{He^+ (g) \longrightarrow He^{2+} (g) + e^-}$$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J atom^{-1}.

Ans. For H–like particles, $E_n = \dfrac{2\pi^2 mZ^2 e^4}{n^2 h^2}$

For H–atom, I.E. $= E - E_1 = 0 - \left(-\dfrac{2\pi^2 me^4}{1^2 \times h^2}\right)$

$$= \frac{2\pi^2 me^4}{h^2} = 2.18 \times 10^{-18}\, J\, \text{atoms}^{-1} \text{(Given)}$$

For the given process, Energy required

$$= E_n - E_1 = 0 - \left(-\frac{2\pi^2 m \times 2^2 \times e^4}{l^2 \times h^2}\right)$$

$$= 4 \times \frac{2\pi^2 me^4}{h^2} = 4 \times 2.18 \times 10^{-18} = 8.72 \times 10^{-18} J$$

2.35 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across the length of scale of length 20 cm long.

Ans. Diameter of carbon atom = 0.15nm

$= 0.15 \times 10^{-9}$ m $= 1.5 \times 10^{-10}$m

Length along which atoms are to be placed

$= 20$cm $= 20 \times 10^{-2}$m $= 2 \times 10^{-1}$ m

$\therefore$ No. of C-atoms which can be placed along the length

$$= \frac{2 \times 10^{-1}}{1.5 \times 10^{-10}} = 1.33 \times 10^9$$

2.36 **2×10^8 atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.**

Ans. Total length = 2.4 cm.

Total number of atoms along the length = 2×10^8

$$\therefore \text{ Diameter of each atom } = \frac{2.4 \text{ cm}}{2\times10^8} = 1.2\times10^{-8}$$

$$\therefore \text{ Radius of the atom } = \frac{1.2\times10^{-8}\text{cm}}{2}$$

$$= 0.6\times10^{-8}\text{ cm} = 0.6\times10^{-9}\text{ m} = 0.6\text{ nm.}$$

2.37 **The diameter of zinc atom is 2.6 Å. Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.**

Ans. (a) Radius $= \frac{2.6\text{Å}}{2} = 1.3\text{Å}$

$= 1.3\times10^{-10}\text{m} = 130\times10^{-12}\text{ m} = 130\text{ pm.}$

(b) Diameter of one atom = 2.6Å = 2.6×10^{-10} m.

$\therefore$ No. of atoms present along the length

$$= \frac{1.6\times10^{-2}}{2.6\times10^{-10}} = 6.154\times10^7$$

2.38 **A certain particle carries 2.5×10^{-16}C of static electric charge. Calculate the number of electrons present in it.**

Ans. Charge carried by one electron = 1.6022×10^{-19}C.

Electrons present in particle carrying 2.5×10^{-16} C of charge

$$= \frac{2.5\times10^{-16}}{1.6022\times10^{-19}} = 1560$$

2.39 **In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X–rays. If the static electric charge on the oil drop is -1.282×10^{-18} C, calculate the number of electrons present on it.**

Ans. As in Q. 38 above , electrons present

$$= \frac{-1.282\times10^{-18}\text{C}}{-1.6022\times10^{-19}\text{C}} = 8$$

2.40 **In Rutherford's experiment, generally the thin foil of heavy atoms like gold, platinum, etc., have been used to be bombarded by the α–particles. If the thin foil of light atoms like aluminium, etc., is used, what difference would be observed from the above results?**

Ans. Heavy atoms have a heavy nucleus carrying a large amount of positive charge. Hence some α-particles are easily deflected back on hitting the nucleus. Also a number of α–particles are deflected through small angles because of large positive charge on the nucleus. If light atoms are used, their nuclei will be light and moreover, they will have small positive charge on the nucleus. Hence, the number of particles deflected back and those deflected through some angle will be negligible or lesser.

2.41 **Symbols $^{79}_{35}$Br and ^{79}Br can be written whereas symbols $^{35}_{79}$Br and ^{35}Br are not acceptable. Answer briefly.**

Ans. Atomic number of Bromine is fixed i.e, 35. However, different Bromine atoms may have different mass numbers (isotopes). Hence, it is essential to indicate mass number.

2.42 **An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.**

Ans. Mass number = 81, i.e., p + n = 81

If protons = x, then neutrons $= x + \frac{31.7}{100}x = 1.317x$

$\therefore\ x + 1.317x = 81$

or $2.317x = 81$

or $x = \frac{81}{2.317} = 35$

Thus, Protons = 35, i.e., atomic no. = 35

Hence, the symbol is $^{81}_{35}$Br

2.43 **An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion.**

Ans. Suppose number of electrons in the ion = x

Then number of neutrons $= x + \frac{11.1}{100}x = 1.111x$

No. of electrons in the neutral atom = x – 1

$\therefore$ No. of protons = x – 1

Mass number = No. of neutrons + No. of protons

$\therefore$ 37 = 1.111x + x – 1 or 2.111x = 38 or x = 18

Hence, the symbol of the ion will be $^{37}_{17}\text{Cl}^{-1}$

2.44 **An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion.**

Ans. Suppose number of electrons in the ion, M^{3+} = x

$\therefore$ No. of neutrons $= x + \frac{30.4}{100}x = 1.304x$

No. of electrons in the neutral atom = x + 3

$\therefore$ No. of protons = x + 3

Mass no. = No. of protons + No. of neutrons

56 = x + 3 + 1.304 x or 2.304 x = 53 or x = 23

$\therefore$ No. of protons = Atomic no. = x + 3 = 23 + 3 = 26

Hence, the symbol of the ion will be $^{56}_{26}\text{Fe}^{3+}$.

2.45 **Arrange the following type of radiations in increasing order of frequency:**

(a) radiation from microwave oven
(b) amber light from traffic signal
(c) radiation from FM radio
(d) cosmic rays from outer space and
(e) X–rays.

Ans. Cosmic rays > X–rays > amber light > microwave > FM

2.46 **Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.**

Ans. $E = Nh\nu = Nh\frac{c}{\lambda}$

$$= \frac{(5.6\times10^{24})(6.626\times10^{-34}\text{Js})(3.0\times10^8\text{ms}^{-1})}{(337.1\times10^{-9}\text{m})} = 3.3\times10^6\text{J}$$

2.47 **Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate**

(a) the frequency of emission
(b) distance traveled by this radiation in 30 s
(c) energy of quantum and
(d) number of quanta present if it produces 2 J of energy.

Ans. $\lambda = 616\text{ nm} = 616\times10^{-9}\text{m}$

(a) Frequency, $\nu = \frac{c}{\lambda} = \frac{3.0\times10^8\text{ms}^{-1}}{616\times10^{-9}\text{m}} = 4.87\times10^{14}\text{s}^{-1}$

(b) Velocity of the radiation = $3.0 \times 10^8\ ms^{-1}$

$\therefore$ Distance travelled in 30 s

$= 30\ s \times 3 \times 10^8\ ms^{-1} = 9.0 \times 10^9 m$

(c) $E = h\nu = h\dfrac{c}{\lambda}$

$$= \frac{(6.626 \times 10^{-34}\ Js) \times 3.0 \times 10^8\ ms^{-1}}{616 \times 10^{-9}\ m} = 32.27 \times 10^{-20} J.$$

(d) No. of quanta in 2 J of energy

$$= \frac{2}{32.27 \times 10^{-20}} = 6.2 \times 10^{18}$$

2.48 In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of 3.15 × 10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.

Ans. Energy of one photon $= h\nu = h\dfrac{c}{\lambda}$

$$= \frac{(6.626 \times 10^{-34}\ J\,s)(3 \times 10^8\ ms^{-1})}{(600 \times 10^{-9}\ m)} = 3.313 \times 10^{-19}\ J$$

Total energy received $= 3.15 \times 10^{-18} J$

$\therefore$ No. of photons received $= \dfrac{3.15 \times 10^{-18}}{3.313 \times 10^{-19}} = 9.51 = 10$

2.49 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2ns and the number of photons emitted during the pulse source is 2.5× 10^{15}, calculate the energy of the source.

Ans. Frequency $= \dfrac{1}{2 \times 10^{-9}\ s} = 0.5 \times 10^9\ s^{-1}$

Energy = N hν = $(2.5 \times 10^{15})\ (6.626 \times 10^{-34} Js)\ (0.5 \times 10^9\ s^{-1}) = 8.28 \times 10^{-10} J$

2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.

Ans. $\lambda_1 = 589nm = 589 \times 10^{-9}\ m.$

$$\therefore \nu_1 = \frac{c}{\lambda_1} = \frac{3.0 \times 10^8\ ms^{-1}}{589 \times 10^{-9}\ m} = 5.093 \times 10^{14}\ s^{-1}$$

$\lambda_2 = 589.6\ nm = 589.6 \times 10^{-9} m$

$$\therefore \nu_2 = \frac{c}{\lambda_2} = \frac{3.0 \times 10^8\ ms^{-1}}{589.6 \times 10^{-9}\ m} = 5.088 \times 10^{14}\ s^{-1}$$

$\Delta E = E_2 - E_1 = h\ (\nu_1 - \nu_2)$

$= (6.626 \times 10^{-34} Js)\ (5.093 - 5.088) \times 10^{14}\ s^{-1} = 3.31 \times 10^{-22}\ J$

2.51 The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

Ans. Work function $(W_0) = h\nu_0$

$$\therefore \nu_0 = \frac{W_0}{h} = \frac{1.9 \times 1.602 \times 10^{-19}\ J}{6.626 \times 10^{-34}\ Js}$$

$(1eV = 1.602 \times 10^{-19}) = 4.59 \times 10^{14}\ s^{-1}$

(a) $\lambda_0 = \dfrac{c}{\nu_0} = \dfrac{3.0 \times 10^8\ ms^{-1}}{4.59 \times 10^{14}\ s^{-1}} = 6.54 \times 10^{-7} m$

$= 654 \times 10^{-9}\ m = 654\ nm$

(b) K.E. of ejected electron = $h\ (\nu - \nu_0)$

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) = (6.626 \times 10^{-34}\ J\,s)(3.0 \times 10^8\ ms^{-1})$$

$$\left(\frac{1}{500 \times 10^{-9}\ m} - \frac{1}{654 \times 10^{-9}\ m}\right)$$

$$= \frac{6.626 \times 3.0 \times 10^{-26}}{10^{-9}}\left(\frac{154}{500 \times 654}\right) J = 9.36 \times 10^{-20}\ J$$

$$K.E. = \frac{1}{2}mv^2 = 9.36 \times 10^{-20}\ J \text{ or } kg\ m^2\ s^{-2}$$

$$v = \sqrt{\frac{2KE}{m}}$$

$$\therefore \frac{1}{2} \times (9.11 \times 10^{-31}\ kg)v^2 = 9.36 \times 10^{-20} kg\ m^2 s^{-2}$$

or $v^2 = 2.055 \times 10^{11}\ m^2\ s^{-2} = 20.55 \times 10^{10} m^2 s^{-2}$

or $v = 4.53 \times 10^5\ ms^{-1}$.

2.52 Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and (b) Planck's constant.

λ (nm)	**500**	**450**	**400**
$v \times 10^{-5} (cms^{-1})$	**2.55**	**4.35**	**5.35**

Ans. Suppose threshold wavelength $= \lambda_0\ nm = \lambda_0 \times 10^{-9}\ m$

Then $h(\nu - \nu_0) = \dfrac{1}{2}mv^2$ or $hc\left(\dfrac{1}{\lambda} - \dfrac{1}{\lambda_0}\right) = \dfrac{1}{2}mv^2$

Substituting the given results of the three experiments, we get

$$\frac{hc}{10^{-9}}\left(\frac{1}{500} - \frac{1}{\lambda_0}\right) = \frac{1}{2}m(2.55 \times 10^{-7})^2 \quad \ldots(i)$$

$$\frac{hc}{10^{-9}}\left(\frac{1}{450} - \frac{1}{\lambda_0}\right) = \frac{1}{2}m(4.35 \times 10^{-7})^2 \quad \ldots(ii)$$

$$\frac{hc}{10^{-9}}\left(\frac{1}{400} - \frac{1}{\lambda_0}\right) = \frac{1}{2}m(5.35 \times 10^{-7})^2 \quad \ldots(iii)$$

Dividing eqn. (ii) eqn. (i), we get

$$\frac{\lambda_0 - 450}{450\lambda_0} \times \frac{500\lambda_0}{\lambda_0 - 500} = \left(\frac{4.35}{2.55}\right)^2$$

or $\dfrac{\lambda_0 - 450}{\lambda_0 - 500} = \dfrac{450}{500}\left(\dfrac{4.35}{2.55}\right)^2 = 2.619$

or $\lambda_0 - 450 = 2.619\lambda_0 - 1309.5$

or $1.619\ \lambda_0 = 859.5$

$\therefore$ $\lambda_0 = 531\ nm$

Substituting this value in eqn. (iii), we get

$$\frac{h \times (3 \times 10^8)}{10^{-9}}\left(\frac{1}{400} - \frac{1}{531}\right)$$

$= \dfrac{1}{2}(9.11 \times 10^{-31})(5.35 \times 10^{-7})^2$ or $h = 6.66 \times 10^{-34}\ J\,s$

2.53 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

Ans. Energy of the incident radiation = Work function + Kinetic energy of photoelectron

Energy of incident radiation (E)

$$= h\nu = h\frac{c}{\lambda} = \frac{(6.626\times10^{-34}\,\text{Js})(3.0\times10^{8}\,\text{ms}^{-1})}{(256.7\times10^{-9}\,\text{m})}$$

$= 7.74\times10^{-19}\,\text{J} = 4.83\,\text{eV}$ ($1\,\text{eV} = 1.602\times10^{-19}\,\text{J}$)

The potential applied gives the kinetic energy to the electron.

Hence, kinetic energy of the electron = 0.35 eV

∴ Work function = 4.83 eV – 0.35 eV = 4.48 eV

2.54 If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of 1.5×10^7 m s^{-1}, calculate the energy with which it is bound to the nucleus.

Ans. Energy of the incident photon

$$= \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{Js})(3.0\times10^{8}\,\text{ms}^{-1})}{(150\times10^{-12}\,\text{m})} = 13.25\times10^{-16}\,\text{J}$$

Energy of the electron ejected $= \frac{1}{2}mv^2$

$$= \frac{1}{2}(9.11\times10^{-31}\,\text{kg})(1.5\times10^{7}\,\text{ms}^{-1})^2 = 1.025\times10^{-16}\,\text{J}$$

Energy with which the electron was bound to the nucleus

$= 13.25\times10^{-16}\,\text{J} - 1.025\times10^{-16}\,\text{J} = 12.225\times10^{-16}\,\text{J}$

$$= \frac{12.225\times10^{-16}}{1.602\times10^{-19}}\,\text{eV} = 7.63\times10^{3}\,\text{eV}.$$

2.55 Emission transitions in the Paschen series end at orbit n = 3 and start from orbit n and can be represented as $\nu = 3.29 \times 10^{15}$ (Hz) $[1/3^2 - 1/n^2]$. Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

Ans. $$\nu = \frac{c}{\lambda} = \frac{3.0\times10^{8}\,\text{m s}^{-1}}{1285\times10^{-9}\,\text{m}} = 2.33\times10^{14}\,\text{s}^{-1} \quad ....(i)$$

According to question, $\nu = 3.29\times10^{15}\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$

By comparing equation (i) and (ii), we get, ...(ii)

$$\text{or}\quad \frac{1}{n^2} = \frac{1}{9} - \frac{3.0\times10^{8}}{1285\times10^{-9}} \times \frac{1}{3.29\times10^{15}}$$

$$= 0.111 - 0.071 = 0.04 = \frac{1}{25}$$

or $n^2 = 25$ or $n = 5$

2.56 Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

Ans. Radius of *n*th orbit of H–like particles

$$= \frac{0.529n^2}{Z}\,\text{Å} = \frac{52.9n^2}{Z}\,\text{pm}$$

$r_1 = 1.3225\,\text{nm} = 1322.5\,\text{pm} = 52.9\,n_1^2$

$$r_2 = 211.6\,\text{pm} = \frac{52.9n_2^2}{Z}$$

$$\therefore \frac{r_1}{r_2} = \frac{1322.5}{211.6} = \frac{n_1^2}{n_2^2} = 6.25 \quad \text{or} \quad \frac{n_1}{n_2} = 2.5$$

∴ If $n_2 = 2$, $n_1 = 5$. Thus, the transition is from 5th orbit. It belongs to **Balmer series**.

$$\bar{\nu} = 1.097\times10^{7}\,\text{m}^{-1}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 1.097\times\frac{21}{100}\times10^{7}\,\text{m}^{-1}$$

$$\text{or}\quad \lambda = \frac{1}{\bar{\nu}} = \frac{100}{1.097\times21\times10^{7}}\,\text{m} = 434\times10^{-9}\,\text{m} = 434\text{nm}$$

Thus, it lies in the visible region

2.57 Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is $1.6 \times 10^6 ms^{-1}$, calculate de Broglie wavelength associated with this electron.

Ans. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{kg m}^2\,\text{s}^{-1}}{(9.11\times10^{-31}\,\text{kg})(1.6\times10^{6}\,\text{ms}^{-1})}$$

$= 4.55\times10^{-10}\,\text{m} = 455\,\text{pm}$

2.58 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.

Ans. Mass of neutron = 1.675×10^{-27} kg

$$\lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\times\lambda}$$

$$= \frac{6.626\times10^{-34}\,\text{kg m}^2\text{s}^{-1}}{1.675\times10^{-27}\,\text{kg}\times(800\times10^{-12}\,\text{m})} = 4.94\times10^{2}\,\text{ms}^{-1}$$

2.59 If the velocity of the electron in Bohr's first orbit is 2.19×10^6 ms^{-1}, calculate the de Broglie wavelength associated with it.

Ans. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{kg m}^2\text{s}^{-1}}{(9.11\times10^{-31}\,\text{kg})(2.19\times10^{6}\,\text{ms}^{-1})}$$

$= 3.32\times10^{-10}\,\text{m} = 332\times10^{-12}\,\text{m.} = 332\,\text{pm}$

2.60 The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate the wavelength associated with this velocity?

Ans. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{kg m}^2\text{s}^{-1}}{(0.1\text{kg})(4.37\times10^{5}\,\text{ms}^{-1})} = 1.516\times10^{-38}\,\text{m}$$

2.61 If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is h/4π m × 0.05 nm, is there any problem in defining this value.

Ans. $\Delta x = 0.002\,\text{nm} = 2\times10^{-3}\,\text{nm} = 2\times10^{-12}\,\text{m}$

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\therefore\ \Delta p = \frac{h}{4\pi\Delta x} = \frac{6.626\times10^{-34}\,\text{kg m}^2\text{s}^{-1}}{4\times3.14\times(2\times10^{-12}\,\text{m})}$$

$= 2.638\times10^{-23}\,\text{kg ms}^{-1}$

Actual momentum

$$= \frac{h}{4\pi \times 0.05\text{nm}} = \frac{h}{4\pi \times 5 \times 10^{-11}\text{m}}$$

$$= \frac{6.626 \times 10^{-34}\,\text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 5 \times 10^{-11}\text{m}} = 1.055 \times 10^{-24}\,\text{kg ms}^{-1}$$

This value cannot be defined as the actual magnitude of the momentum is smaller than the uncertainty in momentum, which is impossible.

2.62 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination (s) has/have the same energy

(i) $n = 4,\ \ell = 2,\ m_\ell = -2,\ m_s = -1/2$
(ii) $n = 3,\ \ell = 2,\ m_\ell = -1,\ m_s = +1/2$
(iii) $n = 4,\ \ell = 1,\ m_\ell = 0,\ m_s = +1/2$
(iv) $n = 3,\ \ell = 2,\ m_\ell = -2,\ m_s = -1/2$
(v) $n = 3,\ \ell = 1,\ m_\ell = -1,\ m_s = +1/2$
(vi) $n = 4,\ \ell = 1,\ m_\ell = 0,\ m_s = +1/2$

Ans. The orbitals occupied by the electrons are (i) 4 *d* (ii) 3 *d* (iii) 4*p* (iv) 3 *d* (v) 3*p* (vi) 4*p*. Their energies will be in the order: (v) < (ii) = (iv) < (iii) = (vi) < (i)

2.63 The bromine atom possesses 35 electrons. It contains 6 electrons in 2*p* orbital, 6 electrons in 3*p* orbital and 5 electrons in 4*p* orbital. Which of these electron experiences the lowest effective nuclear charge?

Ans. 4*p* electrons being farthest from the nucleus experience the lowest effective nuclear charge.

2.64 Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge?
(i) 2*s* and 3*s*   (ii) 4*d* and 4*f*   (iii) 3*d* and 3*p*

Ans. (i) 2*s* is closer to the nucleus than 3*s*. Hence 2*s* will experience larger effective nuclear charge.
(ii) 4*d*
(iii) 3*p* (for same reason)

2.65 The unpaired electrons in Al and Si are present in 3p orbital. Which electrons will experience more effective nuclear charge from the nucleus?

Ans. Silicon has greater nuclear charge (+4) than aluminium (+3). Hence, the unpaired 3p electron of silicon will experience more effective nuclear charge.

2.66 Indicate the number of unpaired electrons in :
(a) P (b) Si (c) Cr (d) Fe and (e) Kr

Ans. (a) $_{15}\text{P} = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1 3p_y^1 3p_z^1$.
No. of unpaired electrons = 3

(b) $_{14}\text{Si} = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1 3p_y^1$.
No. of unpaired electrons = 2

(c) $_{24}\text{Cr} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5 4s^1$.
No. of unpaired electrons = 6

(d) $_{26}\text{Fe} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$ number of unpaired electrons = 4 in (3*d*).

(e) $_{36}$Kr = Noble gas. All orbitals are filled. Unpaired electrons = 0

2.67 (a) How many sub–shells are associated with *n* = 4?
(b) How many electrons will be present in the sub–shells having m_s value of –1 / 2 for *n* = 4 ?

Ans. (a) $n = 4,\ \ell = 0, 1, 2, 3$ (4 subshells , viz., *s*, *p*, *d* and *f*)
(b) No. of electrons in 4th shell.
$= n^2 = 4^2 = 16$
Each orbital has one electron with
$m_s = -1/2$
Hence there will be 16 electrons with $m_s = -½$.

Practice Questions

Very Short Answer Questions [1 Mark]

1. How does the intensity of spectral line vary with wave length?
2. What is Stark effect?
3. What is Zeeman effect?
4. From the following nuclei, select the isotopes and isobars:
$^{238}_{92}\text{U},\ ^{234}_{90}\text{Th},\ ^{234}_{92}\text{U},\ ^{234}_{91}\text{Pa}$
5. How many electrons in the p-orbital of argon (Z = 18) have same spin?
6. Can an electron have the quantum number values as $n = 2$, $l = 2$, $m_l = +2$?
7. What in the sequence of energies of 3*s*, 3*p* and 3*d* orbitals in
   (a) a hydrogen atom
   (b) a multielectron atom
8. Which energy level do not have p-orbital?
9. Name a species which has no neutron.
10. What type of spectrum is obtained when light emitted from discharge tube containing hydrogen gas is analysed with a spectroscope?
11. Which orbital is non-directional in nature?
12. Explain why are Bohr's orbitals also called energy levels?
13. What is the lowest shell which has an *f*-subshell?
14. What is value of angular momentum for an electron in 5th orbit according to Bohr's theory?
15. How are d_{xy} and $d_{x^2-y^2}$ orbitals related?
16. Which experiment led to the discovery of neutrons?
17. The atomic number of Uranium is 92. How many electrons are there in the neutral atom? How many electrons and protons are there in the U^{+2} ion?
18. Which has the greater energy–a photon of violet light or a photon of green light?
19. What is the maximum number of emission lines when the excited electron of a H-atom in *n* = 6 drops to the ground state?
20. Name the experiment evidence to support the wave nature of light.
21. What is the probability of finding a 4*d* electron right at the nucleus?
22. What is the maximum number of electrons that can occupy *g* subshell ($l = 4$) ?

23. Which one Fe^{3+}, Fe^{2+} is more paramagnetic and why?

24. Arrange X-rays, cosmic rays and radio waves according to frequency.

25. What type of metals are used in photoelectric cells? Give one example.

26. What is difference between the notations l and L ?

27. Name the element whose isotope has mass number 14 and 8 neutrons.

28. An element of atomic weight Z consists of two isotopes of mass number $Z - 1$ and $Z + 2$. Calculate the % of higher isotope.

29. Why is 4s orbital filled before 3d orbital?

30. How many quantum numbers specify an (a) electron, (b) orbital? Name them

31. How is photon different from proton?

32. State physical significance of ψ^2.

33. When moving with the same velocity which one of the following particles has the largest de Broglie wavelength and why? (a) Electron (b) Proton (c) α-particle

34. The electronic configuration of $N(7)$ is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ and not $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1$. Why?

35. Give an example of a neutral molecule which is iso–electronic with ClO^{-1}?

36. What did Rutherford's alpha scattering experiment prove?

37. One photon of ultraviolet light can eject a photo electron from the surface of a certain metal. When the same metal is irradiated with 2 photons of red light having total energy equal to that of ultraviolet light; will photoelectron be ejected?

38. Calculate the radius of first two orbits of Li^{2+}?

39. What would you predict for the atomic number of the noble gas beyond Rn, if such an element had sufficient stability to be prepared or observed? Assume that 'g' orbitals are still not occupied in the ground states of the preceding elements.

40. Explain why chromium has only one electron in its 4s sub–shell?

41. Which properties of the elements depend on the electronic configuration of the atoms and which do not?

42. If the electron absorbs 12.1 eV of energy, it will jump to which orbit? (Given energy of electron is –13.6eV)

43. What is the ratio of mass of electron to the mass of proton?

44. How many protons and neutrons are in an element which is represented by the symbol $^{125}X_{56}$ have in its nucleus?

45. If the wavelength of green light is about 5000 Å, what is its frequency? ($c = 3 \times 10^8$ m/s)

46. Calculate the kinetic energy of the ejected electron when ultra-violet radiation of frequenc $1.6 \times 10^{15}\ s^{-1}$ strikes the surface of potassium metal. Threshold frequency of potassium is $5 \times 10^{14}\ s^{-1}$. ($h = 6.63 \times 10^{-34}$ Js)

47. What is the difference between angular momentum of an electron present in 2p and in 3p orbital?

Short Answer Questions [2 & 3 Marks]

1. Explain how can you say electrons and protons are fundamental particles of all the atoms.

2. What is the origin of anode rays in the discharge tube? Name the particles which form anode rays.

3. Describe the drawback of Rutherford's model of atom.

4. Calculate and compare the energies of two radiations one with a wavelength of 800 nm and other with wavelength of 400 nm.

5. Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 100 million volts. ($1\ eV = 1.6 \times 10^{-19}$ J, $m_e = 9.1 \times 10^{-31}$ kg, $h = 6.6 \times 10^{-34}$ Js, $c = 3.0 \times 10^8\ ms^{-1}$)

6. In photoelectric effect experiment irradiation of a metal with light of frequency $5 \times 10^{20}\ s^{-1}$ yields electrons with maximum K.E. $= 6.63 \times 10^{-14}$ J. Calculate v_0 (threshold frequency) for the metal.

7. With what velocity must an electron travel so that its momentum is equal to that of a photon of wavelength = 5200 Å?

8. Using Aufbau principle, write the ground state electronic configuration of following atoms.

(i) Boron ($Z = 5$), (ii) Neon ($Z = 10$),
(iii) Aluminium ($Z = 13$), (iv) Chlorine ($Z = 17$),
(v) Calcium ($Z = 20$) (vi) Rubidium ($Z = 37$)

9. What is the wavelength for the electron accelerated by 1.0×10^4 volts ?

10. The first member (H_α line) of the Balmer series of hydrogen has a wavelength of 6563 Å. Calculate the wavelength of the second member (H_β line).

11. 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 $I_2 = 240\ kJ\ mol^{-1}$)

12. Energy in a Bohr orbit is given to be equal to $-\dfrac{B}{n^2}$, where B $= 2.179 \times 10^{-18}$ J. Calculate the wavelength of the emitted radiation when electron jumps from the third orbit to the second.

13. A sheet of silver is illuminated by monochromatic ultraviolet radiations of wavelength = 1810 Å. What is the maximum energy of the emitted electron ? Threshold wavelength of silver is 2640 Å.

14. 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.

15. Two particles A and B are in motion. If the wavelength associated with particle A is 5×10^{-8}m, calculate the wavelength associated with particle B if its momentum is half of A.

17. What is the evidence that cathode rays are a part of all matter?

18. A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate

(a) the energy of the photon in eV.
(b) the kinetic energy of the emitted electron in joules.
(c) the velocity of the photoelectron.
($1\ eV = 1.6020 \times 10^{-19}$ J)

19. One of the lines in the Balmer series of the hydrogen atom emission spectrum is at 397 nm. It results from a transition from an upper energy level to $n = 2$. What is the principal quantum number of the upper level?

20. Ionization energy of a H-atom is 13.6 eV/atom. It requires a photon of energy 1.5 times the minimum which is required to remove the electron. Calculate the wavelength of the emitted electron.

21. What is the frequency and wave-length of a photon emitted during a transition from the $n = 5$ state to the $n = 2$ state in the hydrogen atom.

22. How many degenerate atomic orbitals are there that can be designated
(i) $6p$ (ii) $5d$ (iii) $6f$?

23. (i) An atomic orbital has $n = 3$. What are the possible values of l and m ?
(ii) List the quantum numbers (m and l) of electron for $3d$ orbital.
(iii) Which of the following orbitals are not possible ?
1s, 2p, 1p, 3f

24. (i) Write the electronic configurations of the following ions.
(a) H^- (b) Na^+ (c) O^{2-} (d) F^-
(ii) What are the atomic numbers of elements whose outermost electrons are represented by
(a) $3s^1$; (b) $2p^3$; (c) $3d^6$?

25. Calculate (i) wave number (ii) frequency of yellow radiation having wavelength of 5800 Å.

26. What are the main points of Planck's quantum theory?

27. The ionization energy of He^+ is 19.6×10^{-18} J atom^{-1}. calculate the energy of the stationary state of Li^{2+}.

28. Differentiate between orbit and orbital.

29. On the basis of Heisenberg Uncertainty principle, show that an electron cannot exist within the nucleus having a radius = 10^{-15} m. ($h = 6.626 \times 10^{-34}$Js)

30. Discuss the similarities and differences between 1s and 2s orbital.

31. Why does the charge to mass ratio of positive rays depends on the gas taken in the discharge tube whereas charge to mass ratio of cathode rays is same for all gases?

32. Which of the following relate to light as wave, particle, or both?
A) diffraction B) photoelectric effect
C) $E = mc^2$ D) $E = h\nu$.

33. An electron in a hydrogen atom in its ground state absorbs 1.5 times as much energy as the minimum required for it to escape from the atom. What is the wavelength of the emitted electron?

34. An electron and a proton are possessing the same amount of kinetic energy. Which of the two have greater wavelength?

35. Calculate the wavelength of de–Broglie waves associated with a proton of kinetic energy 500eV. (given : $m_p = 1.67 \times 10^{-27}$kg, $h = 6.626 \times 10^{-34}$Js and 1eV = 1.6×10^{-19}J)

36. Which out of Cu^{2+}, Fe^{2+}, Cr^{3+} has highest para–magnetism and why? (Given At.No. Cu = 29, Fe = 26, Cr = 24)

37. When light of frequency v is thrown on a metal surface with threshold frequency v_0, photo-electrons are emitted with maximum kinetic energy = 1.3×10^{-18}J. If the ratio, $v : v_0 = 3 : 1$, calculate the threshold frequency v_0.

38. An electron has a speed of 500 ms^{-1} with an uncertainty of 0.02%. What is the uncertainty in locating its position?

39. Define (i) Photo–electric effect (ii) Black body radiations.

Long Answer Questions [5 Marks]

1. (i) Calculate the wavelength of photon which will be emitted when the electron of hydrogen atom jumps from the fourth shell to the first shell. The ionization energy of hydrogen atom is 1.312×10^3 kJ mol^{-1}.
(ii) Which orbital in each of the following pairs is lower in energy in a multi-electron system?
(a) 2s,2p (b) 3p, 3d (c) 3s, 4s (d) 4d, 5f

2. Complete the following statements:
(a) Two electrons in the same —————— must have opposite spins.
(b) The presence of unpaired electrons in an atom gives rise to —————— .
(c) When 'l' = 3, m_l may have value from —————— to ——————.
(d) The neutral fourth–period atom having a total of six 'd' electrons is ————.
(e) Orbitals with the same energy are said to be ——————.
(f) The electronic configuration of Sn is [Kr] ——————.
(g) The 2p orbitals of an atom have identical shapes but differ in their ——————.
(h) A nodal surface is one at which the probability of finding an electron is ————.
(i) Electronic configuration of Li is not $1s^3$, it is in accordance with ————.
(j) Balmer series in hydrogen spectrum is observed in the ——— region.

3. (i) Find the number of photons emitted per second by a 25 watt source of monochromatic light of wavelength 6000 Å ?
(ii) A certain photochemical reaction is found to require 7.61×10^{-17}J energy per molecule. Calculate the number of photons per molecule for light of wavelength 300nm that is just sufficient to initiate the reaction.

4. (i) What are the two longest wavelength lines (in nanometers) in the Lyman series of hydrogen spectrum ?
(ii) In a hydrogen atom, the energy of an electron in first Bohr's orbit is 13.12×10^5 J mol^{-1}. What is the energy required for its excitation to Bohr's second orbit ?

5. What were the weaknesses or limitations of Bohr's model of atoms ? Briefly describe the quantum mechanical model of atom ?

6. (i) What is an emission spectrum ?
(ii) Explain the hydrogen spectrum.

7. (i) Write outer electronic configuration of Cr atom. Why are half filled orbitals more stable ?
(ii) State Heisenberg's uncertainty principle. An electron has a velocity of 50 ms^{-1} accurate upto 99.99%. Calculate the uncertainty in locating its position.
(Mass of electron = 9.1×10^{-31} kg, $h = 6.6 \times 10^{-34}$ Js)

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. How many nodal spheres does a 5*s* electron charge cloud have? **[HOTS]**

2. Why splitting of spectral lines takes place when the source giving the spectrum is placed in a magnetic field? **[HOTS]**

3. Which has more potential energy : an electron close to an atomic nucleus or one far from an atomic nucleus? **[HOTS]**

4. An electron jumps from 5th shell to 2nd shell. How many state of transition are possible. **[HOTS]**

5. Which of the following quantum numbers for orbitals in hydrogen atom has a greater energy for electrons? **[HOTS]**
(i) $n = 3, l = 2$ and $m = +1$
(ii) $n = 3, l = 2$ and $m = -1$

6. Why cathode rays are produced only when the pressure of the gas inside the discharge tube is very low? **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. (a) Two particles *A* and *B* are moving with the same velocity but wavelength of *A* is found to be double than that of *B*. What do you conclude?
(b) Why the ball hit with a hockey by a player does not make a wave? **[HOTS]**

2. A 25 watt bulb emits monochromatic yellow light of wave length 0.57 μm. What is the rate of emission of quanta per second? **[HOTS]**

3. State whether the following statement is correct or not. "Every atom with even atomic number has all paired electrons".
Justify your answer. Also name the rule on which you have relied to answer this question. **[HOTS]**

4. According to de Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball and explain why it does not show wave nature. **[Exemplar]**

5. Table-tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4% what will be the uncertainty in speed and position? **[Exemplar]**

6. Hydrogen atom has only one electron, so mutual repulsion between electrons is absent. However, in multielectron atoms mutual repulsion between the electrons is significant. How does this affect the energy of an electron in the orbitals of the same principal quantum number in multelectron atoms? **[Exemplar]**

Long Answer Questions [5 Marks]

1. (a) The frequency of violet light is about twice that of red light. Compare the energy of violet photon with the energy of a red photon.
(b) Which has a greater energy? A photon of violet light or a photon of green light? **[HOTS]**

2. (i) Calculate the shortest and the longest wavelengths of the Lyman series. Given, Rydberg constant = 10967700 m^{-1}.
(ii) Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectrum of hydrogen atom. **[HOTS]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. Distinguish between a photon and quantum.

2. Calculate the mass and charge of one mole of electron.

3. How many orbitals are in subshells with 'l' equal to (a) 0, (b) 2 ?

4. Explain why is electronic energy negative?

5. Electro–magnetic radiation of wavelength 242 nm is just sufficient to ionize the sodium atom. Calculate the ionization energy of sodium in kJ/mol ($h = 6.626 \times 10^{-34}$ Js ; $c = 3\times10^{8}$ ms^{-1}).

6. Why can't we overcome the uncertainty predicted by Heisenberg's principle by building more precise devices to reduce the error in the measurement below the h / 4 p limit?

7. Which of the four quantum number (n , l , ml , ms) determine (a) the energy of orbital in hydrogen atom and in multi–electron atom, (b) the size of orbital , (c) the shape of an orbital, (d) the orientation of orbital in space (e) orientation of the spin of the electron ?

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. With the decrease in the wavelength of light the intensity decreases.
2. The phenomenon of splitting up of a spectral line into closely spaced lines under the influence of an electric field is called Stark effect.
3. It is the phenomenon of splitting up of a spectral line into closely spaced lines under the influence of a magnetic field.
4. Isotopes = $^{238}_{92}\text{U}, ^{234}_{92}\text{U}$

   Isobars = $^{234}_{90}\text{Th}, ^{234}_{91}\text{Pa}, ^{234}_{92}\text{U}$
5. Six electrons
6. No, it is not possible.
7. (a) $3s = 3p = 3d$

   (b) $3s < 3p < 3d$.
8. First energy level.
9. Hydrogen
10. Emission line spectrum.
11. *s*-orbital
12. This is because each of them is associated with a definite amount of energy.
13. Fourth.
14. $\frac{5h}{2\pi}$
15. The d_{xy} orbital is exactly like $d_{x^2-y^2}$ orbital except that its lobes are at an angle of 45° to the lobes of $d_{x^2-y^2}$ orbital.
16. Neutrons were discovered by Chadwick in 1932. Neutrons are produced when Chadwick bombarded a thin foil of beryllium with fast moving α-particles. These neutral particles were found to have mass 1.675×10^{-27} kg.

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \rightarrow ^{12}_{6}\text{C} + ^{1}_{0}\text{n}$$

17. For a neutral atom, *U*,

   Atomic number = number of protons – number of electrons

   ∴ Number of electrons = 92

   ∴ U^{+2} has 90 electrons whereas the number of protons = 92
18. A photon of violet light has shorter wavelength and thus a higher energy.

$$\left[E = h\nu = h\frac{c}{\lambda}\right].$$

19. No. of spectral lines = $\frac{n(n-1)}{2}$ $n = 6$

   ∴ No. of spectral lines = $\frac{6(6-1)}{2}$ = 15 lines.
20. The phenomenon of interference and diffraction support the wave nature of light.
21. There is no probability of finding a *d* electron right at the nucleus.
22. For *g* subshell, $l = 4$ so $m = 2l + 1 = 9$.

   There are 9 atomic orbitals in a *g* subshell. According to Pauli's exclusion principle, an orbital can accommodate a maximum of two electrons. Hence, the population of *g* subshell is 18 electrons.
23. As Fe^{3+} contains 5 unpaired electrons while Fe^{2+} contains only 4 unpaired electrons. Fe^{3+} is more paramagnetic.
24. Cosmic rays > X-rays > radio waves.
25. The metals with low ionisation enthalpies are used in photoelectric cells. Cesium (Cs) an alkali metal is most commonly used in photoelectric cells.
26. '*l*' signifies the secondary quantum number and

   '*L*' signifies second energy level ($n = 2$).
27. Atomic number = Mass number – Number of neutrons

   Atomic no. = 14–8 = 6, so the element is carbon
28. Let the % of higher isotope (Z + 2) is *x*, other isotope (Z – 1) will be (100 – *x*)

   Average atomic weight (Z) = $\frac{x(Z+2)+(100-x)(Z-1)}{100}$

   $= 100Z = Zx + 2x + 100Z - 100 - Zx + x$

   $3x = 100 \Rightarrow x = 33.33\%$
29. 4*s*-orbital has $(n + l) = 4 + 0 = 4$, which is lower than that of 3*d*, i.e., $3 + 2 = 5$.
30. (a) Four quantum numbers '*n*', '*l*', '*m*' and '*s*' specify an electron.

   (b) Three quantum numbers principal (*n*), azimuthal (*l*) and magnetic (*m*) quantum number specify an orbital.
31. A photon is the quantum of light and its energy is equal to $h\nu$, while a proton is a positively charged particle present in nucleus of an atom.
32. ψ^2 represents probability of finding electron.
33. Electron will have largest wavelength because it has least mass.
34. N(7) has electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ and not $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1$ because latter violates Hund's rule which states degenerate (having equal energy) orbitals are first singly filled and then pairing starts so as to avoid repulsion.
35. ClO^{-1} has total of (17 + 8 + 1) = 26 electrons. Hence the iso–electronic molecule would be HOCl, OF_2 or C_2H_5OH.
36. Atoms contain massive, positively charged centers called nuclei and most of the space inside the atom is empty.
37. No, because threshold frequency of electron will not be crossed by red photons, and one electron interacts with only one photon.
38. $r_n = n^2a_0/Z = n^2 \times 0.529Å/Z$, $r_1 = 1 \times 0.529/3 = 0.176Å$

   $r_2 = 2^2 \times 0.529/3 = 0.705Å$
39. The electronic configuration of the element will be [Rn] $7s^2\ 5f^{14}\ 6d^{10}\ 7p^6$. Thus the element has 32 electrons after atomic number 86, or it has atomic number will be 118.
40. The $3d^5\ 4s^1$ configuration has two exactly half filled sub-shells, which leads to greater stability than the (expected) $3d^4\ 4s^2$ configuration, which has only one fully filled sub-shell.
41. Chemical and physical properties depend upon electronic configuration whereas nuclear properties do not.
42. Energy of electron after absorption is

   = –13.6 eV + 12.1 eV = –1.5 eV

   For hydrogen $E_n = -13.6 / n^2$

   Thus, $-1.5 = -13.6 / n^2$

   or $n^2 = 9$ or n = 3 i.e. i.e. it would jump to 3rd orbit.
43. $\frac{9.1 \times 10^{-28}\text{ g for electron}}{1.67 \times 10^{-24}\text{ g for proton}} = 5.45 \times 10^{-4} = 1/1837$

44. Atomic mass = number of neutrons + number of protons
125 = number of neutrons + 56
Number of neutrons = 125 – 56 = 69.

45. $\nu = c/\lambda = 3.0 \times 10^8 \text{m/s} / (5000 \times 10^{-10}\text{m}) = 6.0 \times 10^{14}\ \text{sec}^{-1}$.

46. Given that, $v = 1.6 \times 10^{15}\ \text{s}^{-1}$;
$v_0 = 5 \times 10^{14}\ \text{s}^{-1}$; $h = 6.63 \times 10^{-34}\text{Js}$

$$\text{K.E.} = h(v - v_0) = 6.63 \times 10^{-34} (16 \times 10^{14} - 5 \times 10^{14})$$
$$= 6.63 \times 10^{-34} \times 11 \times 10^{14} = 7.29 \times 10^{-19}\text{J}$$

47. Angular momentum $= \dfrac{h}{2\pi}\sqrt{l(l+1)}$

Since, it is independent of the value of 'n', so its value will be the same for $2p$ and $3p$ orbitals.

Short Answer Questions

1. The charge over mass ratio of negatively charged particles remains the same irrespective of nature of gas used in discharge tube and material of electrodes which shows that electrons are fundamental particle of all the atoms. Atom, as a whole is neutral and electrons are present in all the atoms, therefore, there must be equal number of positively charged particles in all the atoms.

2. They are obtained by ionisation of gas with the help of cathode rays. They consist of positively charged particle called protons.

3. Maxwell proved that when charged particle revolves under force of attraction, it continuously radiates energy. Electron is a charged particle and revolving under force of attraction, it should radiate energy and ultimately it should fall into the nucleus which actually does not happen. It means there is something wrong with Rutherford's model of atom.

4. $E_1 = h\dfrac{c}{\lambda}$

$$\text{E}_1 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{800 \times 10^{-9}\ \text{m}} = 2.48 \times 10^{-19}\ \text{J};$$

$$\text{E}_2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{400 \times 10^{-9}\text{m}} = 4.97 \times 10^{-19}\ \text{J}$$

$$\frac{\text{E}_1}{\text{E}_2} = \frac{1}{2} \quad \text{or} \quad \text{E}_2 = 2E_1$$

5. K.E. of the electron = 100 MeV = 100×10^6 eV
$= 10^8\text{eV.} = 10^8\ \text{eV} \times 1.6 \times 10^{-19}\ \text{J/eV} = 1.6 \times 10^{-11}\ \text{J}$

$$\lambda = \frac{hc}{K.E.} = \frac{6.6 \times 10^{-34}\ \text{Js} \times 3 \times 10^8\ \text{ms}^{-1}}{1.6 \times 10^{-11}\ \text{J}}$$

$\lambda = 1.24 \times 10^{-14}\text{m}$

6. $hv = hv_0 + K.E.,\ h(v - v_0) = K.E.$

$$v - v_0 = \frac{K.E.}{h} = \frac{6.63 \times 10^{-14}\text{J}}{6.63 \times 10^{-34}\text{Js.}} = 1 \times 10^{20}\text{s}^{-1}$$

$$5 \times 10^{20} - 1 \times 10^{20} = v_0 \Rightarrow v_0 = 4 \times 10^{20}\text{s}^{-1}\text{or Hz}$$

7. According to de Broglie equations, $\lambda = \dfrac{h}{mv}$

Momentum of electron, $mv = \dfrac{h}{\lambda}$

$$= \frac{(6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-1})}{(5200 \times 10^{-10}\ \text{m})}$$

$= 1.274 \times 10^{-27}\ \text{kg ms}^{-1}$ …(i)

The momentum of electron can also be calculated as $= mv = (9.1 \times 10^{-31}\ \text{kg}) \times v$ …(ii)

Comparing (i) and (ii)

$(9.1 \times 10^{-31}\ \text{kg}) \times v = (1.274 \times 10^{-27}\ \text{kg ms}^{-1})$

$$v = \frac{(1.274 \times 10^{-27}\ \text{kg ms}^{-1})}{(9.1 \times 10^{-31}\ \text{kg})} = 1.4 \times 10^3\ \text{ms}^{-1}$$

8.
(i) Boron ($Z = 5$); $1s^2\,2s^2\,2p^1$
(ii) Neon ($Z = 10$); $1s^2\,2s^2\,2p^6$
(iii) Aluminium ($Z = 13$); $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$
(iv) Chlorine ($Z = 17$); $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$
(v) Calcium ($Z = 20$); $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$
(vi) Rubidium ($Z = 37$); $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6 5s^1$.

9. Calculation of the velocity of electron

Energy (kinetic energy) of electron = 1.0×10^4 volts
$= 1.0 \times 10^4 \times 1.6 \times 10^{-19}$ J
$= 1.6 \times 10^{-15}\ \text{J} = 1.6 \times 10^{-15}\ \text{kg m}^2\text{s}^{-2}$

or $1/2\ mv^2 = 1.6 \times 10^{-15}\ \text{kg m}^2\ \text{s}^{-2}$

$$\text{or} \quad v = \left(\frac{2 \times 1.6 \times 10^{-15}\ \text{kg m}^2\text{s}^{-2}}{9.1 \times 10^{-31}\ \text{kg}}\right)^{1/2} = 5.93 \times 10^7\ \text{ms}^{-1}$$

Calculation of the wavelength of electron

According to de Broglie equation, $\lambda = \dfrac{h}{mv}$;

$$\lambda = \frac{(6.626 \times 10^{-34}\ \text{kg m}^2 s^{-1})}{(9.1 \times 10^{-31}\ \text{kg}) \times (5.93 \times 10^7\ \text{ms}^{-1})} = 1.22 \times 10^{-11}\ \text{m}$$

10. Given that, $\lambda_1 = 6563$ Å

According to Bohr's theory, the wavelengths of the Balmer series are given by

$$\bar{v} = \frac{1}{\lambda} = R_H \left\{\frac{1}{2^2} - \frac{1}{n_i^2}\right\}$$

For first member, $n_i = 3$

$$\therefore \quad \frac{1}{\lambda_1} = R_H \left\{\frac{1}{2^2} - \frac{1}{3^2}\right\} = \frac{5R_H}{36}$$

And for second member, $n_i = 4$

$$\therefore \quad \frac{1}{\lambda_2} = R_H \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R_H}{16}$$

Dividing the two equations,

$$\frac{\lambda_2}{\lambda_1} = \frac{5R_H}{36} \times \frac{16}{3R_H} = \frac{20}{27}$$

$$\therefore \quad \lambda_2 = \frac{20}{27}\lambda_1 = \frac{20}{27} \times 6563 = 4861.5\ \text{Å}$$

11. Given that,
$\lambda = 4500 \times 10^{-10}$ m
$h = 6.626 \times 10^{-34}$ Js (constant)
$\text{c} = 3 \times 10^8\ \text{ms}^{-1}$ (constant)

Energy absorbed by each iodine molecule is given by,

$$\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}} = 4.417 \times 10^{-19}\ \text{J}$$

Also given, Bond energy of $\text{I}_2 = 240 \times 10^8\ \text{J mol}^{-1}$

$$\therefore \quad \text{Bond energy of I}_2\ \text{molecule} = \frac{240 \times 10^3}{6.023 \times 10^{23}}$$

$= 3.984 \times 10^{-19}\text{J}$

$\therefore$ K. E. of iodine molecule $= 4.417 \times 10^{-19} - 3.984 \times 10^{-19}$
$= 0.433 \times 10^{-19}$ J

And, K.E. of iodine atom = $\frac{0.433\times10^{-19}}{2}$ = 0.2165×10^{-19} J

12. We are given that, $E_n = -\frac{B}{n^2}$

When an electron jumps from the third orbit ($n = 3$) to the second ($n = 2$), then energy of photon is given by,

$$E = h\nu = E_3 - E_2 = -\frac{B}{3^2} - \left\{-\frac{B}{2^2}\right\} = B\left\{\frac{1}{4}-\frac{1}{9}\right\} = \frac{5B}{36}$$

But $h\nu = h\frac{c}{\lambda}$

$$\therefore \quad \frac{hc}{\lambda} = \frac{5B}{36}$$

$$\text{or} \quad \lambda = \frac{36\,hc}{5B} = \frac{36\times6.63\times10^{-34}\times3\times10^{8}}{5\times2.179\times10^{-18}}\ \text{m}$$

$= 6572 \times 10^{-10}$ m = 6572 Å

13. According to Einstein's photoelectric equation, the maximum energy of the emitted electron is given by

$$E_m = h(v - v_0) = h\left(\frac{c}{\lambda_1}-\frac{c}{\lambda_2}\right) = hc\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)$$

Here,
λ_1 = 1810 Å = $1810 \times 10^{-10}\,m$
λ_2 = 2640 Å = $2640 \times 10^{-10}\,m$
$h = 6.63 \times 10^{-34}$ Js
$c = 3 \times 10^{8}\ \text{ms}^{-1}$

Hence, maximum energy of the emitted electron,

$$E_m = 6.63 \times 10^{-34} \times 3 \times 10^{8}\left[\frac{1}{18\times10^{-10}} - \frac{1}{2640\times10^{-10}}\right]\text{J}$$

$$= 19.89\times10^{-26}\left[\frac{2640\times10^{-10} - 1810\times10^{-10}}{1810\times2640\times10^{-20}}\right]\text{J}$$

$= 3.4553 \times 10^{-19}$ J

= 2.16 ev (∴ 1 ev = 1.6×10^{-19} J)

14. Here, $\frac{1}{2}mV^2 = eV$

$$\text{or} \quad \frac{1}{2}m\frac{h^2}{m^2\lambda^2} = eV \qquad \left[\because \lambda = \frac{h}{mV}\right]$$

$$\text{or} \quad V = \frac{1}{2}\frac{h^2}{m\lambda^2 e}$$

Given that,
λ = 1.54 Å = 1.54×10^{-10} m
$h = 6.626 \times 10^{-34}$ Js
$m = 9.108 \times 10^{-31}$ kg
$e = 1.602 \times 10^{-19}$ C

$$\therefore \quad V = \frac{1}{2}\times\frac{\left(6.626\times10^{-34}\right)^2}{9.108\times10^{-31}\times\left(1.54\times10^{-10}\right)^2\times1.602\times10^{-19}}$$

= 63.3 Volts

15. According to de Broglie's equation, $\lambda = \frac{h}{mv} = \frac{h}{p}$

For particle A

$$\lambda_A = \frac{h}{p_A}$$

For particle B,

$$\lambda_B = \frac{h}{p_B}$$

$$\therefore \quad \frac{\lambda_A}{\lambda_B} = \frac{h}{p_A}\cdot\frac{p_B}{h}$$

$$\frac{\lambda_A}{\lambda_B} = \frac{p_B}{p_A}$$

But $p_B = \frac{1}{2}p_A$

$$\frac{\lambda_A}{\lambda_B} = \frac{1}{2}\frac{p_A}{p_A}$$

$$\frac{\lambda A}{\lambda_B} = \frac{1}{2}$$

$\therefore \quad \lambda_B = 2\lambda_A = 2 \times 5 \times 10^{-8}$

$\lambda_B = 10^{-7}$ m

17. Cathode rays are particles of matter with a definite mass-to-charge ratio. Cathode rays are independent of the gas in the discharge tube or the kind of material making up the electrodes. These are the evidences to prove that cathode rays are part of all matter.

18. $\lambda = 4 \times 10^{-7}$ m

(a) Energy of the incident photon

$$E = h\frac{c}{\lambda}$$

$$E = \frac{6.626\times10^{-34}\ \text{Js}\times3.0\times10^{8}\ \text{ms}^{-1}}{4\times10^{-7}\ \text{m}} = 4.9695 \times 10^{-19}\ \text{J}$$

$$E = \frac{4.9695\times10^{-19}}{1.6020\times10^{-19}}\ \text{eV} = 3.102\ \text{eV.}$$

(b) Kinetic energy KE = Energy of photon – Work function
= 3.102 – 2.13 = 0.972 eV
= 0.972 × 1.6020 × 10^{-19} J = 1.557×10^{-19} J

(iii) Velocity of the photoelectron = $v = \sqrt{\frac{2\text{KE}}{m_e}}$

$$v = \sqrt{\frac{2\times1.557\times10^{-19}}{9.1\times10^{-31}}} \Rightarrow v = 5.85\times10^{5}\ \text{m s}^{-1}$$

19. For Balmer series

$$\frac{1}{\lambda} = 1.0097\times10^{7}\left(\frac{1}{2^2}-\frac{1}{n_H^2}\right)$$

$$\frac{1}{3.97\times10^{-7}\ \text{m}} = 1.97\times10^{7}\left(\frac{1}{4}-\frac{1}{n_H^2}\right)$$

$$\therefore \quad \frac{1}{4}-\frac{1}{n_H^2} = \frac{1}{3.97\times10^{-7}\ \text{m}\times1.097\times10^{7}\ \text{m}^{-1}} = 0.23$$

$$\therefore \quad \frac{1}{n_H^2} = \frac{1}{4} - 0.23 = 0.02$$

$$n_H^2 = \frac{1}{0.02} = 50$$

$\therefore \quad n_H = 7$

20. I.E. = Work function = 13.6 eV

Energy of the photon = 1.5 × *IE*
= 1.5 × 13.6 eV

We know that
$h\nu = W + \text{KE}$

$\therefore$ $KE = hv - W = (1.5 \times 13.6) - 13.6$

$KE = 0.5 \times 13.6\,eV = 6.8\,eV$

$KE = 6.8 \times 1.6 \times 10^{-19}\,J$

But $6.8 \times 1.6 \times 10^{-19} = \dfrac{mv^2}{2}$

$$\therefore \quad v = \left(\frac{2 \times 6.8 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}\right)^{1/2}$$

$v = 1.55 \times 10^{6}\,m\,s^{-1}$

From de Broglie equation, we can write

$$\lambda = \frac{h}{mv} = \frac{6.26 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.55 \times 10^{6}}$$

$\lambda = 4.71 \times 10^{-10}\,m$

$\lambda = 471\,pm$

21. Since $n_L = 2$ and $n_H = 5$. This transition gives rise to a spectral line in the Balmer series.

We have

$$\Delta E = 2.178 \times 10^{-18}\left[\frac{1}{n_L^2} - \frac{1}{n_H^2}\right]J$$

$$= 2.178 \times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 2.178 \times 10^{-18} \times \frac{21}{100}$$

$\Delta E = 4.57 \times 10^{-19}\,J$

The frequency of a photon is given by

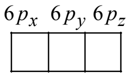
$$\upsilon = \frac{\Delta E}{h} = \frac{4.57 \times 10^{-19}\,J}{6.626 \times 10^{-34}\,Js} = 6.90 \times 10^{14}\,s^{-1}$$

and the wavelength

$$\lambda = \frac{c}{v} = \frac{3.0 \times 10^{8}\,ms^{-1}}{6.90 \times 10^{14}\,s^{-1}} = 4.35 \times 10^{-7}\,m = 435\,nm$$

22. The degeneracy of atomic orbitals depends upon the magnetic quantum number m

(i) $6p$, $n = 6$ $l = 1$, $m = 3$ and as $m = 3$, there are three degenerate atomic orbitals p_x, p_z and p_z. The orbital diagram is



(ii) $5d$, $n = 5$, $l = 2$, $m = 2l + 1$. There are five degenerate d atomic orbitals. Each of them have an $n = 5$ and $l = 2$.

(iii) $6f$: $n = 6$, $l = 2$, $m = 7$. The degeneracy of the f-subshell is 7(–3, –2, –1, 0, +1, +2, +3). The n and l value is same for all the degenerate atomic orbitals.

23. (i) For $n = 3$, $l = 0\ 1, 2$

For $l = 0$, $m = 0$

For $l = 1$ $m = +1, 0, -1$

For $l = 2$ $m = +2, +1, 0, -1, -2$.

(ii) For electron in $3d$ orbital

$l = 2$ and $m = -2, -1, 0, +1, +2$.

(iii) $1p$ and $3f$ are not possible.

24. (i) (a) H^- $1s^2$

(b) Na^+ $1s^2\,2s^2\,2p^6$

(c) O^{2-} $1s^2\,2s^2\,2p^6$

(ii) (a) $3s^1$ Atomic number = 11

(b) $2p^3$ Atomic number = 7

(c) $3d^6$ Atomic number = 26

25. (i) wave number $\overline{\nu} = 1/\lambda = 1/5800 \times 10^{-10}m$

$= 1.724 \times 10^{6}\,m^{-1}$

(ii) v (frequency) $= c/\lambda = \dfrac{3 \times 10^{8}\,ms^{-1}}{5800 \times 10^{-10}\,m}$

$= 5.172 \times 10^{14}\,s^{-1}$

26. The main points of this theory are as follows:

(i) The radiant energy is emitted or absorbed not continuosly but discontinuosly in the form of small discrete packets of energy. Each such packet of energy is called a quantum. In case of light, the quantum of energy is called photon.

(ii) The energy of each quantum is directly proportional to the frequency of radiation i.e. $E \propto \nu$ or

$E = h\,v$ where 'h' is Planck's constant and its value is 6.626×10^{-34}Js.

27. $(E_{He^+}) = Z^2_{(He)} \times$ constant and

$(E_{Li^{2+}}) = Z^2_{(Li)} \times$ constant

Hence energy of the first orbit of

$$Li^{2+}, (E_{Li^{2+}}) = \frac{Z^2_{(Li)} \times (E_{He^+})}{Z^2_{(He)}} = \frac{3^2 \times 19.6 \times 10^{-18}}{2^2}$$

$= 4.41 \times 10^{-17}\,J\,atom^{-1}$

28.

Orbit	Orbital
An orbit is a well defined circular path around the nucleus in which the electrons revolve.	An orbital is the three dimensional space around the nucleus within which the probability of finding is maximum.
It represents the planar motion of an electron around the nucleus.	It represents the three dimensional motion of an electron around the nucleus.
The concept of an orbit is not in accordance with the wave character of electrons and uncertainty principle.	The concept of an orbital is in accordance with the wave character of electrons and uncertainty principle.
All orbits are circular and disc like.	Different orbitals have different shapes i.e. s-orbital is spherical, p-orbitals are dumble shape and so on.
The maximum number of electrons in any orbit is given by $2n^2$ where 'n' is the number of orbit.	The maximum number of electrons present in any orbital is two.

29. If the electron has to exist within the nucleus; the maximum uncertainty in its position would have been 10^{-15}. Taking the mass of electron as 9.1×10^{-31}kg, the minimum uncertainty in velocity can be calculated by applying uncertainty principle.

$\Delta x.\Delta v \approx h/4\pi\Delta m$ or $v = h/4\pi m\Delta x$

$$= \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 10^{-15}} = 5.77 \times 10^{10}\,ms^{-1}$$

As this value is much higher than the velocity of light ($3 \times 10^{8}\,ms^{-1}$) . Thus electron cannot exist within the nucleus.

30. Similarities : (i) Both orbitals have spherical shape.

(ii) Both orbitals have same angular momentum.

Differences : (i) 1s orbital has no node while 2s orbital has one node. (ii) Energy of 2s orbital is greater than 1s orbital.

31. Cathode rays, no matter what the source is , are composed of electrons– all of which have same charge to mass ratio. The ions formed after the loss of electrons might have the same magnitude of charge, but different masses. Hence they will have different charge to mass ratio.

32. A) wave motion B) particle C) particle D) both

33. Since 13.6eV is needed to ionize H–atom, its 1.5 times (i.e., 13.6 × 1.5) 20.4eV have been absorbed by electron in hydrogen atom. Of this energy, 6.8eV is converted to kinetic energy. The velocity of the electron is as follows:

$6.8\text{eV} = 6.8(1.6 \times 10^{-19}\text{C})\ (1\text{V}) = 1.088 \times 10^{-18}\ \text{J}$

$$\text{KE} = \frac{1}{2}\text{mv}^2$$

$$\text{or}\quad \text{v} = \sqrt{2\text{KE}/\text{m}}$$

$$= \sqrt{2(1.088 \times 10^{-18}\ \text{J})/9.1 \times 10^{-31}\ \text{kg}} = 1.55 \times 10^6\ \text{m/s}$$

According to de Broglie equation

$$\lambda = \frac{\text{h}}{\text{mv}} = \frac{6.63 \times 10^{-34}\ \text{Js}}{(9.1 \times 10^{-31}\text{kg})(1.55 \times 10^6\ \text{m/s})} = 4.7 \times 10^{-10}\ \text{m}$$

34. The kinetic energy of a particle is given by,

$$\text{KE} = \frac{1}{2}\text{mv}^2 \qquad \ldots(1)$$

Multiply and divide eqn(1) by 'm'

$$= \frac{1}{2}\text{m}^2\text{v}^2/\text{m} = \text{p}^2/2\text{m} \qquad \ldots(2)$$

We Know that $\lambda = \text{h}/\text{p}$ or $\text{p} = \text{h}/\lambda$

By substituting value of p in eq (2) we get,

$$\text{K. E.} = \frac{\text{h}^2}{2\text{m}\lambda^2}$$

$$\text{KE for electron} = \frac{\text{h}^2}{2\text{m}_\text{e}\lambda_\text{e}{}^2}$$

$$\text{And KE for proton} = \frac{\text{h}^2}{2\text{m}_\text{p}\lambda_\text{p}{}^2}$$

Since KE for electron = KE for proton

$$\frac{\text{h}^2}{2\text{m}_\text{e}\lambda_\text{e}{}^2} = \frac{\text{h}^2}{2\text{m}_\text{p}\lambda_\text{p}{}^2}$$

$$\text{or}\quad \frac{\lambda_\text{e}}{\lambda\text{p}} = \frac{\sqrt{\text{m}_\text{p}}}{\sqrt{\text{m}_\text{e}}}$$

As $\text{m}_\text{p} > \text{m}_\text{e}$ thus $\lambda_\text{e} > \lambda\text{p}$

35. Given that $\text{KE} = 500\ \text{eV} = 500 \times 1.6 \times 10^{-19}\text{J}$;

$\text{m}_\text{p} = 1.67 \times 10^{-27}\ \text{kg}$

$$\text{KE} = \frac{1}{2}\text{mv}^2$$

$$\text{or}\quad 2\text{KE} = \text{mv}^2 \qquad \ldots(1)$$

Multiply eqn(1) with m we get

$2\text{mKE} = \text{m}^2\text{v}^2$

$\text{or mv} = \sqrt{2\text{mKE}}$

By de–Broglie equation $\lambda = \text{h}/\text{mv} = \text{h}/\sqrt{2\text{mKE}}$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times 500 \times 1.6 \times 10^{-19}}}$$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{26.72 \times 10^{-44}}} = \frac{6.626 \times 10^{-34}}{5.169 \times 10^{-22}} = 1.28 \times 10^{-12}\ \text{m}$$

36. Cu^{2+} has configuration = [Ar] 3d^9 hence Cu^{2+} has one unpaired electron,

Fe^{2+} has configuration = [Ar] 3d^6 hence Fe^{2+} has four unpaired electron and

Cr^{3+} has configuration = [Ar] 3d^3 hence has three unpaired electrons. Thus Fe^{2+} has highest para-magnetism.

37. Given that, $\text{K.E.} = 1.3 \times 10^{-18}\text{J}$; $v = 3v_0$;

$\text{h} = 6.626 \times 10^{-34}\ \text{Js}$

Kinetic energy of electron = $\text{h}(v - v_0)$

$1.3 \times 10^{-18} = 6.626 \times 10^{-34}(3v_0 - v_0)$

$$\text{v}_0 = \frac{1.3 \times 10^{-18}}{6.626 \times 10^{-34} \times 2} = 9.81 \times 10^{14}\ \text{Hz.}$$

38. $\Delta\text{V} = 0.02\%\ \text{of}\ 500\ \text{ms}^{-1} = \dfrac{500 \times 0.02}{100} = 0.1\ \text{ms}^{-1}$

$\text{h} = 6.6 \times 10^{-34}\text{Js}$ and mass of electron 'm' $= 9.1 \times 10^{-31}\text{kg}$

$$\Delta\text{x} \times \Delta\text{P} \geq \frac{\text{h}}{4\pi}$$

$$\Delta\text{x} \times \Delta(\text{mv}) \geq \frac{\text{h}}{4\pi}$$

$$\Delta\text{x} = \frac{\text{h}}{4\pi\text{m}\Delta\text{v}} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.1} = 5.77 \times 10^{-4}\text{m}$$

39. (i) The phenomenon of emission of electrons from the metal surface when a light of suitable frequency equal to or greater than the threshold frequency strikes on it is called photo-electric effect. The emitted electrons are called photo-electrons.

(ii) A black body is a substance which absorbs all the light radiation falling on it and when it is heated to a high temperature it emits all the radiations. The radiations emitted by a black body are called black body radiations.

Long Answer Questions

1. (i) For H atom ,

$\text{E}_\text{n} = -1.312 \times 10^3\ \text{kJmol}^{-1} = -1.312 \times 10^6\ \text{Jmol}^{-1}$

$$= -\frac{1.312 \times 10^6}{6.023 \times 10^{23}}\ \text{J atom}^{-1} = -2.18 \times 10^{-18}\ \text{J atom}^{-1}$$

Here, $\text{n}_\text{final} = 1$; $\text{n}_\text{initial} = 4$

$$\text{E}_\text{initial} = -\frac{2.18 \times 10^{-18}}{(4)^2} = -0.136 \times 10^{-18}\ \text{J atom}^{-1}$$

$$\text{E}_\text{final} = -\frac{2.18 \times 10^{-18}}{(1)^2} = -2.18 \times 10^{-18}\ \text{J atom}^{-1}$$

$\Delta\text{E} = \text{E}_\text{final} - \text{E}_\text{initial}$

$= -2.18 \times 10^{-18}\ (-0.316 \times 10^{-18}) = -1.864 \times 10^{-18}\ \text{J}$

Also, $\Delta\text{E} = \text{hc}/\lambda$

$$\lambda = \text{hc}/\Delta\text{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.864 \times 10^{-18}} = 10.66 \times 10^{-8}\ \text{m}$$

(ii) (a) 2s < 2p (b) 3p < 3d

(c) 3s < 4s (d) 4d < 5f

2. (a) orbital (b) para-magnetism
(c) –3 to +3 (d) Fe
(e) degenerate (f) $5s^2\,4d^{10}\,5p^2$
(g) orientations in space
(h) zero
(i) pauli's exclusion principle
(j) visible.

3. (i) We are given that P(Power) = 25 W ; t = 1 sec ; $\lambda = 6000\text{Å} = 6000 \times 10^{-10}\,\text{m} = 6 \times 10^{-7}\,\text{m}$

Energy of one photon is $E = h\nu = hc/\lambda$

$$= \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{6 \times 10^{-7}} = 3.315 \times 10^{-19}\,\text{J}$$

∴ Number of photons emitted per second

$$= \frac{\text{Total energy emitted per sec}}{\text{Energy of one photon}} = \frac{25 \times 1}{3.315 \times 10^{-19}}$$

$= 7.54 \times 10^{19}$

(ii) Given that, $E = 7.61 \times 10^{-17}\,\text{J}$;
$\lambda = 300\,\text{nm} = 300 \times 10^{-9}\,\text{m}$;
$h = 6.626 \times 10^{-34}\,\text{Js}$
$c = 3 \times 10^{8}\,\text{ms}^{-1}$

According to Planck's equation
$E = nh\nu = nhc/\lambda \; n = E\lambda/hc$

$$= \frac{7.61 \times 10^{-17} \times 300 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 115 \text{ photons}$$

4. (i) According to Rydberg-Balmer equation.

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = R\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$$

The wavelength (λ) will be longest when n_2 is the smallest i.e., $n_2 = 2$ and 3 for two longest wavelength lines.

For $n_2 = 2$:

$$\frac{1}{\lambda} = \left(1.097 \times 10^{-2}\ \text{nm}^{-1}\right)\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$= \left(1.097 \times 10^{-2}\ \text{nm}^{-1}\right) \times \frac{3}{4}$$

$$= 8.228 \times 10^{-3}\ \text{nm}^{-1} \text{ or } \lambda = 121.54\,\text{nm}$$

For $n_2 = 3$:

$$\frac{1}{\lambda} = \left(1.097 \times 10^{-2}\ \text{nm}^{-1}\right)\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

$$= \left(1.097 \times 10^{-2}\ \text{nm}^{-1}\right) \times (8/9)$$

$$= 9.75 \times 10^{-3}\ \text{nm}^{-1};\ \lambda = 102.56\ \text{nm}$$

(ii) The expression for the energy of hydrogen of electron is :

$$E_n = -\frac{2\pi^2 me^4}{n^2 h^2}$$

When $n = 1,\ E_1 = -\dfrac{2\pi^2 me^4}{(1)^2 h^2} = -13.12 \times 10^{5}\ \text{J mol}^{-1}$

When $n = 2,\ E_2 = -\dfrac{2\pi^2 me^4}{(2)^2 h^2} = -\dfrac{13.12 \times 10^{5}}{4}\ \text{J mol}^{-1}$

$$= -3.28 \times 10^{5}\ \text{J mol}^{-1}$$

The energy required for the excitation is :

$$\Delta E = E_2 - E_1 = \left(-3.28 \times 10^{5}\right) - \left(-13.12 \times 10^{5}\right)$$

$$= 9.84 \times 10^{5}\ \text{J mol}^{-1}.$$

5. Limitations of Bohr's model of an atom :
(i) It could not explain spectrum of multi-electron atoms.
(ii) It could not explain Zeeman and stark effect.
(iii) It could not explain shape of molecules.
(iv) It was not in accordance with Heisenberg's uncertainty principle.

Quantum Mechanical Model : It was developed on the basis of Heisenberg's uncertainty principal and dual behaviour of matter.

Main features of this model are given below :
(i) The energy of electrons in an atoms is quantized *i.e.* can have certain values.
(ii). It existence of quantized electronic energy levels is a direct result by the wave litre properties of electrons.
(iii) Both the exact position of exact velocity of an electron in an atom cannot be determined simultaneously.
(iv) The orbitals are filled increasing order of energy. All the information about the electron than atom is stored in orbital wave function Ψ.
(v) From the value of Ψ^2 at different points within atom, it is possible to predict the region around the nucleus where electron most probably will found.

5. Refer text.

7. (i) Cr(24) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^5$
Half filled orbitals are more stable because of symmetrical distribution of electrons and exchange energy is maximum.

(ii) It is impossible to determine the exact position and momentum of first moving sub-atomic particle like electron simultaneously.

$$\Delta V = 50 \times [(100 - 99.99)\%]$$

$$= 50 \times \frac{0.01}{100} = 50 \times 10^{-4} = 5 \times 10^{-3}\,\text{ms}^{-1}$$

$$\Delta x.\Delta V = \frac{h}{4m\pi}$$

$$\Rightarrow \Delta x = \frac{6.6 \times 10^{-34}\ \text{Js}}{4 \times 9.1 \times 10^{-31}\text{kg} \times 3.142 \times 5 \times 10^{-3}\ \text{ms}^{-1}}$$

$$\Delta x = \frac{6.6}{571.844} = 1.154 \times 10^{-2}\,\text{m}.$$

HOTS / EXEMPLAR QUESTIONS

Very Short Answer Questions

1. The number of nodal spheres for an *ns*-orbital is *n*–1. The 5s electron charge cloud will have four nodal spheres.

2. In the presence of the magnetic field, the orbitals present in the sub–shells which were degenerate take up different orientations. In other words, degeneracy is broken.

3. An electron has more potential energy when it is far from an atomic nucleus than when it is close to the atomic nucleus.

4. Possible transitions $\Sigma\Delta n = \Sigma(5-2) = \Sigma 3 = 1 + 2 + 3 = 6$

5. Same energy but different orientations.

6. At higher pressure (e.g., at 1 atmospheric pressure), no electric current flows through the tube because gases are poor conductor of electricity.

Short Answer Questions

1. (a) Mass of A is half that of B.
   (b) Mass of the ball is large and so wavelength is negligible (because $\lambda \propto \frac{1}{m}$).

2. The power of a 25 watt bulb is 25 Js^{-1} [1 watt = Js^{-1}]

$\therefore$ Energy of one photon,

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3.0\times10^{8}}{0.57\times10^{-6}}\text{J}$$

or $E = 3.487 \times 10^{-19}$ J [$\because$ 1 µm = 10^{-6} m]

$\therefore$ Rate of emission of quanta per second $= \frac{25}{3.487\times10^{-9}}$

= **7.169×10^{19} s^{-1}**

3. **No,** the given statement is **not** correct.

Let us take the case of **carbon** (z = 6). Its electronic configuration is $1s^2 2s^2 2px^1 2py^1 2pz^0$. It is quite stable. It have an even atomic number (z = 6) but all its electrons are not paired as it contains 2 unpaired electrons. The rule on which we relied is **Hund's rule**.1.

4. $\lambda = \frac{h}{mv}$

m = 100 g = 0.1 kg.

$$v = 100\text{ km/hr} = \frac{100\times1000\text{ m}}{60\times60\text{ s}} = \frac{1000}{36}\text{ ms}^{-1}$$

$h = 6.626 \times 10^{-34}$ Js

$$\lambda = \frac{6.626\times10^{-34}\text{ Js}}{0.1\text{ kg}\times\frac{1000}{36}\text{ ms}^{-1}}$$

$$= 6.626\times10^{-36}\times36\text{ m}^{-1} = 238.5\times10^{-36}\text{ m}^{-1}$$

Since the wavelength is very small, the wave nature cannot be detected.

5. Uncertainty in the speed of ball $= \frac{90\times4}{100} = \frac{360}{100} = 3.6\text{ms}^{-1}$

Uncertainty in position $= \frac{h}{4\pi m\Delta v}$

$$= \frac{6.626\times10^{-34}\text{ Js}}{4\times3.14\times10\times10^{-3}\text{Kg g}^{-1}\times3.6\text{ms}^{-1}}$$

$= 1.46\times10^{-33}$ m

6. The energy of electron is determined by the value of n in hydrogen atom and by n + l in multielectron atom. So for a given principal quantum number electron of s, p, d and f orbitals have different energy.

Long Answer Questions

1. (a) Let the frequency of violet light = f

Then frequency of red light $= \frac{f}{2}$

[frequency of violet light is twice that of red light]

Now, Energy of violet photon = hf (h = Planck's constant), $[E = hf]$

Energy of red photon $= \frac{h.f}{2}$

Thus $\frac{\text{Energy of violet photon}}{\text{Energy of red photon}} = \frac{h.f}{h.f/2}$ **= 2**

(b) Since the wave length of a photon of violet light is shorter as compared to that of a photon of green light so *a photon of violet light has higher energy.*

$$\left[E = h\nu = \frac{hc}{\lambda}\right]$$

2. (i) For Lyman series n_1 = 1 and for shortest wavelength $n_2 = \infty$

$$1/\lambda = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$1/\lambda = 10967700\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = 10967700$$

$\lambda = 1/R = 1/10967700 = 910 \times 10^{-10}$ m = 910 Å

For longest wavelength n_2 = 2

$$1/\lambda = 10967700\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 10967700\times\frac{3}{4}$$

or $\lambda = \frac{4}{3\times10967700} = 1210\times10^{-10}$ = 1210 Å

(ii) The intensity of the lines decreases as the wavelength decreases or the frequency increases. The line with lowest frequency corresponds to transition n_L = 1 to n_H = 2.

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{n_L^2} - \frac{1}{n_H^2}\right]$$

$$\frac{1}{\lambda} = \bar{v} = 1.097\times10^7\left[\frac{1}{1^2} - \frac{1}{2^2}\right]\text{m}^{-1} = 8.23\times10^6\text{ m}^{-1}$$

$$\therefore \quad \lambda = \frac{1}{8.23\times10^6}\text{ m} = 1.215\times10^{-7}\text{ m} = 121.5\text{ nm}$$

$$v = \frac{c}{\lambda} = \frac{3.00\times10^8\text{ ms}^{-1}}{1.215\times10^{-7}\text{ m}} = 2.468\times10^{15}\,s^{-1}$$

Energy, $E = hv$

$= 6.63 \times^{-34}$ J/s $\times 2.468 \times 10^{15}$ s^{-1} = 1.64×10^{-18} J.

CHAPTER TEST

1. A quantum is a bundle of energy but not necessarily of light energy while a photon is quantum of light energy.

2. Mass of 1 electron = 9.1×10^{-31} kg

$\therefore$ Mass of 6.02×10^{23} (1 mole) of electrons

$= 9.1 \times 10^{-31} \times 6.02 \times 10^{23} = 5.48 \times 10^{-7}$ kg

Charge on 1 electron = 1.602×10^{-19} C

$\therefore$ Charge on 6.02×10^{23} (1 mole) of electrons

$= 1.602\times10^{-19} \times 6.02 \times 10^{23} = 9.64 \times 10^4$ C

3. (a) For l = 0 i.e. 's' sub–shell has 1 orbitals.

(b) For $l = 2$ i.e. 'd' sub–shell has 5 orbitals.

4. When the electron is far off from the nucleus (i.e. $n = \infty$), there are no forces of interaction between nucleus and electron. Hence energy of electron = 0 . As the electron approaches the nucleus, attraction takes place, some energy is released. That is why the electronic energy is negative.

5. Energy of one photon is given by $E = h\nu = hc/\lambda$;

$\lambda = 242\text{ nm} = 242 \times 10^{-9}\text{ m}$

$$E = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{242 \times 10^{-9}} = 8.214 \times 10^{-19}\text{ J}$$

This energy is just sufficient to ionize sodium atoms.

Thus, ionization energy of sodium in kJ/mol

$= 8.214 \times 10^{-19} \times 6.023 \times 10^{23} = 4.946 \times 10^{5}\text{ J mol}^{-1}$

$= 494 \times 10^{3} = 494\text{ kJ/mol}$

6. To pin-point the position of electron, we have to use light when the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the collison, the position as well as the velocity of the electron is disturbed. According to the principle of optics, the accuracy with which the position of a particle can be measured depends upon the wavelength of light used. The uncertainty in position is $\pm\lambda$. The shorter the wavelength, the greater is the accuracy. But shorter wavelength means higher frequency and hence higher energy. This high energy photon on striking the electron changes its speed as well as the direction.

This will result in greater uncertainty in velocity of the electron. On the other hand, decreasing the momentum means increasing the wavelength which will lead to greater uncertainty in position.

7. (a) Energy of orbital in hydrogen atom is determined by 'n' and in multi-electron atom by 'n' and 'l' $(n + \ell)$

(b) size of orbital is determined by 'n'.

(c) shape of an orbital is determined by 'l'.

(d) Orientation of the orbital is determined by 'm_l'.

(e) ms refers to orientation of the spin of the electron.

3
Chapter

Classification of Elements and Periodicity in Properties

INTRODUCTION

Upto the end of seventeenth century, only a few elements were known and thus it was easy to study and remember their individual properties. However, with the discovery of a large number of new elements (as many as 112 elements are known at present), it was realised that there should be some simple way to study the properties of these elements and a large number of their compounds. After numerous attempts the scientists were finally successful in arranging the elements in various groups.

This arrangement of formulation of periodic table. Thus, periodic table may be defined as the arrangement of all the known elements according to their properties in a tabular form.

DEVELOPMENT OF THE PERIODIC TABLE

Initially the elements were classified by Lavoisier as metals and nonmetals. The first resonable classification of elements was given by Dobereiner as triad.

According to Dobereiner, when elements of same properties are kept in the increasing order of their atomic weights, the atomic weight of middle element is equal to the mean atomic weight of remaining two elements. Such a group of elements is called Dobereiner's triad.

Triad of atoms			Mean of first and last element
Li 7	Na 23	K 39	$\frac{7+39}{2}=23$
Be 9	Mg 24	Ca 40	$\frac{9+40}{2}=24.5$

Dobereiner could arrange only a few elements as triads and there are some elements present in a triad, whose atomic weights are approximately equal, e.g.

Fe Co Ni
Ru Rh Pd

Therefore, this hypothesis was not acceptable for all elements.

NEWLAND'S RULE OF OCTAVES

As in music, the eighth note is same as the first note. If the elements are arranged in the increasing order of atomic weights, on starting with an element, the first element will exhibit similarities with the eighth element e.g.,

	सा	रे	ग	म	प	ध	नि
Symbol of element	Li	Be	B	C	N	O	F
	7	9	11	12	14	16	19
Symbol of element	Na	Mg	Al	Si	P	S	Cl
	23	24	27	28	31	32	35.5

It is clear from the above table that sodium is the eighth element from lithium, whose properties resemble that of lithium.

Similarly Mg is eighth element for Be, Al for B and so on.

LOTHAR MEYER'S VOLUME CURVES

The graphs of atomic volumes against atomic weights are known as Lothar Meyer volume curves. The elements with similar properties occupy similar position on the curve. The alkali metals have highest atomic volumes. Alkaline earth metals (Be, Mg, Ca, Sr, Ba, etc.) which are relatively a little less electropositive, occupy positions on the descending part of the curve.

Halogens and the noble gases (except helium) occupy positions on the ascending part of the curve. Alkali metals have highest volume hence they are present at the peaks of graph. Transition elements have very small volumes and therefore these are present at the bottom of the curve.

MENDELEEV'S PERIODIC LAW

According to Mendeleev's periodic law, *the physical and chemical properties of elements are periodic function of their atomic weights.*

Mendeleev's Periodic Table

Periodic table is based on atomic weight. In the periodic table, the horizontal lines are called periods and the vertical lines are called groups. The periodic table consists of seven periods and nine groups. The earlier periodic table had only 8 groups. The noble gases were added later in the zero group because these were not discovered when Mendeleev put forward his periodic table. All the groups (except VIII and Zero groups) are divided into subgroups A and B. 2, 8, 18 and 32 are called magic numbers.

Merits of Mendeleev's periodic table:

(a) Mendeleev's periodic table simplified and systematized the study of the elements and their compounds.
(b) He left some blank positions for undiscovered elements
(c) It helped in correcting the doubtful atomic masses of some elements based on their position in Mendeleev's periodic table

Demerits of Mendeleev's periodic table:

(a) The position of hydrogen could not be justified.
(b) The position of isotopes was not clear
(c) It has been found that some elements with higher atomic mass precedes the elements with lower atomic mass.
(d) Some disimilar atoms are grouped together while some similar atoms are separated. e.g. Li, Na, K (alkali metal) are groups together with Cu, Ag and Au (Coinage metal)
(e) The position of lanthanides and actinides are not properly assigned.
(f) No proper place has been alloted to nine element of group VIII.

MODERN PERIODIC LAW AND MODERN PERIODIC TABLE

Moseley proved that the square root of frequency (ν) of the rays, which are obtained from a metal on showering high velocity electrons is proportional to the nuclear charge of the atom. This can be represented by the following expression.

$\sqrt{\nu} = a(Z - b)$, where Z is nuclear charge on the atom and a and b are constants. The nuclear charge on an atom is equal to the atomic number. Plot of $\sqrt{\nu}$ versus Z gave a straight line. This led Moseley to conclude that atomic number was a better fundamental property than atomic weight. According to modern periodic law, "*The properties of elements are the periodic functions of their atomic numbers*".

Modern or Long form of Periodic Table

Long form of periodic table is based upon the Modern Periodic law. This is also known as Bohr's table as it is based on Bohr's scheme for the arrangement of various electrons around the nucleus.

Following are some important structural features of the long form of the periodic table.

Periods: Period is a horizontal row in the periodic table. There are seven periods in the periodic table. The elements in a period have same number of electron shells i.e., **principal quantum number (n).**

- The first period is the shortest period containing 2 elements.
- The second and third are short period containing 8 elements. **Typical elements:** Elements of third period are known as typical elements e.g. Na, Mg, Al, Si, P,S, and Cl. Properties of all elements present in a particular group (e.g., IA) resemble with the properties of the corresponding typical element (e.g. Na.) **Bridge Elements:** (Diagonal relationship). Elements of second period are known as bridge elements Properties of the bridge elements resemble with the properties of the diagonal elements of the third period (i.e. typical elements). For example, Li resembles Mg; Be resembles Al; boron resembles Si, etc.
- The fourth and fifth periods are long period containing 18 elements.
- The sixth period is the incomplete period.

Groups: Group is a vertical column in the periodic table. There are eighteen groups in the periodic table. It constitutes a series of elements whose atoms have the same outermost electronic configuration.

- The subshell which receives the last electron refers to the block to which element belong.
- Group is predicted from the number of electrons in the outermost or penultimate shell i.e. last but one or (n –1) shell

Merits of Long form of Periodic Table over Mendeleev's Periodic Table

(i) **Positions of isotopes and isobars** - Isotopes have same atomic number and the modern periodic table is based on atomic numbers. Therefore, various isotopes of the same element will occupy the same position in the periodic table. Isobars have same atomic weights but different atomic numbers and therefore they have to be placed at different positions.

(ii) The positions of actinoids and lanthanoids is more clear now because these have been placed in group 3 and due to paucity of space, these are written at the bottom of the periodic table. The general electronic configurations of the elements remains same in group.

Defects of Long Form of Periodic Table

(i) The position of hydrogen is still disputable as it was there in Mendeleev's periodic table in group 1 as well as 7.
(ii) Helium is an inert gas but its configuration is different from that of the other inert gas elements.
(iii) Lanthanoids and actinoids series could not be adjusted in the main periodic table and therefore they had to be provided with a place separately below the table.

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

According to IUPAC the nomenclature can be derived using numerical roots for 0 and numbers 1-9 for atomic numbers of elements.

The roots are put together in order of digits which make the atomic number and 'ium' is added at the end. Use the following table

Digit	Name	Abbrevation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Example : Name the IUPAC name of the element of atomic number 108 : Name will be **Unniloctium** and **symbol** - UnO

(2) Example – Name the element with atomic number 115.

Name will be - **Ununpentium** and **symbol** UuP

CLASSIFICATION OF ELEMENTS INTO *s*, *p*, *d* and *f* BLOCK ELEMENTS

s-Block Elements

The elements of the periodic table in which the last electron enters in *s*–orbital, are called *s*–block elements. *s*-orbital can accommodate maximum two electrons. Their general electronic configuration is ns^{1-2}, where n = (1 to 7).

Group 1 elements are known as alkali metals because they react with water to form alkali. Group 2 elements are known as alkaline earth metals because their oxides react with water to form alkali and these are found in the soil or earth. The total number of *s*-block elements are 14. Fr^{87} and Ra^{88} are radioactive elements while H and He are gaseous elements. Cs and Fr are liquid elements belonging to *s*-block.

p - Block Elements

The elements of the periodic table in which the last electron gets filled up in the *p*-orbital are called *p*-block elements. A *p*-orbital can accommodate maximum of six electrons. Therefore, *p*-block elements are divided into six groups which are 13, 14, 15, 16, 17 and 18. The general electronic configuration of *p* block elements are ns^2np^{1-6} (where n = 2 to 6)

The 18 group elements having general electronic configuration ns^2np^6 are inert, because their energy levels are fully filled. The total number of *p*-block elements in the periodic table is 30 (excluding He). There are nine gaseous elements (Ne, Ar, Kr, Xe, Rn, F_2, Cl_2, O_2 and N_2) belonging to *p*-block. Gallium (Ga) and bromine (Br_2) are liquids. The step-like thick lines drawn in the periodic table in the *p*-block divides elements into metals, nonmetals and metalloids.

The *p*-block elements together with *s*-block elements are called Representative elements or Main Group Elements.

d-Block Elements

The elements of the periodic table in which the last electron gets filled up in the *d*-orbital, are called *d*-block elements. The *d*-block elements are placed in groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. In *d*-block elements, the electrons gets filled up in the *d*-orbital of the penultimate shell. They form a bridge between chemically active metals of *s*-block and less active elements of *p*-block. That is why these elements are known as transition elements. Though the total number of d block elements is 33 in the periodic table but there are only 30 transition elements. Because only those elements are considered as transition elements in which *d*-orbital is partially filled. Zn, Cd and Hg though are *d*-block elements but do not known as transition elements because in these elements is *d*-orbitals are fully filled. The general electronic configuration of these elements is $(n–1)d^{1–10}\ ns^{0–2}$ where n = 4 to 7. All of these elements are metals. Out of all the *d* block elements mercury is the only liquid element.

f-Block Elements

The elements of the periodic table in which the last electron gets filled up in the *f*-orbital, are called *f*-block elements. The *f*-block elements are from atomic number 58 to 71 and from 90 to 103. There are 28 *f*-block elements in the periodic table. The elements from atomic number 58 to 71 are called *lanthanoids* because they come after lanthanum (57). The elements from 90 to 103 are called *actinoids* because they come after actinium (89). The lanthanoids occur in nature in low abundance and therefore, these are called rare earth elements. All the actinoid elements are radioactive. All the elements after atomic number 92 (i.e., U^{92}) are *transuranium* elements.

The general formula of these elements is $(n-2)f^{1-14}\ (n-1)\ d^{0-1}\ ns^2$

Metals & Non-metals

Metals comprise more than seventy five percent of the known elements.

(a) Metals appear on the left side of the periodic table.
(b) Metals are usually solid at room temperature except mercury. Mercury is the only metal that is liquid at room temperature.
(c) Metals have high M.P. and B.P. Gallium, Cs and Fr are low melting solids.
(d) Metals are good conductors of heat and electricity.
(e) Metals are malleable and ductile.
(f) Non–metals are about twenty percent of the known elements. These are located at the top right of the periodic table.Following are the characteristics of non-metal.
(g) Non-metals are usually solids or gases at room temperature. Bromine is a non-metal which is liquid at room temperature.
(h) Low M.P. and B.P.
(i) Poor conductors of heat and electricity
(j) Generally brittle.
(k) Semi-metals or metalloids lie at the border line between metals and non-metals (e.g. Si, Ge, As).
(l) Out of 105 elements, 22 are non-metals and about 83 are metals.

PERIODIC PROPERTIES OF ELEMENTS

The Periodicity is the recurrence of similar properties of the elements after certain regular intervals when they are arranged in the order of increasing atomic numbers. Cause of periodicity is the repetition of similar electronic configuration of the atom in the valence shell after certain regular intervals.

Atomic Radius

The distance of the outermost orbit from the centre of the nucleus of an atom is called atomic radius.

Types of Atomic Radius

(i) Covalent radius: It is one half of the distance between the centers of nuclei of the similar atoms bonded by a single covalent bond. For example,

$$\text{Atomic radius of chlorine} = \frac{\text{Bond distance between Cl} - \text{Cl}}{2}$$

(ii) Metallic radius: It is one half of the internuclear distance separating the metal ions in the metallic crystal.

van der Waal's Radius is one half of the distance between two adjacent non-bonded atoms belonging van der Waal's radius to the nearest neighbouring molecules of the substance in the solid state.

Factors affecting atomic radius

The atomic radius depends upon the following factors.

(i) Number of orbits : The increase in the number of orbit (s) in an atom increases the atomic size.

(ii) Effective nuclear charge : The increase in the number of protons increases the effective nuclear charge. This results in the decrease of atomic radius because protons attracts the electrons present in the outermost orbit with greater force.

(iii) Shielding effect/screening effect : The electrons of inner shell repel the electrons of valence shell and prevent them from coming closer to the nucleus. Due to this, the atomic radius increases. This is called shielding effect. When an atom has more number of shells, the shielding provided to outermost electrons will be greater.

Periodic trends in atomic radius

(i) In a period : Atomic radii decreases with increase in atomic number in a given period. This is due to the increase in magnitude of nuclear charge while the number of shells remain the same. Fr is the largest element in the periodic table.

(ii) In a group : The atomic radii of an element increases as we move down a group. This is due to the addition of an extra shell.
van der Waal's radius > Metallic radius > Covalent radius.

Ionic radii

Ionic radius is the distance between the nucleus and the point upto which nucleus influences the electron cloud scattered around the nucleus in an ion.

Types of ionic radii

(i) Cationic radius : An atom forms a cation on loss of electron (s). The cationic radius can be defined as the distance between the nucleus and the point upto which nucleus influences the electron cloud scattered around the nucleus. The size of a cation is smaller in comparison to the size of its corresponding atom.

For Examples

(1) $Mn > Mn^{+2} > Mn^{+3} > Mn^{+4} > Mn^{+6} > Mn^{+7}$

(2) $Pb^{+2} > Pb^{+4}$

(ii) Anionic radius : When a neutral atom gains electron (s) it becomes a negatively charged ion called an anion. The distance between the nucleus of an anion and the point upto which nucleus influences the electron cloud scattered around the nucleus, is called its anionic radius. The size of an anion is greater than the size of its corresponding atom.

Variation of size in isoelectronic species : The species, which have same number of electrons but different nuclear charges, constitute an isoelectronic series. In the isoelectronic species with the increase in effective nuclear charge, the size of ion goes on decreasing.

$N^{3-} > O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$

$P^{3-} > S^{2-} > Cl^{-} > K^{+} > Ca^{2+} > Sc^{3+}$

Ionisation Potential

The energy required to remove the most losely bound electron from the outermost orbit of isolated gaseous atom of an element, is called ionisation potential (IP). This ionisation is an endothermic or energy-absorbing process.

The energy required to remove one electron from a neutral gaseous atom to convert it to monopositive cation, is called first ionisation potential (Ist IP). The energy required to convert a monopositive cation to a dipositive cation is called second ionisation potential (IInd IP).

$$I^{st}\ IP < II^{nd}\ IP < III^{rd}\ IP$$

Factors affecting ionisation potential :

(i) Number of shells : With the increase in number of shells the atomic radius increases i.e. the distance of outermost shell electron(s) from the nucleus increases and hence the ionisation potential decreases.

(ii) Effective nuclear charge : Atomic size decreases with increase in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron(s) of the outermost orbit and higher will be the ionisation potential.

(iii) Shielding effect : The electrons of internal orbits repel the electron(s) of the outermost orbit due to which the attraction of the nucleus towards the electron(s) of the outermost orbit decreases and thus atomic size increases and the value of ionisation potential decreases.

Periodic trends in ionisation potential

(i) In a period : The value of ionisation potential normally increase on going from left to right in a period, because effective nuclear charge increases and atomic size decreases.

Exceptions : In second period ionisation potential of Be is greater than that of B, and in the third period ionisation potential of Mg is greater than that of Al due to high stability of fully filled orbitals. In second period ionisation potential of N is greater than that of O and in the third period ionisation potential of P is greater than that of S, due to stability of half filled orbitals. The increasing order of the values of ionisation potential of the second period elements is

$$Li < B < Be < C < O < N < F < Ne$$

The increasing order of the values of ionisation potential of the third period elements is

$Na < Al < Mg < Si < S < P < Cl < Ar$

Ionisation potential of transition elements

In transition elements, the value of ionisation potential has very little increase on going from left to right in a period because the outermost orbit remains the same as electrons gets filled up in the $(n-1)d$ orbitals resulting in very little increase in the values of ionisation potential.

In series of transition elements, the first ionisation potential normally increases with increase in atomic number on going from left to right, but this periodicity is not uniform.

The value of ionisation potential increases with increase in effective nuclear charge. The value of ionisation potential decreases with increase in shielding effect when the number of electrons increases in $(n-1)d$ orbitals.

In the first series of transition elements, the first ionisation potential normally increases on going from left to right from Sc to Cr because shielding effect is much weaker in comparison to effective nuclear charge. The value of first ionisation potential of Fe, Co and Ni remains constant, because shielding effect and effective nuclear charge balances each other. The value of ionisation potential shows slight increase for Cu[Ar]$3d^{10}4s^1$ and Zn[Ar]$3d^{10}4s^2$ because of their stable electronic configuration. The value of first ionisation potential of Mn is maximum because it has maximum stability due to fully filled *s* and half filled *d*-orbitals.

Inner transition elements

The size of inner transition elements is greater than that of *d*-block elements. Therefore the value of ionisation potential of *f*-block elements is smaller than that of *d*-block elements and due to almost constant atomic size of *f*-block elements in a period the value of their ionisation potential remains more constant than that of *d*-block elements.

(ii) In a group : The value of ionisation potential normally decreases on going from top to bottom in a group because both atomic size and shielding effect increases.

Electron Affinity

Electron gain enthalpy is the enthalpy change accompanying the addition of an electron to a gaseous atom to form a gaseous negative ion :

$$X(g) + e^- \longrightarrow X^-(g)$$

The magnitude of E.G.E. is the force with which the atom can hold the electron i.e. greater the E.G.E. value greater is the tendency of atom to accept the electron. The unit of E.G.E is kJ/ mole or eV.

Factors affecting electron affinity

(i) Atomic size or atomic radius : When the size or radius of an atom increases, the electron entering the outermost orbit is more weakly attracted by the nucleus and thus the value of electron affinity decreases.

(ii) Effective nuclear charge : When effective nuclear charge is more, then the atomic size is less. Then the atom can easily gain an electron and has higher electron affinity.

(iii) Stability of fully-filled and half-filled orbitals : The stability of the configurations having fully-filled orbitals (s^2, p^6, d^{10} and f^{14}) and half-filled orbitals (p^3 , d^5 and f^7) is relatively higher than that of other configurations. Hence such type of atoms have less tendency to gain an electron, therefore their electron affinity values will be very low or zero.

Trends in electron affinity

(i) In a period : The atomic size decreases with increase in effective nuclear charge and hence electron affinity increases.

(ii) In a group : On moving down the group the atomic size decreases and hence the incoming electron feels less attraction. Thus electron affinity decreases down the group.
However in halogens, electron affinity of fluorine is smaller than chlorine. According to size fluorine should have higher value of electron affinity than chlorine. This is due to small size.

Note:
- Noble gases have large positive E.G.E. This is because noble gases have completely filled orbitals. As a result, they show very little tendency to gain electrons. So, energy has to be supplied to add an additional electron.
- Halogens have highest electron affinities because their electronic configuration is $ns^2\ np^5$ i.e. only one electron is short from the noble gas configuration thus has maximum tendency to accept electrons.
- Alkaline earth metals have almost zero electron affinity.
- Electron affinity of N and P are extremely low due to their small atomic size and stable outer electronic configuration.
- Cl is the element with most negative electron gain enthalpy in the periodic table.
- Neon has the largest positive electron gain enthalpy.

Electronegativity

The measure of the capacity or tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called electronegativity of that atom. Pauling was the first scientist to put forward the concept of electronegativity.

Factors affecting electronegativity

(i) Atomic size : Electronegativity of a bonded atom decreases with increase in size. With increase in size, the force of attractions on valence shell electrons decreases and hence electronegativity decreases.

(ii) Nuclear charge : The higher the nuclear charge. More will be the electronegativity value of an element. Since the nucleus will be able to attract or pull more electrons towards itself.

(iii) Screening effect or shielding effect : If the outermost electrons shields the nucleus effectively, the electronegativity of the element decreases.

Periodic trends in electronegativity

(i) In a group : On moving down the group atomic size increases and hence electronegativity decreases.

(ii) In a period : On moving along the period, atomic size decreases and electronegativity increases.

Note:
- The alkali metals possess the lowest value while the halogens have the highest value of electrognegativity.
- Noble gases have zero electronegativity. If the two atoms have similar electronegativity, the bond between them will be covalent.
- If the two atoms have a large difference in electronegativities, they will form an ionic bond.
- Greater the electronegativity of an element, greater is its tendency to gain electrons and hence more is its non-metallic character.
- F is most electronegative element in the periodic table.
- Cs is the least electronegative element in the periodic table.

PERIODIC TRENDS IN CHEMICAL PROPERTIES

Periodicity of Valence or Oxidation States

Valency can be understood in terms of electronic configuration of elements. The valence of representative elements is usually equal to the number of electrons in outermost orbital or equal to eight minus the number of outermost electrons. Nowadays, the term oxidation state is used for valency.

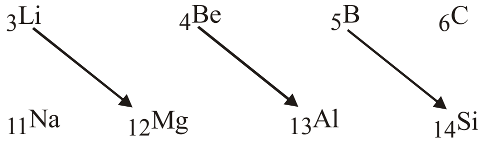
There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids.

(i) In a period : As we move across a period from left to right, the number of valence electrons increases from 1 to 8, but the valence of elements with respect to H or O first increases from 1 to 4 and then decreases to zero.

(ii) In a group : When we move down the group, the number of valence electrons remain the same, therefore, all the elements in a group exhibit the same valence. For example, all elements of group 1 exhibit valence of one while those of group 2, exhibit valence of two. Noble gases present in group 18 are zerovalent, i.e., their valence is zero since these elements are chemically inert.

Anomalous Properties of Second Period Elements

Some elements of second period like Li, Be, B show dissimilarities with other elements of their group but shows similarities with elements of third group like Mg, Al, Si situated diagonally to them. It is called diagonal relationship.



This anomolous behaviour of first member of each group is due to small size, large charge radius ratio, high electronegativity and absence of *d*-orbitals in valence shells.

Similarities between properties of Li and Mg are as follows:

(i) Li and Mg both react directly with nitrogen to form lithium nitride (Li_3N) and magnesium nitride (Mg_3N_2) whereas other alkali metals of group 1 do not form nitrides.

(ii) Fluoride, carbonate and phosphate of Li and Mg are insoluble in water whereas these compounds of other alkali metals are soluble.

(iii) Li and Mg both are hard metals, whereas other metals of group 1 are soft.

(iv) LiOH and $Mg(OH)_2$ both are weak bases, whereas hydroxides of other elements of group 1 are strong bases.

(v) They both do not form peroxide and superoxide.

(vi) Their melting and boiling points are high.

(vii) By thermal disintegration of $LiNO_3$ and $Mg(NO_3)_2$, Li_2O and MgO is obtained respectively.

(viii) Thermal stability of Li_2CO_3 and $MgCO_3$ is very less compared to other alkali metal carbonates and they liberate CO_2 gas easily.

Similarly, Be shows similarity with Al of group 13, which are as follows:

(i) These both elements do not provide colour to Bunsen burner flame.

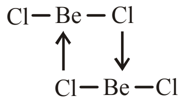
(ii) They both are comparatively stable in air.

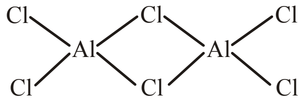
(iii) Both are insoluble in NH_3 therefore do not form blue coloured solution.

(iv) There is no tendency to form peroxide and superoxide.

(v) Reducing power of both Be and Al is very less due to low value of standard electrode potential in the form of oxidation potential.

(vi) Be and Al both form halogen bridge halides.





PERIODIC TRENDS AND CHEMICAL REACTIVITY

Chemical reactivity is highest at the two extremes of a period and is lowest in the centre. The maximum reactivity at the extreme left is exhibited by the loss of an electron (s) forming a cation and at extreme right by the gain of an electron(s) forming an anion.

Variation Along a Period:

(i) Metallic and Non-metallic character: On moving along a period metallic character decreases whereas non-metallic character increases.

(ii) Nature of oxides: On moving along a period basic nature of oxides decreases whereas acidic nature of oxides increases.

Variation Along a Group

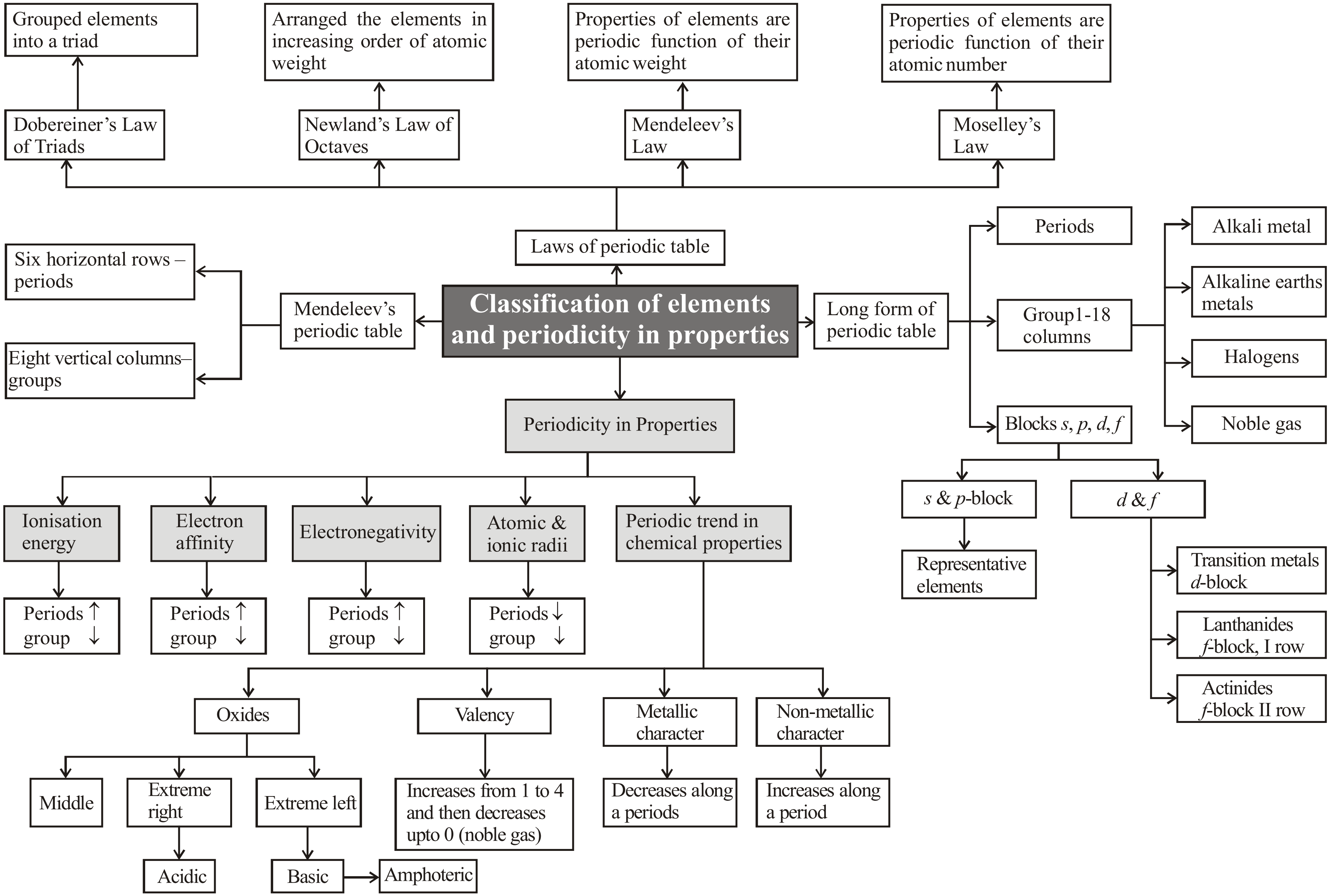
(i) Metallic & non-metallic character: On moving from top to bottom metallic character generally increases due to increase in atomic size and decrease in ionisation enthalpy. Whereas non-metallic character generally decreases down a group.

(ii) Acidic & basic character of oxides: On moving down in a group basic character of oxides increases whereas acidic character decreases.

(iii) Reactivity of metals: Generally increases down a group. As the ionisation enthalpy of metals decreases from top to bottom.

(iv) Reactivity of non-metals: Generally decreases down a group. As the electronegativity decrease from top to bottom in a group.

CONCEPT MAP


Classification of elements and periodicity in properties
Laws of periodic table
Dobereiner's Law of Triads
Grouped elements into a triad
Newland's Law of Octaves
Arranged the elements in increasing order of atomic weight
Mendeleev's Law
Properties of elements are periodic function of their atomic weight
Moselley's Law
Properties of elements are periodic function of their atomic number
Mendeleev's periodic table
Six horizontal rows – periods
Eight vertical columns– groups
Long form of periodic table
Periods
Group1-18 columns
Blocks s, p, d, f
Alkali metal
Alkaline earths metals
Halogens
Noble gas
s & p-block
Representative elements
d & f
Transition metals d-block
Lanthanides f-block, I row
Actinides f-block II row
Periodicity in Properties
Ionisation energy
Periods ↑ group ↓
Electron affinity
Periods ↑ group ↓
Electronegativity
Periods ↑ group ↓
Atomic & ionic radii
Periods ↓ group ↓
Periodic trend in chemical properties
Oxides
Middle
Extreme right
Acidic
Extreme left
Basic
Amphoteric
Valency
Increases from 1 to 4 and then decreases upto 0 (noble gas)
Metallic character
Decreases along a periods
Non-metallic character
Increases along a period

Textbook Exercises

3.1 What is the basic theme of organisation in the periodic table?

Ans. The basic theme of organisation of elements in the periodic table is to simplify and systematize the study of the properties of all the elements and millions of their compounds. On the basis of similarities in chemical properties, the various elements have now been divided into different groups. This has made the study simple because the properties of elements are now studied in form of groups rather than individually.

3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that ?

Ans. Mendeleev used atomic weight as the basis of classification of elements in the periodic table. He arranged known elements in order of increasing atomic weights grouping together elements with similar properties.

3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law ?

Ans. Mendeleev Periodic Law states that the physical and chemical properties of the elements are periodic function of their atomic weights while Modern Periodic Law states that physical and chemical properties of the elements are a periodic function of their atomic numbers. Thus, the basic difference in approach between Mendeleev's Periodic Law and Modern Periodic Law is the change in the basis of classification of elements from atomic weight to atomic number.

3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.

Ans. In the modern periodic table, each period starts with the filling of a new principal energy level. Thus, the sixth period begins with the filling of principal quantum number, $n = 6$. When $n = 6$, l = 0,1, 2,3. But according to Aufbau's principle, the energy of 6d subshell is higher than that of 7s–subshell but energies of 5*d*– and 4*f* sub shells are lower than that of 6*p*–subshell. Therefore, in 6th period, electrons can be filled in only 6*s*, 4*f*, 5*d* and 6*p*–subshells whose energies increase in the order : $6s < 4f < 5d < 6p$. Now *s*-subshell has one, *p*-subshell has three, *d*-subshell has five and *f*-subshell has seven orbitals. Hence, in all, there are 16 (1 + 3 + 5 + 7) orbitals that can be filled in this period. Since according to Pauli's exclusion principle each orbital, at the maximum, can accommodate two electrons, therefore, 16 orbitals, at the maximum, can have 32 electrons and hence sixth period has 32 elements.

3.5 In terms of period and group, where would you locate the element with Z = 114 ?

Ans. The filling of the 6th period ends at $_{86}$Rn. Thereafter, the filling of 7th period starts. Like in 6th period, in 7th period also, the filling of four sub–shells, *i.e.,* 7*s*, 7*p*, 6*d* and 5*f* occurs. But according to Aufbau's principle, their energies increase in the order: $7s < 5f < 6d < 7p$. Therefore, after $_{86}$Rn, the next two elements with Z = 87 and Z = 88 are s-block elements, the next fourteen, i.e. Z = 90–103 are *f*-block elements, the next ten, *i.e.* Z = 104 –112 are d–block elements and the last six, i.e., Z = 113 –118 are *p*-block elements. Therefore, the element Z = 114 is the second *p*-block element (*i.e.* group 14) of the 7th period. Thus, the location of the element with Z = 114 in the period table is

Period = 7th   Block : *p*   Group : 14

3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

Ans. In the third period the filling up of only 3*s*– and 3*p*-orbitals occurs. Therefore, in this period there are only two *s* -and six *p*-block elements. Since third period starts with Z = 11 and ends at Z = 18, therefore, elements with Z = 11 and Z = 12 are *s*-block elements. The next six elements with Z = 13 to 18 are *p*-block elements and belong to groups 13,14,15,16,17 and 18. Therefore, the element which will lie in seventeenth group will have Z = 12 + 5 = 17

3.7 Which element do you think would have been named by

(i) Lawrence Berkeley Laboratory

(ii) Seaborg's group ?

Ans. (i) Lawrencium (Z = 103) and
Berkeliuin (Z = 97)
(ii) Seaborgium (Z = 106)

3.8 Why do elements in the same group have similar physical and chemical properties ?

Ans. Elements in the same group have similar electronic configuration and hence have similar physical and chemical properties

3.9 What does atomic radius and ionic radius really mean to you ?

Ans. Atomic radius literally means size of the atom. It can be measured either by X–ray or by spectroscopic methods. In case of non–metals, atomic radius is called covalent radius. It is defined as one–half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule. For example, the internuclear distance between two chlorine atoms in chlorine molecule is 198 pm. Therefore, the covalent radius of chlorine atom is 198/2 =99 pm (0.99 Å). In case of metals, atomic radius is called metallic radius. It is defined as one– half the distance between the two adjacent atoms in the crystal lattice. For example, the distance between two adjacent copper atoms in solid copper is 256 pm, therefore, the metallic radius of copper is 256/2 = 128 pm (1.28 Å). Ionic radius means size of the ion. An ion can be a cation or an anion. The size of a cation is always smaller than that of the parent atom because loss of one or more electrons increases the effective nuclear charge. As a result, force of attraction increases and hence the ionic size decreases. On the other hand, the size of the anion is larger than the parent atom because the addition of one or more electrons decreases the effective nuclear charge. As a result, the force of attraction decreases and hence the ionic size increases. For example, the ionic radius of Na^+ is 95 pm while the atomic radius of sodium is 186 pm. On the other hand, ionic radius of fluoride ion is 136 pm whereas the atomic radius of fluorine atom is only 72 pm.

3.10 How do atomic radius vary in a period and in a group ? How do you explain the variation?

Ans. The atomic radius increases down the group. This is because a new energy shell (i.e. principal quantum number increases by unity) is added at each succeeding element while the number of electrons in the valence shell remains to be the same. In other words, the electrons in the valence shell of each succeeding element lie farther and farther away from the nucleus. As a result, the force of attraction of the nucleus for the valence electrons decreases and hence the atomic size increases.In contrast, the atomic size decreases as we move from left to right in a period. This is because that within a period the outer electrons remain in the same shell but the nuclear charge increases by one unit at each succeeding element. Due to this increased nuclear charge, the attraction of the nucleus for the outer electrons increases and hence the atomic size decreases.

3.11 What do you understand by isoelectronic species? Name the species that will be iso-electronic with each of the following atoms or ions.

(i) F^- (ii) Ar (iii) Mg^{2+} (iv) Rb^+

Ans. Ions of different elements which have the same number of electrons but different magnitude of the nuclear charge are called isoelectronic species.

(i) F^- has 10 (9 + 1) electrons. Therefore, the species nitride ion, N^{3-} (7 + 3); oxide ion; O^{2-} (8 + 2), neon, Ne (10 + 0); sodium ion, Na^+ (11 – 1); magnesium ion, Mg^{2+} (12 – 2); aluminium ion, Al^{3+} (13 – 3) etc. each one of which contains 10 electrons, are isoelectronic with it.

(ii) Ar has 18 electrons. Therefore, the species phosphide ion, P^{3-} (15 + 3), sulphide ion; S^{2-}(16 + 2); chloride ion, Cl^- (17 + 1), potassium ion, K^+ (19 – 1), calcium ion, Ca^{2+} (20 – 2), etc., each one of which contains 18 electrons, are isoelectronic with it.

(iii) Mg^{2+} has 10 (12 – 2) electrons, therefore, the species N^{3-}, O^{2-}, F^-, Ne, Na^+, Al^{3+}, etc. each one of which contains 10 electrons, are isoelectronic with it.

(iv) Rb^+ has 36 (37 – 1) electrons. Therefore, the species bromide ion, Br^- (35 + 1), krypton, Kr (36 + 0) and strontium Sr^{2+}(38 – 2) each one of which has 36 electrons, are isoelectronic with it.

3.12 Consider the following species: N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}.

(i) What is common in them ?

(ii) Arrange them in the order of increasing ionic radii ?

Ans. (i) Each one of these ions contains 10 electrons and hence all are isoelectronic ions.

(ii) The ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge. For example, consider the isoelectronic ions:
N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}.
All these ions have 10 electrons but their nuclear charges increase in the order:
N^{3-} (+ 7), O^{2-} (+ 8), F^- (+ 9), Na^+ (+ 11), Mg^{2+} (+ 12) and Al^{3+} (+ 13). Therefore, their ionic radii decrease in the order:
$N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$.

3.13 Explain why cation are smaller and anions are larger in radii than their parent atoms.

Ans. The ionic radius of a cation is always smaller than the parent atom because the loss of one or more electrons increases the effective nuclear charge. As a result, the force of attraction of nucleus for the electrons increases and hence the ionic radii decrease. In contrast, the ionic radius of an anion is always larger than its parent atom because the addition of one or more electrons decreases the effective nuclear charge. As a result, the force of attraction of the nucleus for the electrons decreases and hence the ionic radius increases.

3.14 What is the significance of the terms –'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy ?

Ans. (i) Ionization enthalpy is the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom so as to convert it into a gaseous cation is called ionization enthalpy. The force with which an electron is attracted by the nucleus of an atom is appreciably affected by presence of other atoms within its molecule or in the neighborhood. Therefore, for the purpose of determination of ionization enthalpy, it is essential that these inter–atomic forces of attraction should be minimum. Since in the gaseous state, the atoms are widely separated, therefore, these inter–atomic forces are minimum. Further since it is not possible to isolate a single atom for the purpose of determination of its ionization enthalpy, therefore, the inter–atomic distances are further reduced by carrying out the measurement at a low pressure of the gaseous atom. It is because of these reasons, that the term isolated gaseous atom has been included in the definition of ionization enthalpy.

(ii) Electron gain enthalpy is the energy released when an isolated gaseous atom in the ground state accepts an extra electron to form the gaseous negative ion.

The term isolated gaseous atom has already been explained above. The term ground state here means that the atom must be present in the most stable state, i.e., the ground state. The reason being that when the isolated gaseous atom is in the excited state, lesser amount of energy will be released when it gets converted into gaseous anion after accepting an electron. Therefore, for comparison purposes, the electron gain enthalpies of gaseous atoms must be determined in their respective most stable state, i.e., ground state.

3.15 Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.

Hint : Apply the idea of mole concept to derive the answer.

Ans. The energy required to remove an electron in the ground state of hydrogen atom

$= -$ (its energy in the ground state)

$= -(-2.18 \times 10^{-18}\ \text{J}) = 2.18 \times 10^{-18}\ \text{J}$

Ionization energy per mole of hydrogen atoms

$$= \frac{2.8\times10^{-18}\times6.02\times10^{23}}{1000} = 1312.36\ \text{kJ mol}^{-1}$$

$= 1312.36 \times 10^{3}\ \text{J mol}^{-1}$

3.16 Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne.

Explain why

(i) Be has higher $\Delta_i H$ than B

(ii) O has lower $\Delta_i H$ than N and F ?

Ans. (i) The ionization enthalpy, among other things, depends upon the type of electron to be removed from the same principal shell. In case of Be ($1s^2 2s^2$) the outermost electron is present in 2s-orbital while in B ($1s^2 2s^2 2p^1$) it is present in 2p-orbital. Since 2s-electrons are more strongly attracted by the nucleus than 2p-electrons, therefore, lesser amount of energy is required to knock out a 2p-electron than a 2s-electron. Consequently, $\Delta_i H$ of Be is higher than that $\Delta_i H$ of B.

(ii) The electronic configuration of N ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) in which 2p-orbitals are exactly half-filled is more stable than the electronic configuration of O ($1s^2 2s^2 2p_x^2, 2p_y^1, 2p_z^1$) in which the 2p-orbitals are neither half-filled nor completely filled. Therefore, it is difficult to remove an electron from N than from O. As a result, $\Delta_i H$ of N is higher than that of O. Further, the electronic configuration of F is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. Because of higher nuclear charge (+9), the first ionization enthalpy of F is higher than that of O.

3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

Ans. The electronic configurations of Na and Mg are:

Na : $1\ s^2 2s^2 2p^6 3s^1$ Mg: $1\ s^2 2s^2 2p^6 3s^2$

Thus, the first electron in both the cases has to be removed from the 3s–orbital but the nuclear charge of Na (+ 11) is lower than that of Mg (+ 12), therefore, the first ionization energy of sodium is lower than that of magnesium. After the loss of first electron, the electronic configuration of Na^+ is $1s^2 2s^2 2p^6$. Here, the electron is to be removed from inert (neon) gas configuration which is very stable and hence removal of second electron from sodium is very difficult. However, in case of magnesium, after the loss of first electron, the electronic configuration of Mg^+ is $1s^2 2s^2 2p^6 3s^1$. Here, the electron is to be removed from a 3s orbital which is much easier than to remove an electron from inert gas configuration. Therefore, the second ionization enthalpy of sodium is higher than that of magnesium.

3.18 What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down the group ?

Ans. Within the main group elements, the ionization enthalpy decreases regularly as we move down the group due to the following two factors.

(i) **Atomic size**. On moving down the group, the atomic size increases gradually due to the addition of one new principal energy shell at each succeeding element. As a result, the distance of the valence electrons from the nucleus increases. Consequently, the force of attraction of the nucleus for the valence electrons decreases and hence the ionization enthalpy decreases.

(ii) **Screening effect**. With the addition of new shells, the number of inner electron shells which shield the valence electrons increase. In other words, the shielding effect or the screening effect increases. As a result, the force of attraction of the nucleus for the valence electrons further decreases and hence the ionization enthalpy decreases.

3.19 The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :

B	**Al**	**Ga**	**In**	**Tl**
801	**577**	**579**	**558**	**589**

How would you explain this deviation from the general trend ?

Ans. On moving down the group 13 from B to Al, the ionization enthalpy decreases as expected due to an increase in atomic size and screening effect which outweigh the effect of increased nuclear charge.

However $\Delta_i H$ of Ga is only slightly higher (2 kJ mol^{-1}) than that of Al while that of Tl is much higher than those of Al, Ga and In. These deviations can be explained as follows:

Al follows immediately after. s–block elements while Ga and In follow after d–block elements and Tl after *d*– and *f*– block elements. These extra *d*–and *f*–electrons do not shield(or screen) the outer shell–electrons from the nucleus very effectively. As a result, the valence electrons remain more tightly held by the nucleus and hence larger amount of energy is needed for their removal. This explains why Ga has higher ionization enthalpy than Al. Further on moving down the group from Ga to In, the increased shielding effect (due to the presence of additional 4*d*–electrons) outweighs the effect of increased nuclear charge (49 – 31 = 18 units) and hence the $\Delta_i H_1$ of In is lower than that of Ga. Thereafter, the effect of increased nuclear charge (81 – 49 = 32 units) outweighs the shielding effect due to the presence of additional 4f and 5d electrons and hence the $\Delta_i H_1$ of Tl is much higher than that of Al, Ga and In.

3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy?

(i) O or F (ii) F or Cl

Ans. (i) Both O and F lie in 2nd period. As we move from O to F, the atomic size decreases and the nuclear charge increases. Both these factors tend to increase the attraction of the nucleus for the incoming electron and hence electron gain enthalpy becomes more negative. Further, gain of one electron by F gives F^- ion ($1s^2 2s^2 2p^6$) which has stable inert gas configuration while the gain of one electron by O gives O^- ion ($1s^2 2s^2 2p^5$)

which does not have stable inert gas configuration. Consequently, the energy released is much higher in going from F → F^- than in going from O → O^-. In other words, electron gain enthalpy of F is much more negative (– 328 kJ mol^{-1}) than that of oxygen (–141 kJ mol^{-1}).

(ii) In general, the electron gain enthalpy becomes less negative on moving down the group. But the electron gain enthalpy of chlorine (–349 kJ mol^{-1}) is more negative than that of fluorine (–328 kJ mol^{-1}). The reason for this deviation is the small size of F atom. Due to its small size, the electron–electron repulsions in the relatively compact 2p–subshell are comparatively large and hence the incoming electron is not accepted with the same ease as is the case with larger Cl atom. Consequently, electron gain enthalpy of Cl is more negative than that of F.

3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.

Ans. The second electron gain enthalpy of O is positive as explained below:

When an electron is added to O atom to form O^- ion, energy is released. Thus, first electron gain enthalpy of O is negative.

$O(g) + e^-(g) \rightarrow O^-(g); \Delta_{eg}H = -141 \text{ kJ mol}^{-1}$

But when another electron is added to O^- to form O^{2-} ion, energy is absorbed to overcome the strong electrostatic repulsion between the negatively charged O^- ion and the second electron being added. Thus, the second electron gain enthalpy of oxygen is positive.

$O^-(g) + e^-(g) \longrightarrow O^{2-}(g);$

$\Delta_{eg}H = +78 \text{kJ mol}^{-1}$

3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity ?

Ans. Both electron gain enthalpy and electro-negativity refer to the tendency of the atom of an element to attract electrons. Whereas electron gain enthalpy refers to the tendency of an isolated gaseous atom to accept an additional electron to form a negative ion, electronegativity refers to the tendency of the atom of an element to attract the shared pair of electrons towards it in a covalent bond.

3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

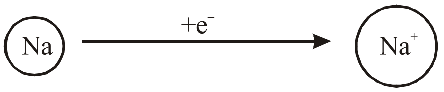
Ans. The electronegativity of any given atom is not constant. Therefore, the statement that the electro negativity of N on Pauling scale is 3.0 in all nitrogen compounds is wrong. Actually electronegativity varies with the state of hybridization and the oxidation state of the element. The electronegativity increases as the percentage of s–character of a hybrid orbital increases or the oxidation state of the element increases. For example, the electronegativity of N increases as we move from, sp^3 to sp^2 to sp hybrid orbital. Similarly, the electronegativity of N in NO_2 where oxidation state of N is +4 is higher than in NO where the oxidation state of N is +2.

3.24 Describe the theory associated with the radius of an atom as it (a) gains an electron (b) loses an electron.

Ans. (a) When a neutral atom gains one electron to form an anion, its radius increases. The reason being that the number of electrons in the anion increases while its nuclear charge remains the same as the parent atom. Since the same nuclear charge now attracts greater number of electrons, therefore, force of attraction of the nucleus on the electrons of all the shells decreases (i.e., effective nuclear charge decreases) and hence the electron cloud expands. In other words, the distance between the centre of the nucleus and the last shell that contains electrons increases thereby increasing the ionic radius. Thus,

Atom	Anion
17 Electrons	18 Electrons
+ 17 Nuclear charge	+ 17
99pm Ionic size	181 pm

(b) When a neutral atom loses one electron to form a cation, its atomic radius decreases. The reason being that the number of electrons in the cation decreases while its nuclear charge remains the same as the parent atom. Since the same nuclear charge now attracts lesser number of electrons, therefore, the force of attraction of the nucleus on the electrons of all the shells increases (i.e., effectivenuclear charges increases) and hence the size of cation decreases. Thus



Atom	Cation
11 Electrons	10
+ 11 Nuclear charge	+ 11
156 pm Ionic size	95 pm.

3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different ? Justify your answer.

Ans. Two isotopes of the same element have same no. of electrons, same nuclear charge, same size and hence they are expected to have same ionization enthalpy.

3.26 What are the major differences between metals and non-metals ?

Ans. Elements which have a strong tendency to lose electrons to form cations are called metals while those which have a strong tendency to accept electrons to form. anions are called non–metals. Thus, metals are strong reducing agents, they have low ionization enthalpies, have less negative electron gain enthalpies, low electronegativity, form basic oxides and ionic compounds.

Non–metals, on the other hand, are strong oxidizing agents, they have high ionization enthalpies, have high negative electron gain enthalpies, high electronegativity, form acidic oxides and covalent compounds.

3.27 Use the periodic table to answer the following questions.

(a) Identify an element with five electrons in the outer subshell.

(b) Identify an element that would tend to lose two electrons.

(c) Identify an element that would tend to gain two electrons.

(d) Identify the group having metal, non-metal, liquid as well as gas at room temperature.

Ans. (a) The general electronic configuration of the elements having five electrons in the outer subshell is $ns^2 np^5$. This electronic configuration is characteristic of elements of group 17, i.e., halogens and their examples are F, Cl, Br, I, At, etc.

(b) The elements which have a tendency to lose two electrons must have two electrons in the valence shell. Therefore, their general configuration should be ns^2. This electronic configuration is characteristic of group2 elements, i.e., alkaline earth metals and their examples are Mg, Ca, Sr, Ba, etc.

(c) The elements which have a tendency to accept two electrons must have six electrons in the valence shell. Therefore, their general electronic configuration is $ns^2 np^4$. This electronic configuration is characteristic of group 16 elements and their examples are O and S.

(d) A metal which is liquid at room temperature is mercury. It is a transition metal and belongs to group 12. A non–metal which is a gas at room temperature is nitrogen (group 15), oxygen (group 16), fluorine, chlorine (group 17) and inert gases (group 18).

A non–metal which is a liquid at room temperature is bromine (group 17).

3.28 The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.

Ans. The elements of group 1 have only one electron in their respective valence shells and thus have a strong tendency to lose this electron. The tendency to lose electrons, in turn, depends upon the ionization enthalpy. Since the ionization enthalpy decreases down the group, therefore, the reactivity of group 1 elements increases in the same order: Li < Na < K < Rb < Cs. In contrast, the elements of group 17, have seven electrons in their respective valence shells and thus have a strong tendency to accept one more electron. The tendency to accept electrons, in turn, depends upon their electrode potentials. Since the electrode potentials of group 17 elements decrease in the order: F (+ 2.87 V) > Cl (1.36 V), Br (1.08 V) and I (+ 0.53V), therefore, their reactivity also decrease in the same order :

F > Cl > Br > I.

3.29 Write the general outer electronic configuration of *s*–, *p*–, *d*– and *f*–block elements:

Ans. (i) *s*–Block elements: ns^{1-2} where n = 2 – 7

(ii) *p*–Block elements: $ns^2\ np^{1-6}$ where n = 2 – 6

(iii) *d*–Block elements: $(n-1)\ d^{1-10}\ ns^{0-2}$ where n = 4 – 7

(iv) *f*–Block elements :

$(n-2)f^{-14}\ (n-1)\ d^{0-1}\ ns^2$ where n = 6 – 7

3.30 Assign the position of the element having outer electronic configuration,

(i) $ns^2\ np^4$ for n = 3

(ii) $(n-1)\ d^2\ ns^2$ for n = 4 and

(iii) $(n-2)f^7\ (n-1)\ d^1\ ns^2$ for n = 6 in the periodic table.

Ans. (i) When n = 3 , it suggests that the element belongs to third period. Since the last electron enters the p–orbital, therefore, the given element is a p–block element. Further since the valence shell contains 6 (2 + 4) electrons, therefore, group number of the element = 10 + no. of electrons in the valence shell = 10 + 6 = 16. The complete electronic configuration of the element is $1s^2 2s^2\ 2p^6\ 3s^2\ 3p^4$ and the element is S (Sulphur)

(ii) n = 4 suggests that the element lies in the 4th period. Since the d–orbitals are incomplete, therefore, it is a d–block element. The group number of the element = no. of d–electrons + no. of s –electrons = 2 + 2 = 4. Thus, the elements lies in group 4 and 4th period. The complete electronic configuration of the element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$ and the element in Ti (Titanium).

(iii) n = 6 means that the element lies in the sixth period. Since the last electron goes to the f–orbital,therefore, the element is a f–block element. All f– block elements lie in group 3. The complete electronic configuration of the element is $[Xe]\ 4f^7\ 5d^1\ 6s^2$. The atomic number of the element 54 + 7 + 1 + 2 = 64 and the element Gd (Gadolinium).

3.31 The first ($\Delta_i\ H_1$) and the second ($\Delta_i.\ H_2$) ionization enthalpies (in kJ mol $^{-1}$) and the (Δ_{eg}H) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Elements	$\Delta_i H_1$	$\Delta_i H_2$	Δ_{eg} H
I	**520**	**7300**	**– 60**
II	**419**	**3051**	**– 48**
III	**1681**	**3374**	**– 328**
IV	**1008**	**1846**	**– 295**
V	**2372**	**5251**	**+ 48**
VI	**738**	**1451**	**– 40**

Which of the above elements is likely to be:

(a) the least reactive element

(b) the most reactive metal

(c) the most reactive non–metal

(d) the least reactive non–metal

(e) the metal which can form a stable binary halide of the formula MX_2 (X = halogen)

(f) the metal which can form a predominantly stable covalent halide of the formula MX (X = halogen) ?

Ans. (a) The element V has highest first ionization enthalpy $(\Delta_i\ H_1)$ and positive electron gain enthalpy $(\Delta_g\ H)$ and hence it is the least reactive element. Since inert gases have positive $\Delta_i\ H_1$, therefore, the element V must be an inert gas. The values of $\Delta_i\ H_1$, $\Delta_i H_2$ and Δ_{eg} H match that of He.

(b) The element II which has the least first ionization enthalpy $(\Delta_i\ H_1)$ and a low negative electron gain enthalpy $(\Delta_{eg}\ H)$ is the most reactive metal. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg}H$ match that of K (potassium).

(c) The element III which has high first ionization enthalpy (Δ_1 H_1) and a very high negative electron gain enthalpy (Δ_{eg} H) is the most reactive non–metal. The values of $\Delta_i H_1$, $\Delta_i H_2$ and $\Delta_{eg}H$ match that of F (fluorine).

(d) The element IV has a high negative electron gain enthalpy (Δ_{eg} H) but not so high first ionization enthalpy (Δ_i H_i). Therefore, it is the least reactive non–metal. The values of Δ_i H_1 , $\Delta_i H_2$ and $\Delta_{eg}H$ match that of I (Iodine).

(e) The element VI has low first ionization enthalpy ($\Delta_i H_1$) but higher than that of alkali metals. Therefore, it appears that the element is an alkaline earth metal and hence will form binary halide of the formula MX_2 (where X = halogen). The values of Δ_i H_1 , $\Delta_i H_2$ and $\Delta_{eg}H$ match that of Mg (magnesium).

(f) The element I has low first($\Delta_i H_1$) but a very high second ionization enthalpy ($\Delta_i H_2$), therefore, it must be an alkali metal. Since the metal forms a predominantly stable covalent halide of the formula MX (X = halogen), therefore, the alkali metal must be least reactive. The values of Δ_i H_1 $\Delta_i H_2$ and $\Delta_{eg}H$ match that of Li (lithium).

3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.

(a) Lithium and oxygen

(b) Magnesium and nitrogen

(c) Aluminium and iodine

(d) Silicon and oxygen

(e) Phosphorus and fluorine

(f) Element 71 and fluorine.

Ans. (a) Lithium is an alkali metal (Group 1). It has only one electron in the valence shell, therefore, its valency is 1. Oxygen is a group 16 element with a valence of 2. Therefore, formula of the compound formed would be Li_2O (Lithium oxide).

(b) Magnesium is an alkaline earth metal (Group 2) and hence has a valence of 2. Nitrogen is a group 15 element with a valence of 8 – 5 = 3.Thus, the formula of the compound formed would be Mg_3N_2 (Magnesium nitride).

(c) Aluminium is group 13 element with a valence of 3 while iodine is a halogen (group 17) with a valence of 1. Therefore, the formula of the compound formed would be AlI_3 (Aluminium iodide).

(d) Silicon is a group 14 element with a valence of 4 while oxygen is a group 16 element with a valence of 2. Hence the formula of the compound formed is SiO_2 (Silicon dioxide).

(e) Phosphorus is a group 15 element with a valence of 3 or 5 while fluorine is a group 17 element with a valence of 1. Hence the formula of the compound formed would be PF_3 or PF_5.

(f) Element with atomic number 71 is a lanthanoid called lutetium (Lu). Its common valence is 3. Fluorine is a group 17 (halogen) element with a valence of 1. Therefore, the formula of the compound formed would be LuF_3 (Lutetium fluoride).

3.33 In the modern periodic table, the period indicates the value of :

(a) atomic number

(b) atomic mass

(c) principal quantum number

(d) azimuthal quantum number

Ans. In the modern periodic table, each period begins with the filling of a new shell. Therefore, the period indicates the value of principal quantum number. Thus, option (c) is correct.

3.34 Which of the following statements related to the modern periodic table is incorrect?

(a) The *p*–block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a *p*–shell.

(b) The *d*–block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a *d*–subshell.

(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(d) The block indicates value of azimuthal quantum number (*l*) for the last subshell that received electrons in building up the electronic configuration.

Ans. Statement (b) is incorrect while other statements are correct. The correct statement is: the *d*-block has 10 columns, because a maximum of 10 electrons can occupy all the orbitals in a *d*-subshell.

3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell

(a) Valence principal quantum number (n)

(b) Nuclear charge (Z)

(c) Nuclear mass

(d) Number of core electrons.

Ans. Nuclear mass does not affect the valence shell because nucleus consists of protons and neutrons. Where protons i.e. nuclear charge affects the valence shell but neutrons do not. Thus, option (c) is wrong.

3.36 The size of isoelectronic species – F^-, Ne and Na^+ is affected by

(a) nuclear charge (Z)

(b) valence principal quantum number (n)

(c) electron–electron interaction in the outer orbitals

(d) none of the factors because their size is the same.

Ans. The size of the isoelectronic ions depends upon the nuclear charge (Z). As the nuclear charge increases the size decreases. For example, F^-(+ 9) > Ne (+ 10) > Na^+ (+ 11). Therefore, statement (a) is correct while all other statements are wrong.

3.37 Which one of the following statements is incorrect in relation to ionization enthalpy?

(a) Ionization enthalpy increases for each successive electron.

(b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.

(c) End of valence electrons is marked by a big jump in ionization enthalpy.

(d) Removal of electron from orbitals bearing lower *n* value is easier than from orbital having higher *n* value.

Ans. Statement (d) is incorrect. The correct statement is: Removal of electron from orbitals bearing lower n value is difficult than from orbital having higher n value. All other statements are correct.

3.38 Considering the elements B, Al, Mg and K, the correct order of their metallic character is :

(a) B > Al > Mg > K (b) Al > Mg > B > K

(c) Mg > Al > K > B (d) K > Mg > Al > B

Ans. In a period, metallic character increases as we move from right to left. Therefore, metallic character of K, Mg and Al decreases in the order: K > Mg > Al. However, within a group, the metallic character, increases from top to bottom. Thus, Al is more metallic than B. Therefore, the correct sequence of decreasing metallic character is:
K > Mg > Al > B, i.e., option (d) is correct.

3.39 Considering the elements B, C, N, F and Si, the correct order of their non–metallic character is

(a) B > C > Si > N > F (b) Si > C > B > N > F

(c) F > N > C > B > Si (d) F > N > C > Si > B

Ans. In a period, the non–metallic character decreases from right to left . Thus, among B, C, N and F, non–metallic character decreases in the order: F > N > C > B. However, within a group, non–metallic character decreases from top to bottom. Thus, C is more non–metallic than Si. Therefore, the correct sequence of decreasing non–metallic character is : F > N > C > B > Si, i.e., option (c) is correct.

3.40 Considering the elements F, Cl, O and N the correct order of their chemical reactivity in terms of oxidizing property is:

(a) F > Cl > O > N (b) F > O > Cl > N

(c) Cl > F > O > N (d) O > F > N > Cl

Ans. Within a period, the oxidizing character increases from left to right. Therefore, among F, O and N, oxidizing power decreases in the order: F > O > N. However, within a group, oxidizing power decreases from top to bottom. Thus, F is a stronger oxidizing agent than Cl. Further because O is more electronegative than Cl, therefore, O is a stronger oxidizing agent than Cl. Thus, over all decreasing order of oxidizing power is :
F > O > Cl > N i.e., option (b) is correct.

Practice Questions

Very Short Answer Questions [1 Mark]

1. Why Group –2 elements have positive electron gain enthalpy?
2. Ga atom loose electron(s) to form Ga^+ , Ga^{2+}, Ga^{3+} ions.Which step will have highest ionization energy?
3. Name a species which is iso electronic with Al^{3+}.
4. Compare the size of Al^{3+} , Mg^{2+} and Ca^{2+}.
5. Which p- block elements exist as liquid at room temperature?
6. Arrange the acids in order of increasing acidic strength; HI, HBr, HCl, HF. Give reason for your answer.
7. Arrange the given compounds in order of increasing acidic strength; CH_4, NH_3, H_2O, HF. Give reason for your answer.
8. Arrange the anions in order of increasing radius; Cl^-, Br^-, N^{3-}, O^{2-}. Give reason for your answer.
9. Arrange the oxides in order of increasing basic character; BeO, MgO, CaO,BaO . Give reason for your answer.
10. Arrange the oxides in order of increasing acidic character; Li_2O, BeO, B_2O_3, CO_2. Give reason for your answer.
11. Why were the names eka-aluminium and eka-silicon given to gallium and germanium by Mendeleev?
12. Helium has a electronic configuration of $1s^2$ but it is placed in *p*-block in group 18. Explain.
13. Lanthanoids and actinoids are placed in separate rows at the bottom of the Periodic Table. Explain the reason for this arrangement.
14. Arrange the following elements in the increasing order of metallic character.
    B, Al, Mg, K
15. Arrange the following elements in the increasing order of non-metallic character.
    C, Si, N, F
16. Which of the following ion has the smallest radius ?
    Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}
17. Which is smaller in size ? Li or F and why ?
18. Define (i) metallic radius (ii) covalent radius.
19. Explain the meaning of a positive electron gain enthalpy.
20. Why are electron gain enthalpies of Be and Mg positive ?
21. What are representative element ?
22. What are inner transition metals ?
23. Name third chalcogen and fifth noble gas.
24. Why *d*-block elements are called transition elements ?
25. Name the elements with the lowest and the highest ionisation energy.
26. What is the difference between Mendeleev's and the modern periodic law ?
27. Give the symbols of two anions and cations isoelectronic with Ne.
28. Name the element having highest electro-negativity in the periodic table.
29. Which is shorter out of covalent radius and van der Waal's radius ?
30. Define van der Waal's radius of an atom.
31. Predict the position of the element in the Periodic Table satisfying the electronic configuration $(n-1)\,d^1\,ns^2$ for $n = 4$.
32. State Dobereiner's law of triads, giving examples.
33. What is meant by Newland's law of octaves ?
34. What is meant by periodicity of properties ?
35. With which quantum number does every period in periodic table begin ?
36 To which series do man-made elements belong ?
37. Which of Lanthanoids is man-made element ?

38. Why do noble gases have bigger atomic size than halogens ?

39. Among (the non-radioactive) halogens the element that has the lowest electron affinity is ....

40. Name the radioactive element of group 17 and group 18.

41. The solubility of alkali metal carbonates.......... as one goes down the group.

42. How do the basic character and solubility in water vary from Be $(OH)_2$ to Ba $(OH)_2$?

43. Which out of F or Cl has a more negative electron gain enthalpy ? Explain.

44. Give two reasons, why the number of elements in first period is only 2 ?

45. Halogens have high electron gain enthalpies . Explain.

46. Write equations to demonstrate the difference between electron affinity and the reverse of ionization potential.

Short Answer Questions [2 & 3 Marks]

1. Explain why the first ionization potential for copper is higher than that of potassium, whereas the second ionization potentials for both metals are in the reverse order.

2. Arrange the following set of atoms in order of increasing ionization energy: Zn, Ga, K. Also discuss the reason.

3. Although most of the elements in '*d*' block has 2 electrons in their valence '*s*' shell yet their ionization energies are higher than Group 2 elements.

4. The first (IE_1) and second (IE_2) ionisation energies (kJ/mol) of a new element designated by Roman numerals are shown below :

	IE_1	IE_2
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of these elements is likely to be (a) a reactive metal, (b) a reactive non-metal, (c) a noble gas, (d) a metal that forms a binary halide of the formula, AX_2?

5. Give four defects of Mendeleev's periodic table.

6. Give the order in which the melting points of halides of sodium decrease and why ?

7. Why are group 1 elements called alkali metals and group 17 are called halogens ?

8. Arrange the following in increasing order :

(i) $BeCO_3$, $BaCO_3$, $CaCO_3$, $MgCO_3$ (Thermal stability)

(ii) $BeCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$ (Ionic character).

9. Among the elements of the third period Na to Ar pick out the element :

(a) with highest first ionisation enthalpy

(b) with largest atomic radius

(c) that is most reactive non-metal

(d) that is most reactive metal.

10. (a) Why do Group I metals have lower ionisation enthalpy than corresponding Group II metals ?

(b) Why is an anion larger in size than its neutral atoms ?

11. The first ionisation energy of carbon atom is greater than that of boron whereas the reverse is true for the second ionisation energy. Explain.

12. What is meant by 'diagonal relationship' in the periodic table ? What is it due to ?

13. (i) Name the most metallic element in second period and most non-metallic element.

(ii) The element with (a) largest atomic radius, (b) smallest atomic radius in third period.

(iii) The element having general electronic configuration ns^2np^4 in fourth period.

14. The first $(1E_1)$ and second $(1E_2)$ ionisation enthalpies (kJ mol^{-1}) of three elements I, II and III are given below :

	I	II	III
$1E_1$	403	549	1142
$1E_2$	2640	1060	2080

Identify the element which is likely to be (a) non-metal (b) an alkali metal (c) an alkaline earth metal.

15. Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

16. What is screening or shielding effect ? How does it influence the ionization enthalpy ?

17. Use the Periodic Table to determine the number of electrons in each of the *s*, *p* and *d* orbitals outside the precious noble gas core of the following elements.

(i) Silicon (ii) Chlorine (iii) Manganese

(iv) Cobalt

18. The elements Z = 117 and Z = 120 have not yet been discovered. In which family/group would you place these elements and also give the electronic configuration in each case.

19. What are isoelectronic species ? The following species are isoelectronic with the noble gas. Arrange these in order of increasing size. K^+, S^{2-}, Cl^-, Ca^{2+}

20. Why is the covalent radius shorter than the metallic radius ?

21. The ions Na^+ and Mg^{2+} occur in chemical compounds, but the ions Na^{2+} and Mg^{3+} do not. Explain.

22. Give reason : ionic compounds of the halogen contain singly charged X^- ion and not doubly charged X^{2-} ion.

23. Consider the ground state electronic configuration of the five elements I to V given below :

Elements	Electronic Configuration
I	$1s^2\ 2s^2\ 2p^5$
II	$1s^2\ 2s^2\ 2p^4$
III	$1s^2\ 2s^2\ 2p^6\ 3s^2$
IV	$1s^2\ 2s^2\ 2p^6\ 3s^1$
V	$1s^2\ 2s^2\ 2p^6$

(i) Which of the above configuration is associated with the highest and which is associated with the lowest ionisation enthalpy ?

(ii) Arrange the above five elements is order of increasing electron gain enthalpy.

24. From the elements : Cl, Br, F, O, Al, C, Li, Cs and Xe; choose the following :

(i) The element which forms largest number of compounds.

(ii) The element with highest electron affinity.

(iii) The element which is liquid at room temperature.

(iv) The element with smallest atomic radius.

25. Arrange the following in the decreasing order of property indicated :

(i) F, Cl, Br and I (electron affinity)

(ii) Mg, Al, Si and Na (ionization energy)

(iii) C, N, O and F (second ionization energy)

26. How much energy in kJ will be required to convert all the magnesium atoms into magnesium ions present in 12 mg of the metal vapours ? IE_1, IE_2 for Mg being 7.646 and 15.035 eV respectively.

27. Calculate the electron affinity of iodine in electron volts if 4.9×10^{-3} J of energy is released when one million atoms of iodine are converted into iodide ions according to the equation :

$$I(g) + e^- \rightarrow I(g)^-$$

28. What are the defects in Modern Periodic Table?

29. Predict the formula of a stable binary compound that would be formed by the following pairs of elements
(a) aluminum and phosphorous
(b) lithium and nitrogen
(c) calcium and sulphur

Long Answer Questions [5 Marks]

1. Name the four blocks of elements in the periodic table and list the difference in their electronic configurations. Give examples of each type of elements. Write at least four characteristics of each block.

2. Discuss the trends in atomic sizes of elements in periodic table.

3. (i) Explain the terms (a) screening effect, (b) penetration effect, (c) metallic character.
(ii) Why are electron affinities of noble gases zero ? Arrange halogens in increasing order of electron affinity.

4. The second ionization enthalpy (IE_2) of the elements of the second period are given below :

Element :	**IE_2 (kJ/mol) :**
Li	7294
Be	1756
B	2430
C	2354
N	2856
O	3396
F	3377
Ne	3966

(i) Explain
  (a) Why is IE_2 of Li so much higher than for all other elements of this period ?
  (b) What is the general trend from Be to Ne of increasing IE_2?
  (c) Why IE_2 of F is just about the same or very slightly less than that of oxygen ?
(ii) Would you predict the IE_2 of Na in kJ/mol is
  (a) greater than 7294
  (b) between 3966 and 7294 or
  (c) less than 3966 ? Explain.

5. What are the IUPAC rules for writing the names and symbols of the elements having atomic numbers more than 100 ?

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. In the ionic compound KF, the K^+ and F^{-1} ions are found to have practically identical radii, about 1.34Å each. What do you predict about the relative atomic radii of K & F? **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. PtF_6 is a powerful oxidizing agent, capable of effecting the following reaction: **[HOTS]**

$$O_2(g) + PtF_6(s) \longrightarrow O_2PtF_6(s)$$

Compare the first ionization energy of O_2 (12.5 eV) with those of the noble gases. Which, if any, of the noble gases might undergo a comparable reaction with PtF_6?

2. All the lanthanoid elements form stable compounds containing the +3 cation. Of the few other ionic forms known, Ce forms the stable + 4 series of ionic compounds and Eu the stable + 2 series. Account for these unusual ionic forms in terms of their electronic configurations. **[HOTS]**

3. Identify the group and valency of the element having atomic number 119. Also predict the outermost electronic configuration and write the general formula of its oxide. **[Exemplar]**

4. Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionisation enthalpy than nitrogen. Explain. **[Exemplar]**

5. Explain the following :
(a) Electronegativity of elements increase on moving from left to right in the periodic table.
(b) Ionisation enthalpy decrease in a group from top to bottom. **[Exemplar]**

6. Among the elements B, Al, C and Si :
(a) Which has the highest first ionisation enthalpy ?
(b) Which has most negative electron gain enthalpy ?
(c) Which has the largest atomic radius ?
(d) Which has the most metallic character ? **[Exemplar]**

Long Answer Questions [5 Marks]

1. Find the best choice in the following list and give brief reason for your answer
(i) highest IE_1; Se, S, Te
(ii) smallest radius; Cl^-, Br^-, I^-
(iii) most parmagnetic; Fe, Co, Ni
(iv) smallest atom; Sn, I, Bi
(v) lowest IE_2 ; Ar, K, Ca **[HOTS]**

2. How much energy, in kJ, will be produced when 7.1g of chlorine atoms are converted to Cl^- ions in gaseous state? [**Given :** Electron affinity of chlorine = – 3.7 ev; 1 ev = 96.49 kJ/mole] **[HOTS]**

3. Why is copper having completely filled *d*-orbitals ($3d^{10}$) regarded as a transition metal? **[HOTS]**

4. How do you explain that $_{31}$Ga has slightly higher energy than $_{13}$Al, although it occupies lower position in group? **[HOTS]**

5. Helium, He, is a nonmetallic gas and the second element in the periodic table. Rather than being placed adjacent to hydrogen, H, however, helium is placed on the far right of the table. why? **[HOTS]**

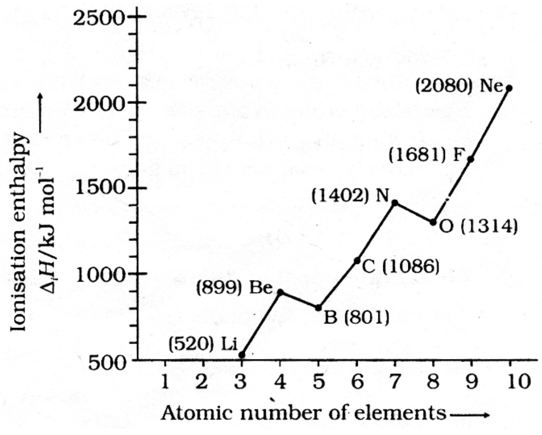
6. In the periodic table we come across *diagonal relationship* where by the top member of each group resembles the second member of next group. For example *Boron* resembles *silicon.* Can it be explained on the basis of I.E. and charge density data? Explain your answer. **[HOTS]**

7. Explain the followings?
   (a) IE_2 for alkali metals shows a jump whereas IE_3 for alkaline earth metals shows a jump.
   (b) Electronegativity for $Fe^{3+} > Fe^{2+}$.
   (c) The atomic radius decreases along the period but inert gases has maximum atomic radius in a period.
   (d) EA_2 of halogens is zero.
   (e) $SnCl_2$ is ionic and $SnCl_4$ is covalent. **[HOTS]**

8. Arrange the elements N, P, O and S in the order of -
   (i) increasing first ionisation enthalpy.
   (ii) increasing non-metallic character.
   Given reason for the arrangement assigned. **[Exemplar]**

9. Among alkali metals which elements do you expect to be least electronegative and why? **[Exemplar]**

10. How would you explain the fact that first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium? **[Exemplar]**



CHAPTER TEST

Time : *30 min.* **Max. Marks :** *15*

Directions :
- *(i) Attempt all questions*
- *(ii) Questions 1 to 3 carry 1 mark each.*
- *(iii) Questions 4 and 5 carry 2 marks each.*
- *(iv) Question 6 carry 3 marks*
- *(v) Question 7 carry 5 marks*

1. What is the relationship between the ionization enthalpy and metallic properties?
2. Why electron gain enthalpy has a negative value in most cases?
3. The first ionization enthalpy in electron volts of nitrogen and oxygen are respectively given by
   (a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6
4. Explain why the electron gain enthalpy of O is unexpectedly less negative than that of S.
5. Which will have lower ionization enthalpy and why (i) Be^+ or Mg^{2+} (ii) I or I^{-1}
6. Name the species which are iso–electronic with (i) Cl^-(18) (ii) Ca^{2+}(18) (iii) Ne(10)
7. A,B,C are three elements, B is an inert gas element other than helium; with this information complete the table:

Table:

Element	Atomic number	No. of electrons in the valence shell	Group to which the element belongs
A	Z–1		
B	Z		
C	Z+1		

Also explain the following:
(i) Electron gain enthalpy of element A is more negative than that of C.
(ii) Electron gain enthalpy of B has positive value.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. Since they have fully filled *s*–subshell thus they have no tendency to accept electron.

2. $Ga^{2+} \longrightarrow Ga^{3+} + e^-$

3. $Mg^{2+} = 12 - 2 = 10\ e^-$, is isoelectronic with
$Al^{3+} = 13 - 3 = 10\ e^-$

4. $Al^{3+} < Mg^{2+} < Ca^{2+}$

5. Ga and Br.

6. HF < HCl < HBr < HI. Bond strength decreases down the group, from F to I. Thus the release of H^+ becomes easier as we move from HF to HI.

7. $CH_4 < NH_3 < H_2O <$ HF. Electronegativity increases across a period. Thus electronegativity difference between hydrogen and other element increases. More will be the electronegativity difference more will be acidic character.

8. $O^{2-} < N^{3-} < Cl^- < Br^-$. Ionic radius increases down a group and decreases across a period

9. BeO < MgO < CaO < BaO. On moving down a group metallic character increases. Metallic oxides are basic in nature. Ba is most metallic.

10. $Li_2O < BeO < B_2O_3 < CO_2$ on moving across a period non-metallic character increases. Non-metallic oxides are acidic in nature. C is most non-metallic.

11. Mendeleev named these elements as eka-aluminium and eka-silicon because he believed that they would be similar to aluminium and silicon respectively in their properties.

12. The position of helium in *p*-block along with other group 18 elements is justified because it has a completely filled valence shell and as a result, exhibits properties characteristics of other noble gases.

13. Lanthanoids and actinoids are placed separately at the bottom of the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

14. Metallic character increases down the group and decreases along the period. The correct order is

$$B < Al < Mg < K$$

15. The correct order is

$$Si < C < N < F$$

16. Be^{2+}. Be is a second period element, thus smaller than higher period elements (Na^+, K^+, Mg^{2+}). The Be^{2+} is isoelectronic with Li^+ but has a greater nuclear charge. Therefore, Be^{2+} is smaller in size than Li^+.

17. F is smaller in size than Li because the effective nuclear charge increases while the number of core electrons remains same. Consequently, the size of the outermost orbital and the radius of the atom decreases.

18. (i) *Metallic radius* is defined as the half the internuclear distance separating the metal ions in the metallic crystal.

(ii) *Covalent radius* is defined as the half the distance between the centre of the nuclei of the two bonded atoms in a covalent bond. 

the covalent radius $= \frac{a}{2}$.

19. The positive electron gain enthalpy means that the energy is required rather than released during the addition of an electron to a neutral gaseous atom to form gaseous ion.

20. They have fully filled *s*-orbitals and hence have no tendency to accept an additional electron. That's why energy is needed if an extra electron has to added. Therefore electron gain enthalpies of Be and Mg are positive.

21. The elements of group 1 (alkali metals) group 2 (alkaline earth metals) and group 13 to 17 constitute the representative elements. They are elements of *s*-block and *p*-block.

22. Lanthanoids (the fourteen elements after Lanthanum) and actinides (the fourteen elements after actinium) are called inner transition elements.

23. Selenium (Se), Xenon (Xe).

24. They represent change or transition from strongly metallic *s*-block to largely covalent *p*-block elements.

25. Cs, He.

26. Mendeleev's Periodic Law was based on atomic masses while the modern periodic law was based on the atomic number.

27. O^{2-}, F^-, Na^+ and Mg^{2+}.

28. Fluorine.

29. Covalent radius is shorter than van der Waal's radius.

30. It is one half of the distance between the centres of nuclei of two nearest non-bonded atoms of the adjacent molecules of the element in the solid state.

31. $(n-1)\,d^1\,ns^2 = 3d^1\,4s^2$

$\therefore$ It lies in the 4th period and III B (or 3rd) group.

32. It states that those triads in which the atomic weight of middle element was average of the atomic weight of first and third, such elements resemble in the physical and chemical properties, e.g.

Li	Na	K
7	$\frac{7+39}{2} = 23$	39

33. It states if elements are arranged in increasing order of their atomic weights, properties of every 8th element resemble with the first element.

34. The reccurrence of similar properties after a definite interval is called periodicity of properties.

35. Principal quantum number.

36. Actinoid series (*f*-block elements).

37. Promethium (Pm), atomic number 61 is man-made element.

38. Noble gases have bigger atomic size than halogens because van der Waal's radii are bigger than covalent radii.

39. Iodine.

40. Astatine (At), Radon (Rn).

41. Increases.

42. Basic character and solubility increases from $Be(OH)_2$ to $Ba(OH)_2$ because hydration energy is more than lattice energy.

43. Cl has more negative electron gain enthalpy. It is because there is more inter-electronic repulsion between valence electrons of Fluorine due to smaller size than Chlorine.

44. It is because 1st energy level have only 1*s* orbital which can have two electrons. When $n = 1$, then $l = 0$

45. This is due to the reason that the valence shell electronic configuration of the halogens is $ns^2\ np^5$ and as they require one only more electron to acquire stable inert gas configuration, they have a strong tendency to accept an additional electron and hence their electron gain enthalpies are highly negative.

46. Electron affinity : $A + e^- \rightarrow A^-$

Reverse of ionization potential; $A^+ + e^- \rightarrow A$

Short Answer Questions

1. Copper and potassium both belongs to 4th period. Copper is present in group 11 whereas potassium is present in group 1. Thus first ionisation energy of copper will be higher as ionisation energy increases on moving left to right in a period. In case of second ionisation energy potassium acquire inert gas ($ns^2\ np^6$) configuration. Thus removal of second electron will be difficult from $3s^2\ 3p^6$ configuration of potassium in comparison to $3d^{10}$ configuration of copper.

2. K < Ga < Zn. K having the largest atomic radii out of given elements. Thus has least ionization energy. The electron removed from Zn is from a completely filled 4s orbital while in case of Ga it is from partially filled 4p orbital. The 4p electrons is at higher energy and is less tightly held by nucleus than 4s electron. Thus, it is more easily removed.

3. This is because in 'd' block elements the radii are smaller due to poor screening electrons present in 'd'-orbitals, thus the valence 's' electrons are tightly held by the nucleus.

4. (a) II (b) IV (c) I (d) III.

5. (a) Isotopes should be given separate place because they have different atomic mass.

(b) The increasing order of atomic weight is not maintained.

(c) Some elements in the same group differ in their properties.

(d) The position of hydrogen is not justified.

6. NaF > NaCl > NaBr > NaI. Greater the difference in electronegativity, more will be ionic character, higher will be melting point due to high lattice energy.

7. Group 1 elements are called alkali metals because their hydroxides form soluble bases called alkalies and their ashes are alkaline in nature.

Group 17 are called halogens because they are salt-producer.

8. (i) $BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3$

(ii) $BeCl_2 < CaCl_2 < SrCl_2 < BaCl_2$.

9. (a) Ar has highest first ionisation enthalpy.

(b) Na has largest atomic radius (covalent radius).

(c) Cl is most reactive non-metal in third-period.

(d) Na is most reactive metal in third period.

10. (a) Group I elements are larger in size than alkaline earth metals (Group II elements), therefore, there is less force of attraction between nucleus and valence electron, that is why their ionisation energy is lower.

(b) Anions are larger than neutral atom because electrons are more than protons, therefore, effective nuclear charge is less, therefore, distance between centre of nucleus and valence electrons is more.

11. $C = 1s^2\ 2s^2\ 2p^2 \quad B = 1s^2\ 2s^2\ 2p^1$.

Nuclear charge is more in C, as a result it is smaller in size, *i.e.*, $I.E._1$ is higher in C than B.

After the removal of first electron, second electron to be removed in C atom is from 2*p* whereas in B atom is from 2*s*. Now as a result second ionisation energy of B is higher than C.

12. The resemblance of elements of second period with diagonally situated elements of neighbouring group is called diagonal relationship. It is due to similar charge/radius ratio, therefore, similarity in properties.

13. (i) Most metallic element is Li and most non-metallic element is F.

(ii) Na has largest atomic radius, Cl has smallest atomic radius.

(iii) Se(34) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$ is element in fourth period with general electronic configuration $ns^2\ np^4$.

14. (a) III is non-metal.

(b) I is an alkali metal.

(c) II is alkaline earth metal.

15. Na_2O reacts with water to form sodium hydroxide which turns red litmus blue.

$$\underset{\text{Sod. oxide}}{Na_2O} + H_2O \longrightarrow \underset{\text{Sod. hydroxide}}{2NaOH}$$

Therefore, Na_2O is a basic oxides.

In contrast, Cl_2O_7 reacts with water to form perchloric acid which turns blue litmus red.

$$Cl_2O_7 + H_2O \longrightarrow \underset{\text{perchloric acid}}{2HClO_4}$$

Therefore, Cl_2O_7 is an acidic oxide.

16. In a multielectron atom, the electrons present in the inner shells shield the electrons in the valence shell from the attraction of the nucleus or they act as a screen between the nucleus and these electrons. This is known as shielding effect or screening effect.

As the screening effect increases, the effective nuclear charge decreases. Consequently, the force of attraction by the nucleus for the valence shell electrons decreases and hence the ionization enthalpy decreases.

17. (i) Si(Z = 14) : [Ne] $3s^2\ 3p^2$

Number of electrons in *s*-orbital = 2

Number of electrons in *p*-orbital = 2

(ii) Cl(Z = 17) : [Ne] $3s^2\ 3p^5$

Number of electrons in *s*-orbital = 2

Number of electrons in *p*-orbital = 5

(iii) Mn (Z = 25) : [As] $3d^5\ 4s^2$

Number of electrons in *d*-orbital = 5

Number of electrons in *s*-orbital = 2

(iv) Co (Z = 27) : [Ar] $3d^7\ 4s^2$

Number of electrons in *d*-orbital = 5

Number of electrons in *s*-orbital = 2

18. The element with Z = 117 would belong to group 17 and halogen family. The electronic configuration would be $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$

The element with Z = 120 belong to group 2 (alkaline earth metal) family with a electronic configuration would be [Uuo] $8s^2$

19. The species having the same number of electrons are called isoelectronic species.

Since, all these ions have equal number of electrons, greater the nuclear charge, smaller the size, the correct order is

$$Ca^{2+} < K^{+} < Cl^{-} < S^{2-}$$

20. The formation of covalent bond involves the sharing of electron between the two atoms. It is shorter than the metallic radius due to the fact that metallic bond is weaker than a covalent bond and the internuclear distance between two metal ions in a metallic lattice is larger than the internuclear distance between the atoms held by a covalent bond.

21. Na^{2+} and Mg^{3+} do not occur in chemical compounds because Na^{+} and Mg^{2+}, both have a stable noble gas configuration of neon. The removal of electron either from Na^{+} (to form Na^{2+}) or Mg^{2+} (to form Mg^{3+}) requires a very large amount of energy.

22. Halogens are short of one electron to complete nearest noble gas electronic configuration. And they can attain the noble gas configuration by picking up an electron and from X^{-}. Once the shell is complete, then additional electron would have to begin a new shell which leads to unstable electronic configuration. That's why X^{2-} does not exist.

23. (i) Highest ionisation enthalpy → element V

Lowest ionisation enthalpy → element IV

(ii) The correct order of increasing electron gain enthalpy is $V < III < IV < II < I$.

24. (i) Carbon (ii) Chlorine

(iii) Bromine (iv) Fluorine

25. (i) $Cl > F > Br > I$

(ii) $Si > Mg > Al > Na$

(iii) $O > F > N > C$

26. $IE_1 + IE_2$ for Mg = 7.646 + 15.035 or 22.681 eV

or $22.681 \times 96.49 = 2188.489\ kJ\ mol^{-1}$

1 mole of Mg (24g) ≡ 2188.5 kJ

$$1.2 \times 10^{-3}g \text{ of Mg} \equiv \frac{2188.5}{24} \times 12 \times 10^{-3}\ kJ = 1094.25\ J$$

27. 10^6 atoms of I when change to I^{-}, energy released is 4.9×10^{-13} J.

$$1\text{mole of atoms} = \frac{4.9 \times 10^{-13}}{10^6} \times 6.023 \times 10^{23}\ J$$

$$= 29.5 \times 10^4 \times 10^{-3} = 295\ kJ\ mol^{-1}$$

$$= \frac{295}{96.49} = 3.057\ eV.$$

28. The defects are:

(i) Position of hydrogen is uncertain, since although it has been placed in Group–1 with alkali metals but it also shows properties similar to elements of Group–17.

(ii) Lanthanides and actinides have not been accommodated in main body of the periodic table.

29. (a) AlP (aluminum phosphide)

(b) Li_3N (lithium nitride)

(c) CaS (calcium sulphide)

Long Answer Questions

1. Four blocks of periodic table are known as s-, p- d- and and f -block elements.

General characteristics of *s*-Block elements :

General electronic configuration ns^{1-2}.

(i) They are soft metals with low melting and boiling points.

(ii) They are highly reactive metals and forms univalent and bivalent ions by losing one or two valence electrons respectively.

(iii) They have low ionisation energies and thus are highly electropositive.

(iv) They act as strong reducing agents. Examples are : Na, Mg, etc.

General characteristics of *p*-Block elements :

General electronic configuration ns^2np^{1-6}

(i) p-Block elements include both metals and non-metals. The metallic character decreases and non-metallic nature of elements increases as we move along a period from left to right.

(ii) Their ionisation energies are relatively higher as compared to s-block elements.

(iii) They form covalent compounds.

(iv) Majority of them show more than one oxidation state in their compounds. Examples are : O, F, etc.

General characteristics of d-Block elements :

General electronic configuration $ns^2(n–1)d^{1-10}$

(i) They are hard metals having high melting and boiling points.

(ii) They exhibit several oxidation states.

(iii) Their ionisation energies lie between s- and p-block elements.

(iv) They form both the ionic and covalent compounds. Examples are : Cr, Fe, etc.

General characteristics of *f*-Block elements :

General electronic configuration $(n–2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$

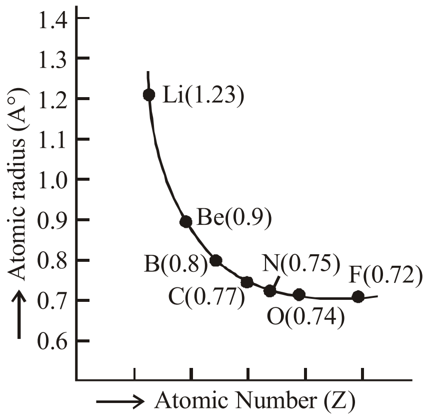
(i) They are heavy metals.

(ii) They show high melting and boiling points.

(iii) They show variable oxidation states.

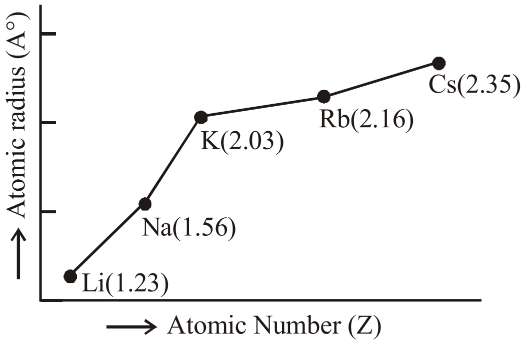
(iv) They have the tendency to form complexes.

2. **Variation of atomic radii in a period : Atomic radii (covalent or vander Waal's) decreases with increase in the atomic number in a given period**. The decrease of atomic radii along a period is due to increase in magnitude of nuclear charge while the number of shells remain the same. Due to increased nuclear charge on moving left to right along a period the electrons of all the shells are pulled closer to the nucleus resulting into decrease in size of atomic radii.



Variation of atomic radii in a period

Variation of atomic radii in a group : The atomic radii of elements increases from top to bottom in a given group. The increase in size on descending a group is due to addition of extra shell (i.e. the number of principal quantum number increases) which outweights the effect of increased nuclear charge. Consequently, the distance of the outermost electron from the nucleus gradually increases down a group i.e. size of atom increases on going down a group.



(Variation of atomic radius down a group)

3. (i) (a) **Screening effect.** The inner electrons between valence electron and nucleus shield the valence electron from nucleus; it is called shielding effect.

(b) **Penetration effect.** Due to shape of the orbital, *s* electron penetrates nearer to the nucleus than *p*, *d* or *f*-electrons and are more tightly held.

(c) **Metallic character.** Lower the ionisation energy, more will be tendency to lose electron, higher will be metallic character.

(ii) The electron affinity of noble gases is zero because they have stable electronic configurations. Cl > F > Br > I is increasing order of electron affinity.

4. (i) (a) For lithium, the outer electron is 2*s* electron, but for Li^+ the outer electron is a 1*s* electron, closer to the nucleus and lower in energy than the 2*s* electron. Moreover, it is difficult to break the noble gas configuration in Li^+. Hence, IE_2, for Li is so much higher than for all other elements of their period.

(b) Once the first electron is removed, the effective nuclear charge increases, and the size of M^+ is less than a M-atom. So, the electrons in M^+ are more strongly held by the nucleus. Hence IE_2 increases from Be to Ne.

(c) After the removal of one electron, the O^+ has an electronic configuration of $1s^2\ 2s^2\ 2p^3$ whereas F^+ has an electronic configuration of $1s^2\ 2s^2\ 2p^3$. As 2*p* subshell is half-filled in O^+, so, O^+ is more stable than F^+. Hence, more energy is required to remove an electron from O^+ than from F^+.

(ii) The IE_2 of Na is between 3960 and 7294 kJ/mol (it is 4560 kJ/mol). The Na^+ has a noble gas core than Na which has one loosely held electron in 3*s*-subshell. The energy needed to remove an electron from the noble-gas core of an atom is always much larger than that needed to remove a valence electron. The core electrons having lower principal quantum numbers are so close to the nucleus that they are strongly attracted to it.

5. These are :

(i) The names are derived from the atomic numbers using the roots for 0 and the numbers from 1 to 9. The suffix ium is added to the name.

(ii) In some cases, the names are shortened.
For example, biium is shortened to bium.

(iii) The symbol of element is then obtained from the first letters of the roots of numbers which make up the atomic number of the given element. The symbol of the element consists of three letters.
Roots for the IUPAC names of the elements are :

Digit	Root	Abbreviations
0	nil	*n*
1	un	*u*
2	bi	*b*
3	tri	*t*
4	quad	*q*
5	pent	*p*
6	hex	*h*
7	sept	*s*
8	oct	*o*
9	enn	*e*

The IUPAC names of the elements having atomic numbers 101 to 120 are :

Atomic No. (Z)	IUPAC Name	Symbols
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uun
112	Ununbium	Uuu
113	Ununtrium	Uub
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilum	Ubn

HOTS / EXEMPLAR QUESTIONS

Very Short Answer Questions

1. The atomic radius of K should be much greater than 1.34 Å, and that of F should be comparitively much smaller, since atomic cations are smaller than their parent atoms, while atomic anions are bigger than their parent. The observed atomic radii of K and F are 2.31 and 0.64Å, respectively.

Short Answer Questions

1. Xe has an ionization energy comparable to O_2. The "inert gas" configuration was thought to prevent reaction of the noble gases before the experiment was actually performed by Bartlett,

Ionization Energies of Noble Gases

gas	IE, eV
helium	24.46
neon	21.47
argon	11.68
krypton	11.93
xenon	12.08
radon	10.70

2. Ce^{4+} has the stable electronic configuration of the noble gas Xe. Eu^{2+}, with 61 electrons, acquire the configuration [Xe] $4f^7$, with the added stability of a exactly half-filled $4f$ sub-shell.

3. Group : 1, Valency : 1

Outermost electronic configuration = $8s^1$

Formula of Oxide = M_2O

4. The outermost electronic configuration of nitrogen $\left(2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1\right)$ is very stable because p-orbital is half filled. Addition of extra electron to any of the $2p$ orbital requires energy.

Oxygen has 4 electrons in $2p$ orbitals and acquires stable configuration i.e., $2p^3$ configuration after removing one electron.

5. (a) Decrease in size of atom and increase in nuclear charge.
(b) Increase in atomic size.

6. (a) Carbon has highest first ionisation enthalpy.
(b) Carbon has most negative electron gain enthalpy.
(c) Al has largest atomic radius.
(d) Al has most metallic character.

Long Answer Questions

1. (i) S, it has smallest atomic size
(ii) Cl^-, number of shells is least
(iii) In case of Fe, the number of unpaired electrons is maximum.
(iv) I, since atomic radius decreases across a period. Sn and I are in the same period. Bi has an extra shell.
(v) Ca, by losing the second electron it acquires stable noble gas configuration.

2. 7.1 g of chlorine $= \dfrac{7.1}{35.5}$ moles = 0.2 moles

Energy produced when 1 mole of Cl (g) is converted to Cl^- $= 3.7 \times 96.49$ kJ = 357.01 kJ

$\therefore$ Energy produced when 0.2 mole of Cl (g) is converted to $Cl^- = 357.01 \times 0.2$ kJ = **71.4 kJ.**

3. In most of its properties copper (Cu) resembles the d-block elements i.e. it forms complex compounds, coloured ions in aqueous solution and also exhibits variable valency (+2 and +1). Due to this it is considered as a transition element.

4. The electronic configurations are

$_{13}Al$: $1s^2 2s^2 2p^6 3s^2 3p^1$

$_{31}Ga$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$

In Ga, 10 electrons present in $3d$-orbitals do not shield the outer electrons from the nucleus effectively. As a result effective nuclear charge in Ga increases. This explains why I.E. of Ga is slightly more than that of Al.

5. Helium is a non metallic gas under all conditions thus it should placed on right of periodic table. secondly it is inert gas and show properties resembling group 18 elements.

$\therefore$ it is placed on extreme right, group 18 of periodic table and not p-2.

6. **Yes.** We can explain the diagonal relationship on the basis of I.E. and charge density data.

I.E. of pairs like *boron* and *silicon* (which show diagonal relationship) are indeed quite close. So the diminishing effect of I.E. of descending a group is compensated for by the increasing effect on I.E. of moving to right in a period.

It is also interesting to note that the pairs of elements that show diagonal relationship have *similar charge densities.* Moving to right and down puts up both charge and size respectively.

7. (a) The jump in IE values are noticed when the successive removal of electrons occurs from different shells. in alkali metals (ns^1) removal of I and II electrons occurs from n, $(n - 1)$ shells respectively and thus shows a jump in IE_2 values. This condition occurs during removal of II and III electrons from alkaline earth metals (ns^2).
(b) Due to more effective nuclear charge
(c) Atomic radii of inert gases are van der Waals radii whereas for rest all atoms covalent radii are determined experimentally. van der Waals radii should not be compared with covalent radii.
(d) After addition of one electron, halogen acquires nearest noble gas configuration. Addition of 2nd electron is not possible and thus $EA_2 = 0$

X : $ns^2\ np^5$ X^- : $ns^2\ np^6$ X^{2-} : Not possible

(e) Sn^{4+} is smaller in size than Sn^{2+} and therefore it causes more polarisation of Cl^- ion. According to Fajan's rule, more is polarisation, more is covalent character.

8. (i) $S < P < N < O$
(ii) $P\ S < N < O$

9. Electronegativity decreases in a group from top to bottom. Thus, ceasium is the least electronegative element.

10. After removing 1 electron from the sodium atom the ion formed acquires the configuration of inert gas, neon. The second electron is removed from one of the $2p$-orbitals which are completely filled i.e., have a total of 6 electrons and are closer to the nucleus.

CHAPTER TEST

1. Metallic character decreases with increase in ionization enthalpy.

2. When an electron is added to a neutral gaseous atom to convert it into a negative ion, energy is released due to attraction from the nucleus.

3. (a) 14.6, 13.6

4. This is because when an electron is added to O, the incoming electron goes to a small size O atom and faces a significant repulsion from the other electrons present. On the other hand S has a large size and the added electron faces less repulsion due to this, electron gain enthalpy of O is less negative than that of S.

5. (i) Be^+ has lower ionization enthalpy then Mg^{2+} because Mg^{2+} has a stable inert gas configuration.

(ii) I will have lower ionization enthalpy than I^- because I^- has a stable inert gas configuration hence in order to remove an electron will require more energy.

6. (i) Cl^- (18) is iso–electronic with Ar(18)

(ii) Ca^{2+}(18) is iso–electronic with K^+(18)

(iii) Ne(10) is iso–electronic with Na^+(10)

7. Let B be neon with atomic number Z = 10. Therefore atomic number of
A = 9(halogen) and of C = 11(alkali metal)

$A_9 = 1s^2, 2s^2, 2p^5$ (Number of electrons in the valence shell = 7)

$B_{10} = 1s^2, 2s^2, 2p^6$

(Number of electrons in the valence shell = 8)

$C_{11} = 1s^2, 2s^2, 2p^6, 3s^1$ (Number of valence shell = 1)

Groups:
Element A belongs to Group – 17 (Halogens)
Element B belongs to Group – 18 (Noble gas)
Element C belongs to Group – 1(alkali metals)

(i) The element A (fluorine) requires only one electron to acquire noble gas configuration. Thus, electron gain enthalpy of A becomes more negative than that of C.

(ii) Noble gas (B) has a stable configuration due to which it would experience a force of repulsion when an electron is introduced. Hence, it has a positive value of electron gain enthalpy.

4

Chapter

Chemical Bonding and Molecular Structure

INTRODUCTION

It is well known fact that no element exists as independent atom, except for noble gases, under ordinary conditions.

Most of these elements exist as molecules.

The questions.

- Why do atoms combine and form bonds ?
- How do atoms combine to form molecule ?
- Why a molecule is more stable than the individual atoms ?

Such doubts will be discussed in this chapter. To answer above questions many theories have been put forward by various scientists time to time

KOSSEL – LEWIS APPROACH TO CHEMICAL BONDING

G.N. Lewis, an American chemist, along with Kossel gave a satisfactory explanation about the cause of chemical combination between atoms. This theory is also known as Electronic theory of valency.

As per the theory noble gases is stable because they have eight electrons in their outer most shell. Thus other atoms having valence electrons less than 8 combines with each other to achieve 8 electrons in their valence shell. The urge of atoms to attain stable electronic configuration of eight electrons in their valence shells is the key factor for chemical combination.

Octet Rule

The *octet rule* is defined as the tendency of atoms of different elements to acquire 8 electrons in their outermost shell. It is therefore concluded that s^2p^6 configuration in the outer energy level constitutes a structure of maximum stability or minimum energy. This can occur in two ways

(a) Complete transference of electron(s) from one atom to another leading to formation of electrovalent or ionic bond.

(b) By sharing of electrons which further occurs by two ways,

  (i) When the shared electron are contributed by the two combining atoms equally, the bond formed is called covalent bond.

  (ii) When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a **coordinate bond**, also called **dative bond**.

Lewis Symbol

G. N. Lewis represented the atom by simple symbol and the outer shell electrons as dots surrounding the symbol of atom. These symbols are called ***Lewis symbols or electron dot symbols*** For example, $_6C$ has electronic configuration [He] $2s^2\ 2p^2$. Its electron dot symbol shows 4 valence electrons as shown.

For example, the Lewis symbols for the elements of second period are as under:

The common valency of the element is either equal to the number of dots in the Lewis symbol (if dots are equal to or less than 4) or it is 8 minus the number of dots (if dots are greater than 4)

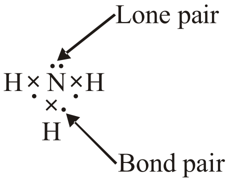
Langmuir, in 1919 improved the Lewis concept by suggesting that when both the atoms taking part in a chemical combination are short of electrons than the nearest noble gas configuration, they can share their electrons in order to complete their octets.

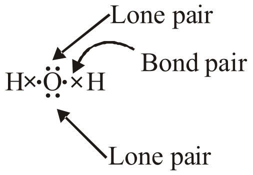
Covalent Bond

A covalent bond may be defined as the bond formed by mutual sharing of electrons between the combining atoms (which are short of electrons) of comparable electronegativity.

Structures represented by lines (–) or dashes are known as **Couper structures**. For example, H–H.

Compounds having covalent bond are known as covalent compounds. The shared pairs of electrons are present between the atoms i.e. covalent bonds are called **bond pairs**. On the other hand, the valence electrons which are not involved in bonding or mutual sharing are termed as **lone pairs** or **non-bonded electrons**.





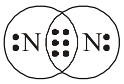
Lewis dot structure can be written for different molecules if the following conditions are satisfied

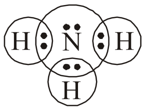
(a) Bond should be formed between two atom as a result of sharing of electrons

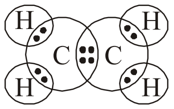
(b) Each atom contribute one electron to shared pair

(c) Combining atoms should achieve noble gas configuration.

(d) If two atom share more than one electron pair i.e., two and three covalent bond between them is referred as double and triple bond respectively. Following are few examples







The following steps are followed in constructing dot formulae for molecules and polyatomic ions.

(a) For writing Lewis dot structure find out total number of valence electrons by adding valence electrons of combining atoms.

(b) One positive charge shows loss of one electron and one negative charge shows gain of one electron, for example : NO_2^- shows addition of one electron.

(c) Write a symmetrical 'skeleton' for the molecules

(d) The least electronegative element is usually taken as the central element except H.

(e) After writing the number of electrons as shared pairs forming single bonds, the remaining electron pairs are used either for multiple bonds or for lone pairs.

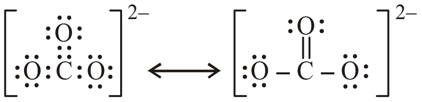
For example : CO_3^{2-}

$C(2s^22p^2), O(2s^22p^4)$

(i) Total number of electrons = 4 + (3 × 6) + 2 = 24 electrons

(ii) Skeletal structure of CO_3^{2-} = $\begin{matrix} & O & \\ O & C & O \end{matrix}$

(iii) Lewis dot structure for CO_3^{2-} is



Formal Charge

It is the difference between the number of valence electrons in an isolated atom and no. of electrons assigned to that atom in Lewis structure.

Formal charge on atom in a molecule/ion = Total no. of valence electrons in the free atom-Total no.of electrons of lone pairs (non-bonding electrons) $-\frac{1}{2}\times$ Total no. of shared electrons (bonding electrons).

Exception to Octet Rule

(i) Incomplete octet : (or electron deficient molecule)

In which octet (of outer most orbit of central atom) is not complete.

Compounds having 6 e^-s in outer most shell are called, Sextet. For example – Halides of IIIA group like BF_3, BCl_3, $AlCl_3$ other example is $BeCl_2$ with 4e^-s in the outermost shell

(ii) Expansion of octet : The compound whose central atom have more than 8 e^-s in its outer most shell shows the expansion of octet. These are mostly 3rd period elements having vacant *d*-orbitals.

For example : PCl_5, SF_6, IF_7. The central atom P, S, I contain 10, 12 and 14 e^-s respectively.

(iii) Pseudo inert gas configuration :

(a) – cations of transition metal which contain 18 e^-s in outer most shell.

For example, Ga^{+3}, Cu^+, Ag^+, Zn^{+2}, Sn^{+4}, Pb^{+4} etc.

(b) – Cations having electrons between 9 to 17 in their outer most shell.
For example, Mn^{+2}, Fe^{+2}, Fe^{+3}, Ti^{+2} etc.

(iv) Odd electron molecules : They have an unpaired electron or odd no. ($7e^-$, $11e^-$ etc.) of electrons. For example, NO, NO_2, ClO_2 etc.

IONIC OR ELECTROVALENT BOND

Ionic bond is formed by complete transfer of one or more electrons from an electropositive atom to an electronegative atom so as to complete their octet.

or

Electrostatic force of attraction between cation and anion is called **ionic bond or electrovalent bond**. The force of attraction is equal in all direction, so ionic bond is non–directional.

When metallic atom loses an electron (i.e. no. of protons > no. of electrons) it becomes positively charged ion known as cation. This process requires energy and is called endothermic process.

$$M + \text{Energy} \longrightarrow M^+ + e^- \text{(endothermic)}$$

When electrically neutral non-metallic atom gain an electron (i.e. no. of electrons > no. of protons), the atom becomes negatively charged ion or anion. This process releases energy and is termed as exothermic process.

$$X + e^- \longrightarrow \underset{\text{(Anion)}}{X^-} + \text{Energy(Exothermic)}$$

Combination of cations and anions is again an exothermic process. More the distance between two elements in periodic table more will be ionic character of bond. The number of electrons (s) lost or gained by the atom to form ionic compound is known as valency of the respective atom in that compound.

Formation of Ionic Bond is Favoured by Following Three Factors

(a) Low ionisation energy of metals : Low I.E. means greater tendency to form cations.
(b) High electron affinity of non-metals : High E.A. means greater tendency to form anions.
(c) High lattice energy

Lattice energy: It is the amount of energy released when one mole of ionic solid is formed by combination of requisite number of cations and anions. Higher the value of lattice energy, greater will be the stability of ionic compound and thus greater will be the ease of its formation. The value of lattice energy depends upon the following two factors.

(i) **Size of the ions :** Smaller the size of the ions, lesser is the internuclear distance and hence greater will be the interionic attraction. Therefore, the magnitude of lattice energy will be large.
(ii) **Charge on the ions :** Larger the magnitude of charge on the ions, greater will be force of attraction between ions. Consequently, higher is the value of lattice energy.

BOND PROPERTIES

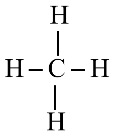
Bond Energy

Bond dissociation energy is the energy required to separate the two atoms. It is directly proportional to bond order.

Case–I : In diatomic molecule : Bond energy = Bond dissociation energy

Example : $N_2 > O_2 > H_2 > F_2$

Case – II : For polyatomic molecule : Bond energy $\approx$ bond dissociation energy (D)

Example : In  $\underset{\text{H}}{\overset{\text{H}}{\text{H}-\overset{|}{\underset{|}{\text{C}}}-\text{H}}}$; Bond energy per C—H bond is 99.5 k Cal/mole.

Theoretical values of bond dissociation energy (D) of individual C—H bonds in CH_4 are given below :–

$D(CH_3–H) = 102$ kcal/mole
$D(CH_2 – H) = 105$ kcal/mole
$D(CH–H) = 108$ kcal/mole
$D(C—H) = 83$ kcal/mole

Hence, mean bond energy per C–H bond in methane

$$= \frac{398}{4} = 99.5 \text{ kcal/mole.}$$

Factors affecting the bond energy

(a) **Δ Electronegativity :–** Bond energy $\propto$ ΔEN

(b) **Bond order :** Bond energy $\propto$ Bond order

(c) **Atomic size :** Bond energy $\propto \frac{1}{\text{Atomic size}}$

(d) **Bond Polarity :** Bond energy $\propto$ Bond polarity

(e) **Hybridisation :** Bond energy $\propto$ % of s–character in hybrid orbitals.

(f) **Lone pair of electrons :**

Bond energy $\propto \frac{1}{\text{Lone pair of electrons}}$

(g) **Resonance :** Bond energy increases due to resonance.

Bond Length

Bond length is the distance between the centres of two bonded nuclei. It is inversely proportional to bond order i.e. as bond order increases, bond length decreases.

$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

Factors affecting the bond length

(a) **Δ Electronegativity :**

Bond length $\propto \frac{1}{\Delta\text{EN}}$ (While B.E. $\propto$ ΔEN)

(b) **Number of bonds :**

Bond length $\propto \frac{1}{\text{Number of bonds or bond order}}$

(c) **Hybridization** : Bond length $\propto \frac{1}{'s'\ \text{character}}$

Bond Angle

The angle between any two adjacent bonds is known as bond angle.It is represented in degree (º), minute (') and second (")

Factors affecting the bond angle

(a) **Number of bonds :**

Bond angle $\propto$ Number of bonds (Bond order)

(b) **Hybridization :**

Case-I : When hybridization is same, bonded atoms are same, central atom and lone pairs of $e^{-1}s$ are different, then

Bond angle $\propto \frac{1}{\text{No.of lone pairs of } e^{-1}\text{s}}$

Case-II : When hybridization is same, bonded atoms are same lone pair of e^{-1}s is same but central atom is different, then

Bond angle $\propto$ Electronegativity of central atom

Case-III : When hybridization is same, lone pair of $e^{-1}s$ are same, central atom is same, bonded atoms are different, then

Bond angle $\propto \frac{1}{\text{electronegativity of bonded atom(s)}}$

Bond Order

It is defined as the number of covalent bonds by which the two atoms are joined in the molecule. It is calculated as given below.

$$\text{Bond order} = \frac{1}{2}\left[\begin{matrix}\text{Number of electrons in bonding M.O.}\\ \text{i.e.}N_b\end{matrix}\right.$$

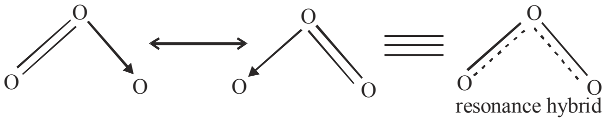
$$\left.\begin{matrix}-\text{Number of electrons in antibonding M.O.}\\ \text{i.e.}N_a\end{matrix}\right]$$

$\therefore$ Bond order $= \frac{1}{2}[N_b - N_a]$

Resonance

In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. The phenomenon is called resonance.

Let us discuss resonance in ozone. It should have one single bond (O–O : 1.48 Å) and one double bond (O = O : 1.21 Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.

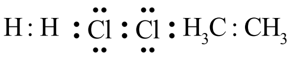


Resonating structures have similar positions of atoms but different arrangement of electrons. These structures have same no. of unpaired electrons and almost equal energy. Resonance hybrid has lower energy than any of the contributing structures and hence possess greater stability.

Resonance energy is the energy difference between resonance hybrid and that of the most stable contributing structure.

Polarity of Bonds

Polar and non-polar covalent bonds : When a covalent bond is formed between two similar atoms, the shared pair of electrons are equally attracted by the bonded atoms. Hence the electron pair is situated exactly in the middle of two identical nuclei as represented below.



$$H:H \; :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \; H_3C:CH_3$$

This type of covalent bond is termed as **non-polar covalent bond** for example, bond in H_2, O_2, N_2, Cl_2, F_2, etc.

A covalent molecule made up of two dissimilar atoms having different electronegativities, the shared pair of electrons does not lie in the middle but shifts towards the more electronegative atom. This type of bond is called ***polar covalent bond***.

As a result of polarisation, the molecule possesses the dipole moment.

Dipole moment: Dipole moment is defined as the product of charge on any one of the atom and the distance between the centre of two atoms. It is usually represented by Greek letter 'μ'. Mathematically.

$$\textbf{Dipole moment } (\mu) = \textbf{ charge (q)} \times \textbf{distance between two atoms (d)}$$

$$\mu = q \times d$$

The charge '*q*' is of the order of 10^{-10} e.s.u. and the internuclear distance '*d*' is of the order of 10^{-8} cm (Å). Therefore, the dipole moment 'μ' is of the order of $10^{-10} \times 10^{-8} = 10^{-18}$ e.s.u. cm. This quantity is known as one Debye.

$$1D = 1 \times 10^{-18} \text{ e.s.u. cm}$$

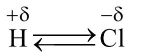
$$1D = 3.33564 \times 10^{-30} \text{ Cm}$$

Where C → coulomb, m → metre

Dipole moment is a vector quantity, i.e., it has magnitude as well as direction. It is often represented by an arrow with its tail at the positive centre and head pointing towards the negative end (+ → –).

Dipole moment in diatomic molecules :

As a polar diatomic molecule posseses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond. For example in case of HCl, the molecular dipole moment is equal to the dipole moment of H–Cl bond i.e., 1.03 D. Thus.

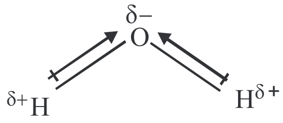


$$\overset{+\delta}{H} \rightleftarrows \overset{-\delta}{Cl} \quad \mu = 1.03 \text{ D}$$

Dipole moment in polyatomic molecules

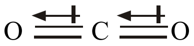
(a) As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all individual bonds.

(b) For example, dipole moment of H_2O is 1.84 D which is equal to the resultant dipole moment of two O–H bonds.



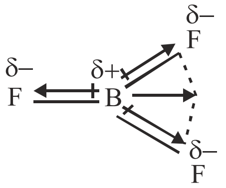
μ = 1.84D

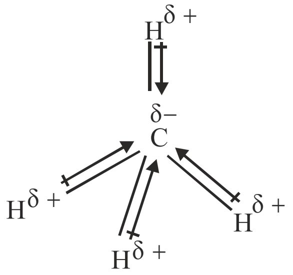
(c) Consider the CO_2 molecule, though C = O bond is polar due to electronegativity difference but the resultant dipole moment of molecule is zero as the individual dipole moments are of equal magnitude and opposite sign. This shows that CO_2 is a linear molecule.

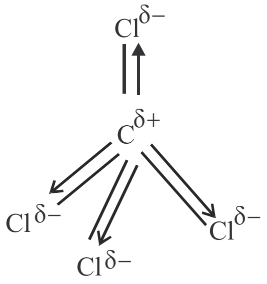


$$O \overset{\leftarrow\!\!+}{=\!=} C \overset{\leftarrow\!\!+}{=\!=} O$$

(d) Again in case of symmetrical molecules such as BF_3, CH_4 and CCl_4 the molecular dipole moment is found to be Zero. This is again because of the fact that individual dipole moments cancel out on account of the symmetry of the molecule.







Applications of dipole moment

(a) In determining the polarity of bonds :

As $\mu = q \times d$,

greater is the magnitude of dipole moment, higher will be the polarity of the bond. But in the strict sense, this concept is applicable to molecules containing only one polar bond. Further in case of non polar molecules like H_2, O_2, N_2 etc. the dipole moment is found to be zero. This is because there is no charge separation in these molecules.

(b) In the calculation of ionic character :

(i) A covalent bond develops a polar character due to the difference in the electronegativity of the atoms forming the bond.

(ii) If the electronegativity difference between two atoms is large, the bond will be highly polar.

(iii) It has been observed that when the electronegativity difference is 1.7, the bond existing between two atoms is 50% ionic and 50% covalent.

(iv) The percentage of ionic character of a bond can be calculated from the ratio of the observed dipole moment to the calculated dipole moment (considering 100% ionic character)

i.e., % ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment considering 100\% ionic character}} \times 100$$

(c) Determination of shape or symmetry of molecule :

Dipole moment is an important factor in determining the shape of molecules containing three or more atoms. For instance, if any molecule possesses two or more polar bonds, it will not be symmetrical if it possesses some molecular dipole moment as in case of water ($\mu = 1.84D$) and ammonia ($\mu = 1.49$ D). But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero, it indicates that the molecule is symmetrical e.g., CH_4, CCl_4 etc.

Fajan's Rule

As we discussed that there is some ionic character in polar covalent bonds. Similarly ionic bonds also possess some partial covalent character which is discussed by Fajan's in terms of following rules;

The power of an ion (cation) to distort the other ion is known as its **polarising power** and tendency of the ion (anion) to get polarised by the other ion is known as its ***polarisability***. Greater the polarisation power or polarisability of an ion, greater will be its tendency to form covalent bond. Formation of covalent bond is favoured by the following factors.

(i) **Small size of cation :** *Smaller the size of cation greater is its polarising power i.e. greater will be the covalent nature of the bond.*

$$\text{Covalent nature}\xrightarrow[\text{Solubility in water}]{\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}}\text{Ionic nature}$$

$$\xrightarrow[\text{m.p. increases}]{}$$

(ii) **Large size of anion :** *Larger the size of anion greater is its polarizing i.e. greater will be the covalent nature of the bond.* This explains the following order for covalent nature of lithium

$$\text{Covalent nature}\xrightarrow[\substack{\text{Solubility in water increases} \\ \text{m.p. of compounds increases}}]{\text{LiI}>\text{LiBr}>\text{LiCl}>\text{LiF}}\text{Ionic nature}$$

(iii) **Charge on the ion :** As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases with the result, its ability for forming the covalent bond increases. Thus covalence increases in the order :

$$Na^+Cl^- < Mg^{2+}Cl_2^{2-} < Al^{3+}Cl_3^{3-}$$

(iv) **Electronic configuration of the cation**: For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e. 18 electrons in the outermost shell) will be more polarising than a cation with noble gas configuration (i.e. 8 electrons outermost shell). Thus copper (I) chloride is more covalent than sodium chloride although Cu^+ ion (0.96 Å) and Na^+ ion (0.95Å) have almost same size and charge. AlI_3 is more covalent than $AlCl_3$. $FeBr_3$ is more covalent than $FeCl_3$. This is due to Fajan's rule.

VSEPR THEORY SIDWICK AND POWELL

VSEPR Theory Sidwick and Powell (1940) has provided a highly useful idea for predicting geometries of molecules known as *VSEPR theory*. The main postulates of *VSEPR* theory are:

(a) The geometry of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom

(b) Pairs of electrons in valence shell repel one another since their electron clouds are negatively charged.

(c) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

(d) The valence shell is taken as a sphere with electron pairs localising on the spherical surface at maximum distance from one another.

(e) A multiple bond is treated as if it is a single electron pair

(f) Where two or more resonance structures can represent a molecule, VSEPR model is applicable to any such structure.

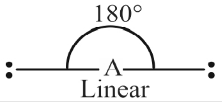
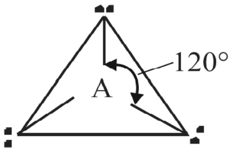
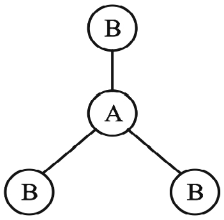
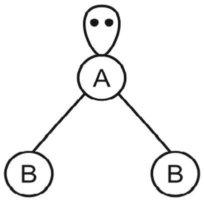
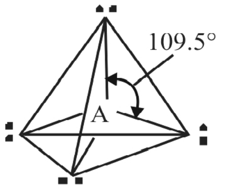
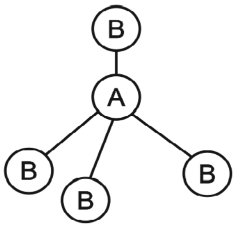
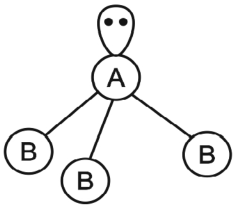
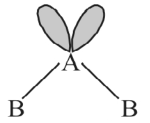
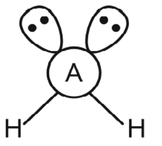
(g) The decreasing order of repulsive interaction of electron pairs is $lp - lp > lp - bp > bp - bp$ where $lp \rightarrow$ lone pair and $bp \rightarrow$ bond pair

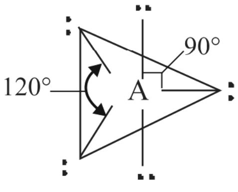
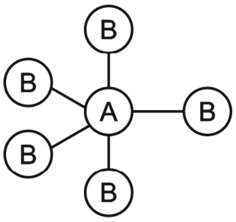
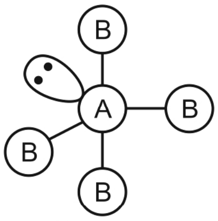
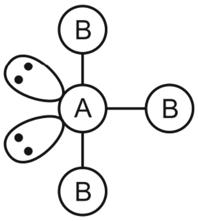
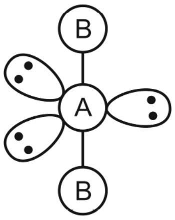
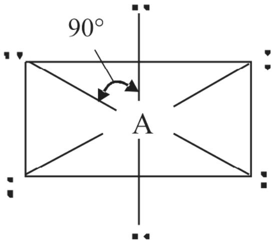
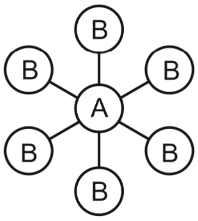
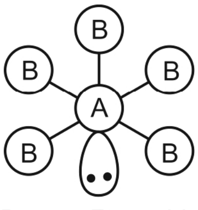
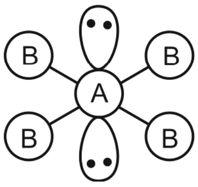
For prediction of geometrical shape of molecules, it is divided in two categories :

(i) molecules in which central atom has no lone pair(s)

(ii) molecules in which central atom has one or more lone pair(s).

Geometrical shapes of molecules containing bond pairs and lone pairs

Total Number of Electron pairs	Geometry of the electron pairs	Bond pairs	Lone pairs	Geometry of the molecule	Examples
2	 Linear	2	0	 Linear	BeF_2, $HgCl_2$
3	 Trigonal planar	3	0	 Trigonal planar	BeF_3, $AlCl_3$
		2	1	 Bent or v-Shaped	SO_2, O_3
4	 Tetrahedral	4	0	 Tetrahedral	CH_4, SiF_4
		3	1	 Pyramidal	NH_3
		2	2	 V shaped Tetrahedral	

5	5  Trigonal bipyramidal	0	 Trigonal bipyramidal	PCl_5, AsF_5
	4	1	 See saw	SF_4
	3	2	 T-shaped	ClF_3
	2	3	 Linear	XeF_2
6	6  Octahedral	0	 Octahedral	SF_6
	5	1	 Square Pyramidal	ClF_5 BrF_5
	4	2	 Square Planar	XeF_4

Nylon and Gillespie further refined this theory by stating that lone pairs are localised on central atom whereas bonded pair is shared between two atoms. Thus lone pair of electrons occupy more space as compared to bond pair of electrons. Thus lp-lp repulsion is greater than lp-bp and bp-bp repulsion.

VSEPR theory is able to explain the shape of simple molecules but it also fails in number of cases and have limited application. In order to overcome these limitations two important theories based on quantum mechanical principles are introduced. These theories are (a) Valence Bond Theory (b) Molecular Orbital Theory

VALENCE BOND THEORY

Valence bond theory was introduced by Heilter and London (1927) and developed by Pauling and others. It based on the concept of atomic orbitals and the orbital configuration of the atoms.

Let us consider the formation of hydrogen molecule based on valence-bond theory.

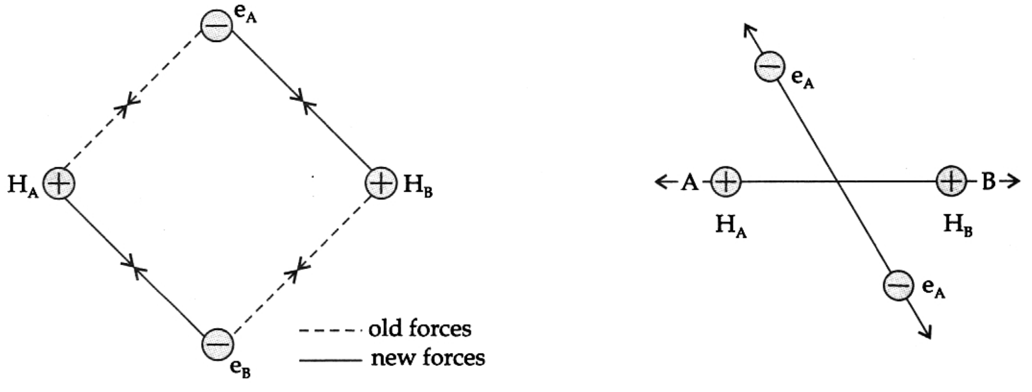
Let two hydrogen atoms A and B having their nuclei N_A and N_B and electrons present in them are e_A and e_B.

As these two atoms come closer, new attractive and repulsive forces begin to operate.

(a) The nucleus of one atoms is attracted towards the electron of the other and vice versa.

(b) Repulsive forces arise between the electrons of two atoms and nuclei of two atoms.

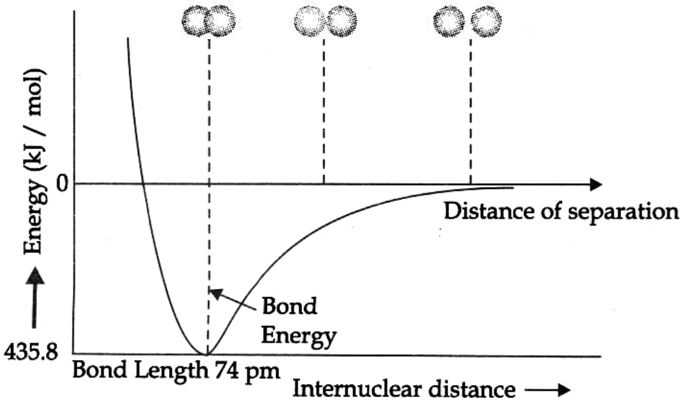
Attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart.



Attractive Forces **Repulsive Forces**

Forces of attraction and repulsion during the formation of H_2 molecule.

Experimental result shows that the magnitude of attractive forces is more. Thus when two atoms approach each other the overall potential energy of the system decreases. When the bond is formed between two hydrogen atoms. The hydrogen molecule is more stable than that of isolated hydrogen atoms. The bond energy of H-H (g) is 433 kJ/mole. Same energy is needed to break the molecules into the atoms is known as bond dissociation energy.



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

Orbital Overlap Concept

A covalent bond is formed by the partial overlapping of two half filled atomic orbitals containing electrons in opposite spins. This can be illustrated by considering the formation of hydrogen molecule.

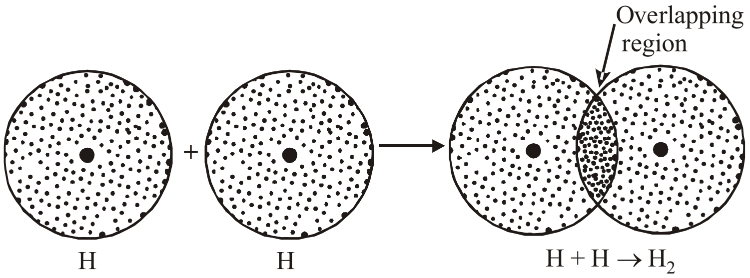


Fig. Overlapping of orbitals to form H_2 molecule.

The hydrogen atom has one electron in 1s-orbital. When two such atoms containing one electron each with opposite spins approach each other, then they merge to form a new orbital known as ***molecular orbital***. These two electrons have greater probability of their presence in the region of overlap and thus get stabilised i.e. ***during overlapping energy is released***.

Thus,

(a) Covalent bond is formed by overlapping of half filled atomic orbitals of atoms involved in bonding.
(b) The orbitals participating in bonding must have electrons with opposite spins. This is the reason why no covalent bond is formed between two helium atoms because they have fully filled orbitals.
(c) Overlapping of orbitals results in decrease of energy.
(d) Strength of covalent bond depends upon the extent of overlapping i.e. greater the extent of overlapping, more is the release of energy and hence stronger will be the covalent bond.

Therefore, according to this theory, the number of covalent bonds formed by an element will be equal to the number of half filled orbitals present in the valence shell of its atoms.

Types of Orbital Overlap

VBT also explains the shape, formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3, and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

Depending upon the type of overlapping the covalent bonds are of two types known as sigma (σ) and pi (π) bonds.

HYBRIDISATION

Characteristics of Hybridisation

(a) Only orbitals of almost similar energies and belonging to the same atom or ion undergo hybridisation.
(b) The number of hybrid orbitals produced is equal to the number of pure orbitals mixed during hybridisation, e.g. four hybrid orbitals are produced by mixing one s and three p(p_x, p_y, and p_z) pure orbitals.
(c) In the excited state, the number of unpaired electrons must correspond to the oxidation state of the central atom in the molecule.
(d) Both half filled orbitals or fully filled orbitals of equivalent energy can be involved in hybridisation. *s*-orbital of equivalent energy always participate in the process of hybridisation.
(e) Orbitals involved in π bond formation do not participate in hybridisation.
(f) Most of the hybrid orbitals are similar in shape, size and energy.
(g) Hybridisation never takes place in an isolated atom but it occurs only at the time of bond formation.
(h) The hybrid orbitals are distributed in space as far as possible resulting in a definite geometry of molecule.
(i) Hybridised orbitals possess lower energy.
(j) Hybridised orbitals provide efficient overlapping than overlapping of pure *s*, *p* and *d*-orbitals.

Method for Finding the Type of Hybridisation

The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation :

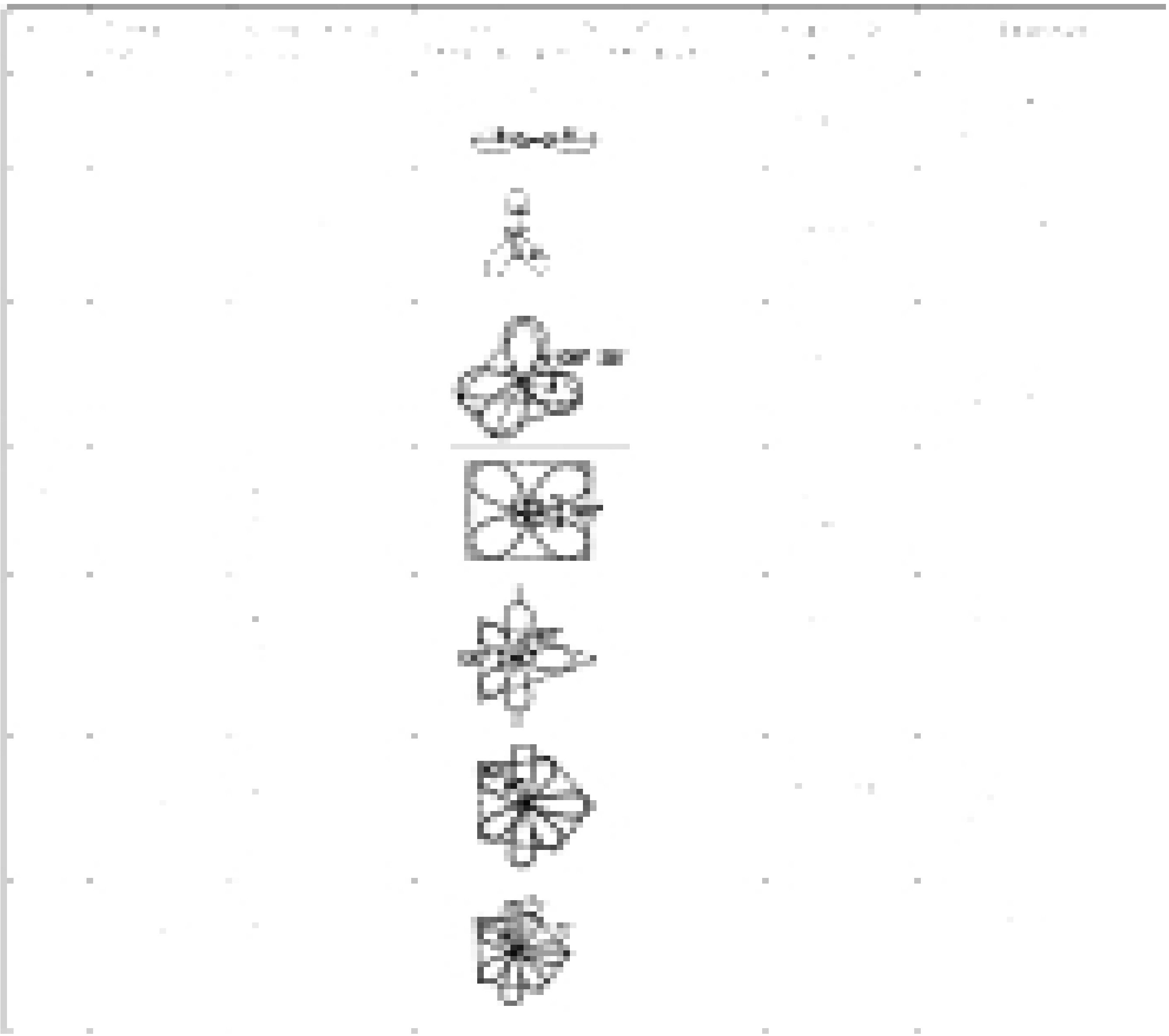
$$H = \frac{1}{2}(V + M - C + A)$$

where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp, sp^2, sp^3, sp^3d, sp^3d^2, sp^3d^3 respectively.

V = Number of electrons in valence shell of the central atom,
M = Number of monovalent atoms,
C = Charge on cation, A = Charge on anion.

Types of Hybridisation

Depending upon the type and number of orbitals involved in intermixing, the hybridisation can be of various types namely sp, sp^2, sp^3, sp^3d, dsp^2, sp^3d^2, sp^3d^3.



GEOMETRY OR SHAPE OF MOLECULES

The shape acquired by a molecule can be explained on the basis of the following two theories.

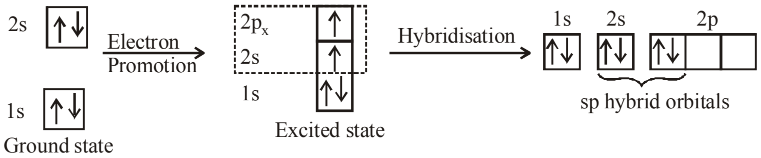
(a) Hybridisation

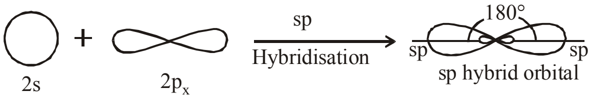
(b) Valence shell electron pair repulsion theory (or *VSEPR* Theory)

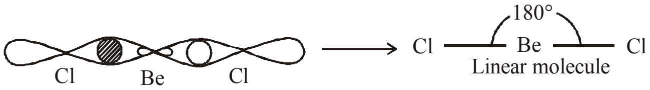
Shapes of Molecules Containing Bond Pairs Only

(i) Shape of beryllium chloride ($BeCl_2$) molecule

(a) On unit a the basis of hybridisation : Electronic configuration of Be (At. No. = 4) is written as $1s^2\ 2s^2$





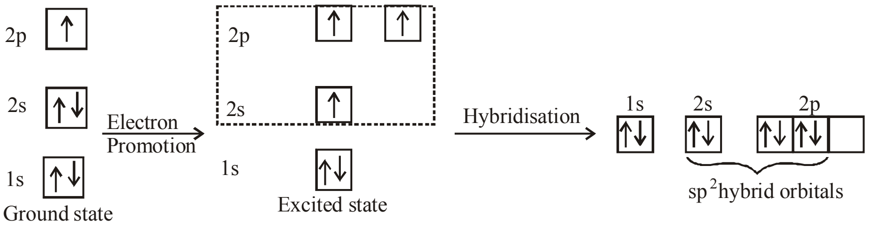


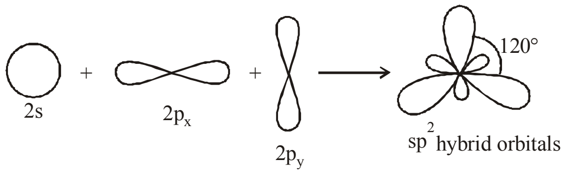
(b) On the basis of VSEPR theory : Linear geometry to $BeCl_2$: In $BeCl_2$, the central Be atom is surrounded by two bond pairs only. According to VSEPR theory, these two bond pairs repel each other and thus go as far as possible to have minimum energy or higher stability. Hence the molecule of $BeCl_2$ acquires a ***linear shape***.

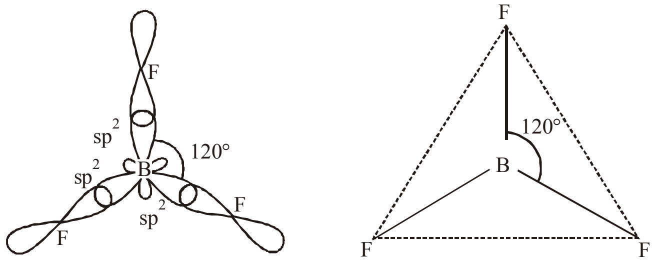
(ii) Shape of boron triflurode (BF_3) molecule:

(a) On the basis of hybridisation:

Electronic configuration of boron (At. No. = 5) is







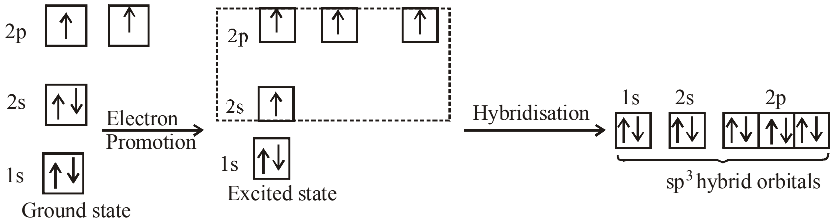
Trigonal planar geometry of BF_3.

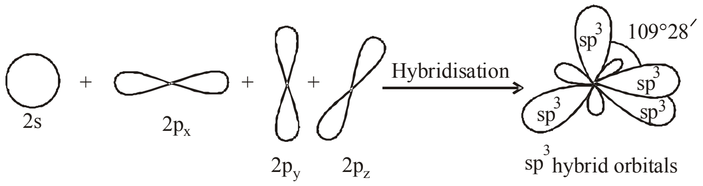
(b) On the basis of VSEPR theory : In BF_3, boron atom is surrounded by three bond pairs. According to VSEPR theory, these bond pairs will repel each other and take up the position of minimum energy at an angle of 120° from each other. Hence BF_3 molecule acquires **trigonal planar geometry.**

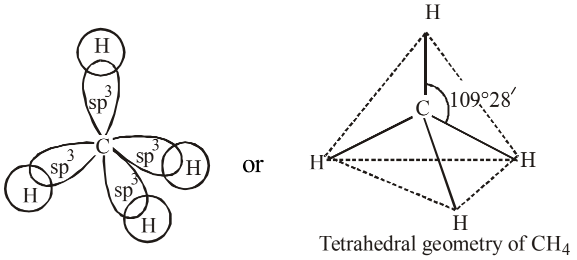
(iii) Shape of methane (CH_4) molecule :

(a) On the basis of hybridisation

Electronic configuration of C (At. No. = 6) is







Tetrahedral geometry of CH_4

(b) **On the basis of VSEPR Theory:** In CH_4, the C atom is surrounded by four bond pairs. According to VSEPR theory, four bond pairs will repel each other and take up the position of minimum energy at an angle of 109°28′ from each other. This provides a tetrahedral geometry to methane.

(iv) **Shape of PCl_5 molecule :** The ground state electronic configuration of phosphorus in PCl_5 is given below:

$$15 \rightarrow P = 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$$

one of the 3s electron gets promoted to 3d orbital giving it the following electronic configuration.

$$1s^2 2s^2 2p^6 \underbrace{3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1,}_{sp^3d \text{ hybrid orbitals}} \ldots\ldots\text{(Hybridisation)}$$

These five sp³d hybrid orbitals overlap with the half filled orbitals of chlorine atoms to forms 5 P—Cl sigma bonds. Thus the molecules of PCl_5 acquires ***trigonal bipyramidal geometry***.

(v) **Shape of sulphur hexafluoride (SF_6):** $_{16}S = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$.......(Ground state)

One electron each from 3s and 3p are promoted to two d-orbitals. So, the elecronic configuration of sulphur atom in the excited state is.

$$_{16}S = 1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1 3d_{yz}^1 \ldots\ldots\text{(Excited state)}$$

$$_{16}S = 1s^2 2s_2^2 p^6 \underbrace{3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1, 3d_{xy}^1,}_{sp^3d^2 \text{ hybrid orbitals}} \ldots\ldots\text{(Hybridisation)}$$

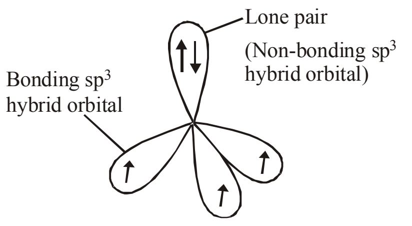
In SF_6, four S—F bonds are directed towards the four corners of a square and the other two S—F bonds lie at right angle above and below the plane of square. Thus, a molecule of SF_6 acquires octahedral geometry.

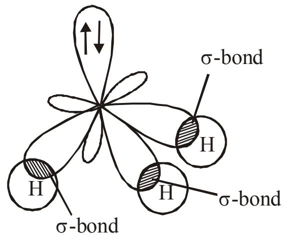
Shapes of Molecules Containing Bond Pairs as well as Lone Pairs

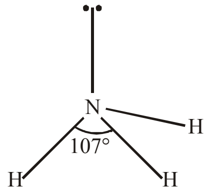
(i) **Shape of ammonia (NH_3) molecule:** In NH_3, the central atom nitrogen, has ground state electronic configuration as follows:

$$_7N = 1s^2 \underbrace{2s^2 2p_x^1 2p_y^1 2p_z^1}_{sp^3\text{hybrid orbitals}} \ldots\ldots\text{(Hybridisation)}$$

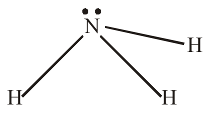
Due to the presence of one lone pair of electrons in one sp³ hybrid orbital, the shape of NH_3 molecule is trigonal pyramidal in which three H-atoms forms the triangular base of pyramid with N-atom at the apex as shown in figure.







or

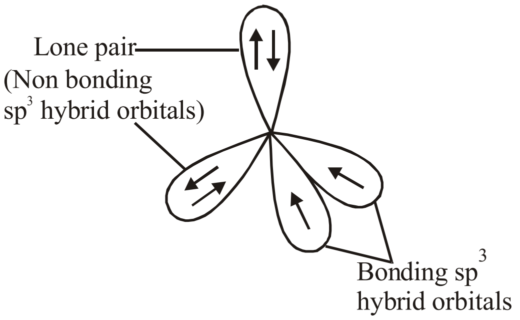


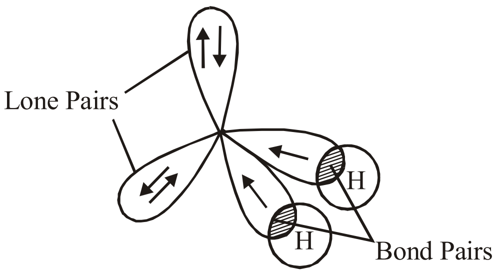
As evident, sp³ hybridisation in NH_3 should give a bond angle of 109°28′ . However the observed bond angle in NH_3 is 107°. Decrease in bond angle may be explained by VSEPR theory. According to this theory lP—bP repulsion > bP—Bp repulsion, therefore the bond angle reduces to 107°.

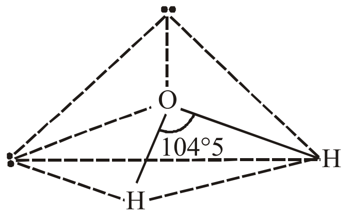
(ii) **Shape of water (H_2O) molecule**

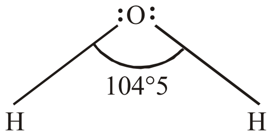
$$_8O = \underbrace{1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1}_{sp^3 \text{ hybridisation}} \ldots\ldots\text{(Ground state)}$$

These four sp³ hybrid orbitals are directed towards the four corners of a regular tetrahdron and thus the bond angle would be 109°28′. However, the experimentally observed bond angle is 104°5. It can be explained on the basis of VSEPR theory. In water molecule, oxygen has two lone pairs and two bond pairs. Since Lp—Lp repulsion > bP—bP repulsion, the H—O—H bond angle decreases to 104°5. Thus H_2O is ***V-shaped*** or ***bent molecule.***









MOLECULAR ORBITAL THEORY

The molecular orbital theory put forward by **Hund and Mulliken** in (1932). According to this theory the atomic orbitals lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals. The salient features of the theory are following

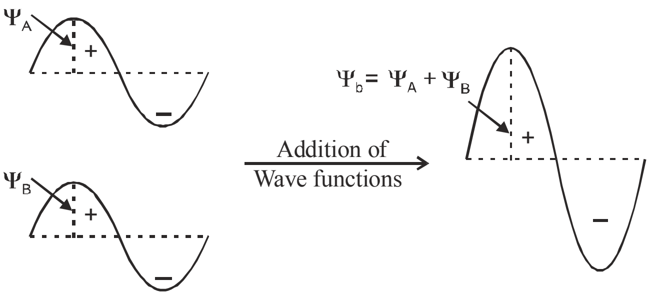
(a) Electrons in a molecule are present in molecular orbital whereas in atoms they are present in atomic orbitals.
(b) Molecular orbitals are formed by overlapping of atomic orbitals of nearly same energy.
(c) Electron in atomic orbital is influenced by one nucleus whereas it is influenced by two or more nuclei in a molecule.
(d) The number of molecular orbitals formed are equal to the number of atomic orbitals involved in overlapping. Electron probability distribution around a nucleus is given by molecular orbital
(e) Molecular orbitals, like atomic orbitals, are characterised by a set of quantum numbers.
(f) Half of the molecular orbitals will have lower energy and are called **bonding molecular orbitals**, while the other half are of higher energy and are termed as **antibonding molecular orbitals.**
(g) Electronic configuration in various molecular orbitals will be governed by the same three rules, i.e. (a) Aufbau's rule. (b) Hund's rule and (c) Pauli's exclusion principle.

Formation of Bonding and Antibonding Molecular Orbitals (LCAO Method) :

(a) An electron in an atom is described by a wave function (Ψ) called atomic orbital. Similarly, the behaviour of an electron in a molecule is described by a molecular wave function called molecular orbital.
(b) The most convenient way of working out the wave functions for molecular orbitals is to adopt the method of linear combination of atomic orbitals (LCAO)
(c) Quantum mechanics shows that linear combination of two functions gives two combinations and hence two molecular orbitals, one bonding orbital and one antibonding orbital, are formed.

(i) Combination by addition :

When the two electron waves are in phase i.e., they have the same sign, they will add up to give a new wave function expressed as Ψ_b.



Addition of wave functions

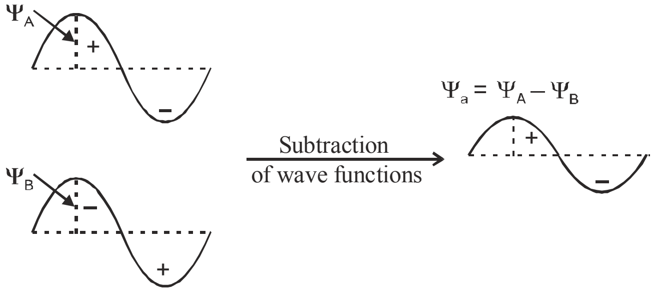
Wave function for bonding molecular orbital is

$$\Psi_b = \Psi_A + \Psi_B$$

Ψ_A = wave function of atom A
Ψ_B = wave function of atom B

(ii) Combination by subtraction :

When the two electron waves are out of phase i.e., they have opposite sign of the wave functions, then they will combine by subtraction and give the resulting wave function Ψ_a.



Subtraction of wave functions

Wave function for antibonding molecular orbital is

$$\Psi_a = \Psi_A - \Psi_B$$

(iii) We know that the probable electron density is given by Ψ^2 and not by Ψ. On squaring we get :

For bonding molecular orbital

$$\Psi^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

and for antibonding molecular orbital $\Psi^{*2} = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$

Here Ψ_A^2 and Ψ_B^2 represent the probable electron density in the two atomic orbitals where as Ψ^2 and Ψ^{*2} indicate the electron density in the two molecular orbitals. It may be noted that the molecular orbital resulting from the addition of the wave functions is known as bonding molecular orbital (Ψ^2) whereas the orbital arising from the subtraction of the wave functions is called antibonding molecular orbital (Ψ^{*2}).

$$\Psi^2 = (\Psi_A + \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

Electron density in a bonding molecular orbital is localised between the nuclei of bonded atoms without any nodal plane whereas in case of antibonding molecular orbital electron density is located away from internuclear space with a nodal plane. Antibonding molecular orbital has more whereas molecular orbital has less energy than parent atomic orbitals.

Comparison between bonding and antibonding molecular orbitals

	Bonding molecular orbital	**Antibonding molecular orbital**
(1)	Bonding molecular orbital is the result of the linear combination of atomic orbitals, when **their wave functions are added.** $\psi_b = \psi_A + \psi_B$	Antibonding molecular orbital is the result of the linear combination of atomic orbitals, when **their wave functions are subtracted.** $\psi_a = \psi_A - \psi_B$
(2)	It usually does not has a node.	It always has a node in between the two nuclei of bonded atoms.
(3)	Charge density increases in between the two nuclei resulting in the attraction between two atoms.	Charge density decreases in between the two nuclei which leads to repulsion between two atoms.
(4)	The energy of the bonding molecular orbital is less than the sum of energies of the two bonded atoms.	The energy of the antibonding molecular orbital is higher than the sum of the energies of the two bonded atoms.
(5)	These are stabilised due to less energy content.	These are destabilised due to higher energy content.

Conditions for the Combination of Atomic Orbitals to Form M.O.

(a) The combining A.O. should be of comparable energy

(b) The combining atomic orbitals must overlap to large extent, greater the overlap, more stable is the molecule formed.

(c) The combining atomic orbitals must have the same symmetry about the molecular axis.

Types of Molecular Orbitals

The molecular orbitals which have cylindrical symmetry around the internuclear axis (bond axis) are termed as σ molecular orbitals. These are formed by additive or subtractive combination of s-orbitals or p-orbitals.

The additive overlap of orbitals gives σ bond (σ_b) to possess lower energy and thus gets stabilized. The subtractive overlap gives antibonding molecular orbitals (σ^* bond) possessing higher energy.

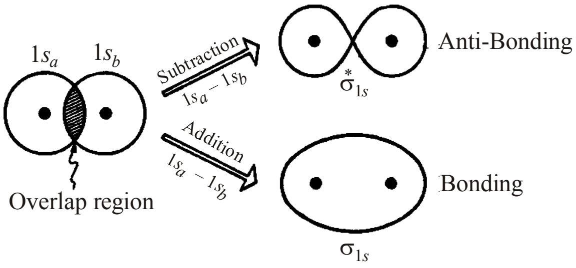


Fig. Formation of bonding and antibonding σ-molecular orbitals

(i) End-on overlapping of p-orbitals: When p_x orbitals of two atoms combine linearly with each other with the assumption that the internuclear axis is x-axis, it results in the formation of a σ bond.

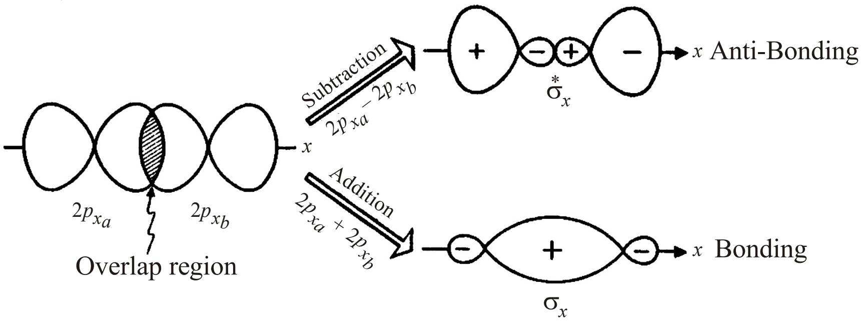


Fig. Formation of σ bonding by overlap of p_x orbitals.

(ii) Sidewise overlap of p -orbital: Molecular orbitals formed by the lateral or sidewise overlap of either two $2p_z$ orbitals are designated as π-molecular orbitals.

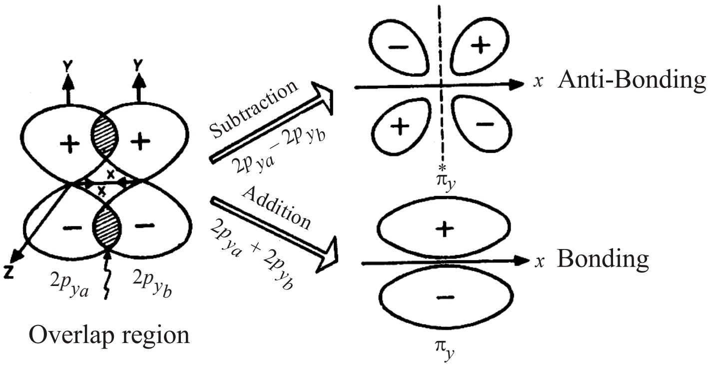


Fig. Overlap of $2p_y$ atomic orbitals.

The +ve sign in orbitals represents that the probability of elecron is maximum in that lobe while the –ve sign corresponds to minimum probability of elecron in that lobe.

Bonding molecular orbital is formed when both lobes rich of electrons, overlap each other, while antibonding molecular orbital is the outcome when one lobe rich in electrons overlaps the lobe deficient in electrons.

Relative Energies of M.O.'s and Filling of e^-s

(a) Two general criteria, which determine the energy of the molecular orbitals are

  (i) Initial energy of the atomic orbitals

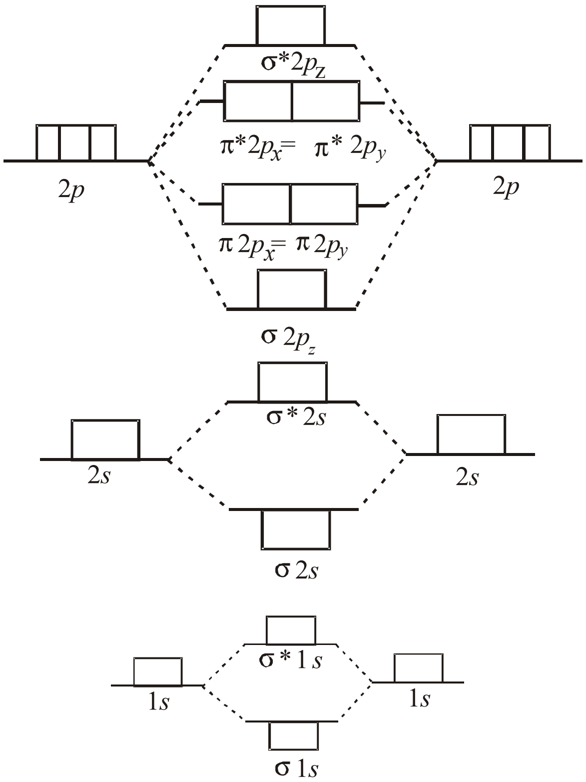
  (ii) The extent of overlap of the atomic orbitals.

(b) It is obvious that molecular orbitals, formed from lower energy atomic orbitals, have lower energy than the molecular orbitals formed from higher energy atomic orbitals.

(c) The sequence or order of increasing energy is given below : (for O_2 and F_2)

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

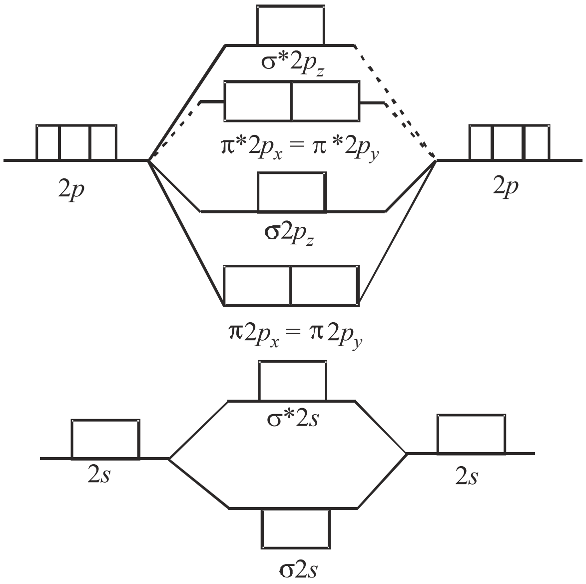
(d) Energy level diagram is shown below :



(e) It has been found experimentally that in some of the diatomic molecules like Li_2, Be_2, B_2, C_2, N_2 etc. $\sigma 2p_z$ M.O. is higher in energy than $\pi 2p_y$ and $\pi 2p_x$ M.O's. Therefore, the order of increasing energy of these M.O's is :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

The new energy level diagram is shown below :



M.O. energy level diagram for Li_2, Be_2, C_2 and N_2 molecules.

(f) The main difference between the two types of sequences in energy level is that for molecules O_2, F_2, the $\sigma 2p_z$ M.O.is lower in energy than $\pi 2p_x$ and $\pi 2p_y$.

(g) The filling of electrons in various M.O. follows rules similar to those for filling A.O.

Stability of Molecules in Terms of Bond Order

(a) The relative stability of molecule is further evaluated by a parameter known as bond order.

(b) Stability of molecule $\propto$ bond order.

(c) Bond order can be defined as the number of covalent bonds formed between two atoms in molecule.

(d) Bond order = 1/2 [No. of electrons in bonding orbitals – No. of electrons in antibonding orbitals]
$= 1/2\,[N_b - N_a]$

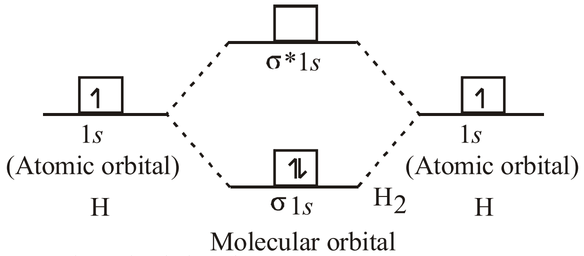
(e) The bond order of 1, 2 and 3 corresponds to single, double and triple bonds respectively. It may be mentioned that according to M.O. theory, even a fractional bond order is possible.

Magnetic Property

If all the electrons in a molecule are paired, then substance is diamagnetic. On the other hand, if there are unpaired electrons in the molecule the substance is paramagnetic. More the number of unpaired electrons in the molecule, greater is the paramagnetism of the substance.

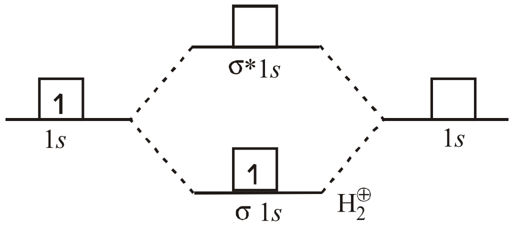
Bonding in Few Molecules/Ions

(i) Hydrogen molecule (H_2) : Having two H atoms with one electron each ($1s^1$)
M.O. configuration of $H_2 = (\sigma\,1s)^2\,(\sigma^*\,1s)^0$



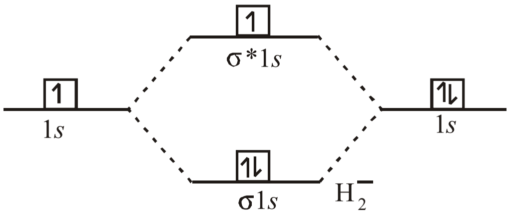
Bond order = $\frac{1}{2}[N_b - N_a] = \frac{1}{2}[2-0] = 1$ i.e., single bond.
Having paired electrons, so diamagnetic.
Stability → quite stable (having single bond)

(ii) H_2^+ ion :



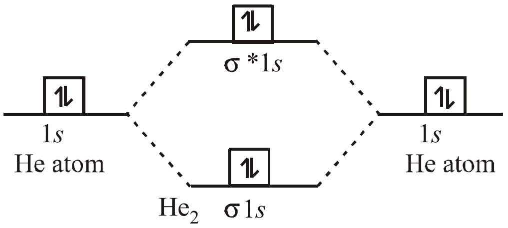
Configuration of $H_2^+ = (\sigma\,1s)^1\,(\sigma^*1s)^0$
One electron in bonding molecular orbital.
Paramagnetic, Bond order = $\frac{1}{2}[1-0] = \frac{1}{2}$
Less stable than H_2 molecule

(iii) H_2^- anion :



M.O. configuration – $(\sigma\,1s)^2\,(\sigma^*1s)^1$
Paramagnetic, Bond order = $\frac{1}{2}[2-1] = \frac{1}{2}$
Stability is equal to $[H_2^+]$

(iv) Helium molecule (He_2) :



M.O. configuration – $(\sigma 1s)^2\,(\sigma^*1s)^2$
Diamagnetic, Bond order = $\frac{1}{2}[2-2] = 0$ (zero)
Bond order zero indicates no linkage between two He atoms.

Hence He_2 molecule does not exist.

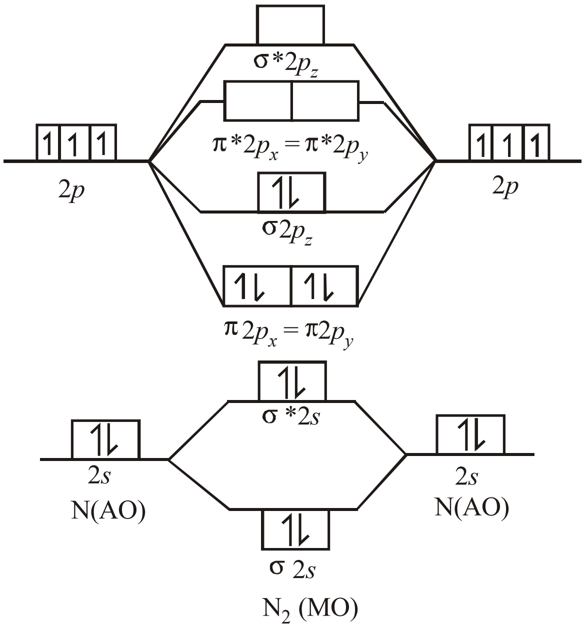
(v) He_2^+ ion :

M.O configuration – $(\sigma 1s)^2(\sigma^* 1s)^1$

Paramagnetic, Bond order = $\frac{1}{2}[2-1]=\frac{1}{2}$

As the bond order is positive, this ion is formed.

(vi) Nitrogen Molecule (N_2) :



M.O. Energy level diagram for N_2 molecule

M.O. configuration = $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

Diamagnetic, Bond order = $\frac{1}{2}[10-4]=3$

N_2 molcule has three bonds, one sigma and two pi bonds.

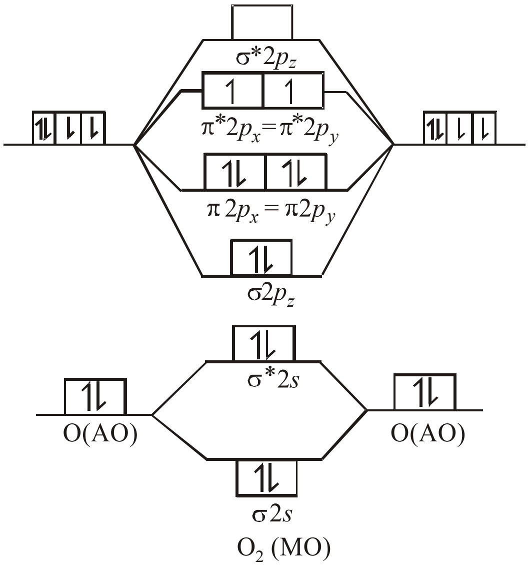
(vii) Nitrogen molecule cation(N_2^+) :

M.O. configuration = $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^1$

Paramagnetic, Bond order = $\frac{1}{2}[9-4]=2.5$

Since bond order of N_2^+ is smaller than bond order of N_2, therefore, it will have larger bond length.

(viii) Oxygen molecule (O_2) :



M.O. Energy level diagram for O_2 molecule

M.O. configuration = KK $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^1(\pi^*2p_y)^1$

Paramagnetic, Bond order = $\frac{1}{2}[8-4]=2$

In oxygen molecule, atoms are held by double bond.

(ix) O_2^+(Oxygen molecule cation) :

M.O. configuration = KK $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^1$

Bond order = $\frac{1}{2}[8-3]=2.5$

Since bond order of O_2^+ is greater than the bond order of O_2, therefore it will have smaller bond length.

(x) O_2^- (Oxygen molecule anion) :

M.O. configuration = KK $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^1$

Paramagnetic, Bond order = $\frac{1}{2}[8-5]=1.5$

Since bond order of O_2^- is smaller than bond order of O_2 therefore it will have larger bond length.

Stability of molecules: *Stability of molecules in directly proportional to bond order.*

$$\text{Stability} \propto \text{Bond order of molecule}$$

Higher the bond order of the molecule more will be the stability of molecule. When bond order is observed to be zero, the molecule does not exist at all.

HYDROGEN BONDING

It is an electrostatic force of attraction between covalently bonded hydrogen atom of one molecule and highly electronegative atom (F, O or N) of other molecule. It is not formed in ionic compounds. H–bond forms in polar covalent compounds, (not in non–polar). It is very weak bond (strength 2–10kcal/mol.) but is stronger than van der Waal's force. It is a special case of dipole–dipole attraction.

$H^{\delta+}-F^{\delta-} .... H^{\delta+}-F^{\delta-} .... H^{\delta+}—F^{\delta-}$

Conditions for Hydrogen Bonding

(a) The molecule must possess a high electronegative atom bonded to hydrogen atom. The greater is the electronegativity difference, more is the polarisation of the bond of the molecule.

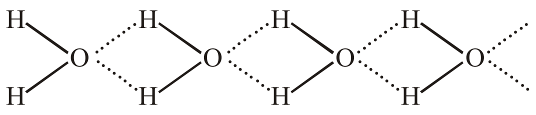
(b) The size of the electronegative atom should be small. Smaller the size of electronegative atom more is the electronegative attraction. These conditions are met only by F, O and N atom and thus only these atoms form effective hydrogen bonding.

Types of Hydrogen Bonding

(i) Intermolecular H–bond : H–bond formation between two or more molecules of either the same or different compounds known as Intermolecular H–bonding. These are of two types :

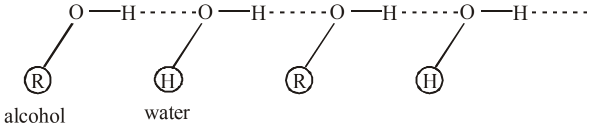
(a) Homo intermolecular : H–bond between molecules of same compounds

Example: H—F........H—F........H—F



(b) Hetero intermolecular : H–bond between molecules of different compounds

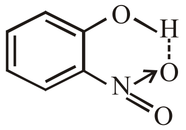
Example : Solution of Alcohol and water.

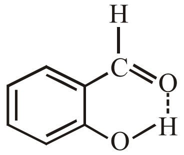


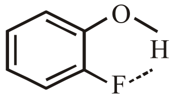
(ii) Intramolecular H–bond :– It takes place within the molecule.

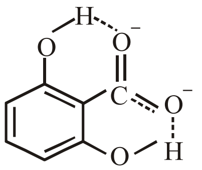
H–atom bonded with electronegative element of a functional group forms H–bond with another electronegative element present on nearest position of the same molecule. This type of H–bond mostly occurs in organic compounds. It results in ring formation (Chelation).

Example:


o-nitrophenol


Salicylaldehyde


o-fluorophenol


2-6 Dihydroxy benzoate

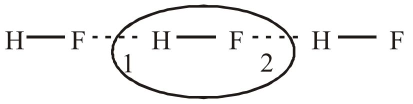
Effects of H-bond on Physical Properties

(i) Physical states :

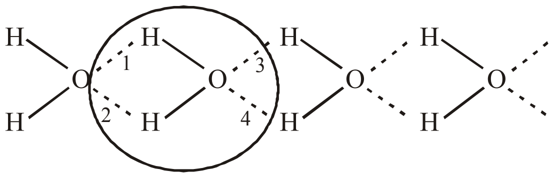
(a) H_2O is a liquid while H_2S is a gas. This is because of H-bonding in H_2O which is missing in H_2S.

(b) For water and Ice : Both have H–bonding even then density of ice is less than water. This is because for the same mass, volume of ice is more as compared to volume of water because of open cage crystal structure of ice.

(c) HF is liquid as it can form only two H–bonds.



On the other hand, H_2O becomes solid due to four hydrogen bonds among water molecules, formed in a tetrahedral manner.



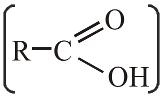
(ii) Melting point and boiling point

Due to intermolecular H-bonding, M.P. & B.P. of compounds increases. For example

(a) $H_2O > CH_3OH > CH_3–O–CH_3$

(b) Trihydric alcohol > dihydric alcohol > Monohydric alcohol

(c) Monocarboxylic acid

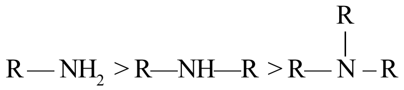


$$\left[R-C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix}\right]$$

form stronger H-bond than alcohol of comparable molecular weight. Therefore B.P. of carboxylic acid is higher than corresponding alcohol.

(d) Decreasing order of M.P. & B.P. in case of amines

1° – amine > 2° amine > 3° – amine



$$R — NH_2 > R—NH—R > R—\overset{\overset{R}{|}}{N}–R$$

(no hydrogen with nitrogen atom)

(e) Boiling points of group 15, 16 and 17 hydrides decreases on decreasing molecular weight.

	group 15	group 16	group 17
Molecular wt.	NH_3	H_2O	HF
decreases	PH_3	H_2S	HCl
Boiling points	AsH_3	SeH_2	HBr
also decreases	SbH_3	TeH_2	HI

Correct order is :

$PH_3 < AsH_3 < SbH_3 < NH_3$

$H_2S < SeH_2 < TeH_2 < H_2O$

$HI < HBr < HCl < HF$

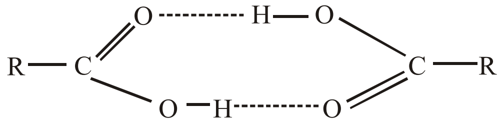
The increase in boiling point of NH_3, H_2O and HF is due to H–bonding.

$H_2O > HF > NH_3$

$PH_3 < H_2S < HCl$

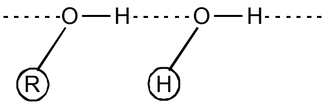
Intramolecular H–bonding gives rise to ring formation, so the force of attraction among these molecule are van der Waal's forces. So there M.P. and B.P. are low .

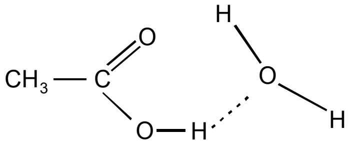
(iii) Molecular weight : Increases due to H–bonding For example : Molecular wt. of CH_3COOH is double to its molecular formula, due to dimer formation caused by H–bonding.



(iv) Solubility :

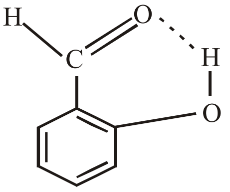
(a) Intermolecular H-bonding : Few organic compounds (Non–polar) are soluble in water (Polar solvent) due to H–bonding.


Alcohol Water


Acetic acid Water

Other examples : Glucose, Fructose etc. dissolve in water. Ketone, ether, alkane etc. are insoluble (no H–bonding). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H–bonding interupts. Order of solubility for amines : Primary amine > Secondary amine > Tertiary amine

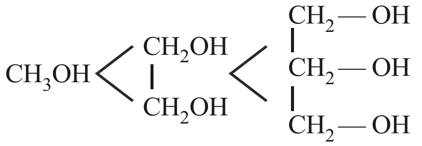
(b) Intramolecular H–bonding : It decreases solubility as it forms chelate by H–bonding, so H–atom is not free for other molecule. It cannot form H–bond with water molecule so cannot dissolve in water.



(Salicylaldehyde), *o*-Hydroxy benzaldehyde

(v) Viscosity and Surface tension – H–bond associates molecules together so viscosity and surface tension increases.

Order of viscosity and surface tension of some molecules :

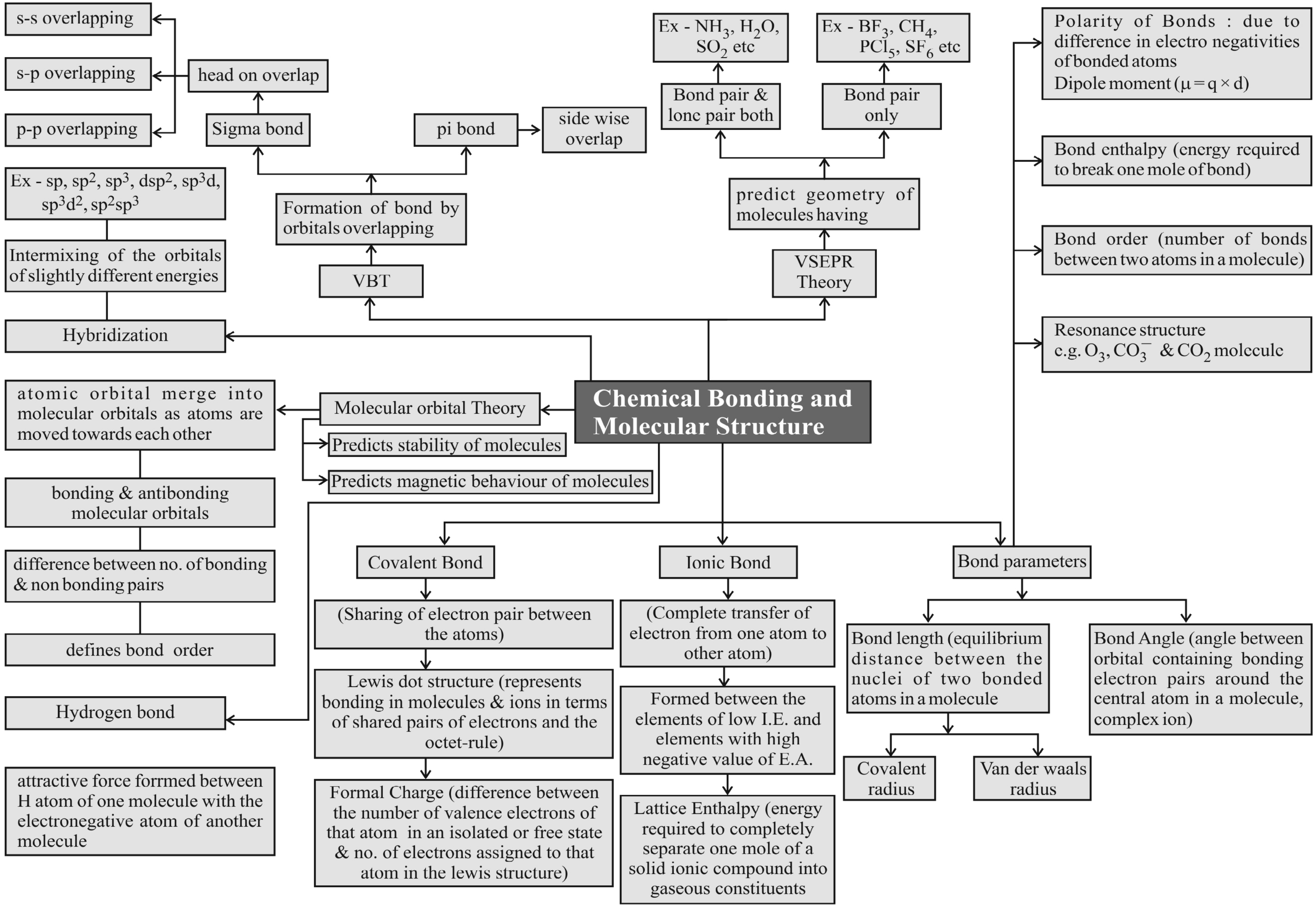


$$CH_3OH < \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} < \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \\ | \\ CH_2-OH \end{matrix}$$

H_2O	>	CH_3OH	>	$CH_3—O—CH_3$
water		alcohol		ether

(vi) Acidic and basic strength : CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ form H–bonds with water. So less hydrolysis occurs. i.e., it gives less OH^- ions. On the other hand, $(CH_3)_4N^+OH^-$ (ammonium compound) will give OH^- ion in large amount due to no H–bonding.

CONCEPT MAP


Chemical Bonding and Molecular Structure
VBT
Formation of bond by orbitals overlapping
Sigma bond
head on overlap
s-s overlapping
s-p overlapping
p-p overlapping
pi bond
side wise overlap
VSEPR Theory
predict geometry of molecules having
Bond pair & lone pair both
Ex - NH_3, H_2O, SO_2 etc
Bond pair only
Ex - BF_3, CH_4, PCl_5, SF_6 etc
Hybridization
Intermixing of the orbitals of slightly different energies
Ex - sp, sp^2, sp^3, dsp^2, sp^3d, sp^3d^2, sp^2sp^3
Molecular orbital Theory
atomic orbital merge into molecular orbitals as atoms are moved towards each other
bonding & antibonding molecular orbitals
difference between no. of bonding & non bonding pairs
defines bond order
Predicts stability of molecules
Predicts magnetic behaviour of molecules
Hydrogen bond
attractive force forrmed between H atom of one molecule with the electronegative atom of another molecule
Covalent Bond
(Sharing of electron pair between the atoms)
Lewis dot structure (represents bonding in molecules & ions in terms of shared pairs of electrons and the octet-rule)
Formal Charge (difference between the number of valence electrons of that atom in an isolated or free state & no. of electrons assigned to that atom in the lewis structure)
Ionic Bond
(Complete transfer of electron from one atom to other atom)
Formed between the elements of low I.E. and elements with high negative value of E.A.
Lattice Enthalpy (energy required to completely separate one mole of a solid ionic compound into gaseous constituents
Bond parameters
Polarity of Bonds : due to difference in electro negativities of bonded atoms
Dipole moment ($\mu = q \times d$)
Bond enthalpy (energy required to break one mole of bond)
Bond order (number of bonds between two atoms in a molecule)
Resonance structure
e.g. O_3, CO_3^- & CO_2 molecule
Bond length (equilibrium distance between the nuclei of two bonded atoms in a molecule
Covalent radius
Van der waals radius
Bond Angle (angle between orbital containing bonding electron pairs around the central atom in a molecule, complex ion)

Textbook Exercises

4.1 Explain the formation of a chemical bond.

Ans. The atoms of different elements combine with each other in order to complete their respective octets or duplet to attain nearest noble gas configuration.

4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

Ans. $_{12}Mg = 2, 8\ 2 \therefore$ Lewis symbol $= Mg:$

$_{11}Na = 2, 8, 1 \therefore$ Lewis symbol $= \dot{N}a$

$_{2}B = 2, 3 \therefore$ Lewis symbol $= .\dot{B}.$

$_{8}O = 2, 6 \therefore$ Lewis symbol $= :\ddot{O}:$

$_{7}N = 2, 5 \therefore$ Lewis symbol $= :\underset{\cdot}{\dot{N}}\cdot$

$_{35}Br = 2,8,18,7 \therefore$ Lewis symbol $= :\underset{\cdot\cdot}{\ddot{Br}}.$

4.3 Write Lewis symbols for the following atoms and ions : S and S^{2-} : Al and Al^{3+} ; H and H^-.

Ans. $_{10}S = 2, 8, 6 \therefore$ Lewis symbol $= :\ddot{S}:$,

S^{2-} ion $= \left[:\underset{\cdot\cdot}{\ddot{S}}:\right]^{2-}$

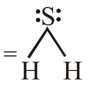
$_{13}A\ell = 2,8,3$

$\therefore$ Lewis symbol $= \cdot\dot{A}\ell\cdot$, $A\ell^{3+}$ ions $= [A\ell]^{3+}$

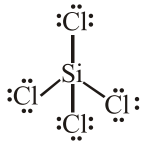
$_{1}H = 1 \therefore$ Lewis symbol = H; H^- ions $= \dot{H}.$

4.4 Draw the Lewis structures for the following molecules and ions : H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

Ans. (i) $H_2S =$

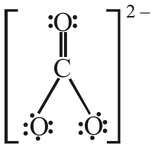


(ii) $SiCl_4 =$

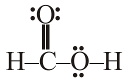


(iii) $BeF_2 = :\ddot{\underset{\cdot\cdot}{F}}–Be–\ddot{\underset{\cdot\cdot}{F}}:$

(iv) $CO_3^{2-} =$



(v) HCOOH =



$H–\overset{\overset{:O:}{\|}}{C}–\ddot{\underset{\cdot\cdot}{O}}–H$

4.5 Define octet rule. Write its significance and limitations.

Ans. Octet Rule: Elements combine with each other in order to complete their respective octets i.e. , 8 electrons in their outermost shell.

Significance of octet rule: It helps to explain why different atoms combine with each other to form ionic compounds or covalent compounds.

Limitations of octet rule: The octet rule fails to explain

(i) the formation of molecules in which the central atom has less than eight electrons in the valence shell such as $BeCl_2$, BF_3, etc.

(ii) the formation of molecules in which the central atom has more than eight electrons in the valence shell such as PF_5 , SF_6, etc.

(iii) the formation of compounds of noble gases especially xenon and krypton such as XeF_2, XeF_6, etc.

(iv) odd electron molecules like NO, NO_2.

4.6 Write the favourable factors for the formation of ionic bond.

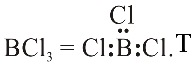
Ans. (i) Low ionization enthalpy of the metal atom.

(ii) High electron gain enthalpy of the non–metal atom.

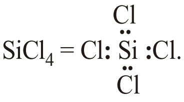
(iii) High lattice enthalpy of the compound formed.

4.7 Discuss the shape of the following molecules using the VSEPR model: $BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

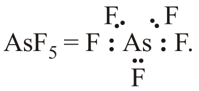
Ans. (i) $BeCl_2$ = Cl:Be :Cl. The central atom has only two bond pairs and no lone pair. Hence linear.

(ii) 

$BCl_3 = Cl:\overset{Cl}{\ddot{B}}:Cl.$ The central atom has only 3 bond pairs and no lone pair. Hence triangular planar

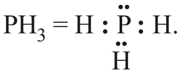
(iii) 

$SiCl_4 = Cl:\overset{Cl}{\underset{Cl}{\ddot{Si}}}:Cl.$ Bond pairs = 4, lone pair = 0. Shape = Tetrahedral

(iv) 

$AsF_5 = F:\overset{F\ \ F}{\underset{F}{As}}:F.$ Bond pairs = 5, lone pair = 0. Shape = Trigonal bipyamidal

(v) $H_2S = H:\underset{\cdot\cdot}{\ddot{S}}:H.$ Bond pairs = 2, lone pairs = 2. Shape = Bent/V– shaped

(vi) 

$PH_3 = H:\underset{H}{\ddot{P}}:H.$ Bond pairs = 3, lone pair = 1. Shape = Trigonal pyramidal

4.8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

Ans. In NH_3, there is only one lone pair on N–atom to repel the bond pairs whereas in H_2O, there are two lone pairs on O–atom to repel the bond pairs. Hence, the repulsions on bond pairs are greater in H_2O than in NH_3 and hence the bond angle is less.

4.9 How do you express the bond strength in terms of bond order?

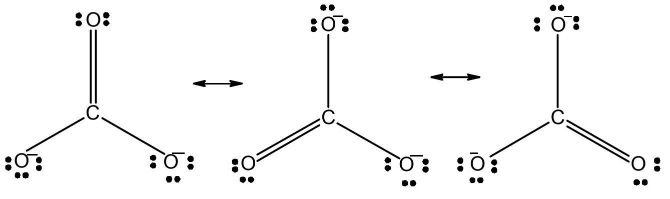
Ans. Greater the bond order, is stronger the bond.

4.10 Define the bond length.

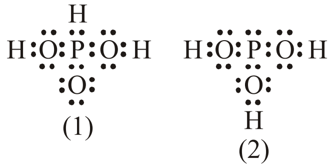
Ans. The equilibrium distance between the centers of nuclei of the two bonded atoms is called its bond length.

4.11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

Ans. CO_3^{-2} has resonance in its structure due to which the bond lengths between C–O are equal.



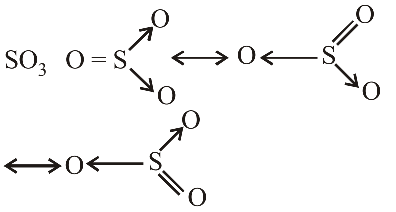
4.12 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same



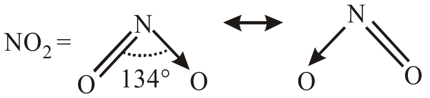
Ans. No, these cannot be taken as canonical forms because the positions of atoms have changed.

4.13 Write the resonance structures for SO_3, NO_2 and NO_3^-.

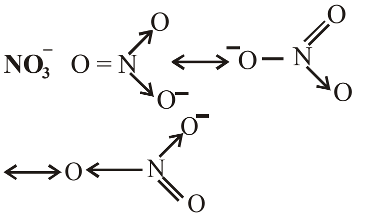
Ans. (i)



(ii)

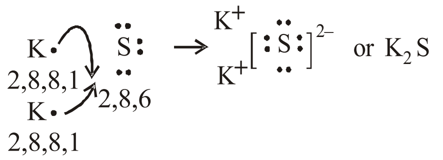


(iii)

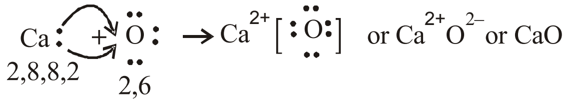


4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions: (a) K and S (b) Ca and O (c) Al and N.

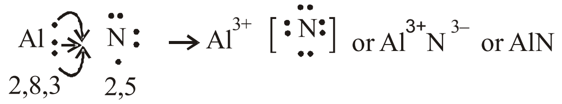
Ans. (a)



(b)



(c)



4.15 Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

Ans. The dipole moment studies show that net dipole moment of CO_2 molecule is zero. This is possible only if CO_2 is a linear molecule ((O = C = O)) so that dipole moments of C–O are equal and opposite and hence cancel out. On the other hand, H_2O molecule is found to have a net dipole moment (1.84 D) though it contains 2 O–H bonds. This shows that it is a bent molecule.

4.16 Write the significance/applications of dipole moment.

Ans. Applications of dipole moment are : (a) in determining polarity of bonds (b) in calculation of percentage ionic character (c) to distinguish between cis and trans isomers (d) to distinguish between ortho, meta and para isomers.

4.17 Define electronegativity. How does it differ from electron gain enthalpy?

Ans. Electronegativity of an element is the tendency of its atom to attract the shared pair of electrons towards itself in a covalent bond.

Electronegativity denotes the relative attraction of covalently bonded atoms for the bonding electron pairs while electron affinity is the energy released when an electron is added to a gaseous atom or ion to form a gaseous ion. Electronegativity is applicable to a compound whereas electron gain enthalpy is applicable to an isolated gaseous atom.

4.18 Explain with the help of suitable example polar covalent bond.

Ans. When two dissimilar atoms having different electronegativities combine together to form a covalent bond, the shared pair of electrons does not lie at equal distances from the nuclei of both the bonded atoms but shifts towards the atom having greater electronegativity. Since the more electronegative atom attracts the electrons more strongly, the distribution of electrons gets distorted. As a result, one end of the molecule, having more electronegative atom becomes slightly negatively charged while the other acquires slightly positive charge. Thus, positive and negative poles are developed and this type of bond is called polar covalent bond.

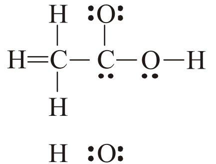
For example in HCl, chlorine being more electronegative than hydrogen will pull bonding electrons towards itself and develop a negative charge while hydrogen will have a partial positive charge.

$$\mathrm{H} \rightarrow\!\!\rightarrow\!\!- \mathrm{Cl} \Rightarrow \overset{\delta^+}{\mathrm{H}}-\overset{\delta^-}{\mathrm{Cl}}-$$

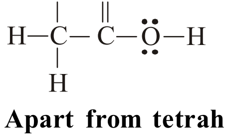
4.19 Arrange the bonds in order of increasing ionic character in the molecules : LiF, K_2O, N_2, SO_2 and ClF_3

Ans. $N_2 < SO_2 < ClF_3 < K_2O < LiF$

4.20 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



Ans.



4.21 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar?

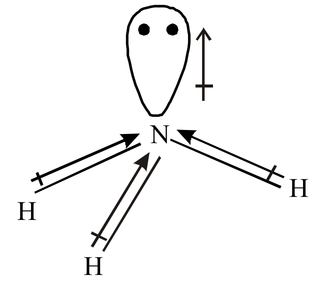
Ans. Electronic configuration of C–atom is $1s^2\ 2s^2 2p_x^1\ 2p_y^1$ Hence, it undergoes sp^3 hybridisation which gives a tetrahedral shape. For square planar, the hybridisation required is dsp^2 which is not possible for C–atom in CH_4

4.22 Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar?

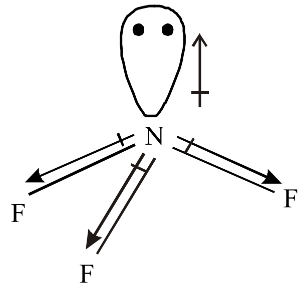
Ans. This is because BeH_2 molecule is linear (H–Be–H) so that the two Be–H bond moments are equal and opposite and hence cancel out.

4.23 Which out of NH_3 and NF_3 has higher dipole moment and why?

Ans.



Resultant of 3N—H bonds



Resultant of 3N—F bonds

NH_3 has higher dipole moment than NF_3. This is explained on the basis of the following two reasons.

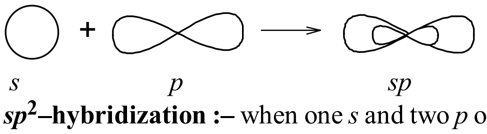
(1) The dipole formed between the lone pair and N atom has to be taken into consideration which is in the direction of the lone pair.

(2) F is more electronegative than N, therefore direction of bond is from N to F whereas N is more electronegative than H, the direction of the bond is from H to N .Thus (see diag.) resultant moment of N – H bonds add up to the bond moment of lone pair, whereas that of 3 N–F bonds partly cancels the resultant moment of lone pair. Hence, the net dipole moment of NF_3 is less than that of NH_3.

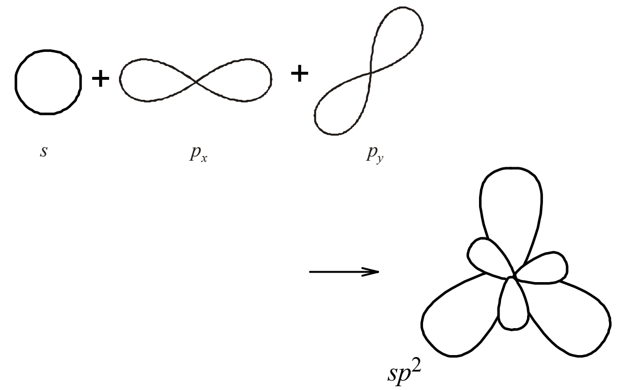
4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of *sp*, sp^2 and sp^3 hybrid orbitals?

Ans. Hybridization is defined as the mixing of the atomic orbitals belonging to the same atom but having slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbitals..

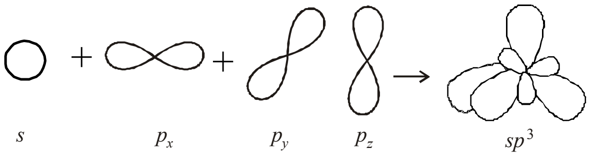
***sp*– hybridization :–** when one s and one p orbital belonging to the same main shell of an atom mix together to form two new equivalent orbitals type of hybridisation is called sp hybridisation.



sp^2–hybridization :– when one *s* and two *p* orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridization is called sp^2 hybrid orbitals.



sp^3–hybridization :– when one *s* and three *p* orbitals of the same shell of an atom mix to form four new equivalent orbitals, the type of hybridization is called sp^3 hybrid orbitals.



4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction :

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

Ans. E.C. of $_{13}Al = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$(Ground state) or $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^{\ 1}\ \ 3p_y^{\ 1}$ (Excited state). Hence, it undergoes, sp^2 hybridization to give it planar triangular structure. To form $AlCl_4^{-1}$, the empty $3p_z$ orbital is also involved so that hybridization is sp^3 and the shape is tetrahedral.

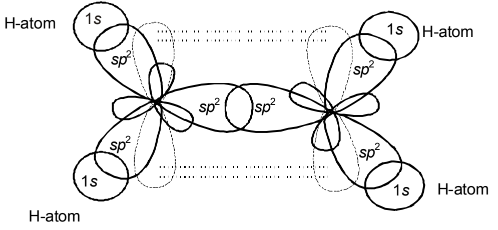
4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction?

$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$

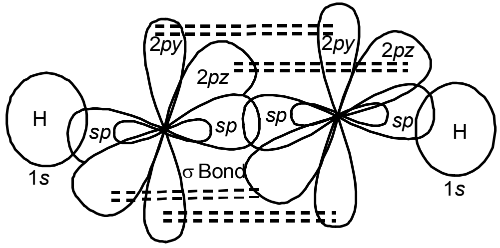
Ans. In BF_3, B is sp^2 hybridized and in NH_3, N is sp^3 hybridized. After the reaction, hybridization of B changes to sp^3 but that of N remains unchanged.

4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

Ans. C_2H_4: —

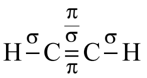


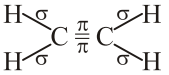
C_2H_2: —



4.28 What is the total number of sigma and pi bonds in the following molecules ?

(a) C_2H_2 **(b)** C_2H_4

Ans. (a) 
$\mathrm{H\overset{\sigma}{-}C\overset{\pi}{\underset{\pi}{\overset{\sigma}{\equiv}}}C\overset{\sigma}{-}H}$ (3σ, 2π)

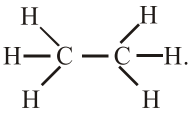
(b) 
(5σ, 1π)

4.29 Considering x–axis as the internuclear axis which out of the following will not form a sigma bond and why ? (a) 1s and 1s (b) 1s and 2p_x (c) 2p_y and 2p_y (d) 1s and 2s.

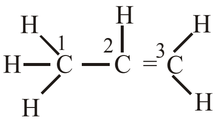
Ans. Only (c) will not form a σ–bond because taking y–axis as the intermolecular axis, there will be lateral (sideway) overlap between the two 2p_y orbitals forming a π bond.

4.30 Which hybrid orbitals are used by carbon atoms in the following molecules ?

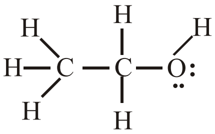
(a) CH_3–CH_3 (b) CH_3–$CH=CH_2$
(c) CH_3–CH_2–OH (d) CH_3–CHO
(e) CH_3COOH.

Ans. (a) 

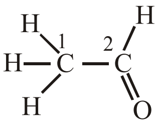
Both C—atoms use sp^3 hybrid orbitals.

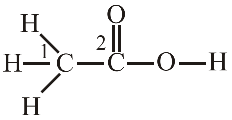
(b) 
,$C_1 = sp^3, C_2 = sp^2$,

$C_3, = sp^2$

(c) 

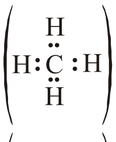
Both C–atoms use sp^3 hybrid orbitals.

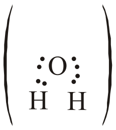
(d) 
. $C_1 = sp^3$, $C_2 = sp^2$

(e) 
. $C_1 = sp^3$, $C_2 = sp^2$

4.31 What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one example of each type?

Ans. Covalent bonds are formed by mutual sharing of electrons between the two atoms. The shared pairs of electrons thus present between the bonded atoms are called bond pairs. All the electrons of an atom may not participate in the bonding. The electron pairs present on the atoms which do not take part in bonding are called lone pairs of electrons. For example, in

CH_4 , there are only 4 bond pairs but in

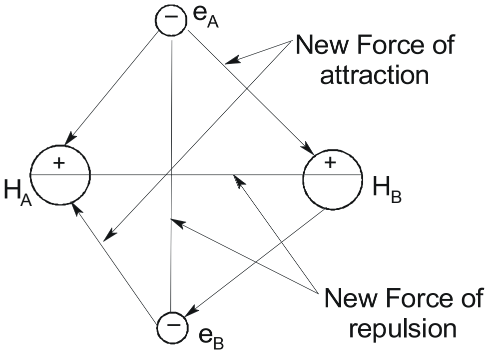
H_2O , there are two bond pairs and two lone pairs.

4.32 Distinguish between a sigma and a pi bond.

Ans.

Sigma bond	Pi bond
1. It is formed by overlap of orbitals along internuclear axis.	1. It is formed by sideways overlapping of orbitals.
2. It is formed by overlapping of s-s orbital, s-p orbital and p-p orbital.	2. It is formed by overlap of p-p and p-d orbitals.
3. The electron cloud of a sigma bond is symmetrical about the internuclear axis and the overlapping is quite large, thus sigma bonds are strong.	3. As the electron clouds overlap above and below the plane of internuclear axis, the overlapping is small, thus pi bonds are weak.
4. Free rotation about a sigma bond is possible.	4. Free rotation about a pi bond is not possible, since on rotating the overlapping vanishes and the bond breaks.
5. Bond length is longer.	5. Bond length is shorter.
6. No preset conditions are required for the formation of bond.	6. Pi bonds are always formed after sigma bonds have formed.

4.33 Explain the formation of H_2 molecule on the basis of valence bond theory.

Ans. 

Consider two hydrogen atoms A and B with electron e_A and e_B respectively. H_A represents the nucleus of hydrogen atom 'A' and H_B for hydrogen atom 'B'. When the two hydrogen atoms approach each other, the following two forces come into existence:

(a) Attractive forces between (i) electron e_A and nucleus H_B (ii) electron e_B and nucleus H_A.

(b) Repulsive forces between (i) electron e_A and electron e_B (ii) nucleus H_A and nucleus H_B.

The attractive forces tend to bring the atom close to each other, whereas repulsive forces tend to push them apart. Since the magnitude of attractive forces is greater than the repulsive forces, as a result, the energy of the system decreases and a molecule of hydrogen is formed.

4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

Ans. The main points are

(i) When two atomic orbitals combine they loose their original identity and form new orbitals which are termed as molecular orbitals.

(ii) Only those atomic orbitals combine to form molecular orbitals which have comparable energies and proper orientation. For example 1s would only combine with 1s and not with 2s. $2p_x$ would only combine with $2p_x$ of other atom and so on.

(iii) The number of molecular orbitals formed is equal to the number of atomic orbitals which combine with one another.

(iv) The two atomic orbitals combine to give bonding molecular orbital and anti–bonding molecular orbital. The bonding molecular orbital has lower energy than anti–bonding molecular orbital and hence greater stability than the other.

(v) The filling up of molecular orbitals takes place according to the same rules as those of atomic orbitals.

4.35 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

Ans. E.C. of $_4Be = 1s^2\,2s^2$

M.O. E.C. of $Be_2 = \sigma_{1s}^2\,\sigma^{*2}_{1s}\,\sigma_{2s}^2\,\sigma^{*2}_{2s}$

$\therefore$ Bond order $= \frac{1}{2}(4-4) = 0$.

Hence, Be_2 does not exist.

4.36 Compare the relative stability of the following species and indicate their magnetic properties:

O_2, O_2^+, O_2^- (superoxide), O_2^{2-} (peroxide)

Ans. The electronic configuration of

$O_2 = KK[\sigma(2s)]^2\,[\sigma^*(2s)]^2\,[\sigma(2p_z)]^2[\pi(2p_y)]^2\,[\pi(2p_x)]^2\,[\pi^*(2p_y)]^1\,[\pi^*(2p_x)]^1$

The number of bonding electrons $(N_b) = 8$, number of anti–bonding electrons $(N_a) = 4$

Bond order $= \frac{N_b - N_a}{2} = 1/2\,(8-4) = 2$,

It is paramagnetic due to presence of 2 unpaired electrons in the $\pi^*(2p_y)$ and $\pi^*(2p_z)$.

The electronic configuration of

$O_2^+ = KK[\sigma(2s)]^2\,[\sigma^*(2s)]^2\,[\sigma(2p_z)]^2[\pi(2p_y)]^2\,[\pi(2p_x)]^2\,[\pi^*(2p_y)]^1$

The number of bonding electrons $(N_b) = 8$, number of anti–bonding electrons $(N_a) = 3$

Bond order $= \frac{N_b - N_a}{2} = 1/2\,(8-3) = 2\frac{1}{2}$,

It is paramagnetic due to presence of 1 unpaired electrons in the $\pi^*(2p_y)$.

The electronic configuration of O_2^{-1} (superoxide) $= KK[\sigma(2s)]^2\,[\sigma^*(2s)]^2\,[\sigma(2p_z)]^2[\pi(2p_y)]^2\,[\pi(2p_x)]^2\,[\pi^*(2p_y)]^2\,[\pi^*(2p_z)]^1$

The number of bonding electrons $(N_b) = 8$, number of anti–bonding electrons $(N_a) = 5$

Bond order $= \frac{N_b - N_a}{2} = 1/2\,(8-5) = 1\frac{1}{2}$,

It is paramagnetic due to presence of 1 unpaired electrons in the $\pi^*(2p_y)$.

The electronic configuration of O_2^{2-} (peroxide) $= KK[\sigma(2s)]^2\,[\sigma^*(2s)]^2\,[\sigma(2p_x)]^2[\pi(2p_y)]^2\,[\pi(2p_z)]^2\,[\pi^*(2p_y)]^2\,[\pi^*(2p_z)]^2$

The number of bonding electrons $(N_b) = 8$, number of anti-bonding electrons $(N_a) = 6$

Bond order $= \frac{N_b - N_a}{2} = 1/2\,(8-6) = 1$,

It is dia–magnetic due to presence of no unpaired electrons.

The relative stability would be $O_2^+ > O_2 > O_2^{-1} > O_2^{2-}$ since higher the bond order more is the stability.

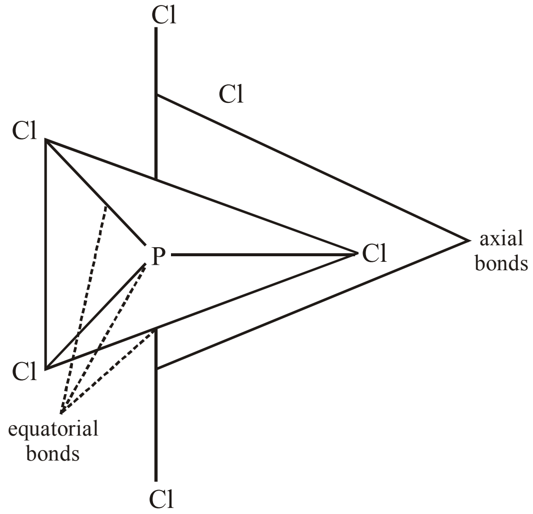
4.37 Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans. As orbitals are represented by wave functions, a plus sign in an orbital represents *a* +ve wave function and a minus sign represents *a* –ve wave function.

4.38 Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?

Ans. In PCl_5 the hybridization is sp^3d, thus it has a trigonal bi–pyramidal structure. This is because one of the 3*s* electron of '*p*' gets promoted to 3*d* orbital giving the electronic configuration $1s^22s^22p^63s^13p_x^13p_y^13p_z^13d^1$, thus it involves sp^3d hybridization.

The equatorial and the axial bond lengths in PCl_5 are different. The axial bond lengths are longer than the equatorial bond length. This is due to minimize bond–pair bond–pair repulsion for the large sized chlorine atoms.



4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces ?

Ans. **Hydrogen bond** – Whenever a molecule contains a hydrogen atom linked to a highly electron-egative atom (F,O,N) , this atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the other H–end becomes slightly positive. The negative end attracts the positive end as a result a weak bond is formed between them. This bond is called hydrogen bond.

...... $H^{\delta+} - X^{\delta-}$ ...... $H^{\delta+} - X^{\delta-}$ ...... $H^{\delta+} - X^{\delta-}$ ......

Hydrogen bond is stronger than the van der Waal's forces.

4.40 What is meant by the term bond order ? Calculate the bond order of: N_2, O_2, O_2^+ and O_2^- ?

Ans. Bond order is defined as half of the difference between the number of electrons present in the bonding and the anti–bonding orbitals i.e. B.O = 1/2 ($N_b - N_a$).

The electronic configuration of

$O_2 = KK[\sigma(2s)]^2 [\sigma^*(2s)]^2 [\sigma(2p_x)]^2 [\pi(2p_y)]^2 [\pi(2p_z)]^2 [\pi^*(2p_y)]^1 [\pi^*(2p_z)]^1$

The number of bonding electrons (N_b) = 8, number of anti–bonding electrons (N_a) = 4

$$\text{Bond order} = \frac{N_b - N_a}{2} = 1/2\,(8-4) = 2,$$

The electronic configuration of

$O_2^+ = KK[\sigma(2s)]^2 [\sigma^*(2s)]^2 [\sigma(2p_x)]^2 [\pi(2p_y)]^2 [\pi(2p_z)]^2 [\pi^*(2p_y)]^1$

The number of bonding electrons (N_b) = 8, number of anti–bonding electrons (N_a) = 3

$$\text{Bond order} = \frac{N_b - N_a}{2} = 1/2\,(8-3) = 2\frac{1}{2},$$

The electronic configuration of O_2^{-1} (superoxide) = $KK[\sigma(2s)]^2 [\sigma^*(2s)]^2 [\sigma(2p_x)]^2 [\pi(2p_y)]^2 [\pi(2p_z)]^2 [\pi^*(2p_y)]^2 [\pi^*(2p_z)]^1$

The number of bonding electrons (N_b) = 8, number of anti-bonding electrons (N_a) = 5

$$\text{Bond order} = \frac{N_b - N_a}{2} = 1/2\,(8-5) = 1\frac{1}{2},$$

The electronic configuration of $N_2 = KK[\sigma(2s)]^2 [\sigma^*(2s)]^2 [\sigma(2p_x)]^2 [\pi(2p_y)]^2 [\pi(2p_z)]^2$

The number of bonding electrons (N_b) = 8, number of anti-bonding electrons (N_{ab}) = 2

$$\text{Bond order} = \frac{N_b - N_a}{2} = 1/2\,(8-2) = 3,$$

The order of stability will be $N_2 > O_2^+ > O_2 > O_2^{-1}$.

Practice Questions

Very Short Answer Questions [1 Marks]

1. How is bond order related to the stability of a molecule?

2. Write the type of hybridisation involve in CH_4, C_2H_4 and C_2H_2.

3. Define covalent bond according to orbital concept?

4. Why ethyl alcohol is completely miscible with water?

5. Which is more polar–CO_2 or N_2O? Give reason.

6. State the types of hybrid orbitals associated with (i) P in PCl_5 and (ii) S in SF_6.

7. Out of bonding and antibonding molecular orbitals which one has lower energy and which one has higher stability?

8. Name the two conditions which must be satisfied for hydrogen bonding to take place in a molecule.

9. Why is solid NaCl non-conductor of electricity?

10. Why is NaCl harder than sodium metal?

11. The H—S—H bond angle in H_2S is 92.2° whereas the H—O—H bond angle in H_2O is 104.5°, why?

12. Define covalent bonds according to quantum theory of valence bond theory (modern concept).

13. Out of NaCl and MgO, which has higher value of lattice energy?

14. Explain why reactions involving covalent compounds are generally slow?

15. Define dipole moment. Is it scalar or vector quantity?

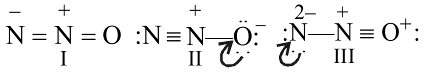
16. Why are dipole moments of CO_2, BF_3, CCl_4, PF_5, SF_6 zero?

17. Can a π-bond be formed in the absence of a sigma bond?

18. What types of hybridisation are involved with the central atom of a molecule having following shapes:

(i) planar, (ii) a regular tetrahedral, (iii) an equilateral triangle.

19. Which of the following structures contributes least towards resonance hybrid?



$\overset{-}{N} = \overset{+}{N} = O \quad :N \equiv \overset{+}{N} — \ddot{O}:^- \quad :\overset{2-}{N} — \overset{+}{N} \equiv O^+:$

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20. Give the structure of an anion which is isostructural with BF_3.

21. How would the bond lengths vary in dicarbon species C_2, C_2^-, C_2^{2-} ?

22. Which of the species have similar shape and why? NO_2^-, NO_2^+, CO_2, O_3.

23. Which one of the following species is not likely to exist? H_2^+, HeH, He_2

24. Write a neutral molecule which is isoelectronic with ClO^-.

25. Why are bond orders of He_2^+ and H_2^- identical?

26. How will you differentiate between the lone pair and a bond pair of electrons?

27. Define lattice enthalpy and how is it related to the stability of the ionic compound.

28. How are bond order and bond length related to each other?

29. Define Pauling electronegativity.

30. How does the concept of formal charge related to the stability of ion/molecule?

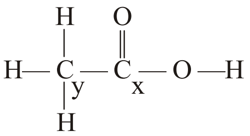
31. What is the decreasing order of repulsion of various electron pairs?

32. Which of the following molecules will have the same shape as SO_2?

$SnCl_2$, CO_2, BeH_2.

33. ClF_3 is T-shape molecule while NF_3 has a trigonal pyramidal shape. Explain.

34. State the hybridisation of the carbon labelled (x) and (y) in acetic acid.



$H—\underset{y}{\overset{H}{C}}—\underset{x}{\overset{O}{C}}—O—H$

35. Which out of the two molecules OCS and CS_2 has a higher dipole moment and why?

36. Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar?

37. Calculate the bonding and antibonding electrons in O_2^{2+} ion on the basis of molecular orbital theory.

38. Why are noble gases monoatomic?

39. How hybridization of 'C' atom changes when ethene is hydrogenated?

40. What is the decreasing order of electronegativi-ties of $C_{sp}3$, $C_{sp}2$ and C_{sp} atoms?

41. H_2S is a gas while H_2O is liquid. Explain

42. Explain BF_3 is planar while NH_3 is tetrahedral.

43. Which of the following has higher dipole moment $H_3C - CH_2 - CH = CH_2$(1–butene) or $H_3C - CH_2 - C \equiv CH$(1–butyne)?

44. Write the correct order of increasing bond length of C – O bond in CO, CO_3^{-2} and CO_2.

45. Which of the given species are isostructural species : – NO_3^{-1} , BF_3 , NH_4^+, $BeCl_2$?

46. How many sigma and pi bond are present in molecule of phenol?

47. How many valence electrons does oxygen atom has? Which electrons are they?

48. Draw Lewis dot structure for $MgCl_2$ and CH_4 .

49. Write Lewis formula for HCHO.

50. In writing Lewis dot structures of molecules, which atom is given central position?

51. What are the conditions of resonating structures?

52. Write two resonance structure of ozone which satisfy octet rule.

53. Which is more stronger and why σ or π bond ?

54. Benzene ring has alternate (C–C) single and double bonds, yet all C–C bonds are of equal length. Why?

55. Ice floats on water why?

56. How many σ and π bonds are present in the compound given below

$H_3C–CH = CH– C \equiv N$

57. Which has got more s–character ethane or acetylene?

58. What could be the nature of A – B bond, if the electronegativities of A, B are 3.5 and 2.5 respectively?

59. The dipole moment of hydrogen halides decreases from HF to HI. Explain this trend.

Short Answer Questions [2 & 3 Marks]

1. "A non-polar molecule can have highly polar bonds". Justify the statement.

2. Chlorine is non-polar while HCl is a polar molecule. Explain.

3. Ethane is stable while ethene is quite reactive, explain why?

4. Name the compounds in each of the following which shows hydrogen bonding:

(a) CH_3COOH and C_2H_6

(b) PH_3 and NH_3

(c) Ortho nitrophenol and meta nitrophenol.

(d) HF and HCl

(e) C_2H_5OH and CH_4

5. Covalent bonds possess some ionic character also, explain why?

6. An ionic bond is an extreme case of polar covalent bond. Justify.

7. Bond angle in NH_3 is more than that in case of PH_3 molecule. Explain.

8. Predict the dipole moment of

(i) A molecule AX_4 with tetrahedral geometry

(ii) A molecule AX_2 with linear geometry

(iii) A molecule AX_3 with distorted tetrahedral geometry.

9. In each of the following pairs, predict which has higher value of the property mentioned:

(i)	HF, HCl	Polar character
(ii)	KCl, KF	Lattice energy
(iii)	NH_3, NF_3	Dipole moment
(iv)	C_2H_6, C_2H_4	s-character in the hybrid orbital.

10. Electronic configurations of the five neutral atoms are given below:

A. $1s^2\,2s^2\,2p^6\,3s^2$. B. $1s^2\,2s^2\,2p^6\,3s^1$.

C. $1s^2\,2s^2\,2p^1$. D. $1s^2\,2s^2\,2p^3$.

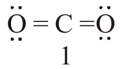
E. $1s^2\,2s^2\,2p^6$.

Write the empirical formula for the substances containing

(i) A and D (ii) B and D (iii) D and D (iv) E and E using proper symbols of the elements.

11. Write formal charges of the atoms in the nitrite ion.

12. Out of the following four resonance structures for the CO_2 molecule, which are important for describing the bonding in the molecule and why?



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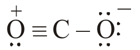

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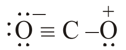

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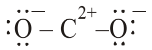

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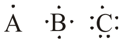
13. Three elements have the following Lewis symbols:



(a) Assign groups of the periodic table to these elements.

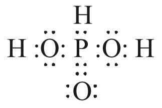
(b) Which elements are expected to form ions and what is the expected charge over these ions?

(c) Write the formulae and Lewis structures of the covalent compounds formed between

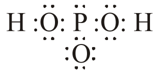
(i) A and B (ii) A and C

14. Distinguish between Atomic orbital and Molecular orbital.

15. H_3PO_3 can be represented by the structures (I) and (II) shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, cite reason for the same.



(I)



(II)

16. Write the electron-dot structures for

(i) CN^- (ii) SO_3^{2-} and (iii) ClO_2^-.

17. Predict the dipole moment of a molecule of the type

(i) AX_4 having a square planar geometry.

(ii) AX_5 having a square pyramidal shape.

(iii) AX_6 having an octahedral geometry.

18. Why is it that in the SF_4 molecule, the lone pair of electrons occupies an equitorial position in the overall trigonal bipyramidal arrangement in preference to the axial position?

19. Why are lone pair-lone pair repulsions stronger than lone pair-bond pair?

20. Explain the formation and difference between a sigma (σ) bond and a pi (π) bond.

21. Explain: $MgCl_2$ is linear while $SnCl_2$ is angular in shape.

22. What do you understand by co-ordinate covalent bond? Give one example.

23. How does the structure of PCl_5 is responsible for its high reactivity?

24. Give the shapes of bonding and antibonding MOs formed by combination of
(i) two *s*-orbitals
(ii) two *p*-orbitals (side to side)

25. Account for the following :
(i) N_2 has a higher bond dissociation energy than NO.
(ii) N_2 and CO both have the same bond order but CO is more reactive than N_2.

26. Arrange the following species in order of increasing stability:

$$Li_2, Li_2^+, Li_2^-$$

27. Account for the following :
(i) He_2 is not found to exist in nature
(ii) N_2^+ is not a diamagnetic substance
(iii) The dissociation energy of He_2^+ is almost the same as that of He_2^+.

28. Define Lattice energy. How is Lattice energy influenced by (i) Charge on the ions (ii) Size of the ions.

29. Explain the diamagnetic behaviour of F_2 molecular on the basis of molecular orbital theory.

30. Covalent bonds are called directional bonds while ionic bonds are called non–directional. Why?

31. Which is more covalent and why : $BeCl_2$ or $MgCl_2$?

32. Give hybridization and shape of
a) XeF_4 b) BrF_3 .

33. Calculate the percent ionic character of HCl. Given that the observed dipole moment is 1.03D and the bond length of HCl is 1.275 Å. Given $q = 4.8 \times 10^{-10}$ esu.

34. What are the conditions for writing the Lewis dot structures for molecules?

35. Use Lewis dot symbols to show electron transfer between the following atoms to form cations and anions:
(a) Na and Cl (b) Ca and O

36. Discuss the factors which favours the formation of ionic bond?

37. Why does Pauli's exclusion principle permit bonding only if the electrons are of different spins?

38. The dipole moment of HBr is 2.60×10^{-30} C.m, and the inter atomic spacing is 1.41 Å. What is the percent ionic character of HBr?

39. The dipole moments of SO_2 and CO_2 are 5.37×10^{-30}C.m and zero respectively. What can be said about the shapes of the two molecules?

40. Give hybridization and shape of the following molecules:
(a) SF_6 (b) CCl_4 (c) BF_3 (d) PCl_5

41. Arrange in order of increasing dipole moment: BF_3 , H_2S , H_2O.

42. Which elements are likely to form ionic bond and why?

43. What do you mean by resonance?

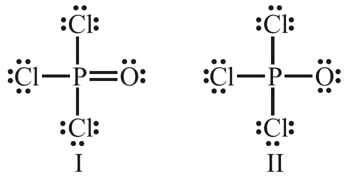
44. Define a single covalent bond and double covalent bond.

Long Answer Questions [5 Marks]

1. Give difference between Bonding Molecular orbital and Anti–bonding molecular orbital.

2. What are the characteristics of resonance?

3. Determine the formal charges on the atoms in the two structures shown below for the molecule $POCl_3$. Which of these two structures is the better structure (i.e., which is preferred)?



4. Select the best Lewis structure(s) for the sulphate ion, SO_4^{2-}.

5. State the hybridization and draw the molecular structure of the following
(a) PF_5 (b) I_3^- (c) NH_3 (d) XeO_3 (e) CH_4

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Why are reactions of ionic compounds very fast? **[HOTS]**

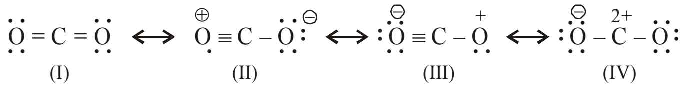
2. Is CaF_2 linear of bent or neither of the two? Justify **[HOTS]**

3. Explain why N2 has greater bond dissociation energy than N_2^+ whereas O_2^+ has greater bond dissociation energy than O_2.

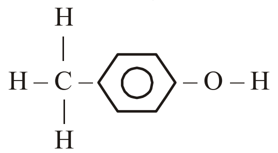
4. BH_4^- and NH_4^+ are isolobal. Explain **[HOTS]**
$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$

5. Account for the following :
The experimentally determined N—F bond length in NF_3 is greater than the sum of the single covalent radii of N and F. **[HOTS]**

6. Out of various resonating structures of CO2 shown below. Which one is wrong and why ? **[HOTS]**



7. Find out the number of σ–bonds and the number of lone pair of electron in the following molecule. **[HOTS]**



8. Write the Lewis structure of thiocyanate ion, NCS^-. **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. Explain why N_2 has greater bond dissociation energy than N_2^+ whereas O_2 has lesser bond dissociation energy than O_2^+. **[HOTS]**

2. The dipole moment of KCl is 3.336×10^{-29} cm which indicates that it is highly polar molecule. The inter-atomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. **[HOTS]**

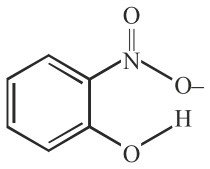
3. BeF_2 and H_2O both are triatomic molecules but their shapes are different. Explain. **[HOTS]**

4. In SF_4 molecule, the lone pair of electrons occupies an equatorial position rather than axial position in the overall trigonal bipyramidal arrangement. Why? **[HOTS]**

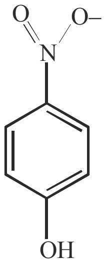
5. Why the bond orders of He_2^+ and He_2^- are identical ? **[HOTS]**

6. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species. **[Exemplar]**

7. Structures of molecules of two compounds are given below :



(I)



(II)

(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding.

(b) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point.

(c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bonds with water easily and be more soluble in it. **[Exemplar]**

Long Answer Questions [5 Marks]

1. Give reasons for following :

(i) What is the decreasing order of lattice energy of various ions?

(ii) $PbSO_4$, $BaSO_4$, AgCl, AgBr, AgI are insoluble in water, why?

(iii) Which is more ionic and why? $FeCl_2$ or $FeCl_3$?

(iv) What is the decreasing order of strengths of bonds between sp^3, sp^2 and sp hybrid orbitals?

(v) What is the order of dipole moment of ortho, meta and para disubstituted derivatives? **[HOTS]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :

(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. Which of the two will have higher boiling point and why. KCl or Cl_2?

2. $CHCl_3$ does not give precipitate with $AgNO_3$ although it has 3 Cl atoms while KCl does. Why?

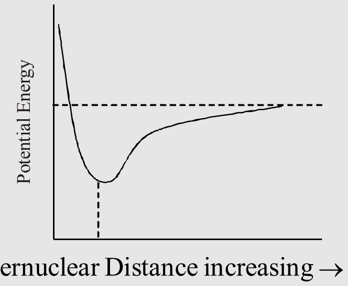
3. Which has a higher dipole moment and why NH_3 or NF_3 ?

4. What is Octet rule? List important exceptions to the Octet rule.

5. o-nitro phenol has lower boiling point than p–nitro phenol. Explain?

6. Select the best Lewis structure for chloric acid, $HClO_3$, in which the chlorine atom is surrounded by three oxygen atoms, one of which is also bonded to a hydrogen atom.

7. Carefully observe the graph given below and answer the following questions



(a) What does the above curve represents?

(b) How will the plot of potential energy vs internuclear distance for the repulsive forces between the atom look like?

(c) What does minimum of the curve represents in the above curve?

(d) How does potential energy relate to the stability of the bond?

(e) How you expect a diagram of potential energy vs internuclear distance to look like for the system where the spins of the electrons are identical?

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

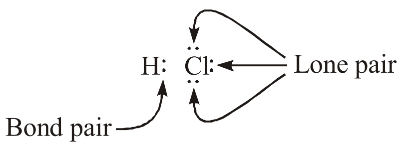
1. Higher the bond order greater is the stability.
2. $CH_4 = sp^3$
   $C_2H_4 = sp^2$
   $C_2H_2 = sp$
3. Covalent bond can be formed by the overlap of the orbitals belonging to the two atoms having opposite spins of electrons.
4. This is because ethyl alcohol forms H-bonds with water.
5. N_2O is more polar than CO_2. This is because CO_2 is linear and symmetrical. Its net dipole moment is zero. N_2O is linear but not symmetrical. It has a net dipole moment of σ116D.
6. (i) sp^3d of P in PCl_5
   (ii) sp^3d^2 of S in SF_6
7. Bonding molecular orbital has lower energy and higher stability.
8. (i) The molecule should contain highly electronegative atom linked to H–atom.
   (ii) The size of electronegative atom should be small.
9. In solid NaCl, Na^+ and Cl^- are not free to move.
10. In NaCl, there is strong ionic bond between Na^+ and Cl^- whereas in Na metal there is weak metallic bond.
11. In H_2S there is less polarity as comared to H_2O because sulphur is bigger in size and less electronegative, therefore b.p. –b.p. repulsion is less in H_2S than in H_2O hence bond angle is less.
12. It is formed by overlapping of half filled atomic orbitals.
13. MgO has higher value of lattice energy.
14. Covalent compounds have high bond dissociation energy that is why they react slowly.
15. Dipole moment is defined as product of charge and distance between atoms. $\boxed{\mu = e \times d.}$ It is a vector quantity.
16. They have symmetrical shape, individual bond moments get cancelled, therefore, net dipole moment is zero.
17. No.
18. (i) sp^2, (ii) sp^3, (iii) sp^2.
19. III, contributes least because like charges reside on adjacent atoms.
20. $[BeF_3]^-$ is isostructural with BF_3.
21. $C_2^{2-} > C_2^- > C_2$ is order of bond lengths.
22. NO_2^+ and CO_2 are '*sp*' hybridised, therefore have linear shape.
23. He_2 is not likely to exist because its bond order is zero.
24. OF_2 is neutral molecule which is isoelectronic with ClO^-.
25. $He_2^+(3) : \sigma 1s^2\, \sigma^* 1s^1 \Rightarrow \text{B.O.} = \frac{1}{2}(2-1) = \frac{1}{2}$

    $H_2^-(3) : \sigma 1s^2 \sigma^* 1s^1 \Rightarrow \text{B.O.} = \frac{1}{2}(2-1) = \frac{1}{2}$

    Since they have same number of bonding and anti-bonding electrons

    ∴ bond order is identical.
26. A lone pair of electrons is a pair of valence electrons that is not used in bonding.

    A bond pair is an electron pair shared between the two atoms. For example:



27. The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of solid ionic compound into gaseous constituent ions.

    The lattice enthalpy qualitatively measure the stability of an ionic compound.
28. Bond order and the bond length are inversely related.

$$\text{Bond order } \alpha \frac{1}{\text{Bond length}}$$

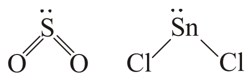
29. Pauling defined the difference in electronegativity of A and B, as

$$|\chi_A - \chi_B| = 0.102\sqrt{\Delta / \text{kJ mol}^{-1}}$$

$$\text{where } \Delta = \text{BE}(A-B) - \frac{1}{2}[\text{BE}(A-A) + \text{BE}(B-B)]$$

30. The lowest energy structure (stable one) is the one, with the smallest formal charges on the atoms.
31. The decreasing order of repulsion is:

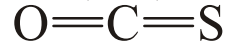
    Lone Pair-Lone Pair (LP-LP) > Lone Pair-Bond pair (LP-BP) > Bond Pair-Bond Pair (BP-BP)
32. Only $SnCl_2$ has the same shape as SO_2. SO_2 and $SnCl_2$ both are AX_2L type molecule. Both have bent structure. While CO_2 and BeH_2 are AX_2 type with linear shape.



33. In ClF_3, Cl, the central atom has five electron pair (three are bond pair and two are lone pair). It is a AX_3L_2 type molecule. NF_3 is AX_3L type molecule and has a trigonal pyramidal shape.
34. The carbon atom x is sp^2 and carbon atom *y* is sp^3 hybridised.
35. OCS will have a higher dipole moment than CS_2 although both are linear in shape. This is due to difference in electronegativity of O and S. In OCS, two dissimilar atoms are bonded to the central C atom.

$\mu_{net} = 0$

or $\mu_1 = \mu_2$



$\mu_{net} \neq 0$

or $\mu_1 > \mu_2$

36. BeH_2 has a zero dipole moment as it is linear in shape. The two bond dipoles cancel each other

$\mu = 0$

37. The electron configuration of O_2^{2+} ion is

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2 \begin{bmatrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{bmatrix}$$

Number of bonding electrons = 10
Number of antibonding electrons = 4

38. Noble gas atoms have no tendency to form a molecule because they have their octet complete.

39. Ethene (C_2H_4) has sp^2 hybridized carbon atoms. On hydrogenation, it changes to ethane (C_2H_6) in which carbon atoms are sp^3 hybridized.

40. The decreasing order of electronegativities of the various C-atoms is $C_{sp} > C_{sp^2} > C_{sp^3}$.

41. There is hydrogen bonding in H_2O due to presence of highly electronegative O atom but no such hydrogen bonding is possible in H_2S.

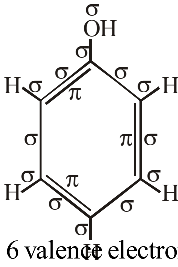
42. In BF_3 central Boron atom has sp^2-hybridisation hence it has trigonal planar structure while in NH_3 N–atom has sp^3-hybridisation and a lone pair of electron thus has a pyramidal shape.

43. In 1–butyne the triply bonded carbon atom is sp–hybridized while in 1–butene the doubly bonded carbon atom is sp^2–hybridized. We know that sp hybridized –Carbon is more electronegative than sp^2 hybridized – Carbon , thus 1 – butyne has more dipole moment than 1 – butene.

44. $CO < CO_2 < CO_3^{-2}$.

45. NO_3^{-1} and BF_3 are isostructural since they both are sp^2 – hybridized.

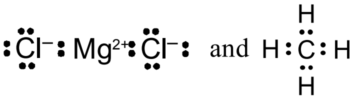
46.



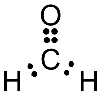
i.e 13 sigma and 3 pi bonds.

47. 6 valence electrons. $2s^2$, $2p^4$. Valence electrons are electrons present in outermost shell.

48.



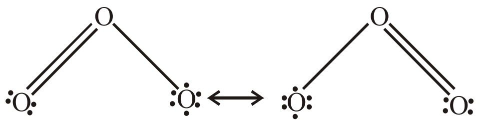
49.



50. Generally least electronegative atom is given central position.

51. Different resonating structures of a substance have : (i) same positions of atoms (ii) same number of shared and unshared electrons (iii) almost equal energy.

52.



53. σ bond is more stronger than π bonds. Because the electron cloud of a sigma bond is symmetrical about the internuclear axis and the overlapping is quite large.

54. Due to resonance the bond lengths between the C atoms becomes equal.

55. In ice, the hydrogen bonding give rise to cage like structure of water molecules. The molecules are not so closely packed as they are in the liquid state. Thus for same mass of water the volume of ice increases and hence the density decreases. Thus it floats over water.

56. 9σ and 3π bonds are present.

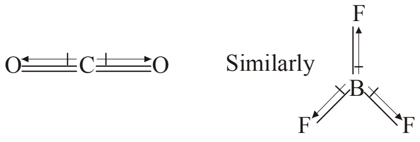
57. Acetylene(C_2H_2) having sp–hybridization has more s–character than ethane (C_2H_6) having sp^3 hybridization.

58. The difference of electronegativities of A, B in AB molecule is 1.0 (3.5 – 2.5), the A – B would be a polar covalent bond.

59. In H—X, X atom is more electronegative than H. Therefore, the H—X bond is polar and the direction of dipole is from H to X. As the electronegativity of X decreases from F to I, the charge separation decreases. Therefore, the dipole moment decreases.

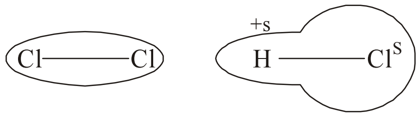
Short Answer Questions

1. A non-polar molecule can have highly polar bonds because molecular dipole is a vector sum of various bond dipoles. For example, in CO_2 there are two strong C = O dipoles but net dipole moment of the molecule is zero.



$\mu = 0$ $\mu = 0$

2. In chlorine molecule, two chlorine atoms with same electronegativity are held by a single covalent bond hence Cl_2 is non-polar. In HCl, the bond is polar due to different electronegativities of H, Cl.



$\mu = 0$ $\mu = 1.03\ D$

3. In ethane molecule, all the bonds are sigma bonds which are quite stable whereas in case of ethene molecule, there is one carbon-carbon double bond, which consists of a strong 'σ' and a weaker π bond, which dissociates readily to form two new sigma bonds and thus readily undergoes addition reactions.

4. (a) CH_3COOH (b) NH_3
(c) Ortho nitrophenol (d) HCl
(e) C_2H_5OH

5. Hundred percent covalent character is found in the covalent bonds between the atoms of the same element, however, in heteroatomic covalent bonds some percentage of ionic character is also present which goes on increasing with the increasing difference in the electronegativities of the bonded atoms.

6. A covalent bond between the atoms of different electronegativities is polar. As the difference in electronegativities increases, the polar character of the covalent bond also increases. As the difference in electronegativities of the bonding atoms exceeds 3.2, complete migration of the shared pair of electrons takes place resulting into the formation of ionic bond.

7. NH_3 and PH_3 both are the hydrides of the members of group 15 of the periodic table. While moving down from N to P, the atomic size increases and the electronegativity decreases due to which these bond pairs of electrons do not repel each other more strongly in PH_3 molecule, therefore $\angle HPH$ in PH_3 is lesser than the $\angle HNH$ in NH_3.

8. (i) Non-polar due to symmetric structure.
(ii) Non-polar due to linear molecular structure.
(iii) Polar due to non-symmetric molecular structure.

9. (i) HF is more polar than HCl.
(ii) KF has higher lattice energy than KCl.
(iii) NH_3 has higher dipole moment than NF_3.
(iv) C_2H_4 has higher s-character in hybrid orbitals.

10. A = Mg, B = Na, C = B, D = N, E = Ne.
(i) Mg_3N_2 (ii) Na_3N
(iii) N_2 (iv) Not formed and remains only Ne.

11. Lewis structure of nitrite ion can be represented as

$$\underset{1}{:\ddot{O}} = \ddot{N} - \underset{2}{\ddot{\underset{..}{O}}:}$$

Formal charge on N-atom $= 5 - 2 - \frac{1}{2} \times 6 = 5 - 2 - 3 = 0$

Formal charge on number 1

Oxygen atom $= 6 - 4 - \frac{1}{2} \times 4 = 6 - 4 - 2 =$ zero

Formal charge on number 2

Oxygen atom $= 6 - 6 - \frac{1}{2} \times 2 = 6 - 6 - 1 = -1$

∴ Lewis structure of nitrite ion and formal charges on the various atoms are as shown below :

$$:\ddot{O} = \ddot{N} - \ddot{\underset{..}{O}}:^{-}$$

12. The resonating structures 1, 2, 3 of the CO_2 molecule are important for describing the bonding in the molecule as both the C–O bond lengths are the same (115 pm) which lies between carbon-oxygen triple bond length (110 pm) and double bond length (121 pm).

13. (a) A – group 1, B – group 14, C – group 17
(b) A, C are expected to form ions A^+ and C^-
(c) (i) $A : \overset{A}{\underset{A}{\ddot{\underset{..}{B}}}} : A$

(ii) $A^+ \left[: \ddot{\underset{..}{C}} : \right]^-$ or A^+Cl

14. Refer to key concepts

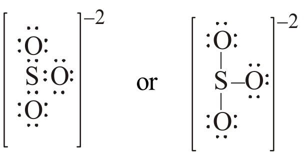
15. These two structures are not the canonical forms. In canonical forms, the position of the atoms remain fixed. In structure I, H-atom is directly bonded to the phosphorus atom while in structure II, there is no H-atom bonded to P-atom. The structure (I) is acceptable because it explains that the H_3PO_3 is a dibasic acid.

16. (a) CN^- ion has 4 + 5 + 1 = 10 electrons (4 from the C atom, 5 from the N atom, and 1 for the additional negative charge).

Therefore, the Lewis structure is

$$\left[:\dot{\underset{\cdot}{C}} + \cdot\dot{\underset{\cdot}{N}} : + \cdot\right]^- \rightarrow \left[:C:::N:\right]^- \rightarrow \left[:C \equiv N:\right]$$

(b) SO_3^{-2} : Total number of electrons $= 6 + 3 \times 6 + 2 = 26$. The Lewis structure is

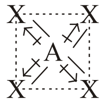


The – 2 charge is present on the entire ion.

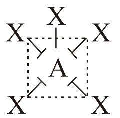
(c) ClO_2^- : The total number of electrons $= 7 + 2 \times 6 + 1 = 20$. The Cl is the central atom and O atoms are bonded to it. The Lewis structure is

$[:\ddot{\underset{..}{O}} : \ddot{\underset{..}{Cl}} : \ddot{\underset{..}{O}} :]^-$ or $[:\ddot{\underset{..}{O}}–\ddot{\underset{..}{Cl}}–\ddot{\underset{..}{O}} :]^-$

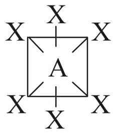
17. (i) Zero dipole moment.



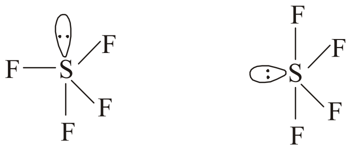
(ii) The molecule will have an appreciable dipole moment.



(iii) Zero dipole moment



18. In SF_4, the central S atom has five electron pairs (four bond pairs and one lone pair) whose arrangement should be trigonal bipyramidal. However, one of the electron pair is lone pair. SF_4 can, therefore, have structure (a) or structure (b).



(a) L.P. in the axial position (b) L.P. in the equitorial position

In structure (a), there are three LP–BP repulsions at 90°. In structure (b), there are only two LP–BP repulsions at 90°. Hence, structure (b) is favoured one. The structure (b) is known as see-saw shape.

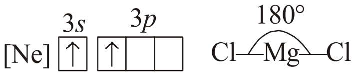
19. The lone pairs are localized on the central atom, while each bonded pair is share between two atoms. Consequently, the lone pair electrons in a molecule occupy more space as compared to the bonding pair electrons. This causes greater repulsion between lone pairs of electrons as compared to the lone pair-bond pair and bond pair-bond pair repulsion.

20.

	σ-bond		π-bond
(a)	σ-bond is formed by the axial overlapping of half-filled atomic orbitals.	(a)	π-bond is formed by the lateral or side-ways overlapping of atomic orbitals.
(b)	It is formed when two s-orbitals overlap or when one orbital with directional character (p-orbital) overlaps along its axis.	(b)	It is formed by the overlapping of two parallel p-orbitals which are available after σ-bonds have been formed.
(c)	A σ-bond has a cylindrical shape about the bond axis.	(c)	A π-bond has an electron distribution above and below the bond axis.
(d)	A σ-bond is a strong bond.	(d)	A π-bond is weaker than σ-bond.
(e)	It allows free rotation.	(e)	It restricts free rotation.

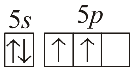
21. The molecule of $MgCl_2$ is linear because valence orbital of Mg is *sp*-hybridized.

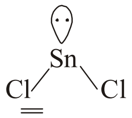
Mg (*excited state*)



$SnCl_2$ is angular because valence orbital of Sn is sp^2 hybridized.

Sn (*ground state*) [Kr]

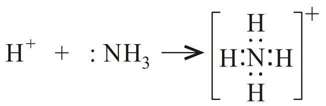




22. Co-ordinate covalent or dative bond is formed by mutual sharing of electrons between the two atoms but the shared pair of electrons is donated only by one atom.

$$A + :B \rightarrow A:B$$

An example is the formation of the ammonium ion, in which all bonds are clearly identical



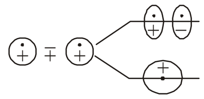
$$H^+ + :NH_3 \rightarrow \left[\begin{array}{c} H \\ H:\ddot{\underset{..}{N}}:H \\ H \end{array}\right]^+$$

23. PCl_5 has a trigonal bipyramid shape in which P atom is at the center and Cl atoms are pointed towards the corner of a trigonal bipyramid.

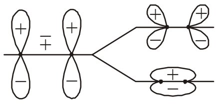
The three P—Cl bonds which makes an angle of 120° with each other are called equitorial bonds. The remaining two P—Cl bonds are perpend-icular to the plane of equitorial bonds, are called axial bonds.

Axial bond pairs suffer more repulsions from the equitorial bond pairs. Therefore, the axial bonds are slightly elongated and hence slightly weaker than the equitorial bonds. This makes PCl_5 quite reactive.

24. (i) two s-orbitals



(ii) two p-orbitals (side-to-side)



25. (i) N_2 molecule has total 14 electrons and the bond order is 3, while in NO, the bond order is 2.5. Due to higher bond order, N_2 has higher bond dissociation energy.

(ii) N_2 and CO both are isoelectronic and have the same bond order. CO is more reactive than N_2 because of high electronegativity difference. CO is more polar than N_2.

26. Stability is directly related to the bond order.

$Li_2 : \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

$Li_2^+ : \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^1$

$$\text{Bond order} = \frac{3-2}{2} = 0.5$$

$$Li_2^- : \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2 \left[\begin{array}{l} \pi 2p_x^1 \\ \pi 2p_y^0 \end{array}\right.$$

$$\text{Bond order} = \frac{5-2}{2} = 1.5$$

The increasing stability order is $Li_2^+ < Li_2 < Li_2^-$

27. (i) In He_2, total 4 electrons are present. Its MO electron configuration is $\sigma 1s^2\, \sigma^* 1s^2$.

As $N_b = N_a$, the bond order is zero. He_2 does not exist.

(ii) The MO electron configuration of N_2^+ (total electrons = 13) is

$$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2 \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array}\right. \sigma 2p_z^1$$

As one unpaired electron is present in $\sigma 2p_z$ MO, N_2^+ cannot be diamagnetic, it is paramagnetic in nature.

(iii) The bond dissociation energy is directly related to the bond order.

The bond order of H_2^+ is $\frac{1}{2}$ and the bond order of $He_2^+ (\sigma 1s^2\, \sigma^* 1s^1)$ is also $\frac{1}{2}$.

As bond order is same, the bond dissociation energy of H_2^+ is almost same as that of He_2^+.

28. Lattice energy is defined as the energy released when one mole of crystalline solid is formed by the combination of oppositely charged ions.

(i) As the magnitude of charge on an ion increases there will be greater force of interionic attraction and hence greater will be the value of Lattice energy.

(ii) Smaller the size of the ions user will be the internuclear distance and thus greater will be the Lattice energy.

29. The orbital electronic configuration of florine $(Z=9) = 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

MO.E.C of flourine

$= [\sigma 2s]^2 [\sigma^* 2s]^2 [\sigma 2p_z]^2 [\pi^2 p_x]^2 [\pi^* 2p_y]^2 [\pi^* 2p_x]^2 [\pi^* 2p_y]^2$

Due to presence of all filled orbitals F_2 is diamagnetic.

30. In covalent bond, the shared pair of electrons are localized between the two atoms and also covalent bonds are formed by overlap of half filled atomic orbitals. Since orbitals are directional in nature covalent bonds are directional; while in ionic bond each ion is surrounded by a number of oppositely charged ions and there is no definite direction.

31. $BeCl_2$ is more covalent than $MgCl_2$. Since Be^{2+} ion is small in size and hence has greater polarizing power.

32. (a) XeF_4–hybridization is sp^3d^2 and shape is octahedral or square planar.

(b) BrF_3–hybridization is sp^3d and shape is T–shaped.

33. $1\ \text{esu} = 3.335 \times 10^{-10}\,C$

$$\therefore\ 4.8 \times 10^{-10}\ \text{esu} = 3.335 \times 10^{-10} \times 4.8 \times 10^{-10} = 16 \times 10^{-20} = 1.6 \times 10^{-19}$$

$$\text{Now, } \mu_{ionic} = q \times d = 1.6 \times 10^{-19} \times 1.275 \times 10^{-10} = 2.04 \times 10^{-29}\ C.m$$

$$\text{Given } \mu_{observed} = 1.03D = 1.03 \times 3.35 \times 10^{-30}\,C.m = 3.45 \times 10^{-30}\,C.m$$

Now percent ionic

$$\text{Character} = \frac{\mu_{obs}}{\mu_{cal}} \times 100 = \frac{3.45 \times 10^{-30}}{2.04 \times 10^{-29}} \times 100 = 16.83\%$$

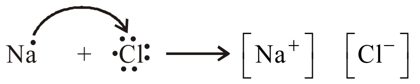
34. The following are conditions for writing Lewis dot structures for molecules :

(i) Each bond is formed as a result of sharing of an electron pair between the atoms.

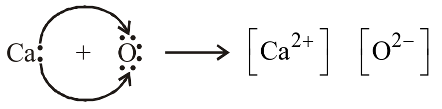
(ii) Each combining atom contributes one electron to the shared pair.

(iii) The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.

35. (a)



(b)



36. (i) The atom forming cation should have low ionization enthalpy so that it can loose electron and form cation easily.

(ii) The other atom forming anion should have high electron gain enthalpy.

(iii) Higher the lattice energy of the resulting ionic compound greater will be its stability and thus more readily it will be formed.

(iv) If (lattice energy + electron gain enthalpy) > ionization energy, the net effect will be release of energy and hence an ionic bond is formed.

37. With the overlap of orbitals, the two electrons exchange and occupy the same orbital. The Pauli exclusion principle states that no two electrons in an atom can have same values for all four quantum numbers. For the electrons to be in that same orbital, three quantum number must be same; therefore the spin quantum number will be different.

38. The dipole moment of a100% ionic molecule at the given internuclear distance would be

$$\mu_{ionic} = q \times d = 1.60 \times 10^{-19}C \times 1.41 \times 10^{-10}m = 2.26 \times 10^{-29}C.m$$

$$\text{Percent ionic character} = \frac{\mu_{oberved}}{\mu_{calculated}} \times 100$$

$$= \frac{2.60 \times 10^{-30}}{2.26 \times 10^{-29}} \times 100 = 11.5\%$$

39. Oxygen is more electronegative than either sulphur or carbon. Thus each sulphur-oxygen and carbon-oxygen bond should be polar, with net negative charge residing on the oxygen atom.

Since CO_2 has no net dipole moment, the dipole moment of two C–O bonds must cancel each other. This can occur only if the two bonds are in a straight line and in opposite direction. Thus CO_2 molecule must be linear in shape. The existence of dipole moment in SO_2 must mean that the molecule is not linear.

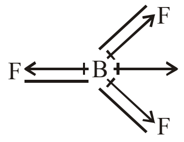
40. (a) SF_6 – the hybridization is sp^3d^2 and shape is octahedral.

(b) CCl_4 – the hybridization is sp^3 and shape is tetrahedral.

(c) BF_3 – the hybridization is sp^2 and shape is trigonal planar.

(d) PCl_5 – the hybridization is sp^3d and shape is trigonal bipyramidal.

41. $BF_3 < H_2S < H_2O$. BF_3 has a zero dipole moment because of its symmetry B – F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third .

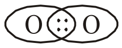


H_2S has a lower dipole moment than H_2O because of the much lower bond polarity of H –S compared to H–O as oxygen has high electronegativity in comparison to sulphur atom.

42. The elements having low ionization enthalpy and high electron gain enthalpy give rise to the formation of ionic bond. Example NaCl. This is because elements with low ionization enthalpy would easily loose electron to form cation while elements, which are having high electron affinity, would pick up the electron easily and form anion. The positive cation would combine with negative anion with the release of energy called lattice enthalpy would result in the formation of ionic crystal.

43. In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule. The actual structure is in between of all these contributing structures and is called resonance.

44. A single covalent bond has only one shared pair of electron between the two atoms. For example 

If two atoms share two pairs of electrons, the covalent bond between them is called a double covalent bond. For example 

Long Answer Questions

1. Refer theory
2. Characteristics of resonance are following
   - (i) The contributing structures do not have any real existence. Only the resonance hybrid has the real existence.
   - (ii) As a result of resonance, the bond lengths of different bonds in a molecule becomes equal.
   - (iii) The resonance hybrid has lower energy and hence greater stability than any of the contributing structures.
   - (iv) Greater is the resonance energy, greater is the stability of the molecule.
   - (v) Greater is the number of canonical forms especially with nearly same energy, greater is the stability of the molecule.
3. Formal change on atom in a Lewis structure is given as

$$= \begin{bmatrix} \text{total number of valence} \\ \text{electrons in the free atom} \end{bmatrix}$$

$$- \begin{bmatrix} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{bmatrix} - \frac{1}{2} \begin{bmatrix} \text{total no. of} \\ \text{bonding (shared pair)} \\ \text{electrons} \end{bmatrix}$$

For calculating the formal charges; we just apply the formula given above. Then, to choose the better structure, we look for the one with the smallest formal charges on the atoms. We begin by calculating the formal charges. For the chlorines, which have valence electrons as isolated neutral atoms, we have

formal charge = 7 – 6 – 1 = 0

Each chlorine has a formal charge of zero in both structures. Now let's examine the other atoms.

For structure I

Phosphorus: formal charge = 5 – 0 – 5 = 0

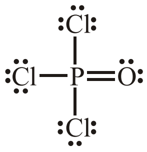
Oxygen: formal charge = 6 – 4 – 2 = 0

For structure II

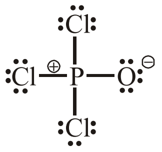
Phosphorus: formal charge = 5 – 0 – 4 = +1

Oxygen: formal charge = 6 – 6 – 1 = –1

Placing these formal charges on the respective Lewis structures gives



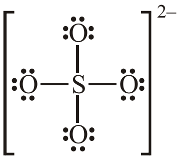
I



II

Finally, since structure I has the smallest formal charges, it is lower in energy and is the better Lewis structure for this molecule.

4. First, let's draw a Lewis structure that obeys the octet rule.



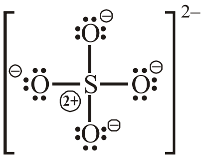
Now let's calculate formal charges.

For sulfur atom

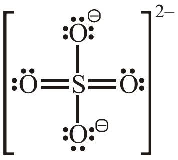
formal charge = 6 – 0 – 4 = +2

For oxygen atom

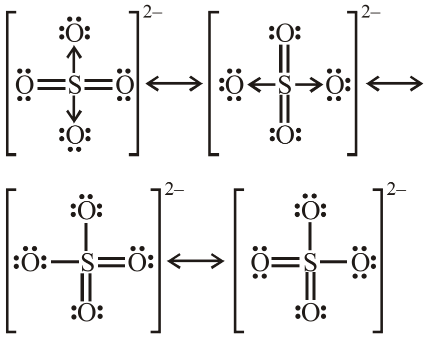
formal charge = 6 – 6 – 1 = – 1 Adding the formal charges to the Lewis structure gives the following structure



Now, we will try to reduce these formal charges. If we move an unshared pair of electrons from oxygen to the S–O bond makes the charge on the oxygen less negative and the charge on the sulfur less positive. Since there are two positive formal charges or sulfur, we need to do this twice to give sulfur a zero formal charge. This results in following structure

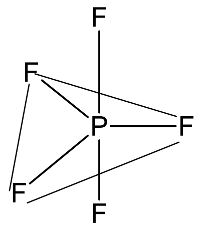


Notice, however, that in creating the double bonds, we had choices as to where locate them. There are four different arrangements for these double bonds, as shown below, are four resonance structures.

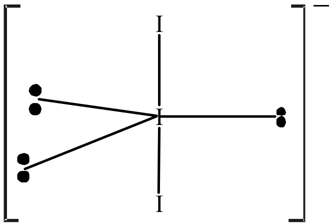


Thus, we consider the sulphate ion to be a resonance hybrid of these contributing structures.

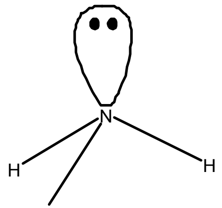
5. (a) PF_5– hybridization sp^3d, molecular shape – Trigonal bipyramidal



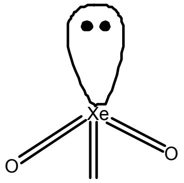
(b) I_3^{-1} – hybridization sp^3d, molecular shape – Linear



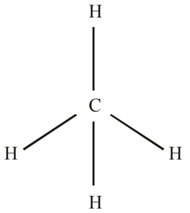
(c) NH_3 – hybridization sp^3, molecular shape – Trigonal pyramidal



(d) XeO_3 – hybridization sp^3, molecular shape– Pyramidal



(e) CH_4 – hybridization sp^3, molecular shape – Tetrahedral



HOTS / EXEMPLAR QUESTIONS

Very Short Answer Questions

1. It is because ionic compounds dissociate into ions very easily in acqueous solution, therefore, react faster
2. CaF_2 is neither linear nor bent molecule because it is ionic compound and ionic bond is non-directional.
3. B.O. of N_2 (3) > B.O. of N_2^+ (2.5) but B.O. of O_2^+ (2.5) > B.O. of O_2 (2). Greater the bond order, greater is the bond dissociation energy.
4. Both have tetrahedral shapes, i.e., four lobes of sp^3 hybridized orbitals.
5. This is because both N and F are small and hence have high electron density. So they repel the bond pairs thereby making the N—F bond length larger.
6. Structure (III) is wrong. The electron pairs on oxygen atom as shown in it are not permissible.
7. Number of σ-bonds = 16
8. $:\ddot{N}::C::\ddot{S}:^{-} \leftrightarrow :N:::C:\underset{..}{\overset{..}{S}}:^{-} \leftrightarrow :\underset{..}{\overset{..}{N}}:C:::S:^{-}$

Short Answer Questions

1. The M.O. electronic configuration are :

$\mathbf{N_2}$: KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$

Bond order = 3

$\mathbf{N_2^+}$: KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1$

Bond order : $2\frac{1}{2}$

Since bond order of N_2 is larger than that of N_2^+, N_2 has greater bond dissociated energy than N_2^+.

$\mathbf{O_2}$: KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$ $(\pi^* 2p_x)^1 (\pi^* 2p_y)^1$

Bond order = 2

$\mathbf{O_2^+}$: KK $[\sigma 2s]^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1$

Bond order = $2\frac{1}{2}$

Since bond order of O_2 is less than that of O_2^+, O_2 has lower bond dissociation energy than O_2^+.

2. $\mu = q \times d$

Dipole moment corresponding to 100% ionic character of KCl = $(1.602 \times 10^{-19} C) \times (2.6 \times 10^{-10} m) = 4.1652 \times 10^{-29}$ Cm

Actual dipole moment of KCl = 3.336×10^{-29} Cm

Percentage ionic character $= \dfrac{3.336 \times 10^{-29}\,\text{Cm}}{4.1652 \times 10^{-29}\,\text{Cm}} \times 100$

= 80.09%.

3. According to **VSEPR** theory, the geometry and shape of a covalent molecule does not depend upon the number of atoms present in a molecule but it depends upon the number of electron pairs that surround the central atom. Molecules having different number of electron pairs surrounding the central atom have different shapes.

In BeF_2, the central atom (Be) is surrounded by two electron pairs where as in H_2O, the central atom (O) is surrounded by four electron pairs. Due to this the shapes of BeF_2 and H_2O are different.

4. The *lp* – *bp* repulsions are less if it occupies equatorial position than if it occupies axial position. As a result, energy is less and stability is more.

5. Molecular ion Molecular orbital configuration

Molecular ion	Molecular orbital configuration
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$
He_2^-	$(\sigma_{1s})^2(\sigma^*_{1s})^2$

Since both He_2^+ and He_2^- have equal number of bonding (N_b) and antibonding (N_a) electrons because of identical molecular orbital configuration, their bond order is given by

$= \frac{1}{2}[N_b - N_a] = \frac{1}{2}[2-1] = \frac{1}{2}$ are identical.

6. (i) According t molecular orbital theory electronic configuration of O_2^+ and O_2^- species are as follows :

$O_2^+ : (\sigma 1s)^2 (\overset{*}{\sigma} 1s^2)(\sigma 2s)^2 (\overset{*}{\sigma} 2s^2)(\sigma 2p_z)^2$
$(\pi 2p_x^2, \pi 2p_y^2)(\overset{*}{\pi} 2p_x^1)$

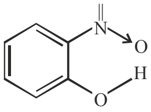
$O_2^- : (\sigma 1s)^2 (\overset{*}{\sigma} 1s^2)(\sigma 2s)^2 (\overset{*}{\sigma} 2s^2)(\sigma 2p_z)^2$
$(\pi 2p_x^2, \pi 2p_y^2)(\overset{*}{\pi} 2p_x^2, \overset{*}{\pi} 2p_y^1)$

Bond order of $O_2^+ = \dfrac{10-5}{2} = \dfrac{5}{2} = 2.5$

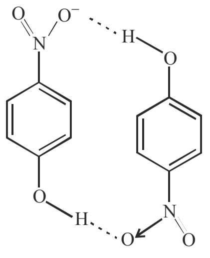
Bond order of $O_2^- = \dfrac{10-7}{2} = \dfrac{3}{2} = 1.5$

Higher bond order of O_2^+ shows that it is more stable than O_2^-. Both the species have unpaired electrons. So both are paramagnetic in nature.

7. (a) Compound (I) will form intramolecular hydrogen bond because NO_2 and OH group are close together in comparison to that in compound (II)



(I)



(II)

(b) Compound (II) will have higher melting point because it forms intermolecular hydrogen bonds. Thus, more and more molecules are joined together through hydrogen bond formation.

(c) Due to intermolecular hydrogen bonding compound (I) will not be able to form hydrogen bonds with water thus will be less soluble in it while compound (II) can form hydrogen bond with water more easily and will be soluble in water.

Long Answer Questions

1. (i) The magnitude of lattice energy of the ion pairs in an ionic compound follows the order.
bivalent – bivalent > univalent – bivalent > univalent.

(ii) Compounds like $PbSO_4$, $BaSO_4$, $AgCl_2$, AgBr or AgI, etc, are although ionic but are insoluble in water because of the high value of lattice energy which exceeds the hydration energy of the central metal ion.

(iii) $FeCl_2$ is more ionic than $FeCl_3$ because msaller Fe^{3+} ion with greater polarizing power than Fe^{2+}, introduces some covalent character in the Fe–Cl bond.

(iv) The hybrid orbitals with greater 'p' character are more directional in nature and the more the directional character of the overlapping hybrid orbital the stronger is the bond. Following is the order of the bond strength of the hybrid orbitals.
$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$

(v) Out of ortho, metal and para disubstituted compounds para isomer is non-polar while the polar character varies as ortho > meta.

CHAPTER TEST

1. KCl has higher boiling point than Cl_2 , because it is ionic compound and the atoms are held together by strong electrostatic force of attraction while Cl_2 is covalent , the forces are much weaker.

2. $CHCl_3$ being covalent compound does not dissociates to give Cl^{-1} ions while KCl which is ionic easily dissociates. Thus KCl gives precipitate with $AgNO_3$.

3. NH_3 has higher dipole moment than NF_3 because in NH_3 the different dipole moments acts in one direction thus the sum of dipole moments is greater than zero. While in NF_3 different dipole gets cancelled out as they acts in opposite direction. Thus net dipole moment is zero.

4. **Octet Rule.** Elements combine with each other in order to complete their respective octets i.e. , 8 electrons in their outer most shell.

Limitations of Octet rule. The Octet rule fails to explain

(i) the formation of molecules in which the central atom has less than eight electrons in the valence shell such as $BeCl_2$, BF_3, etc.

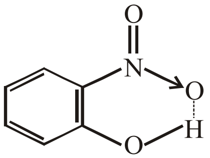
(ii) the formation of molecules in which the central atom has more than eight electrons in the valence shell such as PF_5 , SF_6, etc.

(iii) the formation of compounds of noble gases especially xenon and krypton such as XeF_2, XeF_6, etc.

(iv) odd electron molecules like NO, NO_2.

5. In ortho-nitro phenol intramolecular hydrogen bonding takes place due to which no association with neighbouring molecules occur. Intra molecular hydrogen bonding occurs when H atom is in between the two highly electronegative (F_1O_1N) atoms present within the same molecule.

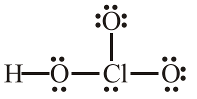
Intramolecular hydrogen bonding in o–nitro phenol is shown below



In para–nitrophenol intermolecular hydrogen bonding takes place due to which the boiling point is high.

6. First, we have to construct a Lewis structure that obeys the octet rule. Next, we have to decide whether it is the most stable Lewis structure that can be drawn. To do this, we will calculate the formal charges on the atoms. If they are zero, we don't need to look further, but if they are non zero, we will look for a way to reduce the formal charges.

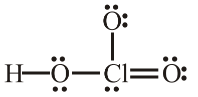
First, let's look at the Lewis structure obtained by following the octet rules. This is



$$\mathrm{H-\ddot{O}-\overset{\overset{\displaystyle :\ddot{O}:}{|}}{Cl}-\ddot{O}:}$$

Now let's assign formal charges to each of the atoms.
Oxygen atom (bonded to H)
formal charge = 6 – 4 – 2 = 0
Other oxygen atoms
formal charge = 6 – 6 – 1 = – 1
Chlorine atom
formal charge = 7 – 2 – 3 = + 2

Now let's see whether we can reduce the number of formal charges on individual atoms in the structure by moving electrons around. If we move an unshared pair of electrons from one of the oxygens not bonded to the hydrogen into the Cl–O bond, thereby creating a double bond, this makes the formal charge on the oxygen less negative and that on the chlorine less positive. Forming two such double bonds gives the following structure

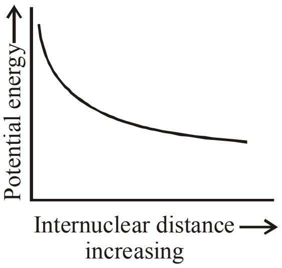


$$\mathrm{H-\ddot{O}-\overset{\overset{\displaystyle \ddot{O}:}{|}}{Cl}=\ddot{O}:}$$

Now, there are no formal charges on the atoms, so we consider it as the preferred structure.

7. (a) This curve is obtained by the interaction of attractive and repulsive forces. This potential energy curve represents the bond energy between two nuclei as a function of internuclear distance.

(b)



(c) The minimum of the curve given in the question represents the internuclear distance at which the potential energy of the system is the lowest. At this distance the attraction between the atoms is greatest.

(d) Lower the potential eneragy the greater is the stability of the bond.

(e) The curve will be similar that shown in answer above in (b). No bonding occurs as there are no attractive forces.

5

Chapter

States of Matter

INTRODUCTION

In the prior chapters you had studied about the properties of individual atoms and molecules. However, most of the properties of matter that we encounter in our routine life has no significance at atomic or molecular level. Further, these physical properties depend upon the state in which that substance exists, for example, solid, liquid or gas (though the chemical properties of the substance remain the same). The three important states of the matter are (i) **Solid state** (ii) **Liquid state** (iii) **Gaseous state**, which can exist together at a particular temperature and pressure e.g. water has three states in equilibrium at 4.58 mm and 0.0098°C.

Some Characteristics of the Three Common Forms of Matter are :

Property	*Gaseous state*	*Liquid state*	*Solid state*
1 **General**	It has definite mass but no definite shape and volume	It has definite mass and volume but no definite shape	It has definite mass, volume and shape.
2. **Forces**	Almost negligible	Weaker than those in solids	Strongest
3. **Density**	Low	Lower than solids	High
4. **Motion**	Molecules have large rotatory, vibratory and translatory motions	Low values of motions	No translatory or rotatory motion. Possess vibratory motion
5. **Packing**	No proper packing	Less closely packed	closely packed
6. **Energy**	Least	Higher than solids	Molecules possess maximum energy
7. **Thermal Expansion**	High	Higher than solid	Least
8. **Compression**	High	Slightly higher than solid	Least compressibility
9. **Intermixing**	Spontaneous	Spontaneous but slow	Least-intermixing
10. **Pressure**	Exert pressure on the walls of container	Negligible	Negligible

INTERMOLECULAR INTERACTIONS

Intermolecular forces are the forces of attraction and repulsion between interacting particles. These forces does not include the electrostate forces (between two oppositely charged ions) and the forces that hold the atoms of a molecule together. Attractive intermolecular forces are known as van der Waal's forces. Different types of van der waal's forces are as follows:

Dispersion Forces or London Forces

These forces occur in atoms and non-polar molecules by momentary displacement of their otherwise symmetrical electronic charge cloud. Dispersion forces are attractive forces that originates as a result of instantaneous dipoles induced in atoms or molecules.

They are inversely proportional to the sixth power of distance between two interacting particles. These forces are important only at short distances and their magnitude depends on the polarisability of the particle.

Dipole-Dipole Forces

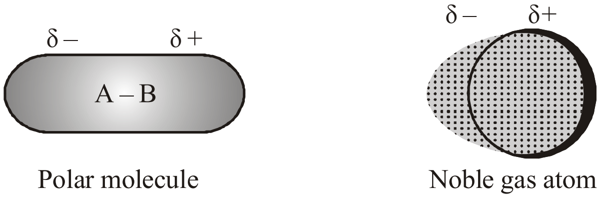
These forces act between molecules possessing permanent dipole. They occur among polar molecules. The positive pole of one molecule is thus attracted by the negative pole of the other molecule. For example:

$$......\overset{\delta+}{H}—\overset{\delta-}{Cl}.......\overset{\delta+}{H}—\overset{\delta-}{Cl}.......\overset{\delta+}{H}—\overset{\delta-}{Cl}.......$$

The strength of dipole-dipole interaction depends upon dipole moment of interacting molecule. Higher the dipole moment stronger is the intermolecular interaction. This interaction is stronger than London forces and weaker than ion-ion interaction.

Dipole Induced Dipole Forces

These forces operate between molecules having permanent dipole and molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electron cloud. Thus an induced dipole is developed in the other molecule. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.



Dipole-induced dipole attractions

Ion-Dipole Interactions

This is the attraction between an iron (cation or anion) and a polar molecule. For example, when NaCl is dissolved in water, the polar water molecules are attracted towards Na^+ ion as well as towards Cl^- ion (a process called hydration of ions). The strength of this interaction depends upon the charge and size of the ion and the magnitude of dipole moment and size of the polar molecule.

Ion-Induced Dipole Interaction

A non-polar molecule may be polarized by the presence of an ion near it, for example, it becomes an induced dipole. The interactions between them are called ion-induced dipole interactions. The strength of these interactions depends upon the charge on the ion and the ease with which the non-polar molecule gets polarized.

Hydrogen Bond

It is a special case of dipole-dipole interaction. Already discussed in 'Chapter - Chemical Bonding'.

Intermolecular forces are also repulsive in nature which comes into significance when molecules are in close content. These repulsive forces makes compression of solids and liquids difficult.

INTERMOLECULAR FORCES VS THERMAL INTERACTIONS

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of the average KE of the particles of matter. The intermolecular forces tends to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are a result of balance between intermolecular forces and thermal energy of molecules.

Predominance of thermal energy and molecular interaction energy of a substance in three states is depicted as follows :

$$\text{Gas} \longrightarrow \text{Liquid} \longrightarrow \text{Solid}$$

Predominance of intermolecular interactions

$$\text{Gas} \longleftarrow \text{Liquid} \longleftarrow \text{Solid}$$

Predominance of thermal energy

GASEOUS STATE

The force of attraction between the gaseous molecules is minimum and hence the molecules are far apart from each other and thus their position is not fixed in gaseous state. This property of gases results in the following important characteristics of gases.

(a) Gases or their mixture are homogeneous in composition
(b) Gases have very low density
(c) Gases exert pressure
(d) Gases possess high diffusibility
(e) Gases have infinite expansibility and high compressibility
(f) Gases can be liquified by cooling under high pressure
(g) All gases undergo similar change with the change of temperature and pressure. This behaviour of gases can be described by certain laws known as **gas laws**.

GAS LAWS

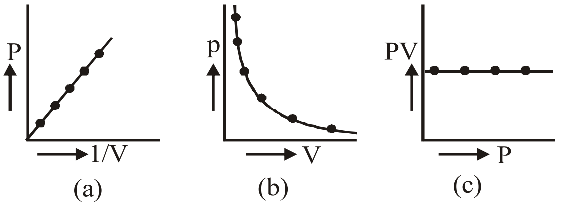
Boyle's Law

Robert Boyle, states that at constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure.

$$V \propto \frac{1}{P} \quad \text{or} \quad PV = k \text{ (constant)} \quad \text{or} \quad P_1V_1 = P_2V_2 \Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

Graphical representation of Boyle's law: According to Boyle's law, $P \propto \frac{1}{V}$ or PV = constant , therefore, Boyle's law has been verified graphically, as

(a) a graph plotted for ***P versus*** $\frac{1}{V}$ shows a ***straight line*** passing through the origin.
(b) a graph for ***P versus V*** at constant temperature shows a ***parabola***.
(c) a graph for ***PV versus P*** shows a horizontal straight line.



At constant temperature, when pressure of a given mass of a gas is plotted against the corresponding volume, a curve is obtained. Such curves at different fixed temperatures are called isotherms.

Boyle's law proves that gases are compressible because when a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that gases becomes denser at higher pressure. Mathematically,

$$P \propto \frac{1}{V} \Rightarrow P \propto \frac{1}{m|d} \qquad [\because V = \frac{m}{d} \quad d \rightarrow \text{density}]$$

$$\Rightarrow \quad P \propto \frac{d}{m} \qquad \text{or} \quad P = \frac{R}{m} d$$

or, $P \propto d$

Significance of Boyle's law: It proves the fact that gases are compressible. The more it is compressed, the denser it becomes.

Charle's Law

This law states that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature.

(Absolute temperature = ºC + 273.15)

Mathematically, $V \propto T$ (at constant pressure)

V = volume of gas

T = Absolute temperature

$$V = KT \quad \text{or} \quad \frac{V}{T} = K$$

Hence, if the volume of a gas V_1 at temperature T_1 changes to V_2 at T_2, pressure remaining constant, we have

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

or $\log V - \log T = \text{constant}$

For each degree change of temperature, the volume of sample of a gas changes by the fraction of 1/273.15 of its volume at 0ºC.

$$\text{so} \quad V_t = V_0 \left[\frac{273.15 + t}{273.15}\right]$$

This equation is called Charles-Gay-Lussac equation.

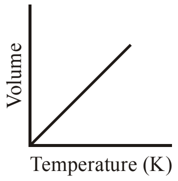
where, V_t = volume of gas at temperature tºC, V_0 = volume of gas at 0ºC temperature, t = temperature in ºC

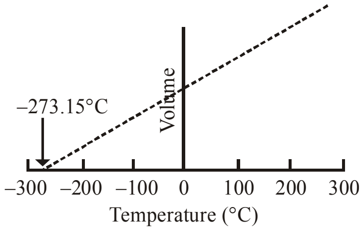
If in the above eqation we put the value of t as –273.15°C the volume of the gas will be zero. It means gas will not exist, which is not possible. In fact all gases get liquified before this temperature is reached. This hypothetical or imaginary temperature at which the gases occupy zero volume is called **absolute zero** (conversion of centigrate to Kelvin; °C + 273 = K; – 273°C + 273 = 0 K). This zero point on the scale is known as **Kelvin scale** (K). More correctly this temperature is – 273.15°C. At absolute zero (0 K or – 273°C) temperature, the volume, pressure, kinetic energy and heat content of a gas is zero.

A plot between volume of the gas against absolute temperature at constant pressure is known as **isobar**; it is always a straight line.

(a) For a definite mass of the gas a plot of V vs T (°K) at constant pressure is a straight line passing through the origin.

(b) A plot of V versus t (°C) at constant pressure is a straight line cutting the temperature axis at – 273.15°C.





Significance of Charle's law:

It proves that gases expand on heating. Since the mass of a gas remains same, the number of molecules per unit volume decreases on heating. In other words, hot air is less dense than cold air, this enables the hot air balloons to rise up by displacing the cooler air of the atmosphere.

Gay Lussac's Law

Gay Lussac states that for a given mass of the gas the pressure is directly proportional to the absolute temperature at constant volume. That is,

$P \propto T$ at constant volume

$\frac{P}{T} = \text{constant}$ where P = Pressure of a gas, T = Absolute temperature

or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

If P_0 and P_t be the pressure of a given mass of a gas at 0°C and t°C respectively maintaining constant volume, then

$$P_t = P_0\left(1+\frac{t}{273}\right)$$

Volume remaining constants the pressure of a given mass of a gas is directly proportional to its temperature in degree Kelvin.
At constant volume, when the pressure exerted by given mass of a gas is plotted against the corresponding absolute temperature, a straight line is obtained. Such straight lines at different fixed volumes as shown in figure are called ***isochores***.

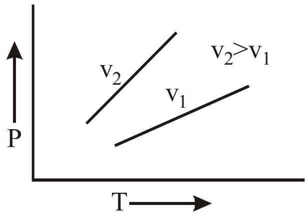


Illustration 1 :

A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of cylinder indicates 12 atmosphere at 27°C. Due to sudden fire in the building the temperature starts rising. At what temeprature, cylinder will explode.

Sol. $\frac{P_1}{T_1}=\frac{P_2}{T_2} \Rightarrow \quad \frac{14.9}{T_1}=\frac{12}{300} \quad \Rightarrow T_1 = 372.5\,K$

Avogadro’s Law

According to this law equal volumes of all gases contain equal number of molecules under same conditions of pressure and temperature. As 1 mole of a gas contains Avodagro’s number of molecules (viz, 6.022×10^{23}), this means that one mole of each gas at the same temperature and pressure should have the same volume.
At STP (298.15 K, 1 bar)
One mole of gas occupies a volume of 22.4 L
It therefore follows that $V \propto n$ (at constant temperature and pressure)
where, V = Volume of the gas, n = Number of moles of gas
$V = kn$

$$V = K\frac{m}{M}\left(n=\frac{m}{M}\right) \text{ or } M = K\frac{m}{V} - Kd\left(\because \text{ density}, d=\frac{m}{V}\right)$$

Thus, density of a gas is directly proportional to its molar mass

IDEAL GAS EQUATION

By combination of Boyle’s law, Charle’s law and Avogadro’s law we get an equation which gives the simultaneous effect of the change of pressure and temperature on the volume of a gas. This is known as ideal gas equation.

$$V \propto n \times T \times \frac{1}{P}$$

$$V = \frac{R \times T \times n}{P}$$

or **PV = nRT** (It is also called equation of state)

where n is the number of moles of the gas and R is molar gas constant. R is same for all the gases and is therefore, also called universal gas constant.
when n = 1 for example for one mole of gas, the ideal gas equation becomes

$$\mathbf{PV = RT}$$

$$R = \frac{PV}{T}$$

Value of R for one mole of an ideal gas:

$$\frac{\left(10^5\,Pa\right)\left(22.71\times10^{-3}\,m^3\right)}{\left(273.15K\right)}$$

$R = 8.314\ JK^{-1}\ mol^{-1}$
$R = 0.082\ L\,atm\,K^{-1}\ mol^{-1}$

Values of Gas Constant (R) in Different Units

Pressure	Volume	Numerical value of R	Units or R
Atmosphere	litre	0.821	Litre atm.K^{-1} $mole^{-1}$
Atmosphere	cm^3	82.1	cm^3 atm. K^{-1} $mole^{-1}$
dynes cm^{-2}	cm^3	8.314×10^7	ergs K^{-1} $mole^{-1}$
dynes cm^{-2}	cm^3	1.987 (or 2.0)	cal K^{-1} $mole^{-1}$
Pa or Nm^{-2}	cm^3	8.314	JK^{-1} $mole^{-1}$

The gases which obey the ideal gas equation are known as ***ideal gases***.

For any gas if P_1, V_1, T_1 are the initial pressure, volume and temperature and P_2, V_2, T_2 are final than we can write,

$$\frac{P_1V_1}{T_1} = nR \text{ and } \frac{P_2V_2}{T_2} = nR \Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Above equation is known as combined gas law.

Ideal Gas Equation in Terms of Density

If m is the mass, M is the molecular mass of the gas, then the moles of gas is

$$n = \frac{m}{M} \quad \text{or} \quad PV = nRT = \frac{m}{M}RT$$

$$P = \frac{m}{V} \times \frac{RT}{M}$$

$$P = \rho\frac{RT}{M} \qquad \left[\therefore \frac{m}{V} = \rho(\text{Density})\right]$$

$$M = \rho\frac{RT}{P}$$

Illustration 2 :

The density of a gas at 30°C and 1.3 atmosphere pressure is 0.027 g/cc. Calculate the molecular weight of the gas.

Sol. $M = \frac{RTd}{P}$; $R = 0.0821$ atm lit K^{-1} mol^{-1};

$d = .027\,g/cc = 27\,g/l$;

$T = 273 + 30 = 303\,K; P = 1.3$ atm

$$M = \frac{27 \times .0821 \times 303}{1.3} = 516.66\,g/mol$$

Dalton's Law of Partial Pressures

The total pressure exerted by a mixture of two or more non-reactive gases in a definite volume is equal to the sum of partial pressures exerted by the individual gases.

$$P = P_1 + P_2 + P_3 + ...$$

Gases are generally collected over water thus they are moist. In order to obtain pressure of dry gas, vapour pressure of water (aqueous tension) is substracted from total pressure of moist gases.

$$P_{\text{Dry gas}} = P_{\text{Total}} - \text{Aqueous Tension}$$

Partial Pressure in Term of Mole Fraction

Let n_1 & n_2 be the no. of moles of two inert gases A and B which are filled in a container of volume 'V' at temperature T. So the total pressure of container 'P' may be calculated as

$PV = (n_1 + n_2) RT$ .... (i)

Partial pressure of individual gas is calculated as

$P_AV = n_1RT$ .... (ii)

$P_BV = n_2RT$ ....(iii)

On the addition of eq. (ii) & (iii) we get,

$(P_A + P_B) V = (n_1 + n_2) RT$ ....(iv)

On the comparison of eq. (i) & (iv)

$$P = P_A + P_B$$

Dividing equation (ii) by (i), we get

$$\frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = x_A$$

$$P_A = x_A P$$

where x_A = mole fraction of 'A'

Similarly dividing (iii) by (i), we get

$$P_B = x_B P$$

so, partial pressure of a component = mole fraction × total pressure

Grahm's Law of Diffusion

Effusion: Effusion is a particular type of diffusion in which the movement of gas molecules take place through a small hole when the gaseous system is subjected to pressure.

Rate of diffusion (or effusion): Rate of diffusion (or effusion) is equal to the volume of gas diffused (or effused) per unit time.

for example

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused (or effused)}}{\text{Time taken}}$$

This law states that at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. That is,

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}}, \quad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

(where r_1 & r_2 are the rates of diffusion and d_1 & d_2 are the vapour densities of the two gases respectively)

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2/2}{M_1/2}} = \sqrt{\frac{M_2}{M_1}}$$ (where M_1 & M_2 are the molecular masses of two gases respectively).

Illustration 3 :

Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6g O_2 and 1.4 g of N_2 at 27°C. Also calculate the partial pressure of the He gas in the cylinder. Assume ideal behaviour of gases, R = 0.0821 atm lit K^{-1} mol^{-1}.

Sol. $PV = (n_1 + n_2 + n_3)RT$

$$P \times 10 = \left(\frac{0.4}{4} + \frac{1.6}{32} + \frac{1.4}{28}\right) \times 0.821 \times 300\ ; P = 0.4926\ \text{atm}$$

Total moles = 0.2

$$p_{He} = \frac{0.1}{0.2} \times 0.4926 = 0.2463\ \text{atm}$$

KINETIC MOLECULAR THEORY OF GASES

The main postulates of the kinetic molecular theory of gases are.

(a) A gas consists of a large number of identical particles, called atoms or molecules.

(b) These particles are so small in size that their actual volume is negligible as compared to the total volume of the gas. This assumption explains the compressibility of gases.

(c) Particles of gas are in a state of rapid constant motion in a straight line in all directions until their directions are changed on collision with each other or with the walls of the container. Pressure is exerted by the gas as a result of collision of particles with the walls of the container.

(d) There is no attractive or repulsive force between the molecules. They move completely independent of each other. This assumption supports the fact that gases expand and occupy all the space available to them.

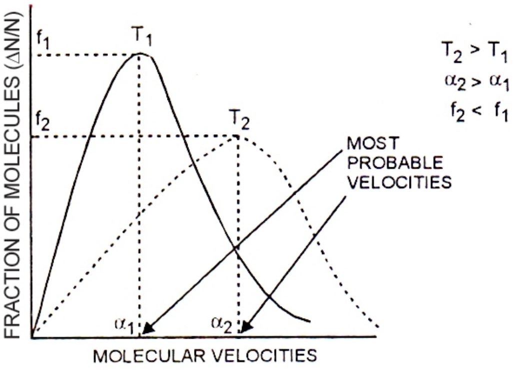
(e) The gravitational force on the gas molecules is almost negligible.

(f) The molecular collision are perfectly elastic and there is no loss of kinetic energy due to their collisions. However, there may be redistribution of energy during such collisions.

(g) The pressure exerted by the gas is due to the bombardment of the moving molecules on the walls of the container.

(h) Different molecules in a container move with different velocities and thus they possess different kinetic energies. However, the average kinetic energy of the gas molecules in directly proportional to the absolute temperature.

Maxwell-Boltzmann Distribution of Molecular Velocities



All the molecules of a given sample of gas do not have the same velocity. This is because of the continuous collisions of the gas molecules with one another and against the walls of the container. When a faster molecule collides with a slower molecule, kinetic energy $\left(\frac{1}{2}mv^2\right)$ is transfered from the faster molecule to the slower molecule. The velocity of the molecule, which gains energy, increases and that of the other decreases. Thus, their velocities keep on changing. Since a very large number of such collisions are taking place per second, only a fraction (percentage) of molecules will have the same particular velocity. The distribution of velocities amongst molecules in a gas was calculated by Maxwell and Boltzmann from the law of probability as shown in figure.

The important features of Maxwell's distribution curve may be summed up as follows:

(i) The small fraction of molecules have very low or very high speeds.

(ii) The maximum fraction of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called the most probable velocity. Therefore, the most probable velocity is defined as a velocity possessed by the maximum fraction of the molecules corresponding to the highest point on maxvelling curve.

(iii) At higher temperature more molecules have higher velocities and less molecules have lower velocities.

Calculation of Kinetic Energy

According to postulates of Kinetic gas equation :

$$PV = \frac{1}{3}mn\bar{u}^2$$

where, P = pressure of the gas

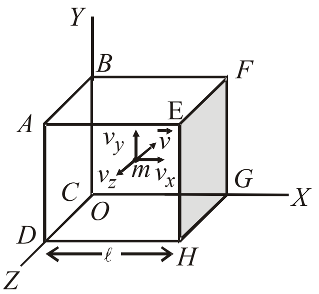
V = volume of the gas

n = no. of molecules present in the given amount of gas

For 1 mole of a gas since $n = N$

where N = Avogadro's number,

the above kinetic equation may be written as



$$PV = \frac{1}{3}Mu^2$$

For one mole of the gas :

$$PV = RT \text{ and } \quad n = N$$

$$\frac{1}{3}Mu^2 = RT \qquad \text{.....(1)}$$

$$u^2 = \frac{3RT}{M}$$

$$u^2 \propto T \qquad (\because R \text{ and } M \text{ are constants})$$

$$u \propto \sqrt{T}$$

Thus, the root mean square velocity of an ideal gas is directly proportional to the square root of the absolute temperature.

Also from eq. (1),

$$\frac{1}{3}\frac{Mu^2}{N} = \frac{RT}{N}$$

$$\frac{1}{3}mu^2 = KT \qquad \left(\because \frac{R}{N} = K, \text{ Boltzmann constant}\right)$$

or $\frac{1}{2}mu^2 = \frac{3}{2}KT$

But $\frac{1}{2}mu^2$ is average kinetic energy per molecule of the gas

$\therefore$ Average K.E. $= \frac{3}{2}KT$

or Average K.E. $\propto T$ ($\because K$ is constant)

Thus, average kinetic energy of one mole of any gas is directly proportional to its absolute temperature.

Again from equation (1), when $u = 0$,

$T = 0$ (**Absolute zero**)

Hence, **absolute zero** may be defined as the temperature at which the velocities of the gas molecules reduce to zero for example, molecular motion ceases at absolute zero. However, note that this is true only in case of an ideal or perfect gas. The gases used in practice are far from the perfect, particularly at such low temperature.

Speed Related to Gaseous State

(i) Root mean square speed (RMS speed) : Square root of the mean of the squares of the speed of all the molecules, for example,

$$u = \frac{\sqrt{u_1^2 + u_2^2 + u_3^2 + ...u_n^2}}{n}$$

where $u_1, u_2, u_3, ..., u_n$ are the velocities of the gas molecules respectively and n is the number of molecules. RMS is directly proportional to square root of absolute temperature and inversely proportional to square root of molecular weight and density.

$$C = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

(ii) Average speed (AVS) : It is the arithmetic mean of the various speeds of the molecules

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi m}}$$

Average speed = .9213 × RMS speed

RMS speed = 1.085 × Average speed

(iii) Most probable speed (MPS) : Speed possessed by maximum number of molecules of a gas at a given temperature.

$$\text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

MPS = .816 × RMS ; RMS = 1.224 MPS

Relation between the three types of velocities

$$\alpha : v : u$$

$$\sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

1.414 : 1.595 : 1.732

1 : 1.128 : 1.234 for example, $\alpha < v < u$.

DEVIATION FROM IDEAL GAS BEHAVIOUR: REAL GASES

A gas which obeys the ideal gas equation (PV = n RT) under all conditions of temperature and pressure is called an ideal gas or a perfect gas. The gases are observed to show ideal behaviour fairly well at low pressure and high temperature. As the temperature becomes low and pressure becomes high, the gases show a deviation from the general gas laws. Thus, the gas which does not obey general gas laws at all temperatures and pressures is called non-ideal gas or real gas.

Real gases deviate from ideal behaviour because of the following two faulty assumptions of kinetic theory.

(i) The actual volume occupied by molecules is negligible as compared to the total volume of the gas.

(ii) The forces of attraction and repulsion between molecules of the gas are negligible.

Above two assumptions are incorrect as if assumption (a) is correct gases would never liquify without any intermolecular interactions but as we known they do liquify.

Similarly if assumption (b) is correct then in fig. (b) two curves should coincide with each other which actually don't.

Van der Waal's Equation

In order to make up for these two faulty assumptions of kinetic theory van der Waals modified the ideal gas equation by applying corrections to make into account

(a) the volume occupied by gas molecules, and

(b) the forces of attraction between the gas molecules.

van der Waals introduced the necessary corrections as follows:

(i) Volume correction : At higher pressure, the volume is much reduced and at this state the volume of gas molecules no longer remains negligible in comparision with the total volume V occupied by the gas. Thus the free space available for motion of molecules is reduced. If V be the volume of the molecules at rest, effective volume when they are in motion must be greater. It has been calculated to be approximately four times the actual volume.

Thus, excluded volume for one molecule in motion = 4v

∴ Excluded volume for 'N' molecules in motion = 4 N.v

∴ Effective or excluded or co-volume of 1 mole = 4N.v = b

Real or compressible or ideal volume of gas = Actual volume of container – Volume occupied by N molecules in motion

∴ Real volume of gas = (V – b)

Thus, gas equation after I correction is, P (V – b) = RT

(ii) Pressure correction : When pressure of the gas is appreciably high, the molecules are closer to each other than thus, molecular attraction among molecules should not be neglected.

van der Waals' pointed out that if molecular attraction are taken into accout, the forces developed due to collisions are somewhat lesser than those which would have been noticed in absence of these forces. This is due to the decrease in speed of molecules which are to collide due to attraction among molecules. Thus,

Real pressure of gas = Pressure developed due to collisions + Pressure loss due to attraction

= P + P′

Pressure loss due to attraction is P′

$P' \propto$ no. of molecules which are being attracted, i.e., n $P' \propto$ no. of molecules which are attracting, i.e., n

∴ $P' \propto n^2$

Since, in gases uniform distribution of molecules occurs

Thus, $P' \propto n^2 \propto d^2 \propto \frac{1}{V^2}$

where d is density of gas and V is volume.

or $P' = \frac{a}{V^2}$

where a is van der Waals' constant of attraction, a characteristic constant for a given gas.

The gas equation after II correction is

$$\left[P + \left(\frac{a}{V^2}\right)\right]\left[V - b\right] = RT \qquad \ldots(1)$$

Similarly, for n moles of gas one can write

$$\left[P + \left(\frac{n^2 a}{V^2}\right)\right]\left[V - nb\right] = nRT \qquad \ldots(2)$$

Eqs. (1) and (2), represents van der Waals' equation for 1 mole and n moles of gas respectively.

Note : In terms of compressibility factor, van der Waals' equation may be written as :

$$\left[P + \frac{n^2 a}{V^2}\right]\left[V - nb\right] = nRT$$

$$P = \frac{nRT}{\left[V - nb\right]} - \frac{an^2}{V^2}$$

Since, $$Z = \frac{V_M}{V_{M\,\text{ideal}}} = \frac{V_M}{n\frac{RT}{P}}$$

$$\frac{PV_M}{nRT} = \left[\frac{nRT}{V_M - nb} - \frac{an^2}{V_M^2}\right] \times \frac{V_M}{nRT}$$

$$Z = \frac{V_M}{V_M - nb} - \frac{an}{RTV_M}$$

The constants a and b : van der Waals' constant for attraction (a) and volume (b) are characteristics constants for a given gas. Some salient features of a and b are given below :

(i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.

(ii) For a given gas van der Waals' constant of attraction 'a' is always greater than van der Waals' constant of volume 'b'.

(iii) The gas having higher value of 'a' can be liquefied easily and therefore, H_2 and He are not liquefied easily.

(iv) The unit of 'a' and 'b' are

Unit of 'a' ($a = P \times V^2$) = atm litre^2 mol^{-2}

= dyne cm^2 mol^{-2}

= newton m^4 mol^{-2}

Unit of 'b' ($b = 4Nv$) $= \text{litre mol}^{-1}$
$= \text{cm}^3\ \text{mol}^{-1}$
$= \text{m}^3\ \text{mol}^{-1}$

(v) The numerical values of 'a' and 'b' are in the order 10^{-1} to 10^{-2} and 10^{-2} to 10^{-3} respectively if reported in atm-litre units.

By applying low pressure the kinetic energy of molecules decreases and get closer till they change to liquid. So also high pressure brings the gas molecules closer so as to permit attractive forces to be large enough to change to liquids.

Illustration 4 :

(a) Calculate the pressure exerted by 5 mol of CO_2 in one litre vessel at 47°C using van der Waal's equation. Also report the pressure of gas if it behaves ideally in nature. Given that $a = 3.592$ atm ltr^2 mol^{-2} . $b = 0.042$ litre mol^{-1}

(b) If volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mol of CO_2 gas at 273K .

Sol. (a) $$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{5^2 \times 3.592}{1}\right)(1 - 5 \times 0.0427) = 5 \times .0821 \times 320$$

$P = 77.218$ atm

when the gas behaves ideally then $PV = nRT$

$P \times 1 = 5 \times .0821 \times 320. \Rightarrow P = 131.36$ atm

(b) For 1 mole $\left[P + \frac{a}{V^2}\right][V - b] = RT$

If b is negligible $P = \frac{RT}{V} - \frac{a}{V^2} = \frac{.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$

$P = 0.9922$ atm

Compressibility Factor

The extent of deviation of real gas from ideal behaviour is conveniently studied by introducting a term of compressibility factor, Z, in the ideal gas equation for example $PV = ZnRT$, $Z = \frac{PV}{nRT}$

Accordingly,

(a) a gas behaves ideally for example $PV = nRT$, when $Z = 1$

(b) a gas behaves non-ideally (real gas) for example $PV \neq nRT$ when $Z \neq 1$.

Thus, the difference between unity and the value of compressibility factor of a gas is a measure of the extent of nonideality of the gas. The compressibility factor can have two values.

(a) $Z > 1$, for example the gas shows positive deviation from ideal behaviour and is less compressible.

(b) $Z < 1$, the gas shows negative deviation form ideal behaviour and is more compressible.

Gases show ideal behaviour at very low pressure when the volume occupied is large so that the volume of the molecules can be neglected.

Illustration 5 :

The compression factor (compressibility factor) for 1 mol of a van der Waal's gas at 0°C and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate the van der Waals constant 'a'.

Sol. $Z = \frac{PV}{nRT}$, $0.5 = \frac{100 \times V}{1 \times .0821 \times 273}$ $\therefore V = 0.112$ litre.

van der Waal's equation when 'b' is negligible

$$\left[P + \frac{a}{V^2}\right]V = RT \text{ or } \left[100 + \frac{a}{(0.112)^2}\right] = 0.0821 \times 273$$

$a = 1.253$ atm litre^2 mol^{-2}

Boyle's Temperature

The temperature at which a real gas obeys ideal gas laws over an appreciable range of pressure is known as Boyle's temperature. It is related to van der Waal's constant shown as below.

$$T_B = \frac{a}{bR}$$

Effect of Pressure on Deviations

At very low pressure Z is equal to 1 and the gases exhibit nearly ideal character. However, at higher pressure CO_2 gas shows a greater dip in the curve indicating that it is most easily liquified.

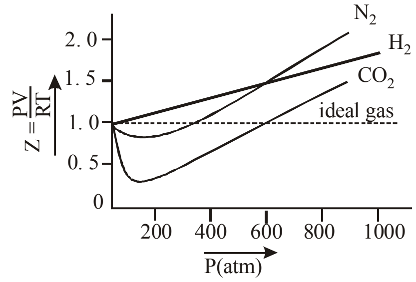


Fig. Z versus P curves for H_2, N_2 and CO_2 at 300K

Effect of Temperature on Deviation

From the shape of the curves, it is clear that deviation from ideal gas nature becomes less and less at high temperature.

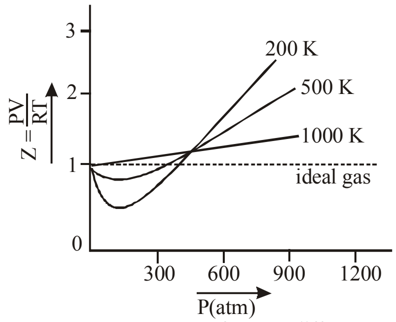


Fig. Z versus P curves for N_2 at different temperatures.

LIQUEFACTION OF GASES

Liquefaction of gases can be achieved either by lowering the temperature or increasing the pressure of the gas simultaneously. By applying low pressure the kinetic energy of molecules decrease and get closer till they change to liquid so also high pressure brings the gas molecules closer so as to permit attractive forces to be large enough to change to liquids.

Thomas Andrews plotted isotherms of CO_2 at various temperatures shows in fig.

Main features of the curve are

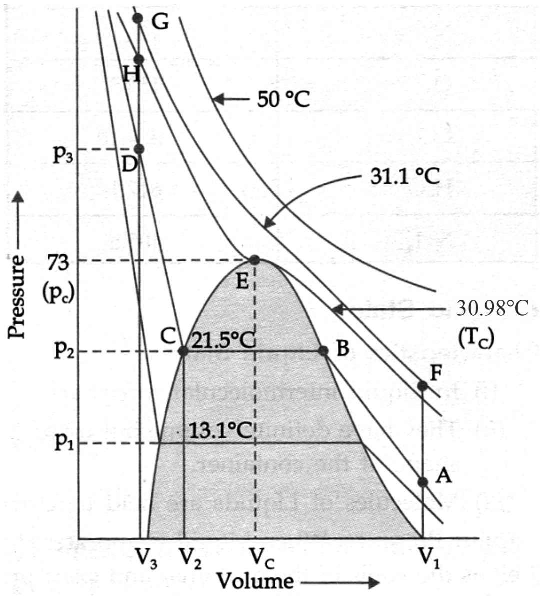
(a) At high temperature isotherm look like that of an ideal gas

(b) At 73 atm and 30.98°C liquid carbon dioxide appears first time indicating critical temperature of carbon dioxide. Further increase in pressure simply compresses the liquid.

(c) At 21.5°C CO_2 remains as a gas only upto point B, At point B liquid CO_2 appears and till C liquid and gas co-exist. Beyond C further application of pressure merely compresses the liquid as shown by steep line (CD)

(d) It is also possible to change a gas into liquid directly by a process, while 'H' a single phase is present by avoiding two-phase equilibrium region

$$A \xrightarrow[\text{temperature}]{\text{By raising}} F \xrightarrow[\text{gas}]{\text{Compressing the}} G \xrightarrow[\text{the temperature}]{\text{By lowering}} D(\text{through H})$$



Critical Constants

(i) Critical temperature (T_c) : The temperature above which gas cannot be liquefied whatever pressure is applied is called critical temperature $T_c = \dfrac{8a}{27bR}$

(ii) Critical pressure (P_c) : The minimum pressure required to liquefy a gas at its critical temperature is called critical pressure.

$$P_c = \frac{a}{27b^2}$$

(iii) Critical volume (V_c) : The volume occupied by one mole of a gas at the critical temperature and critical pressure is called critical volume.

$$V_c = 3b$$

LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids freely moves faster than one another, therefore, liquids can flow and can assume the shape of the container in which these are stored.

Some physical properties of liquids are discussed as below :

Vapour Pressure

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour (above the liquid) in equilibrium with the liquid at that temperature.

It is temperature dependent. As the temperature of a liquid is increased, the vapour pressure of the liquid increases. It is explained on the basis of Maxwell's distribution of energies. At a particular temperature, all the molecules do not have the same energy. Only those molecules can escape from liquid phase to vapour phase which possess kinetic energy equal or greater than a particular value of kinetic energy (E). As a result, the molecules escaping into the vapour phase increases and so does the vapour pressure.

Boiling point of a liquid defined as the temperature at which the vapour pressure of the liquid becomes equal to the external pressure (for example, atmospheric pressure).

When the external pressure is normal atmospheric pressure (for example, 760 mm), the boiling point is called normal boiling point.

When the external pressure is equal to 1 bar, the boiling point is called standard boiling point of the liquid.

Surface Tension

It is defined as the force acting at right angles to the surface along 1 cm length of the surface. Thus, the units of surface tension are dynes per cm (or Nm^{-1} in SI system).

It arises due to the fact that the molecules of the liquid at the surface are in different situation than those inside the liquid. For the molecules at the surface, net attractive force is towards the interior of the liquid. As a result of this inward pull, the surface of the liquid tends to contact to the smallest possible area for a given volume of the liquid.This gives the lowest energy state of the liquid.

To increase the area of surface, some work has to be done against the inward pull. The work required to be done to increase or extend the surface area by one square unit is called **surface energy**.

The lowest energy state of a liquid is when surface area is minimum. Spherical shape satisfies this condition. This is the reason why drops of liquid are spherical in shape.

The magnitude of surface tension depends on the attractive forces between the molecules. When the forces are large, surface tension is large. Increase in temperature increases KE of molecules and effectiveness of attractive forces decreases, so surface tension decreases as the temperature is increased.

Viscosity

It is a measure of resistance to flow which arises due to internal friction between layers of fluid as they slip past one another as the liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient, for example,

$$F \propto A \quad (A \text{ is the area of contact})$$

$$F \propto \frac{du}{dz} \quad \left(\frac{du}{dz}\text{; is velocity gradient for example, change in velocity with distance}\right)$$

$$\therefore \quad F \propto A\frac{du}{dz}$$

$$\Rightarrow \quad F = \eta A\frac{du}{dz}$$

$\eta \rightarrow$ proportionality constant called coefficient of viscosity.

Its SI unit is Nsm^{-2} and in cgs, its unit is poise.

- Greater the viscosity, more slowly the liquid flows. H-bonding and van der Waal's forces are strong enough to cause high viscosity.
- Viscosity of liquids decreases as the temperature rises because at high temperature, molecules have high K.E. and can overcome the intermolecular forces to slip past one another between the layers.

CONCEPT MAP

Intermolecular Interactions Dispersion or London Forces: (act between induced momentary dipoles)
Dipole-Dipole Force:
(act between molecules possessing permanent dipoles)
Dipole-Induced Dipole Forces:
(act between molecules having permanent dipole and molecules lacking it)
Hydrogen Bonding:
(It is a special case of dipole-dipole interactions)

Kinetic Theory of Gases.
All the gases are made up of molecules moving randomly in all the directions.

$$K.E = \frac{3}{2}RT,\ c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi m}} = 0.9213 \times \text{rms speed}$$

$$\text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

$MPs = 816 \times RMS$

Behaviour of Real Gases
Two faulty assumptions of kinetic theory lead van der Waal to modify idea gas equation as,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{Compressibility factor}\quad Z = \frac{PV}{nRT}$$

For ideal gas = Z = 1; For real gas Z^1 1

Z > 1 the gas shows + ve deviation

Z < 1 the gas shows –ve deviation

STATES OF MATTER

Gas Laws

Boyle's Law : $V \propto 1/P$
$P_1V_1 = P_2V_2$, $P \propto d$
Charle's Law: $V \propto T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Gay Lussac's Law: $P \propto T$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Avogadro's Law: V = Kn
M = Kd

Grahm's Law: $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

Liquefaction of Gases

$T_C = \frac{8a}{27bR}$ (temperature above which gas can not be liquified)

$P_C = \frac{a}{27b^2}$ (minimum pressure required to liquify a gas at its critical temperature)

$V_C = 3b$ (Volume occupied by one mole of gas at T_C and P_C

Ideal Gas Equation : PV = nRT
Value of R = 8.314 $JK^{-1}mol^{-1}$, 0.0822 atm K^{-1} mol^{-1}, 8.314 Pa m^3 K^{-1} mol^{-1} and 8.314 × 10^{-2} bar LK^{-1} mol^{-1}
Equation of state :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Dalton's Law $P_{Total} = P_1 + P_2 + P_3 + \ldots$ (at const. T, V)

Liquid State: Intermolecular forces are stronger than gaseous state and have definite volume.
Vapour pressure: Pressure exerted by the vapour in equilibrium with the liquid at that temperature. It increases with increase in temperature.
Surface Tension: Force acting at right angles to the surface along 1 cm length of the surface. Unit dynes per cm or Nm^{-1} SI System. It decreases with increase in temperature.
Viscosity: It is a measure of resistance to flow which arises due to internal friction between layers of fluid as they slip past one another as the liquid flows.

Textbook Exercises

5.1 What will be the minimum pressure required to compress 500 dm³ of air at 1 bar to 200 dm³ at 30°C?

Ans. $P_1 = 1$ bar, $V_1 = 500\ dm^3$

$P_2 = ?$, $V_2 = 200\ dm^3$

As temperature remains constant at 30°C,

$P_1V_1 = P_2V_2$

$1\ bar \times 500\ dm^3 = P_2 \times 200\ dm^3$

$$\text{or}\quad P_2 = \frac{500}{200}\ bar = 2.5\ bar$$

5.2 A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure ?

Ans. $V_1 = 120\ mL$, $P_1 = 1.2\ bar$, $T_1 = 35°C$

$V_2 = 180\ mL$, $P_2 = ?$, $T_2 = 35°C$

As temperature remains constant, $P_1V_1 = P_2V_2$

$(1.2\ bar)(120\ mL) = P_2\ (180\ mL)$

or $P_2 = 0 \cdot 8\ bar$

5.3 Using the equation of state, PV = n RT, show that at a given temperature, density of a gas is proportional to gas pressure, P.

Ans. Using $PV = nRT$

$$PV = \frac{wRT}{M},\ \text{where } n = \text{number of moles}$$

$$= \frac{\text{weight(w)}}{\text{Mol. Mass (M)}} \qquad \therefore\ P = \frac{wRT}{VM}$$

$$P = d\frac{RT}{M},\ \text{where } d = \text{density} = \text{weight / Volume}$$

$$\text{or } d = \frac{MP}{RT}$$

Thus, for a given temperature (M & R are constant) , the density of gas is proportional to gas pressure i.e.

$$d \propto P.$$

5.4 At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide ?

Ans. Using the expression, $d = \frac{MP}{RT}$

$$\therefore\ d_1 = \frac{M_1P_1}{RT_1};\ d_2 = \frac{M_2P_2}{RT_2}.$$

At the same temperature and for same density,

$M_1P_1 = M_2P_2$ (as R is constant) (1 → gaseous oxide, 2 → dinitrogen)

$M_1 \times 2 = 28 \times 5$ (Molecular mass of $N_2 = 28$ u)

or $M_1 = 70$ u

5.5 Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.

Ans. Suppose molecular masses of A and B are M_A and M_B respectively. Then their number of moles will be

$$n_A = \frac{1}{M_A},\ n_B = \frac{2}{M_B}\quad \left(\because n = \frac{\text{given mass}}{\text{molar mass}}\right)$$

$P_A = 2bar,\ P_A + P_B = 3bar,$ i.e., $P_B = 1$ bar

Applying the relation $PV = nRT$

$P_AV = n_ART,\quad P_BV = n_BRT$

$$\therefore\ \frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{1/M_A}{2/M_B} = \frac{M_B}{2M_A}$$

$$\text{or}\ \frac{M_B}{M_A} = 2\times\frac{P_A}{P_B} = 2\times\frac{2}{1} = 4 \text{ or } M_B = 4\ M_A$$

5.6 The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and 1 bar will be released when 0.15 g of aluminium reacts?

Ans. $2Al + 2NaOH + 2H_2O' \rightarrow 2NaAlO_2 + 3H_2$

2×27 $\qquad\qquad$ 3×22400 ml

H_2 produced at STP from 0.15 g Al

$$= \frac{3\times 22400\times 0.15}{54}\ ml = 186.7\ ml$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

(STP) (Required conditions)

We know 1 bar = 0.987 atm

$$\frac{1\,atm\times 186.7 ml}{273K} = \frac{0.987\ atm\times V_2}{293K}\quad \text{or}\ V_2 = 203\ ml$$

5.7 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm³ flask at 27°C ?

Ans. $P = \frac{n}{V}\ RT = \frac{wRT}{MV}$

$$P_{CH_4} = \left(\frac{3.2}{16}\,mol\right)\frac{0.0821\,dm^3\ atm\,K^{-1}\ mol^{-1}\times 300K}{9\,dm^3}$$

$$= 0.55\,atm$$

$$P_{CO_2} = \left(\frac{4.4}{44}\,mol\right)\frac{0.0821\,dm^3 atm\,K^{-1} mol^{-1}\times 300\,K}{9\,dm^3}$$

$$= 0.27\ atm$$

$P_{total} = (0.55 + 0.27)\ atm = 0.82\ atm$

5.8 What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0. 8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1 L vessel at 27°C ?

Ans. Partial pressure of H_2 in 1L vessel

$P_1 = 0.8$ bar, $V_1 = 0.5L$, $P_2 = ?$ $V_2 = 1.0$ L

Temperature remaining constant,

$P_1V_1 = P_2V_2$ (Boyle's Law)

or, $0.8\ bar \times 0.5L = P_2 \times 1.0\ L$

or $P_{H_2} = 0.40$ bar

Partial pressure of O_2 in 1L vessel

$P'_1 = 0.7$ bar, $V'_1 = 2.0$ L, $P'_2 = ?$ $V'_2 = 1.0$ L

Temperature remaining constant

$P'_1V'_1 = P'_2V'_2$

or, $0.7\ bar \times 2.0\ L = P'_2 \times 1.0\ L$

or, $P'_2 = 1.4$ bar or, $P_{O_2} = 1.4$ bar

Total pressure = $P_{H_2} + P_{O_2} = 0.4\ bar + 1.4\ bar = 1.8\ bar$

5.9 Density of a gas is found to be 5.46 g/dm^3 at 27°C at 2 bar pressure. What will be its density at STP ?

Ans. $d = \frac{MP}{RT}$

For the same gas at different temperature and pressure

$$\frac{d_1}{d_2} = \frac{P_1}{T_1} \times \frac{T_2}{P_2}$$

Given that

$d_1 = 5.46 \text{ g dm}^{-3}$, $T_1 = 27° \text{ C} = 300 \text{ K}$, $P_1 = 2 \text{ bar}$

At S.T.P.

$d_2 = ?$, $T_2 = 0°\text{C} = 273\text{K}$, $P_2 = 1 \text{ bar}$

$$\frac{5.46 \text{ g dm}^{-3}}{d_2} = \frac{2 \text{ bar}}{300 \text{ K}} \times \frac{273 \text{ K}}{1 \text{ bar}}$$

or, $d_2 = 3 \text{ g dm}^{-3}$

5.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 0.1 bar pressure. What is the molar mass of phosphorus ?

Ans. Volume at 0°C and 1 bar pressure $= \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or,

$$\frac{0.1 \times 34.05}{546 + 273} = \frac{1 \times V_2}{273}$$

$$V_2 = \frac{0.1 \times 34.05 \times 273}{(546 + 273)}$$

or, $V_2 = 1.135 \text{ mL}$.

∴ Weight of 1.135 mL of vapour at 0°C and 1bar pressure $= 0.0625 \text{ g}$

∴ Weight of 22700 mL of vapour at 0°C and 1bar pressure

$$= \frac{0.0625}{1.135} \times 22700 = 1250 \text{ g}$$

∴ Molar mass $= 125 \text{ g mol}^{-1}$

5.11 A student forgot to add the reaction mixture to the round bottomed flask at 27°C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out ?

Ans. Let us assume that volume of vessel = V cm^3

or, volume of air in the flask at 27°C = V cm^3

Since, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $\frac{V}{300} = \frac{V_2}{750}$

or, $V_2 = 2.5 \text{ V}$

∴ Volume expelled = 2.5 V – V = 1.5 V

∴ Fraction of air expelled $= \frac{1.5\text{V}}{2.5\text{V}} = \frac{3}{5}$

5.12 Calculate the temperature of 4.0 mole of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K^{-1} mol^{-1}).

Ans. PV = nRT

$$\text{or} \quad T = \frac{PV}{nR} = \frac{3.32 \text{ bar} \times 5\text{dm}^3}{4.0 \text{ mol} \times 0.083 \text{ bar dm}^3\text{K}^{-1}\text{mol}^{-1}} = 50 \text{ K}$$

5.13 Calculate the total number of electrons present in 1.4 g of dinitrogen gas

Ans. Gram molecular mass of dinitrogen = 28 g

28 g of dinitrogen contains 6.023 × 10^{23} molecules.

∴ 1.4 g of dinitrogen would contain $= \frac{6.023 \times 10^{23} \times 1.4}{28} =$ 3.011 × 10^{22} molecules

Since 1 atom of nitrogen consists of 7 electrons then one nitrogen molecule would contain 14 electrons 3.011× 10^{22} molecules of nitrogen would contain = 14 × 3.011 ×10^{22} = 4.215 × 10^{23} electrons.

5.14 How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second?

Ans. One Avogadro number of wheat grains

6.022 ×10^{23} grains

Time required to distribute 10^{10} grains = 1 sec

Time required to distribute 6.022 × 10^{23} grains

$$= \frac{6.023 \times 10^{23}}{10^{10}} \text{sec} = 6.022 \times 10^{13} \text{ sec}$$

$$= \frac{6.022 \times 10^{13}}{60 \times 60 \times 24 \times 365} \text{ years} = 19.096 \times 10^5 \text{ years.}$$

5.15 Calculate the total pressure in a mixture of 8 g of dioxygen and 4g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. R = 0.083 bar dm^3 K^{-1} mol^{-1}.

Ans. Molar mass of O_2 = 32g mol^{-1}

∴ 8g of O_2 = 8 / 32 g mol^{-1} = 0.25 mol

Molar mass of H_2 = 2 g mol^{-1}

∴ 4g of H_2 = 4 / 2 g mol^{-1} = 2 mol

∴ Total number of moles (n) = 2 mol + 0.25 mol = 2.25 mol

V = 1 dm^3, T = 27° C = 300 K, R = 0.083 bar dm^3 K^{-1} mol^{-1}

$$PV = n\,RT \text{ or, } P = \frac{nRT}{V}$$

$$= \frac{2.25\text{mol} \times 0.083\text{bar dm}^3\text{K}^{-1}\text{mol}^{-1} \times 300\text{K}}{1\text{dm}^3}$$

= 56.025 bar

5.16 Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3 K^{-1} mol^{-1}).

Ans. Volume of the balloon

$= 4/3\pi r^3 = 4/3 \times 22/7 \times (10\text{m})^3 = 4190.5 \text{ m}^3$

Volume of He filled at 1.66 bar and 27°C = 4190.5m^3

Calculation of mass of He

PV = nRT = (w/M) RT

$$\text{or, } w = \frac{MPV}{RT}$$

$$= \frac{4 \times 10^{-3} \text{kg mol}^{-1} \times 1.66 \text{ bar} \times 4190.5 \times 10^3 \text{ dm}^3}{0.083\text{bar dm}^3\text{K}^{-1}\text{mol}^{-1} \times 300 \text{ K}} = 1117.5 \text{ kg}$$

∴ Total mass of (balloon + He) = 100 + 1117.5 = 1217.5 kg

Maximum mass of the air that can be displaced by the balloon to go up = Volume × Density

or, 4190.5 m^3 ×1.2 kg m^{-3} = 5028.6 kg

payload = 5028.6 –1217.5 kg = 3811.1 kg

5.17 Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. R = 0.083 bar L K^{-1} mol^{-1}.

Ans. $PV = nRT \text{ or, } V = \frac{nRT}{P} = \frac{wRT}{MP} \left(\text{because } n = \frac{w}{M}\right)$

$$V = \frac{8.8\text{g}}{44 \text{g mol}^{-1}} \times \frac{0.083 \text{ bar LK}^{-1}\text{mol}^{-1} \times (273 + 31.1)\text{K}}{1 \text{bar}} = 5.05 \text{ L.}$$

5.18 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas ?

Ans. Let the molar mass of the gas be M_x

We know $P_1 = P_2$ and $V_1 = V_2$ or $P_1V_1 = P_2V_2$

or $n_1RT_1 = n_2RT_2$ or $n_1T_1 = n_2T_2$

or $\frac{W_1}{M_1}T_1 = \frac{W_2}{M_2}T_2$

$$\therefore \frac{2.9}{M_x}\times(95+273) = \frac{0.184}{2}\times(17+273)$$

$$\text{or} \quad M_x = \frac{2.9\times368\times2}{0.184\times290} = 40\text{g mol}^{-1}$$

5.19 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

Ans. $n_{H_2} = 20/2 = 10$ moles, $n_{O_2} = 80/32 = 2.5$ moles

$$\left(\because n = \frac{\text{given mass}}{\text{molar mass}}\right)$$

$$P_{H_2} = \frac{n_{H_2}}{n_{H_2}+n_{O_2}}\times P_{Total} = \frac{10}{10+2.5}\times 1\,\text{bar}. = 0.8\,\text{bar}$$

5.20 What would be the SI unit for the quantity pV^2T^2/n ?

Ans. $\frac{Nm^{-2}\times(m^3)^2\times K^2}{mol} = Nm^4K^2mol^{-1}$

5.21 In terms of Charle's law explain why –273°C is the lowest possible temperature?

Ans. At –273°C, volume of the gas becomes equal to zero, i.e., the gas ceases to exist.

5.22 Critical temperature for carbon dioxide and methane are 31.1°C and – 81.9°C respectively. Which of these has stronger intermolecular forces and why?

Ans. Higher the critical temperature, more easily the gas can be liquefied, i.e., greater are the intermolecular forces of attraction. Hence, CO_2 has stronger intermolecular forces than CH_4.

5.23 Explain the physical significance of the van der Waal's parameters?

Ans. '*a*' is a measure of the magnitude of the intermolecular forces of attraction while b is a measure of the effective size of the gas molecules.

Practice Questions

Very Short Answer Questions [1 Mark]

1. State Charle's Law.
2. Is volume directly or inversely proportional to pressure at constant temperature ?
3. Given are the boiling point of different liquids $CS_2 = 46.3°$ C ; H_2O = 100°C ; CCl_4 = 77°C. In which liquid the intermolecular forces of attraction are weakest?
4. Is the boiling point of water measured at sea level greater than, less than , same as that measured at an elevation of 1 mile.
5. A thermometer is dipped in a dish containing ether and the reading is recorded. After few minutes the volume of ether decreases. Will the temperature shown by the thermometer will be more or less than the initial reading.
6. If the number of moles of gas was doubled and the pressure and temperature remained the same, what would happen to volume?
7. When do real gases behave as ideal gas?
8. Define Boyle's law.
9. Liquids are less compressible than gases. Explain
10. What is the effect of temperature on viscosity?
11. The tyre of automobile is inflated to lesser pressure in summer than in winter. Why ?
12. The size of weather balloon becomes larger and larger as it ascends up into higher altitudes. Why?
13. What is the effect of pressure on (i) viscosity, (ii) surface tension, (iii) density of liquid ?
14. What is boiling point of water at (i) higher altitudes, (ii) in pressure cooker ?
15. Why is moist air lighter than dry air ?
16. State Graham's law of diffusion.
17. What do you mean by Boyle temperature ? Give its expression and its relation with inversion temperature.
18. Give most common application of Dalton's law.
19. Name any three measurable properties of gases.
20. What is an isotherm ?
21. What is an isobar ?
22. Liquid is transferred from a large beaker to a small beaker, what will be the effect on its vapour pressure ?
23. Why does a gas expand indefinitely ?
24. Explain, why the bubbles of a gas in a boiling liquid generally increase in volume as they approach the upper surface ?
25. What is the effect of temperature on the vapour pressure of a liquid ?
26. Define root mean square velocity.
27. What are critical constants of a gas ?
28. What is SI unit of (i) Viscosity (ii) Surface tension.
29. Define critical temperature of gas.
30. What are real gases ?
31. Why liquids diffuse slowly as compared to gases ?
32. What is thermodynamic scale of temperature?
33. Why is it not possible to cool a gas at 0 K ?
34. What is the molar gas volume at STP for an ideal gas ?
35. What is the density of oxygen, O_2 in grams per litre at 25°C and 0.850 atm ?
36. How is the mole fraction of a component gas related its partial pressure and the total pressure.
37. In the van der Waals equation $\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$. The constant '*a*' accounts for what property of molecules of real gases ?
38. Under what conditions $Z \to 1$ for different gases?
39. How does the vapour pressure depend on the amount of a liquid ?
40. Why is it difficult to soften food at hills ?
41. Predict the order of increasing vapour pressure at a given temperature for the following compounds.

(i) $CH_3CH_2CH_2CH_2OH$ (Butanol-1)
(ii) $HOCH_2CH_2CH_2CH_2$ OH (Butan-1, 4-diol)
(iii) $CH_3CH_2—O—CH_2CH_3$ (Diethyl ether)

42. An astronaut in an orbiting space-ships spilled a few drops of his drink, and the liquid floated around the cabin. In what geometric shape is each drop most likely to be found ? Explain.

43. Which will cool at room temperature faster—a closed container of water at 100°C or an open container of water at 100°C ? Explain your answer.

44. Methane, CH_4, reacts with chlorine in the presence of light gives four products: methyl chloride (CH_3Cl), dichloro methane (CH_2Cl_2), trichloromethane ($CHCl_3$) and tetrachloro-methane (CCl_4). Which compound has the lowest vapour pressure at room temperature? Explain.

Short Answer Questions [2 & 3 Marks]

1. A gas is expanded, at constant temperature, from a volume of 400 ml to a volume of 1 litre, where its final pressure is 100 mm of Hg. What was the original pressure?

2. At STP a given quantity of gas occupies 5.00 litres. What is the temperature of this same quantity of gas at the same pressure when it occupies a volume of 10 litres?

3. In the reaction $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$, how many litres of oxygen are necessary to react with 100 litres of methane? How many litres of CO_2 and steam are produced? (Assume all the reactants and products are measured at the same pressure and temperature.)

4. Find the number of moles of gas that would occupy 10.2 litres at a pressure of 3.7 atm and a temperature of 500 K.

5. Using the kinetic theory, account for the observed behaviour of gases described by Dalton's law.

6. Why in case of hydrogen and helium the compressibility factor is always greater than 1?

7. If the density of a certain gas at 30°C and 768 atm pressure is 1.35 kg/m^3, find its density at STP.

8. A gas cylinder contains 370 g oxygen gas at 30 atm pressure and 25°C. What mass of oxygen would escape if first the cylinder were heated to 75°C and then the valve were held open until gas pressure was 1 atm, the temperature being maintained at 75°C?

9. Why glycerin is more viscous than ethanol?

10. A flask was heated from 27°C to 227°C at constant pressure. Calculate the volume of the flask if 0.1 dm^3 of air measured at 227°C was expelled from the flask ?

11. A gas occupying a volume of 100 litres is at 20°C under a pressure of 2 bar. What temperature will it have when it is placed in an evacuated chamber of volume 175 litres ? The pressure of the gas in the chamber is one-third of its initial pressure.

12. The values of the van der Waal's constants for a gas are $a = 4.10\ dm^6\ bar\ mol^{-2}$ and $b = 0.035\ dm^3\ mol^{-1}$. Calculate the values of the critical temperature and critical pressure for the gas.

13. A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture ?

14. Viscosity of a liquid arises due to strong intermolecular forces existing between the molecules. Stronger the intermolecular forces, greater is the viscosity. Name the intermolecular forces existing in the following liquids and arrange them in the increasing order of their viscosities. Also give reason for the assigned order in one line.
Water, hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$), glycerine ($CH_2OHCH(OH)CH_2OH$)

15. What are the two practical implications of the Boyle's law?

16. A perfect gas at 340 K is heated at constant pressure until its volume has increased by 18 per cent. What is the final temperature of the gas?

17. A bacterial culture isolated from sewage produced 41.3 ml of methane, CH_4 at 31ºC and 753 mm Hg. What is the volume of this methane at STP?

18. A 2.50 L flask was used to collect a 5.65g sample of propane gas C_3H_8. After the sample was collected, the gas pressure was found to be 956 mmHg. What was the temperature of the propane in the flask?

19. Chloroform, $CHCl_3$ is a volatile (easily vapourised) liquid solvent. Calculate the density of chloroform vapour at 99ºC and 745 mmHg. Give the answer in gram per litre.

20. How many litres of chlorine gas, Cl_2, can be obtained at 40ºC and 1.03 atm from 9.41 g of hydrogen chloride, according to the following equation?

$$2KMnO_4 (s) + 16HCl (aq) \rightarrow$$
$$8H_2O (l) + 2KCl (aq) + 2MnCl_2 (aq) + 5Cl_2 (g)$$

21. Pressure of 1 g of an ideal gas A at 27ºC is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find a relationship between their molecular masses.

22. What are the causes of deviations from ideal behaviour?

23. Explain why 15g of steam at 100ºC melts more ice than 15g of liquid water at 100ºC?

24. Explain why liquids like ether and acetone are kept in cool places?

25. An open vessel at 27ºC is heated until three-fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.

26. A cylinder contains nitrogen gas and a small amount of liquid water at a temperature of 25ºC (the vapour pressure of water is 23.8 mm Hg). The total pressure is 600 mm Hg. A piston is pushed into the cylinder until the volume is halved. What is the final total pressure?

27. What names are given to the following ideal gas relationships ?
(a) Volume and moles at constant T and p.
(b) Pressure of non-reacting gases in mixture of constant T and V.
(c) Volume and temperature in Kelvin at constant p and n.

28. What is the volume of a sample of oxygen at a pressure of 2.50 atm, if its volume is 3.15 L at 1.00 atm ? The temperature remains constant.

29. A sample of hydrogen gas is found to occupy 906 cm^3 of volume at 300 K. Calculate the temperature at which it will occupy 500 cm^3 of volume? (Assuming amount and pressure remains constant.)

30. A quantity of hydrogen is confined in a chamber of constant volume. When the chamber is immersed in a bath of melting ice, the pressure of the gas is 1000 torr. What is the temperature in Celsius, when the pressure in manometer indicates are absolute pressure of 400 torr ?

31. Calculate the value of R in S.I. units for one mole gas at STP.

Long Answer Questions [5 Marks]

1. (i) Derive the formula to calculate molar mass of gas from ideal gas equation

(ii) Give difference between ideal and real gas.

2. (i) A quantity of hydrogen is confined in a chamber of constant volume. When the chamber is immersed in a bath of melting ice, the pressure of the gas is 1000atm. (a) What is the Celsius temperature when the pressure manometer indicates an absolute pressure of 400 atm? (b) What pressure will be indicated when the chamber is brought to 100 ºC?

(ii) A steel tank containing air at 15 atm pressure at 15° C is provided with a safety valve that will yield at a pressure of 30 atm. To what minimum temperature must the air be heated to blow the safety valve?

3. (i) One mole of the CO_2 occupies 1.5 L at 25ºC. Calculate the pressure exerted by the gas using:

(a) an ideal gas equation

(b) van der Waal's equation if:
$a = 3.012$ atm mol^{-2} and $b = 0.04$ L mol^{-1}.

(ii) The critical temperature and pressure for NO gas are 177 K and 64.5 atm. respectively. Calculate the van der Waal's constants '*a*' and '*b*'.

4. 1 L of O_2 and 1 L of H_2 are taken in a vessel of 2 L capacity at NTP. The gases are made to combine to form water. Calculate:

(i) the moles and weight of water formed.

(ii) the amount of gas left in vessel.

(iii) the total pressure if the vessel is heated to 100ºC.

(iv) moles of O_2 used for the formation of water.

5. Two flasks A and B have equal volume. Flask A contains H_2 and is maintained at 300 K while flask B contains an equal mass of CH_4 gas and is maintained at 600 K.

(a) Which flask contains greater number of molecules? How many times more?

(b) In which flask is the pressure greater? How many times greater?

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Which of the following two graphs will be a straight line at constant temperature?

P versus V or P versus $\frac{1}{V}$ (at constant T)

P versus $\frac{1}{V}$ graph will be a straight line. **[HOTS]**

2. Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas 'A' liquefies but gas B does not liquify even on applying high pressure until it is cooled. Explain this phenomenon. **[HOTS]**

3. While drinking in an orbiting spaceship the astronaut spilled a few drops of his drink. What will be the shape of liquid drops floating in cabin? Explain your answer. **[HOTS]**

4. How can you show incompressible nature of gas molecules? **[HOTS]**

5. Which one out of NH_3 and N_2 will have a larger value of 'a' (van der Waals' constant)? **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. At 15°C and 900 mm pressure, 0.4 gram of a certain gas occupied 3280 mL. If the pressure is changed to 1300 mm at constant temperature. What is the density of the gas? **[Exemplar]**

2. Calculate the vapour density of a gas, 12.8g of which occupies 10L at a pressure of 750 mm at 27°C. **[Exemplar]**

3 Which type of intermolecular forces exist among the following molecules?

(i) H_2S molecules (ii) H_2O molecules

(iii) Cl_2 and CCl_4 molecules (iv) SiH_4 molecules

(v) Helium atoms (vi) He atoms and HCl molecules

[Exemplar]

4. Value of universal gas constant (R) is same for all gases. What is its physical significance? **[Exemplar]**

5. Use the information and data given below to answer the questions (a) to (c) :

Stronger intermolecular forces result in higher boiling point.

Strength of London forces increases with the number of electrons in the molecule.

Boiling point of HF, HCl, HBr and HI are 293 K, 189 K, 206 K and 238 K respectively.

(a) Which type of intermolecular forces are present in the molecules HF, HCl, HBr and HI ?

(b) Looking at the trend boiling points of HCl, HBr and HI, explain out of dipole-dipole interaction and London interaction, which one is predominant here.

(c) Why is boiling point of hydrogen fluoride highest while that of hydrogen chloride lowest? **[Exemplar]**

6. Compressibility factor, Z, of a gas is given as $Z = \frac{pV}{nRT}$

(i) What is the value of Z for an ideal gas ?

(ii) For real gas what will be the effect on value of Z above Boyle's temperature ? **[Exemplar]**

7. For real gases the relation between p, V and T is given by van der Waals equation :

$$\left(p+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

where '*a*' and '*b*' are van der Waals constants, 'nb' is approximately equal to the total volume of the molecules of a gas. '*a*' is the measure of magnitude of intermolecular attraction.

(i) Arrange the following gases in the increasing order of '*b*'. Give reason. O_2, CO_2, H_2, He

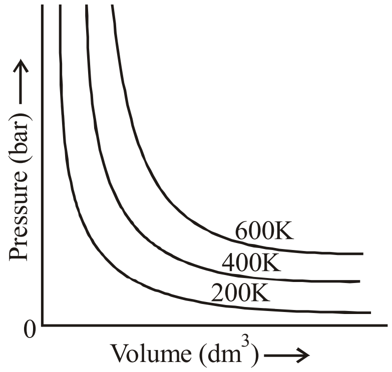
(ii) Arrange the following gases in the decreasing order of magnitude of '*a*'. Give reason.

CH_4, O_2, H_2 **[Exemplar]**

8. The variation of pressure with volume of the gas at different temperature can be graphically represented as shown in figure. On the basis of this graph answer the following questions.

(i) How will the volume of a gas change if its pressure is increased at constant temperature?

(ii) At a constant pressure, how will the volume of a gas change if the temperature is increased from 200 K to 400 K? **[Exemplar]**



Long Answer Questions [5 Marks]

1. (i) A spherical balloon of 21 cm diameter is to be filled with hydrogen at STP from a cylinder containing the gas at 20 atm at 27ºC. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up.

(ii) Two van der Waals gases A and B have volumes 0.112 and 0.111 L mol^{-1} respectively. Calculate the compressibility factors for one mole of each at 273 K and 200 atm and hence state which gas is more compressible. **[HOTS]**

2. An LPG (liquified petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres 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. **[HOTS]**

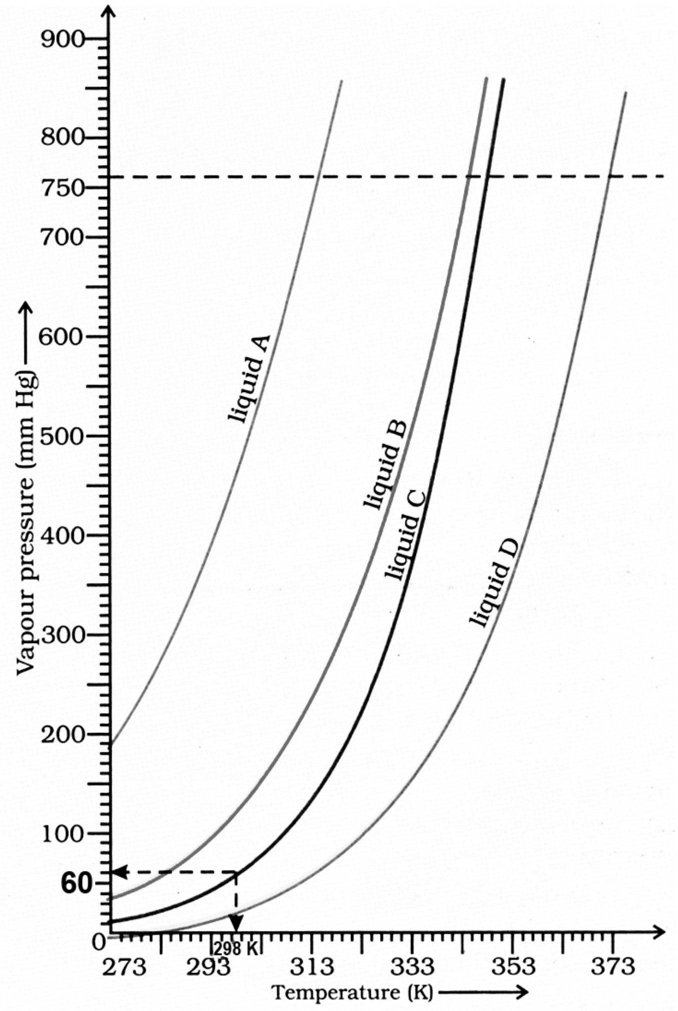
3. The variation of vapour pressure of different liquids with temperature is shown in Fig. 5.6.

(i) Calculate graphically boiling points of liquids A and B.

(ii) If we take liquid C in a closed vessel and heat it continuously. At what temperature will it boil?

(iii) At high altitude, atmospheric pressure is low (say 60 mm Hg). At what temperature liquid D boils?

(iv) Pressure cooker is used for cooking food at hill station. Explain in terms of vapour pressure why is it so?



[HOTS]

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. Draw a graph between V & P at constant T.

2. Tea or coffee is sipped from a saucer when it is quite hot. Explain.

3. Why ethanol has lower vapour pressure than benzene?

4. What is the difference between boiling and evaporation?

5. Liquid ammonia bottle is cooled before opening the seal . Why?

6. Calculate the total pressure in a 10L cylinder which contains 0.4 g Helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27° C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behavior of gases. ($R = 0.082$ L atm K^{-1} mol^{-1})

7. (i) An evacuated glass vessel weighs 50 g when empty, 148 g when filled with a liquid of density 0.98 g/ml and 50.5 g when filled with an ideal gas at 760 mm Hg at 300K. Determine the molecular weight of the gas.
(ii) At 0°C, the density of a gaseous oxide at 2 bar is same as that of nitrogen at 5 bar. What is the molecular mass of oxide.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. At constant pressure the volume of given mass of gas is directly proportional to absolute temperature.

2. Volume is inversely proportional to pressure according to Boyle's law.

3. CS_2

4. Greater

5. Less than the initial reading, since evaporation leads to cooling.

6. Doubled.

7. At high temperature and low pressure real gases behave like ideal gas.

8. The volume of a given mass of gas is inversely proportional to pressure at constant temperature.
$V \alpha 1/P$ or $PV = \text{constant}$.

9. Liquid molecules have stronger intermolecular forces of attraction as compared to gases, thus they are less compressible than gases.

10. Increase in temperature reduces viscosity.

11. Air expands more during summer than winter.

12. At higher altitudes, atmospheric pressure is less, therefore, air inside balloon exerts pressure and it becomes larger and larger.

13. Increase in pressure increases viscosity, surface tension and density because force of attraction increases.

14. (i) < 100°C (ii) > 100°C

15. Moist air has water vapour which has lower vapour density (18/2 = 9) than dry air, which has vapour density equal to 14.4. That is why moist air is lighter than dry air.

16. It states that the rate of diffusion of gases is inversely proportional to square root of molecular masses at constant temperature and pressure.

17. Boyle temperature is a temperature at which most of real gases show ideal gas behaviour over wide range of pressure.

$$T_b = \frac{a}{bR}$$

$$T_i = 2T_b$$

18. The air pressure decreases with increase in altitude. That is why jet aeroplane flying at high altitude need pressurization of the cabin so that partial pressure of oxygen is sufficient for breathing.

19. (i) Volume (ii) Pressure
(iii) Temperature

20. The graph plotted between P and V for a gas at constant temperature is called an isotherm.

21. The graph plotted between V and T at constant pressure is called an isobar.

22. There will be no effect on the vapour pressure of a liquid because vapour pressure is an intensive property.

23. Because the intermolecular forces of attraction among the molecules of a gas are negligible.

24. Because on approach of the upper surface, the pressure on them decreases and hence volume increases.

25. Vapour pressure is directly proportional to the temperature.

26. It is the square root of the mean of the squares of different speeds of all the molecules of a gas.

27. Critical temperature, critical volume and critical pressure are called critical constants of a gas.

28. (i) Unit of viscosity is pas Nm^{-2} S.
(ii) Unit of surface tension Nm^{-1}.

29. The temperature above which a gas cannot be liquefied.

30. A gas which can deviate ideal gas behaviour at higher pressure and lower temperature is called a real gas.

31. In Liquids, the molecules are more compact in comparison to gases.

32. The temperature scale based on absolute zero (0K = – 273.15°C) is known as the thermodynamic scale of temperature.

33. It is not possible to cool gas at 0K because all gases condenses to liquids or solids before this temperature is reached.

34. Molar gas volume (volume of one mole of gas) at 0°C and under 1 atm is 22.4 L or $22.4 \times 10^{-3}\ m^3$.

35. $$d = \frac{PM}{RT}$$

$$d = \frac{0.850\ \text{atm} \times 32.0\ \text{g mol}^{-1}}{0.0821\ \text{L atm mol}^{-1} \times 298\ \text{K}} = 1.11\ \text{gL}^{-1}$$

36. Mole fraction equals the partial pressure divided by the total pressure.

$$x_i = \frac{p_i}{p_{total}}$$

37. '*a*' accounts for intermolecular forces of attraction.

38. Z = 1 for different gas at a very low pressure $(P \to 0)$.

39. The vapour pressure is a kinetic phenomenon. It is independent of the amount of a liquid. It only depends on the temperature.

40. It is difficult to soften food at hills because the external pressure is less than one atmosphere and the water will boil at a lower temperature.

41. The increasing vapour pressure order is $HO\,CH_2\,CH_2\,CH_2\,CH_2\,OH < CH_3\,CH_2\,CH_2\,CH_2\,OH < CH_3\,CH_2—O—CH_2\,CH_3$
Because the hydrogen bonding decreases in magnitude from Butan-1, 4-diol to Diethylether.

42. The drop would be spherical—the shape which gives the smallest surface area per unit volume, in response to surface tension.

43. The water will cool faster uncovered, since it can evaporate that way—Evaporation results in cooling, since the most energetic molecules are the ones that are lost, and they may use energy to push back the atmosphere.

44. Tetrachloromethane (CCl_4) has the lowest vapour pressure at room temperature. This is due to its highest molecular mass and greatest London forces.

Short Answer Questions

1. Temperature is constant, so apply Boyle's law
$P_1V_1 = P_2V_2$
$P_1 = ?$; $V_1 = 400$ ml; $P_2 = 100$ mm of Hg ; $V_2 = 1L = 1000$ ml

$$P_1 = \frac{P_2 \times V_2}{V_1} = \frac{100 \times 1000}{400} = 250 \text{ mm of Hg.}$$

2. Pressure is constant, so apply Charle's law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 5L$; V_2 ; $= 10L$; $T_1 = 273$ K ; $T_2 = ?$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{10 \times 273}{5} = 546\ \text{K}$$

3. As per reaction 1 litre of methane reacts with
= 2 litres of oxygen
∴ 100 litres of methane would react with
= 200 litres of oxygen
For the second part
As 2 litres of oxygen gives
= 1 litre of CO_2 and 2 litres of Steam
∴ 200 litres of oxygen would give
= 100 litres of CO_2 and 200 litres of steam.

4. PV = nRT
P = 3.7 atm ; V = 10.2 L ; n = ? ;
R = 0.082 L atm
K^{-1} $mole^{-1}$; T = 500 K

$$n = PV/RT = \frac{3.7 \times 10.2}{0.082 \times 500} = 0.92 \text{ mole}$$

5. There are no attractive forces between the particles of an ideal gas. In the mixture of gases, each particle strikes the walls same number of times per second as if no other particles were present. Therefore, the pressure of a particular gas in a mixture is not changed by the presence of other gases.

6. H_2 and He being a very small molecules, the intermolecular forces of attraction in them are negligible i.e. 'a' factor is very small so that a / V^2 is negligible. The van der waal's equation reduces to
$P(V - b) = RT$ for 1 mole
or $PV - bP = RT$ or $PV = RT + bP$ ---(1)
Divide eqn (1) by RT we get

$$\frac{PV}{RT} = 1 + \frac{bP}{RT} \text{ We know } PV/RT = Z\text{, thus } Z = 1 + \frac{bP}{RT}$$

i.e. Z > 1 and increases with increase in the value of P.

7. Since the mass does not change, the density is inversely proportional to the volume:

$$= \frac{d_{stp}}{d_{given\ conditions}} = \frac{V_{given\ conditions}}{V_{std}}$$

$$= \frac{T_{given\ conditions} \times P_{std}}{T_{std} \times P_{given\ conditions}}$$

$$= \frac{303K \times 760\,\text{mm Hg}}{273K \times 760 \times 768\,\text{mm Hg}} = 0.0014$$

$d_{stp} = 0.0014 \times d_{given\ conditions}$
$= 0.0014 \times 1.35\ kg/m^3 = 0.00189\ kg/m^3$

8. The volume is found from initial conditions :

$$n = (370g)\left(\frac{1\text{mol}}{32.0g}\right) = 11.56\,\text{mol}$$

$$V = \frac{nRT}{P}$$

$$= \frac{11.56\,\text{mol} \times 0.0821\text{L atm / mol K} \times 298\,\text{K}}{30.0\,\text{atm}} = 9.43\ \text{L}$$

The final number of moles of oxygen is

$$n = PV/RT = \frac{1.00\,\text{atm} \times 9.43\,\text{L}}{0.0821\,\text{L atm / mol K} \times 348\,\text{K}} = 0.330 \text{ mol}$$

Mass of oxygen left

$$= (0.330\,\text{mol})\left(\frac{32.0g}{\text{mol}}\right) = 10.6g$$

Mass of oxygen escaped = (370g initial) – (10.6g final)
= 359.4 g of oxygen escaped.

9. This is because of presence of three –OH groups in glycerol or glycerin as compared to only one –OH group in ethanol. Hence, the hydrogen bonding in glycerin is thrice as compared to alcohol molecule. Thus, there is a greater intermolecular force of attraction in glycerin than in ethanol; therefore, it is more viscous than alcohol.

10. Let the volume of the flask = V dm^3 (after expelling the air)

$V_1 = V\ dm^3$ $T_2 = 27 + 273 = 300\ K$

$V_2 = (V + 0.1)\ dm^3$ $T_2 = 227 + 273 = 500\ K$

Since the pressure of the gas is constant, Charles's law is applicable.

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \text{ or } V_1 = \frac{T_1}{T_2} \times V_2$$

$$\text{or} \quad V = \frac{(300\ K) \times (V + 0.1\ dm^3)}{(500\ K)}$$

$$\text{or} \quad V = \frac{3(V + 0.1)}{5} dm^3$$

$$\text{or} \quad 5V - 3V = 0.3\ dm^3 \text{ or } 2V = 0.3\ dm^3$$

$$\therefore \quad V = \frac{0.3\ dm^3}{2} = 0.15\ dm^3$$

11. From the available data :

$V_1 = 100 L$ $V_2 = 175\ L$

$P_1 = 2$ bar $P_2 = 2 \times 1/3 = 2/3$ bar

$T_1 = 20 + 273 = 293\ K$ $T_2 = ?$

According to Gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or } T_2 = \frac{P_2V_2T_1}{P_1V_1}$$

By substituting the values,

$$T_2 = \frac{(2/3\ bar) \times (175\ L) \times (293\ K)}{(2\ bar) \times (100\ L)}$$

$$= 170.9\ K = 170.9 - 273.0 = -102.1°C$$

12. (i) Calculation of critical temperature (T_c).

$a = 4.10\ dm^6\ bar\ mol^{-2}$

$b = 0.035\ dm^3\ mol^{-1}$

$R = 0.0821\ dm^3\ bar\ mol^{-1}\ K^{-1}$.

Now, critical temperature,

$$T_c = \frac{8a}{27\ Rb}$$

Substituting the values,

$$T_c = \frac{8 \times 4.10}{27 \times 0.0821 \times 0.035}$$

(ii) Calculation of critical pressure (P_c)

$$P_c = \frac{a}{27b^2} = \frac{4.10}{27 \times 0.035 \times 0.035} = 123.96 \text{ bar}$$

13. $$\text{Number of moles of dioxygen} = \frac{70.6\ g}{32\ g\ mol^{-1}} = 2.21\ mol$$

$$\text{Number of moles of neon} = \frac{167.5\ g}{20\ g\ mol^{-1}} = 8.375\ mol$$

$$\text{Mole fraction of dioxygen} = \frac{2.21}{2.21 + 8.375} = \frac{2.21}{10.585} = 0.21$$

$$\text{Mole fraction of neon} = \frac{8.375}{2.21 + 8.375} = 0.79$$

Partial pressure of a gas = mole fraction × total pressure

⇒ Partial pressure of oxygen = 0.21 × (25 bar) = 5.25 bar

Partial pressure of neon = 0.79 × (25 bar) = 19.75 bar

14. In water and glycerine – Hydrogen bonding. Hexane – Dispersion forces / London forces. The order of viscosities of these liquids is hexane < water < glycerine. Hexane has weakest intermolecular forces and glycerine the strongest (three OH groups). Therefore, hexane has minimum viscosity and glycerine has maximum viscosity.

15. The two practical implications of the Boyle's law are:

(i) The density and pressure decreases with the increase in altitude. The decrease in pressure at high altitudes causes altitude sickness (headache, sluggish feeling) due to decrease in the oxygen intake in each breath.

(ii) When a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that the gas becomes denser. Air at the level is denser because it is compressed by the mass of air above it.

16. $$V_1 = V;\ V_2 = \frac{18}{100}V + V = \frac{118}{100}V$$

$T_1 = 340\ K$ $T_2 = ?$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } T_2 = \left(\frac{V_2}{V_1}\right)T_1$$

$$T_2 = \frac{\left(\frac{118V}{100}\right)}{V} \times 340K \qquad T_2 = 401\ K.$$

17. $V_1 = 41.3\ ml$ $V_2 = ?$

$P_1 = 753\ mm\ Hg$ $P_2 = 760\ mm\ Hg$

$T_1 = 31 + 273 = 304\ K$ $P_2 = 273\ K$

$$\therefore \quad V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1 = \frac{753\ mm\ Hg \times 273K \times 41.3\ ml}{760\ mm\ Hg \times 304K}$$

$V_2 = 36.7$ ml.

18. $m = 5.65\ g$

$$P = \frac{956}{760} atm = 1.26\ atm$$

$V = 2.50\ L$

$M = 44\ g\ mol^{-1}$

$PV = nRT$

$$T = \frac{PVM}{mR} = \frac{1.26 atm \times 2.50 L \times 44 g\ mol^{-1}}{5.65 g \times 0.0821 L\ mol^{-1} K^{-1}}$$

$T = 298.8\ K$.

19. $M = 119.5\ g\ mol^{-1}$

$T = 99 + 273 = 372\ K$

$$P = \frac{745}{760} = 0.98\ atm$$

$$d = \frac{PM}{RT}$$

$$= \frac{0.98\ atm \times 119.5 g\ mol^{-1}}{0.0821\ L\ atm\ mol^{-1}\ K^{-1} \times 372K}$$

$d = 3.83\ g\ L^{-1}$.

20. $$n_{HCl} = \frac{9.41 g}{36.5 g\ mol^{-1}} = 0.26\ mol$$

16 mol HCl liberates 5 mol Cl_2

∴ 0.26 mol HCl will liberate

$$5 \times \frac{0.26}{16} = 0.081\ mol\ Cl_2$$

$PV = nRT$

$$V_{Cl_2} = \frac{nRT}{P} = \frac{0.081\,\text{mol} \times 0.0821\,\text{L atm}^{-1}\text{K}^{-1} \times 313\text{K}}{1.03\,\text{atm}}$$

$$V_{Cl_2} = 2.02\,\text{L}.$$

21. For gas A

$$P_A V = \frac{m_A}{M_A} RT \qquad (1)$$

For gas B

$$P_B V = \frac{m_B}{M_B} RT$$

Dividing equation (1) by equation (2) give

$$\frac{P_A}{P_B} = \frac{m_A}{m_B}\frac{M_B}{M_A}$$

$$\frac{M_A}{M_B} = \left(\frac{m_A}{m_B}\right)\left(\frac{P_B}{P_A}\right) = \left(\frac{1\text{g}}{2\text{g}}\right)\left(\frac{1\text{ bar}}{2\text{ bar}}\right)$$

$$\frac{M_A}{M_B} = 1:4$$

22. The causes of deviations from ideal behaviour are:

(a) The molecules of a gas occupy a certain volume as can seen from the fact that gases can be liquified and solidified at low temperatures and high pressure.

(b) The effect of applying high pressure is to bring the molecules closer to one another, thereby increasing the forces of attractions amongst them.

23. More heat is required for vapourisation than for melting. Melting needs only enough energy for the molecules to escape from their sites in the solid. For vapourisation, enough energy must be supplied to break most of the intermolecular attractions. That's why 15g of steam melts more ice than 15g of water at 100ºC.

24. Liquid like ether and acetone are highly volatile due to weak intermolecular forces of attraction. The rate of evaporation of liquid decreases with decrease in temperature. Therefore, ether and acetone are kept in cool place to slow down their evaporation.

25. Given that,

$T_1 = 27ºC = 300\text{K}$

$n_1 = 1\text{ mol}$

$$n_2 = 1 - \frac{3}{5} = 0.4\text{ mol}$$

The volume of the gas remains constant throughout the process therefore pressure also remains constant. Hence from

$$n_1RT_1 = n_2RT_2$$

$$\text{or} \quad T_2 = \frac{n_1}{n_2} \times T_1 = \frac{1}{0.4} \times 300 = 750$$

$T_2 = 477ºC$

26. Given that,

$P_1 = 600 - 23.8 = 576.2\text{ mm of Hg}$

$$V_2 = \frac{V_1}{2}$$

According to Boyle's law,

$$P_1V_1 = P_2V_2$$

$$\therefore \quad 576.2 \times V_1 = P_2 \times \frac{V_1}{2}$$

or $\quad P_2 = 1152.4$

The final total pressure $= 1152.4 + 23.8 = 1176.2$ mm of Hg

27. (a) Avogadro's Law

(b) Dalton's Law

(c) Charles's Law

28.

$$\left.\begin{array}{l} P_1 = 1.00\text{ atm} \\ P_2 = 2.50\text{ atm} \\ V_1 = 3.15\text{ L} \\ V_2 = ? \end{array}\right]\begin{array}{l}\text{Temperature and} \\ \text{an amount of gas} \\ \text{remains constant}\end{array}$$

From Boyle's law, we have

$P_1 V_1 = P_2 V_2$

$$\text{or} \quad V_2 = \frac{1.00\text{ atm} \times 3.15\text{ L}}{2.50\text{ atm}} = 1.26\text{ L}.$$

29.

$T_1 = 300\text{ K} \qquad T_2 = ?$

$V_1 = 906\text{ cm}^3 \qquad V_2 = 500\text{ cm}^3$

Using Charles law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad T_2 = \left(\frac{V_2}{V_1}\right)T_1$$

$$T_2 = \left(\frac{500\text{ cm}^3}{906\text{ cm}^3}\right) \times 300\text{ K}$$

$\therefore \quad T_2 = 166\text{ K}.$

30. As melting ice implies 0°C.

$\therefore \quad T_1 = 273\text{ K} \qquad P_1 = 1000\text{ torr}$

$T_2 = ? \qquad P_2 = 400\text{ torr}$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ (volume and amount of gas remains constant)}$$

$$\therefore \quad T_2 = \left(\frac{P_2}{P_1}\right)T_1 = \left(\frac{400\text{ torr}}{1000\text{ torr}}\right) \times 273\text{ K}$$

$$= 109\text{ K} = -164°\text{C}.$$

31. $R = \dfrac{PV}{nT}$; $P = 1\text{ atm} = 101.325 \times 10^3\ (\text{Nm}^{-2})$

$V = 22.4\text{ L} = 22.4 \times 10^{-3}\text{ m}^3$

$n = 1\text{ mol}, T = 273\text{ K}$

$$R = \frac{101.325 \times 10^3\text{ Nm}^{-2} \times 22.4 \times 10^{-3}\text{ m}^3}{1\text{ mol} \times 273\text{ K}}$$

$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$

Long Answer Questions

1. (i) We know $PV = nRT$ or $PV = \dfrac{wRT}{M}$ where w is the mass of the gas and M is its molar mass.

$$\therefore M = \frac{wRT}{PV}$$

Knowing w, P (its pressure), V(volume), R(gas constant) and T(temperature) molar mass M can be calculated. If density is known then M = dRT / P where d = density = w / M.

(ii) Ideal gas are those which obeys gas laws (Boyle's law, Charle's law etc) or the gas equation PV = nRT strictly for all the values of temperature and pressure. The molecules of ideal gas occupy negligible volume and exert negligible force of attraction on one another.

Real gases does not obey gas laws under all conditions of temperature and pressure. All gases in the universe are real. Real gases approach ideal behaviour only at high temperature and low pressure.

2. (i) (a) Data given $P_1 = 1000$ atm; $P_2 = 400$ atm ; $T_1 = 0°\ C + 273 = 273K$ (since ice melts at 0° C) ; T_2 = ? at constant volume.

$$\frac{P_1}{T_1}=\frac{P_2}{T_2} \quad \therefore T_2=\frac{T_1.P_2}{P_1}=\frac{273\times400}{1000}$$

= 109 K = 109 – 273 = –164° C

(b) Here we have to calculate

$$P_2=\frac{T_2.P_1}{T_1}=\frac{(100+273)\times(1000\,\text{atm})}{(0+273)}$$

$= 1.37 \times 10^3$ atm

(ii) Applying Charles law as volume is constant $\frac{P_1}{T_1}=\frac{P_2}{T_2}$

$P_1 = 15$ atm ; $P_2 = 30$ atm ; T_1 = (15 + 273)K = 288K ; T_2 = ?

$$\frac{15\,\text{atm}}{288K}=\frac{30\,\text{atm}}{T_2} \text{ or } T_2=576\,K$$

= (576 – 273) = 303°C

3. (i)

(a) According to ideal gas equation:

PV = nRT

$$P=\frac{nRT}{V}=\frac{1\times0.0821\times298}{1.5}=16.29\text{ atm.}$$

(b) According to van der Waal's gas equation:

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

$$P=\frac{nRT}{(V-nb)}-\left(\frac{an^2}{V^2}\right)$$

$$=\frac{1\times0.0821\times298}{(1.5-1\times0.04)}-\left(\frac{3.6\times(1)^2}{(1.5)^2}\right)=15.137\text{ atm.}$$

(ii) $T_c = 177K$

$P_c = 64.5$ atm.

van der Waal's constant,

$$a=\frac{27(RT_c)^2}{64P_c}=\frac{27\times(0.0821\times177)^2}{64\times64.5}$$

$= 1.34\ L^2$ atm. mol^{-2}

van der Waal's constant,

$$b=\frac{RT_c}{8P_c}=\frac{0.0821\times177}{8\times64.5}=0.02813\text{ L mol}^{-1}$$

4. $$H_2+\frac{1}{2}O_2\longrightarrow H_2O$$

Before reaction,

Volume of H_2 = 1L

Volume of O_2 = 1L

After reaction,

1 L H_2 reacts with $\frac{1}{2}$ L O_2 to yield 1 L H_2O

∴ Volume of H_2 left = 1 – 1 = 0L

Volume of O_2 left $=1-\frac{1}{2}=\frac{1}{2}$L

Valume of H_2O formed = 1L

(i) According to ideal gas equation,

PV = nRT

or $n(H_2O)=\frac{PV}{RT}=\frac{1\times1}{0.0821\times273}=0.0446$ (at NTP)

Mass of H_2O = n × M = 0.0446 × 18 = 0.8031 g

(ii) At NTP,

22.4 L O_2 weights = 32 g

$\therefore$ 0.5 L O_2 weights $=\frac{32\times0.5}{22.4}=0.7143$g

(iii) Given that, T = 100ºC = 373 K

V = 2L

n (H_2O) = 0.0446

$$n(O_2)=\frac{PV}{RT}$$

$$n(\text{total})=0.0446+0.0223=\frac{1\times0.5}{0.0821\times273}$$

= 0.0223 = 0.0669

$$P=\frac{nRT}{V}=\frac{0.0669\times0.0821\times373}{2}=1.02\text{ atm}$$

(iv) Volume of O_2 that reacts to yield H_2O = 0.5L

At NTP, 22.4 L = 1 mol

$\therefore$ 0.5 L $=\frac{0.5}{22.4}=0.02$ mol O_2

reacts to yield H_2O

5. (a) Mass of gas in each flask = m g

Number of molecules of H_2 in flask A

$$n_{(H_2)A}=\frac{\text{Number of grams of }H_2\times N_A}{\text{molar mass of }H_2}$$

$$=\frac{m\text{ g}\times6.023\times10^{23}\text{ molecules / mol}}{2\text{g mol}^{-1}}$$

$$n_{(H_2)A}=\frac{1}{2}m\times6.023\times10^{23}\text{ molecules}$$

Number of molecules of CH_4 in flask B.

$$n_{(CH_4)B}=\frac{m\text{ g}\times6,023\times10^{23}\text{ molecules / mol}}{16\text{g / mol}}$$

$$=\frac{1}{16}m\times6.023\times10^{23}\text{molecules}$$

$$\therefore \frac{\text{Number of molecules of }H_2}{\text{Number of molecules of }CH_4}$$

$$=\frac{\frac{1}{2}m\times6.023\times10^{23}}{\frac{1}{16}m\times6.023\times10^{23}}=8.$$

Therefore, flask A contains eight times the number of molecules in flask B.

(b) Partial pressure in flask A,

$$p_{(H_2)A}=\frac{n_ART_A}{V}$$

and partial pressure in flask B,

$$p_{(CH_4)B}=\frac{n_BRT_B}{V}$$

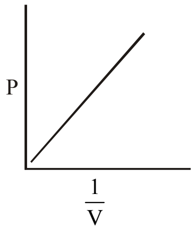
$$\therefore \frac{p_{(H_2)A}}{p_{(CH_4)_B}}=\frac{n_A}{n_B}\times\frac{T_A}{T_B}=8\times\frac{300}{600}=4$$

Therefore, the pressure in flask A is four times that in flask B.

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. P vs $\frac{1}{V}$ graph will be straight line.



2. Gas 'A' is at or below its critical temperature and gas 'B' is at a temperature higher than critical temperature.

3. The shape will be *spherical.*

Spherical shape given the *smallest surface area per unit volume* due to surface tension.

4. The value of '*b*' i.e., van der Waals' constant for volume remains constant over a wide range of *P* and *T*, which implies that gas molecules are incompressible.

5. The value of 'a' will be larger for NH_3 than for N_2. Because of presence of intermolecular hydrogen bonding in NH_3 its 'a' value will be larger.

Since there are more attractive forces in NH_3 as compared to that in N_2.

Short Answer Questions

1. $\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

$\therefore$ Density at 900 mm pressure $= \frac{0.4}{3280}$ g / mL

$= 0.000122$ g/mL

At constant temperature, Density × Pressure

$\therefore \quad \frac{d_1}{P_1} = \frac{d_2}{P_2} \qquad \text{or} \qquad d_2 = \frac{d_1 \times d_2}{P_1}$

$d_1 = 0.000122$ g/mL $\qquad d_2 = ?$

$P_1 = 900$ mm $\qquad P_2 = 1300$ mm

$$\therefore \quad d_2 = \frac{0.000122 \times 1300}{900} = 0.0001762 \text{ g/mL}$$

Hence, density of gas at 1300 mm = 0.0001762 g/mL.

2. $\text{Vapour density (V.D.)} = \frac{W}{2} \times \frac{RT}{PV}$

Given,

$W = 12.8$g

$R = 0.082$ litre-atm degree^{-1} mole^{-1}

$T = 273 + 27 = 300$ K

$P = \frac{750}{760}$ atm

$V = 10$L

Substituting these values, we get

$$\text{V.D.} = \frac{12.8 \times 0.082 \times 300}{\frac{750}{760} \times 10 \times 2} = \mathbf{15.92.}$$

3. (i) Dipole-dipole interactions (because H_2S is polar).

(ii) Hydrogen bonding.

(iii) London dispersion forces (because both are non-polar)

(iv) London dispersion forces (because SiH_4 is non-polar).

(v) London dispersion forces (because He atoms have symmetrical electron clouds).

(vi) Dipole-induced dipole forces (because HCl is polar while He atom has symmetrical electron cloud).

4. Unit of R depends upon those units in which P, V and T are measured, $R = \frac{PV}{nT}$. If pressure is measured in Pascal, per mole volume is measured in m^3 and temperature is measured in Kelvin then. Units of 'R' are Pa m^3 K^{-1} mol^{-1} or J mol^{-1}K^{-1}. Joule is the unit of work done so 'R' is work done per mole per kelvin.

5. (a) In HCl, HBr and HI, dipole-dipole and London forces because molecules possess permanent dipole. In HF dipole-dipole, London forces and hydrogen bonding.

(b) Electronegativity of chlorine, bromine and iodine decreases in the order :

$$Cl > Br > I$$

Therefore, dipole moment should decrease from HCl to HI. Thus, dipole-dipole interaction should decrease from HCl to HI. But boiling point increases on moving from HCl to HI. This means that London forces are predominant. This is so because London forces increase as the number of electrons in a molecule increases and in this case number of electrons as increasing from HCl towards HI.

(c) Hydrogen fluoride has highest dipole moment due to highest electronegativity of fluorine and hydrogen bonding is also present in it. Therefore, HF has highest boiling point.

6. (i) Z = 1 for ideal gas

(ii) For a real gas Z > 1 above Boyle's temperature.

7. (i) $H_2 < He < O_2 < CO_2$ because size increases in the same order.

(ii) $CH_4 > O_2 > H_2$ intermolecular attractions are the highest in CH_4 and lowest in H_2 because intermolecular forces increase with number of electrons in a molecule.

8. (i) The volume of a gas will decrease if the pressure on the gas is increased keeping the temperature constant.

(ii) On increasing temperature, the volume of a gas will increase if the pressure is kept constant.

Long Answer Questions

1. (i) $V_{balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times \left(\frac{21}{2}\right)^3 = 4851 \text{ cm}^3$

$V_{cylinder} = 2.82 \text{ L} = 2820 \text{ cm}^3$

$P = 20$ atm, $T = 300$ K

Correcting the volume to STP.

$$\frac{20 \times 2820}{300} = \frac{1 \times V_2}{273}$$

$\therefore \quad V_2 = 51324 \text{ cm}^3$

When the pressure in the cylinder is reduced to one atmosphere, no more H_2 will be released and hence 2820 cm^3 of H_2will be left in it. Hence V_{H_2} used in filling balloon = 51324 – 2820 = 48504 cm^3

Number of balloons filled $= \dfrac{48504}{4851} = 10.$

(ii) Compressibility factor,

$$Z = \frac{PV}{RT}$$

Given that, P = 200 atm

T = 273K

Volume of A = 0.112 L

Volume of B = 0.111 L

$$\therefore \quad Z_A = \frac{200 \times 0.112}{0.082 \times 273} = 1.00062$$

$$\text{and } Z_B = \frac{200 \times 0.111}{0.082 \times 273} = 0.9917$$

Because $Z_A > Z_B$, therefore B is more compressible.

2. Mass of LPG used = 29.0 kg – 23.2 kg = 5.8 kg = 5,800 g

∴ No. of moles of LPG used = 5.800 g/58 g mol^{-1}

Now, volume of 100 moles of LPG at 27°C (300 K) and 1 atm,

$$V = nRT/P = \frac{100\,\text{mol} \times 0.0821\,\text{L atm mol}^{-1}\ \text{K}^{-1} \times 300\,\text{K}}{1\ \text{atm}}$$

= 2,460 L = 2.46 m^3

Now, number of moles of n-butane before use (n_1) = 14.2 kg/58 g mol^{-1} = 14,200 g / 58 g mol^{-1}

The number of moles of n-butane after use (n_2) = 8.4 kg / 58 g mol^{-1}

Now $P_1V_1 = n_1RT_1$ and $P_2V_2 = n_2RT_2$

But $V_1 = V_2$ and $T_1 = T_2$

∴ $P_1 \propto n_1$ and $P_2 \propto n_2$

or $P_2 = P_1n_2 / n_1$ = 2.5 atm × (8,400 / 14,200) = 1.479 atm.

3. (i) Boiling point of A = approximately 315 K, B = approximately 345 K

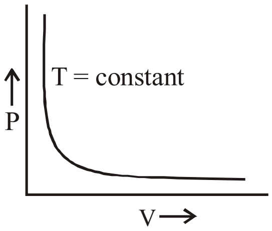
(ii) Will not boil

(iii) approximately 313 K

(iv) A liquid boils when vapour pressure becomes equal to the atmospheric pressure. Water boils at low temperature on hills because atmospheric pressure is low. Therefore even at low temperature vapour becomes equal to atmospheric pressure.

CHAPTER TEST

1.



2. Evaporation causes cooling and the rate of evaporation increases with the increase in the surface area. Since saucer has a large surface area, therefore the hot tea or coffee cools more quickly in it.

3. Ethanol shows hydrogen bonding due to which it has strong intermolecular force of attraction while benzene posses no such hydrogen bonding thus ethanol has a lower vapour pressure than benzene.

4. Boiling occurs at a particular temperature when the vapour pressure of liquid is equal to the atmospheric pressure. It is a bulk phenomenon and its rate does not depends upon surface area of liquid.

Evaporation is a surface phenomenon where liquid molecules escape from the surface of the liquid. It takes place at all temperatures and the rate of evaporation depends on surface area of liquid.

5. Liquid ammonia in a bottle is liquid at ordinary temperature only under high pressure. If a bottle is opened without cooling, the ammonia vapours will come out and cause discomfort as it has a pungent smell and can cause tears in eyes. In order to avoid it, liquid ammonia bottle is cooled before opening the seal so that the pressure inside the bottle decreases and thus its volatility.

6. Volume of vessel = 10L

T = 27 + 273 = 300K

(i) First calculate the number of moles of each gas

Mass of helium = 0.4 g , Molar mass of helium = 4 no. of moles of helium = 0.4 / 4 = 0.1

Mass of oxygen = 1.6 g , Molar mass of oxygen = 32 no. of moles of oxygen = 1.6 / 32 = 0.05

Mass of nitrogen = 1.4 g , Molar mass of nitrogen = 28 no. of moles of nitrogen = 1.4 / 28 = 0.05

(ii) Calculate total pressure

Using ideal gas equation , PV = nRT. Here n = total number of moles of all the gases.

n(total) = n(He) + n(O_2) + n(N_2) = 0.1 + 0.05 + 0.05 = 0.20 moles

P(total) = nRT/V = 0.20 × 0.082 × 300 / 10 = 0.492 atm

(iii) Calculate partial pressure of helium

P(He) = mole fraction of He × P(total)

Mole fraction of He = n(He) /n(Total) = 0.1/0.2 = 0.5

P(He) = 0.5 × 0.492 = 0.246 atm.

7. (i) Volume of liquid

$$= \frac{(148 - 50)}{0.98\text{g / ml}} = 100\text{ ml} = 0.1\text{ liter}$$

This is volume of vessel and hence the volume of gas.

$$\text{For ideal gas, } PV = nRT = \frac{wRT}{M}$$

$$\text{or } M = \frac{wRT}{PV}$$

(T = 300K ; P = 760 mm = 1atm; V = 0.1L; R = 0.0821 Latm K^{-1}mol^{-1})

$$= \frac{0.5 \times 0.082 \times 300}{1 \times 0.1} = 123\text{ g mol}^{-1}$$

(ii) For gaseous oxide $d_1 = \dfrac{P \times M_g}{RT}$,

where M_g = Molecular mass of gaseous oxide.

$$= \frac{2 \times M_g}{RT}$$

$$\text{For nitrogen gas } d_2 = \frac{P \times M_{N_2}}{RT} = \frac{5 \times 28}{RT}$$

Since $d_1 = d_2$

$$\frac{2 \times M_g}{RT} = \frac{5 \times 28}{RT} \text{ or } M_g = 5 \times 28 / 2 = 70\text{ g/mol}$$

6

Chapter

Thermodynamics

INTRODUCTION

When a chemical reaction occurs, it is always associated with energy change. The energy change involved during a reaction is due to the cleavage of old bonds within each of the reactants molecules and the formation of new bonds in each molecule of the products. Energy is absorbed during cleavage of old bonds while energy is evolved when new bonds are formed. Difference between the energy absorbed and energy evolved is the net change in energy accompanying a chemical reaction.

The branch of chemistry which deals with study of energy change associated with various chemical reactions or physical processes is called **chemical energetics**.

According to law of conservation of energy "Total energy of the system and its surroundings remains constant, although it can be transformed from one form to the other."

Chemical Thermodynamics: The branch of chemistry that concerns with the study of flow of heat energy during a chemical reaction is called **chemical thermodynamics.**

THERMODYNAMIC TERMS AND CONCEPTS

System and Surroundings

A system is that specific part of the universe which is under experimental study and separated from surroundings by a boundary. The part of the universe other than the system which is in a position to exchange energy and matter with the system is termed as surroundings.

Boundary

The real or imaginary surface separating the system from the surroundings is termed as boundary *i.e.,* a boundary refers to the limits of the system.

For example, when a reaction is carried out in a beaker, the content of the beaker constitute the system while the entire remaining part of the universe including the empty part of the beaker is surroundings. The surface of the liquid content in the beaker separating the system from surrounding is boundary.

The content of the system may be two types :

(i) **Homogeneous :** When the contents of the system constitute a single phase or is homogeneous throughout then the system is termed as a homogeneous system .

Note: The term phase represents a homogeneous, physically distinct and mechanically separable part of the system.

(ii) **Heterogeneous :** A system consisting of more than one phase unevenly distributed throughout the system. For example, ice in contact with water constitutes two different phases, viz solid ice and liquid water.

Types of System

Systems are classified into three catagories :

(i) **Open system :** The boundary of this type of a system is open and non-insulated. Therefore, an open system can exchange matter as well as energy with the surroundings. For example, tea in a cup or solution of $CuSO_4$ in a beaker.

(ii) **Closed system** : A system that can exchange energy but can not exchange matter with the surrounding is called a closed system. Such a system is non-insulated but sealed. For example, heating of I_2 in a sealed container. Here solid iodine sublimes to iodine vapours but iodine vapours cannot escape from the container.

(iii) **Isolated system :** A system which can neither exchange matter nor energy with the surroundings is called isolated system. Such a system is insulated and sealed e.g., piece of ice in a thermos flask.

State Functions

The thermodynamic parameters which depend upon the initial and final states of the system only and are independent of how the change is accomplished are called state functions. Examples of the state functions are internal energy (E), enthalpy (H), entropy (S), free energy (G), pressure (P), temperature (T) and volume (V), etc. Heat (q) and work (W) are not the state functions being path dependent.

A system in which the state functions (variables) have constant values throughout is said to be in a state of *thermodynamic equilibrium*.
The state functions are of two types :

(i) Intensive variables: The state functions of the system which are independent of the quantity of the substance present in the system are called intensive variables. For example, pressure, temperature, concentration, density, viscosity, surface tension, refractive index and specific heat, etc.

(ii) Extensive Variables: The state variables which depend upon the quantity of the substance present in the system are termed as extensive variables. Volume, mass, internal energy, enthalpy, entropy and work are examples of extensive variables.

An extensive state parameter changes to intensive state parameter when it is specified by unit amount of matter e.g., mass and volume are extensive state parameters but density (mass per unit volume) is an intensive state parameter.

Thermodynamic Processes

The process in which state of system gets changed from one state to the another state. Macro properties get changed in this process. These are of the following types:

(i) Isothermal process – It is the process in which temperature of the system remains constant. In this process, the boundaries of the system are mobile. The energy released in the exothermic process is absorbed by the surroundings and if the process is endothermic the system takes the required energy from the surroundings, therefore the temperature remains constant. Thus, the change in temperature, $dT = 0$

Maximum work done in expansion of n moles of an ideal gas :

$$W_{\max} = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303\, nRT \log \frac{P_1}{P_2}$$

where, V_1 = Initial volume of the gas
V_2 = Final volume of the gas
P_1 = Initial pressure of the gas
P_2 = Final pressure of the gas

(ii) Adiabatic process – In this process there is no exchange of heat between the system the surroundings, i.e., the system is in isolated state. In this process, temperature can increase and can decrease also. Change in heat $(dq) = 0$

(iii) Isobaric process – This process takes place at constant pressure. Change in pressure $(dp) = 0$.
For example : vapourisation of water, heating of water up to its boiling point at same atmospheric pressure.

(iv) Isochoric process – The process which takes place at constant volume. Change in volume, $(dV) = 0$.

(v) Cyclic process – The process in which a system proceeds via many intermediate steps and returns to the initial state. Change in internal energy $(dE) = 0$, change in enthalpy $(dH) = 0$

(vi) Reversible process – This process is slow and unreal. Its direction can be changed at any step and during process of every stage system remains in equilibrium with surroundings.

(vii) Irreversible process – This process is fast and gets completed in a single step. This process cannot be reversed. All the natural processes are of this type.

INTERNAL ENERGY

The energy associated with a thermodynamic system is defined as the internal energy or intrinsic energy of the system.
The internal energy depends upon its chemical nature and its state of existence. Thus, the energy stored within a substance is known as internal energy.
The internal energy of the system is the sum of following different types of energies stored in atoms or molecules of the substance.

(i) Translational energy of molecules (E_t)
(ii) Rotational energy of molecules (E_r)
(iii) Vibrational energy of molecules (E_v)
(iv) Electronic energy (E_e)
(v) Coulombic energy between the electrons and the nuclei in atoms (E_c)
(vi) Potential energy due to interaction of the constituent molecules of the system (E_p).
(vii) Nuclear energy (E_n)

Thus, $U = E_t + E_r + E_v + E_e + E_c + E_p + E_n$.

Internal energy of a definite amount of a particular substance (system)is a state function as its value depends upon the state of the system but does not depend upon how that state is acheived.

WORK AND HEAT

Energy of a system may increase or decrease in several ways. The two common ways are work and heat.

Work

Work is a mode of energy transfer from or to a system with reference to the surroundings. Work is said to have been done whenever the point of application of a force is displaced in the direction of the force. Work is of many types and can be expressed as the product of two factors.

W = (A Generalized force) × (A Generalized displacement)

Two main types of work used in thermodynamics are briefly described below:

(i) **Electrical work:** Electrical work is important in systems where reaction takes place between ions. Here, generalized force is the EMF and the generalized displacement is the quantity of electricity flowing through the circuit. Hence,

Electrical work done = EMF × Quantity of electricity

(ii) **Mechanical work (Pressure-volume work) :** As the name indicates pressure-volume type of work is performed when a system changes its volume in the presence of external pressure. This type of work is the most important form of work used in the study of thermodynamics and involved in systems consisting of gases. It is the work done when the gas expands or contracts against the external pressure (usually, the atmospheric pressure).

Heat

Just as work is a form of energy which is exchanged between the system and the surroundings as a result of expansion or contraction of the gas because of difference in the internal pressure of the gas and external pressure.

Similarly, heat is another mode of energy exchanged between the system and the surroundings, as a result of difference in temperature between them. It is usually represented by the letter Q.

When the heat is given by the system to the surroundings, it is given negative sign (since, there is loss in energy of the system). On the other hand, when heat is absorbed by the system from the surroundings, it is given a positive sign (since there is increase in energy of the system).

Units of Q: Heat is usually measured in calorie. A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C. In the SI system, it is expressed in **joule**.

Remember that energy, work and heat have same units. Energy is a thermodynamic property of the system while work and heat are not.

Difference between heat and work : When heat is supplied to a gas in a system, the molecules start moving faster with greater randomness in different direction. However, when work is done on the system, then initially the molecules start moving down in the direction of the piston. Thus, **work is an organized form of energy while heat is a random form of energy.**

FIRST LAW OF THERMODYNAMICS

According to this law energy can neither be created nor destroyed, it can only be changed from one form to the other i.e.,

Total energy of an isolated system remains constant. Total energy of universe remains constant. Whenever some amount of any form of energy disappears, the same amount of energy is produced in other form.

Mathematical Form :

If energy is absorbed by a system (+q) and work is done on the system (+w) internal energy of the system increases. If E_1 is initial value of internal energy and E_2 the final, then

$$E_2 = E_1 + q + w \text{ or } E_2 - E_1 = q + w$$

or, $$\Delta E = q + W$$

This is the mathematical form of 1st law of thermodynamics

(i) **For isothermic process**

Energy change in system = heat given to system + work done on system

$\Delta E = 0$ as temperature is constant

$\therefore\ 0 = q + W$ or $q = -W$

(ii) **For isochoric process**

$W = 0$ (System does not do any work) ; $\because\ \Delta V = 0$

$\Delta E = q_v + 0$ $\therefore$ heat given to system at constant volume changes internal energy.

(iii) **For adiabatic process**

$Q = 0$;

$\Delta E = 0 + W$ or $\Delta E = W$ i.e., work done on system equals to the change in internal energy

(iv) For isobaric process when a gas expands against a constant pressure, P, then

(a) The work done by the system = $-P\Delta V$ ($\Delta V = V_2 - V_1$)

$$\Delta E = q - P\Delta V$$

Then, W = Litre atmosphere [1 litre atmosphere = 101.3 Joule]

(b) If a gas expands in vacuum, the work done, W = 0, because P = 0.

Applications

To understand the pressure-volume work, consider a cylinder fitted with a frictionless and weightless piston having areas of cross-section equal to A cm. Further, let the volume of the gas in the cylinder is V and pressure (external pressure) acting on the piston is P (or P_{ext}) which is slightly less than the internal pressure of the gas. Due to high internal pressure, the gas expands and the piston moves a small distance dl.

Now, we know that pressure = $\dfrac{\text{Force}}{\text{Area}}$

Force (F) = Pressure (P) × Area (A)

$\therefore$ Work done by the gas (i.e., system) = Force × Distance

$$= P \times A \times dl = P \times dV$$

But $A \times dl = dV$, a small increase in the volume of the gas. Hence, the small amount of work (dW) done by the gas can be written as

$$dW = -P \times dV$$

(negative sign is used for the work done by the system)

If the volume of the gas changes by a finite quantity from volume V_1 to V_2, then total work done, W will be given by

$$W = -\int_{V_1}^{V_2} PdV$$

If the external pressure P against which the gas expands remains almost constant throughout the process, the above expression may be written as

$$W = -\int_{V_1}^{V_2} dV = P(V_2 - V_1) = -P\Delta V$$

where $\Delta V = (V_2 - V_1)$ is the total change in volume of the gas (or the system).

In case, the external pressure (P) is slightly more than the pressure of the gas, the gas will contract, i.e., the work will be done by the surroundings on the system. However the same formula will apply for the work done.

Sign of W

According to latest SI convention,

(i) Work is taken as negative when work is done by the system on the surroundings as in expansion of a gas, i.e., when $V_2 > V_1$

$$W = -P\,\Delta V$$

(ii) Work is taken as positive when work is done on the system as in contraction of gas, *i.e.,* when $V_2 < V_1$.

$$W = P\,\Delta V$$

It is important to note that here P is the external pressure (and not the pressure of the gas) that is used to calculate the work done during expansion or contraction of the gas, and hence, it is sometimes written as P_{ext}. Hence,

$$W = -P_{ext} \times \Delta V$$

Units of W

The units of work are the same as those of energy, viz. erg or joule ($1\ J = 1\ N\ m\ \ 1\ kg\ m^2\ s^{-2}$).

$$\text{Work} = \text{Force} \times \text{Distance} = N \times m = N\,m = 1\ J$$

Alternatively, Work = Force × Distance

= Mass × Acceleration × Distance

$= Kg \times ms^{-2} \times m = kg\,m^2s^{-2}$

Work Done in Isothermal Reversible Expansion of An Ideal Gas

The small amount of work done (δW), when the gas expands through a small volume, dV, against the external pressure P is given by

$$\delta W = -PdV$$

$\therefore$ Total work done when the gas expand from initial volume V_1 to final V_2 will be

$$W = -\int_{V_1}^{V_2} P\,dV$$

For an ideal gas, $PV = nRT$

or $P = \frac{nRT}{V}$

$\therefore$ $W = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$

For isothermal expansion, $T = \text{constant}$

Hence, $W = -nRT\int_{V_1}^{V_2} \frac{1}{V} dV$

$$= -nRT \ln \frac{V_2}{V_1}$$

$$W = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= -2.303\ nRT \log \frac{P_1}{P_2}$$

Note that the negative sign of work indicates work of expansion, or the work is done by the system.

Illustration 1 :

Determine the work done by the gas which expands from 100 mL to 250 mL. under a constant pressure fo 2 atm.

Solution: $W = P\,\Delta V$

$$= 2\ \text{atm}\frac{150}{1000}\text{L} = 0.3\text{L atm} = 0.3 \times 101.3\ \text{J} = 30.39\ \text{J}$$

Free Expansion

Expansion of a gas in vacuum is called free expansion. In free expansion the external pressure (P_{ext}) is zero. No work is done during free expansion of an ideal gas whether the proces is reversible or irreversible.

In case of isothermal expansion of an ideal gas into vacuum, the work done is zero as the P is zero.

Hence, the equation $\Delta V = q + w$ can be written as

(i) For isothermal irreversible change,

$q = -w = P_{ext}\,(V_\delta - V_i)$

(ii) For isothermal reversible change,

$$q = -w = nRT \ln \frac{V_\delta}{V_i} = 2.303\, nRT \log \frac{V_\delta}{V_i}$$

(iii) For adiabatic change,

$q = 0$

$\Delta U = W_{ad}$

ENTHALPY, H

The enthalpy of a system may be defined as the sum of internal energy and the product of pressure and volume of that system. Enthalpy is a state function and is also known as heat content of the system (or substance).

At constant temperature and pressure,

$\Delta H = \Delta E + P\Delta V$

ΔE = Change in internal energy

$P\Delta V = \Delta W$ = Work done

P = External pressure

Most of the chemical reactions occur at constant pressure (1 atmospheric) and in an open vessel . Thus the measured value of heat evolved or absorbed is the enthalpy change ($q_p = \Delta H$)

When $\Delta V = 0$, $\Delta H = \Delta E$

For liquids and solids

$\Delta V = 0 \quad W = 0$

$\Delta H = \Delta E$

For gaseous state

$PV = nRT \qquad P\Delta V = \Delta nRT$

$\Delta H = \Delta E + (\Delta n)\,RT$

(a) $\Delta n = 0 \qquad \Delta H = \Delta E$

(b) $\Delta n = -ve \qquad \Delta H < \Delta E$

(c) $\Delta n = +ve \qquad \Delta H > \Delta E$

$\Delta H = -ve$, (reaction is exothermic)

$\Delta H = +ve$, (reaction is endothermic)

Enthalpy of a system depends on physical state (solid, liquid and gas).

H is a state function. Therefore, it depends only on initial and final states. Absolute value of enthalpy cannot be determined

Enthalpy of monoatomic gas = $\frac{5}{2}$RT per mole.

Change in enthalpy of the products and reactants at 298 K and 1 atmospheric pressure is called **standard molar enthalpy change**.

Exothermic and Endothermic Reactions

The chemical reactions which are accompanied with the evolution of heat are called **exothermic reactions**. e.g.

(i) $C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5\ \text{kJ}$

(ii) $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(g) + 286\ \text{kJ}$

The enthalpy change (ΔH) at constant pressure and constant temperature is given by

ΔH = (Heat content of products) – (Heat content of reactants) = $H_p - H_R$

For an exothermic reaction $H_R > H_P$ i.e. heat content of reactants is more than that of the products.

Therefore, ΔH is negative for exothermic reactions.

The chemical reactions which are accompanied with absorption of heat are called **endothermic reactions**. e.g.

(i) $N_2(g) + O_2(g) + 180.5kJ \longrightarrow 2NO(g)$

(ii) $C(s) + 2S(s) + 92.0kJ \longrightarrow CS_2(l)$

For an endothermic reaction $H_P > H_R$ i.e. heat content of products is more than that of the reactants. Therefore, ΔH is positive for endothermic reactions.

HEAT CAPACITY

It is the amount of energy needed to raise the temperature of a specific substance by 1 degree Celsius. Heat capacity can also be viewed as the ratio of the amount of energy transferred to an object and the resultant temperature rise (ΔT).

$$C = q/\Delta T$$

The units of C are J/degree Celsius. Because the heat capacity of an object is dependent on the mass of the object, heat capacities are often given per 100 g to allow for a comparison between objects of equal mass.

Molar heat capacity : The amount of heat needed to increase the temperature of one mole of a substance by one degree is the molar heat capacity. It is expressed in joules per moles per degrees Celsius (or Kelvin).

Specific heat capacity : The amount of heat needed to increase the temperature of one gram of a substance by one degree is the specific heat capacity. It is expressed in joules per gram per degree Celsius.

Quantity of heat : The quantity of heat is a measurement of the amount of heat is present. The formula of quantity of heat, q, is equal to the mass of substance, m, multiplies with the specific heat and the change in temperature, ΔT.

$$q = \Delta T \times C \times m$$

Heat capacity or specific heat C can never be negative for a substance.

Relation Beween C_P and C_V

The specific heat at constant volume is represent as C_V and the specific heat at constant pressure is represented as C_P. Using the definition of enthalpy ($H = U + PV$) and writing the differential of enthalpy, the relationship between the specific heats for ideal gases is

$$H = U + PV$$

$$dH = dU + d(RT)$$

$$C_p dT = C_V dT + RdT$$

$$C_P = C_V + R$$

where R is the particular gas constant.

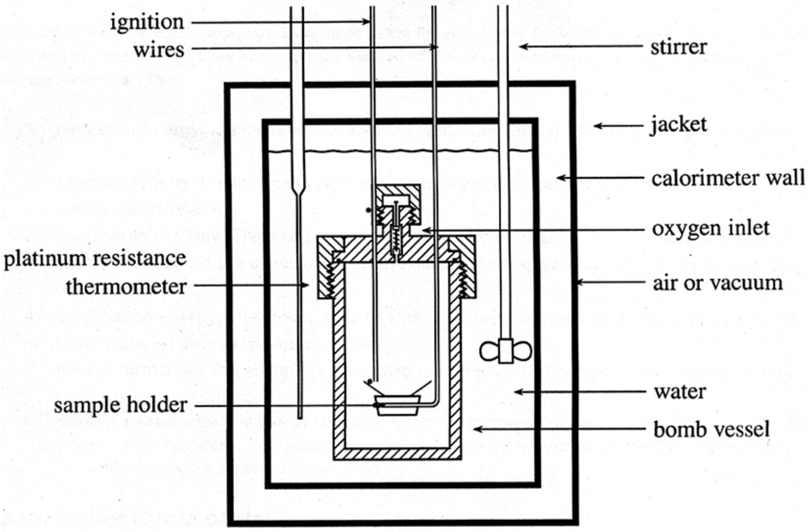
CALORIMETRY

Calorimetry is a method to measure heat effect of a process. Which could be a physical or a chemical change. Calorimeter is an instrument which determines heat effect in it by direct measurement of temperature.

Measurement of DU and DH

Determination of ΔU

The heat changes in a chemical reaction at constant volume can be measured with the help of a bomb calorimeter devised by **Berthelot**. The Calorimeter consists of a strong combuston chamber, called bomb (made up of heavy steel) which can with stand very high pressure. A known quantity of the combustible substance is burnt in the pressure of pure oxygen in the steel bomb.



Bomb Calorimeter

The initial temperature of water is noted before the sample is ignited by an electric current. The heat evolved during combustion raises the temperature of water. The rise in temperature of the water is recorded by the thermometer.
By knowing the heat capacity of calorimeter system and the rise in temperature of the water, the heat of combustion at constant volume can be calculated as

$$\Delta U = q_v = Q \times \Delta T \times \frac{M}{W}$$

Q = Heat capacity of the calorimeter
ΔT = Rise in temperature of water
W = Weight of substance taken
M = Molar mass of the substance.

Determination of ΔH

At constant pressure heat evolved or absorbed is equal to the enthalpy of reaction ΔH.
In exothermic reaction q_p and ΔH both will be negative.
In endothermic reaction q_p and ΔH both will be positive.

HEAT OF REACTION

Heat of reaction is defined as the amount of heat evolved or absorbed when the molar quantities of the reactants as indicated by the chemical equation have completely reacted.
It is represented by ΔH_r. Mathematically,

Enthalpy of reaction (or heat of reaction), $\Delta H_r = \sum H_p - \sum H_R$

Factors Affecting Heat of Reaction

(i) Effect of temperature

According to Kirchoff's equation,
Heat of reaction at temperature $T_1 = \Delta H_1$
Heat of reaction at temperature $T_2 = \Delta H_2$
At constant pressure, $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$
At constant volume, $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$
ΔE_2 and ΔE_1 are internal energy changes at temperatures T_2 and T_1
The heat supplied to a system to raise its temperature through 1°C keeping the volume of the system constant is called **heat capacity at constant volume.** Similarly, the heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called **heat capacity at constant pressure.**

(ii) Effect of physical state

ex: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -58\text{kcal}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell) \qquad \Delta H = -68.4\text{kcal}$

Thus, heat of reaction is different in different physical state of the reactants or the products.

(iii) Effect of pressure and volume

Heat of reaction
At constant volume, q_V $\qquad P\Delta V = 0$
At constant pressure, q_P $\qquad W = P\Delta V$
$q_P = q_V + \Delta nRT$
Heat of reaction is different if different allotropic form is involved in the reaction.

Types of Heat of Reaction

(i) **Heat of Combustion:** The amount of heat change when one mole of the substance (compound or element) is completely burnt or oxidised in excess of oxygen. Heat of combustion is an exothermic process and thus the heat change i.e. ΔH is always negative. For example,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$

Calorific value of food and fuel:

The calorific value of food and fuel is the amount of heat produced when one gram of the substance is completely burnt. It is expressed in J/gm or kJ/gm or cals/gm (1k cal = 4.184 KJ).

Calorific values of some foods and fuels.

Food	Calorific value (kJ/ g)	Fuel	Calorific value (kJ/g)
Butter	30.4	Charcoal	33
Ghee	37.6	Wood	17
Milk	3.2	Dung cake	6 – 8
Curd	2.5	Kerosene	48
Honey	13.3	Fuel Oil	45
Rice	14.5	Hydrogen	150
Egg	7.3	Methane	55
Meat	12.0	Butane (LPG)	55

(ii) Enthalpy of formation : It is defined as the heat change (evolved or absorbed) when one mole of a compound is formed from its constituent elements.It is denoted by ΔH_f. For example,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_f = -393.5 \text{ kJ mol}^{-1}$$

The enthalpy change accompanying the formation of one mole of the compound in standard state from its constituent elements also taken in their standard states i.e. at 298 K and one atmospheric pressure is termed as standard heat of formation.

$$\Delta H^\circ_{\text{Reaction}} = \sum \Delta H^\circ_f(\text{Products}) - \sum \Delta H^\circ_f \text{ (Reactants)}$$

Since the heat of formation of all elements in their standard state are arbitrarily assumed to be zero, therefore, the heat of formation of a compound is the heat of compound itself, i.e.

$$\text{Element} \longrightarrow \text{Compound}$$

$$\begin{aligned} H^\circ_{\text{Reaction}} &= H^\circ_f(\text{Compound}) - H^\circ_f(\text{elements}) \\ &= H^\circ_f(\text{compound}) - 0 = H^\circ_f(\text{compound}) \end{aligned}$$

(iii) Heat of neutralization: It is defined as the heat change (or heat evolved) when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in dilute solution at a given temperature.
For example,

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O \qquad \Delta H = -57.1 \text{ kJ}$$

Thus, the heat of neutralisation of one gm equivalent of HCl with one gm equivalent of NaOH at 25°C is – 57.1 kJ.
The enthalpy of neutralization of strong acid with strong base is constant i.e. $\Delta H = -57.1$ kJ.
However, the ionisation of weak acid or weak base in aqueous solution is not complete. Thus, the heat of neutralization of weak acid with strong base or of strong acid with weak base or both weak is less than 57.1 kJ.

(iv) Heat of solution: It is defined as the amount of heat change (absorbed or evolved) occured when one mole of a substance (solute) is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change.

$$NaCl(s) + H_2O(l) \longrightarrow NaCl(aq) \qquad \Delta H_{\text{solution}} = +5.0 \text{ kJ}$$

The enthalpy of solution is usually endothermic.

(v) Heat of hydration : It is defined as the amount of heat change when one mole of an anhydrous salt combines with the specific number of moles of water so as to change into the hydrated form. For example, heat of hydration of anhydrous copper sulphate may be represented as :

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O \qquad \Delta H = -78.2 \text{ kJ}$$

(vi) Enthalpy of fusion : It is defined as the heat change when one mole of a solid substance is converted into the liquid state at its melting point. For example, the heat of fusion of ice (ΔH_{fusion}) at 0°C (or 273 K) is 6.0 kJ mol^{-1}. This may be represented as:

$$\underset{\text{(ice)}}{H_2O(s)} \longrightarrow \underset{\text{(water)}}{H_2O(l)} \qquad \Delta H_{\text{fusion}} = 6.0 \text{ kJ mol}^{-1}$$

(vii) Heat of vapourisation: It is the enthalpy change involved in the conversion of one mole of liquid into its vapours at its boiling point. For example, when one mole of water is converted into steam at 100°C (373 K), 40.6 kJ of heat is required. It may be represented as.

$$H_2O(l) \longrightarrow H_2O(g), \qquad \Delta H = +40.6 \text{ kJ mol}^{-1}$$

(viii) Heat of sublimation: It is the enthalpy change involved when one mole of a solid is directly converted into vapour phase at a constant temperature. e.g.

$$I_2(s) \longrightarrow I_2(g), \qquad \Delta H = +62.4 \text{ kJ mol}^{-1}$$

(ix) Enthalpy of dilution : It is defined as the heat with drawn from the surroundings when additional solvent is added to the solution. It is dependent on the original concentration of the solution and the amount of solvent added.

(x) Enthalpy of Atomization: It is defined as the amount of heat change when one mole of bond breaks completely and forms atoms in a gas phase.

Example: The atomisation of dihydrogen

$$H_{2(g)} \rightarrow 2H_{(g)}; \Delta H° = 435.0 \text{ kJ mol}^{-1}$$

In case of diatomic molecules, the enthalpy of atomisation is also bond dissociation enthalpy.

(xi) Thermochemical equations: A balanced chemical equation which tells about the amount of heat eolved or absorbed during the reaction is called a **thermochemical equation**. A complete thermochemical equation supplies the following informations :

(a) It tells about the physical state of the reactants and products. This is done by inserting symbol (s), (*l*) and (g) for solid, liquid and gaseous state respectively alongside the chemical formula.

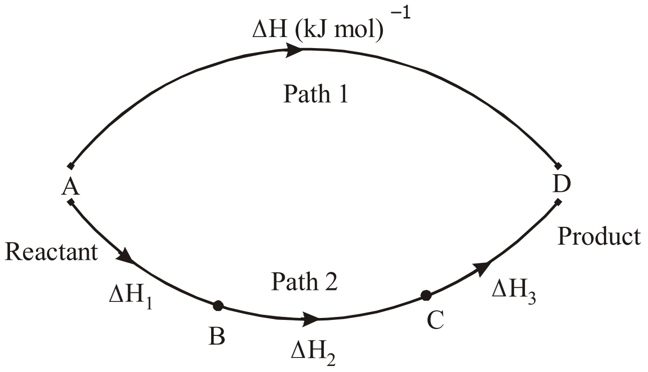
(b) It tells about the allotropic form (if any) of the reactant by inserting the respective allotropic name, e.g., C (graphite) (s).

(c) The aqueous solution of the substance is indicated by the word aq.

(d) It tells whether a reaction proceeds with the evolution of heat or with the absorption of heat, i.e., heat change involved in the system.

Remember that like algebraic equations, thermochemical equations can be reversed, added, substracted and multiplied.

(xii) Hess's law of constant heat summation: Hess's law states that " the total amount of heat absorbed or evolved in a chemical reaction is same whether the reaction takes place in one step or in a number of steps."



Hess's law suggest that the heat change of a chemical reaction depends only on the heat change has taken place.

$\therefore \quad \Delta H = H_1 + H_2 + H_3$

Application of Hess's Law

(i) Heat of formation : With the help of Hess's law, heat of reaction of such reactions can be determined which proceed with many side reactions. For example, heat of formation of CO can be determined by knowing the heat of formation of CO_2 from C and heat of formation of CO_2 from CO. Let the heat of formation of CO from C is Q, then from the above reactions we know that

Q = Heat of formation of CO_2 from C – Heat of formation of CO_2 from CO

$= -94 - (-67.6) = -94 + 67.6 = 26.4$ kcal

$\therefore$ Heat of formation of CO = – 26.4 kcal/mole

(ii) Determination of heat change of slow reactions, e.g., the transformation of rhombic sulphur into monoclinic sulphur.

$$S\text{ (rhombic)} + O_2\text{ (g)} \longrightarrow SO_2\text{ (g)}; \Delta H = -71.1 \text{ kCal} \quad \dots (1)$$

$$S\text{ (monoclinic)} + O_2\text{ (g)} \longrightarrow SO_2\text{ (g)}; \Delta H = -71.7 \text{ kCal} \quad \dots (2)$$

Subtracting Eq. (1) from (2) and rearranging,

$$S\text{ (monoclinic)} \longrightarrow S\text{ (rhombic)}; \Delta H = -0.6 \text{ kCal}$$

$$S\text{ (rhombic)} \longrightarrow S\text{ (monoclinic)}; \Delta H = +0.6 \text{ kCal}$$

Bond Energy

The bond dissociation energy is the amount of energy which is required to break one mole of a particular type of bonds between the atoms in gaseous state.

- For a diatomic molecule (H_2, Cl_2, HCl, etc,) the bond energy is equal to the bond dissociation energy but this is not true for a polyatomic molecule like H_2O , CH_4 , C_2H_5OH etc. A polyatomic molecule contains more than one bond of the same kind but differeing in the bond dissociation values

$$H_2O(g) \rightarrow H(g) + OH(g), \quad \Delta H = 497.8 \text{ kJ}$$

$$OH(g) \rightarrow H(g) + O(g), \quad \Delta H = 428.5 \text{ kJ}$$

- In such cases the average bond dissociation energy required to cleave bonds of a particular type in a substance is called bond energy.
- Bond energy of O — H bond is $\frac{497.8+428.5}{2} = 463.15 \text{kJmol}^{-1}$.

C–H bond in methane is the average of the bond dissociation energies of the four C–H bonds.

Difference between bond dissociation energy and bond energy.

Bond dissociation energy	Bond energy
(a) It is the energy required to break a bond of diatomic molecule in gaseous state,. e.g., H–H, Cl–Cl, O=O, etc. Since there is only one bond between two atoms (may be single, double or triple bond), the energy required to cleave the bond is termed as bond dissociation energy.	(a) Bond energy or average bond energy for a polyatomic molecule is the average amount of energy required to cleave one mole bonds of a particular type in gaseous molecules, e,g., in water molecule the bond dissociation energies of two O– H bond differ from one another. $HO-H(g) \longrightarrow OH(g) + H(g); \Delta H = 497.8 \text{ kJ}$ $O-H(g) \longrightarrow O(g) + H(g); \Delta H = 428.5 \text{ kJ}$ In such cases, the average of bond dissociation energies is termed as bond energy.
(b) It is a definite quantity and is expressed in kJ mol^{-1}.	(b) It is an average of various bond dissociation energies of similar bonds and is expressed as kJ mol^{-1}.

SPONTANEOUS AND NON-SPONTANEOUS PROCESS

A process which can take place by itself under some given set of conditions, or by initiation if necessary, is called a spontaneous process.

All natural processes which occur spontaneously are irreversible in character.

(i) Examples of processes which occur by themselves :

(a) Dissolution of common salt, sugar, etc. in water.

(b) Flow of heat from a hot body to a cold body.

(c) Evaporation of water from an open vessel, pond or sea.

(d) Flow of water down a hill.

(e) Combination of H_2 (g) and I_2 (g) to form HI (g)

(ii) Examples of processes which occur on initiation.

(a) Lifting of water from lower level to higher level.

(b) Lighting of candle involve burning of wax, (initiated by ignitation)

A process that does not occur of its own i.e. a process which does not have any natural tendency to occur is termed as a non-spontaneous process, e.g.

(a) Lifting of water from well to overhead water tank.

(b) Flow of heat from a cold body to a hot body.

(c) Electrolysis of water to produce hydrogen and oxygen.

All these processes or reactions which are accompained by decrease of energy (exothermic reactions, ΔH value negative) occur spontaneously. Hence it seems that decrease in enthalpy (or negative value of Δ H) may be regarded as the driving force for all spontaneous processes.

There are number of endothermic reactions. (i.e.ΔH is positive) which are observed to be spontaneous. For example,

Evaporation of water

$$H_2O(l) \longrightarrow H_2O(g), \qquad \Delta H = +44.0 \text{ kJ mol}^{-1}$$

Some Important Points Related to Spontaneous Changes

(a) These changes occur only in single direction. They do not occur in opposite direction by themselves. For example, water does not flow itself from lower to upper level.

(b) Work can be done by a spontaneous change. For example, motion of a piston by expansion of gas, rotation of a wheel when water falls on it from some height, etc.

(c) For a spontaneous change in an isolated system, ΔS = Positive

(d) When system is not an isolated system

$$\Delta S_{(total)} = \Delta S_{(system)} + \Delta S_{(surrounding)} > 0$$

$$= \Delta S_{universe} > 0$$

(e) Adiabatic expansion : In adiabatic system, q = 0 at each step. Therefore, ΔS = 0. Thus. reversible adiabatic processes are called isoentropic.

(f) Entropy changes during Phase Transition : In phase transition process,

$$\Delta S = S_2 - S_1 = \frac{q\,(\text{Reversible})}{T} = \frac{\Delta H}{T}$$

$$\Delta S(\text{Fusion}) = \frac{\Delta H(\text{Fusion})}{T}$$

Where, ΔH(fusion) = Latent heat of fusion of solid

T = Melting point of solid in Kelvin

$$\Delta S\,(\text{Vapourisation}) = \frac{\Delta H(\text{Vapourisation})}{T}$$

where, ΔH (Vapourisation) = Latent heat of vapourisation

T = Boiling point of liquid in Kelvin

$$\Delta S\,(\text{sublimation}) = \frac{\Delta H(\text{sublimation})}{T}$$

ΔH (sublimation) - Enthalpy of sublimation

T = Temperature in Kelvin.

It is difficult to find out the value of ΔS(Surroundings). Therefore, there is no proper evidence in favour of entropic spontaneous change. Gibbs suggested the another thermodynamic function free energy which is related only to the system. Thus it is convenient to predict spontaneity.

ENTROPY

Entropy is regarded as a measure of the disorder or randomness of a system. It is measured in units of joules per degree kelvin mol^{-1} ($JK^{-1}\ mol^{-1}$).

The change in entropy from initial to the final state of of the system can be represented by ΔS. Thus, $\Delta S = S_{\text{final state}} - S_{\text{intial state}}$

Characteristics of entropy :

(a) Entropy is a state function

(b) Entropy is expressed in the units of $JK^{-1}\ mol^{-1}$.

(c) For any substance, entropy increases as follows

$S_{solid} < S_{liquid} < S_{gas}$

(d) For a chemical reaction, change of entropy is given as $\Delta S = \Sigma S_{products} - \Sigma S_{reactants}$

(e) At absolute zero (i.e. –273ºC), particles of the system attain a perfect order because all types of molecular motion ceases. Thus, Nernst stated that at absolute zero, the entropy of a perfectly crystalline solid is zero. However,at temperatures greater than zero kelvin, the entropy of the substance is positive i.e entropy increases with increase in temperature. At standard state i.e 25^0 C (or 298 K) and 1atm pressure, the entropy is called standard entropy and is represented by S^0.

(f) Change in entropy, ΔS, may be given as the ratio of heat absorbed in a reversible manner to the temperature (T) at which heat is absorbed i.e. $\Delta S = \frac{q_{rev}}{T}$.

$\Delta S_{system} + \Delta S_{surr} \geq 0$, where sign '=' refers to a reversible process (equilibrium) and sign '>' to an irreversible process (spontaneous process).

$\Delta S_f = \Delta H_f / T_f$ and $\Delta S_{vap} = \Delta H_{vap} / T_b$.

FREE ENERGY OR GIBBS FREE ENERGY

William Gibbs introduced another thermodynaymic function, called Gibb's energy and denoted it by symbol G. He defined it as the available energy of the system that can be utilised for doing the useful work. Mathematically, free energy is related to enthalpy (H), entropy (S) and absolute temperature (T) as

$$G = H - TS$$

Thus, the change in free energy (ΔG) which decides for the spontaneity of a process at constant temperature and pressure is written as

$$\Delta G = \Delta H - T\Delta S$$

This equation is known as Gibb's Helmholtz equation and is very helpful in predicting the feasibility of a process.

The most favourable conditions for a spontaneous process are decrease in energy (i.e. negative value of ΔH) and increase in entropy.

$\Delta G° = \Sigma G°(\text{Products}) - \Sigma G°(\text{Reactants})$.

$\Delta S° = \Sigma S°(\text{Products}) - \Sigma S°(\text{Reactants})$.

$-\Delta G = W_{\text{useful}}$.

$\Delta G = -$ ve ; the process (or reaction) is spontaneous.

$\Delta G =$ zero ; the process (or reaction) is in equilibrium state.

$\Delta G = +$ ve ; the process (or reaction) is non-spontaneous.

ΔH	**ΔS**	**ΔG = ΔH –TΔS**	**Remarks**
–	+	–	Reaction is spontaneous at all temperatures.
+	–	+	Reaction is non-spontaneous at all temperatures.
–	–	– (at low T)	Reaction is spontaneous at low temperatures.
–	–	+ (at high T)	Reaction is non-spontaneous at high temperatures.
+	+	+ (at low T)	Reaction is non-spontaneous at low temperatures.
+	+	– (at high T)	Reaction is spontaneous at high temperatures.

In case of endothermic processes, high temperature always favours the spontaneity or feasibility of the process.

In case of exothermic process, low temperature favours the spontaneity of the process.

Standard Free Energy Change

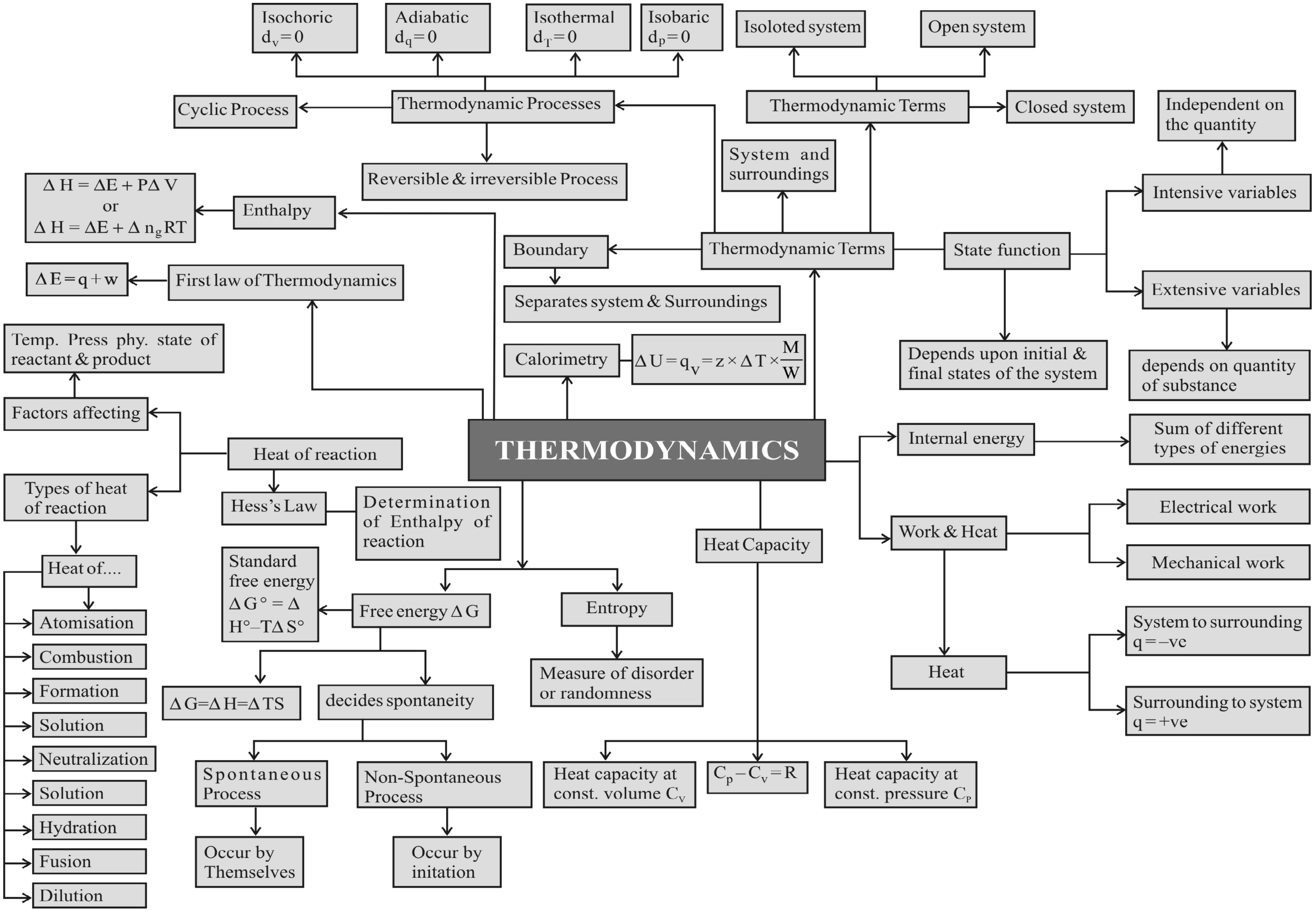
Standard free energy change (ΔG^0) of a reaction is defined as the free energy change when the reactants in their standard state (i.e. at 298 K and 1 atm pressure) are converted into products in their standard states. Thus, Gibbs Helmholtz Equation for standard free energy change can be written by the equation

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

Standard Gibbs energy change is related to equilibrium constant by :

$$\Delta G° = -RT \ln K = 2.303\ RT \log K$$

CONCEPT MAP


THERMODYNAMICS
Thermodynamic Terms
Thermodynamic Terms
Isoloted system
Open system
Closed system
System and surroundings
Boundary
Separates system & Surroundings
State function
Depends upon initial & final states of the system
Intensive variables
Independent on the quantity
Extensive variables
depends on quantity of substance
Thermodynamic Processes
Isochoric $d_V = 0$
Adiabatic $d_q = 0$
Isothermal $d_T = 0$
Isobaric $d_P = 0$
Cyclic Process
Reversible & irreversible Process
Enthalpy
$\Delta H = \Delta E + P\Delta V$ or $\Delta H = \Delta E + \Delta n_g RT$
First law of Thermodynamics
$\Delta E = q + w$
Calorimetry
$\Delta U = q_V = z \times \Delta T \times \frac{M}{W}$
Internal energy
Sum of different types of energies
Work & Heat
Electrical work
Mechanical work
Heat
System to surrounding q=–ve
Surrounding to system q=+ve
Heat Capacity
Heat capacity at const. volume C_V
$C_P - C_V = R$
Heat capacity at const. pressure C_P
Entropy
Measure of disorder or randomness
Free energy ΔG
Standard free energy $\Delta G° = \Delta H° – T\Delta S°$
$\Delta G = \Delta H = \Delta TS$
decides spontaneity
Spontaneous Process
Occur by Themselves
Non-Spontaneous Process
Occur by initation
Heat of reaction
Hess's Law
Determination of Enthalpy of reaction
Factors affecting
Temp. Press phy. state of reactant & product
Types of heat of reaction
Heat of....
Atomisation
Combustion
Formation
Solution
Neutralization
Solution
Hydration
Fusion
Dilution

Textbook Exercises

6.1 Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only.

Ans. (ii) Whose value is independent of path.

6.2 For the process to occur under adiabatic conditions, the correct condition is

(i) $\Delta T = 0$ (ii) $\Delta p = 0$

(iii) $q = 0$ (iv) $w = 0$.

Ans. (iii) $q = 0$

6.3 The enthalpies of all elements in their standard states are :

(i) unity (ii) zero

(iii) < 0 (iv) different for each element.

Ans. (ii) zero

6.4 $\Delta U^{\ominus}$ **of combustion of methane is –X kJ mol^{-1}. The value of** $\Delta H^{\ominus}$ **is**

(i) $= \Delta U^{\ominus}$ **(ii)** $> \Delta U^{\ominus}$ **(iii)** $< \Delta U^{\ominus}$ **(iv)** $= 0$.

Ans. The balanced equation for combustion of methane will be

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$

Thus, $\Delta n_g = (n_p - n_r)_g = 1 - 3 = -2$

$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT = -X - 2RT$ Thus, $\Delta H^{\ominus} < \Delta U^{\ominus}$. Hence, (iii) is the correct answer.

6.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, – 890·3 kJmol^{-1}, –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of CH_4 (g) will be

(i) – 74.8 kJmol^{-1} (ii) – 52.27 kJ mol^{-1}

(iii) + 74.8 kJ mol^{-1} (iv) + 52.26 kJ mol^{-1}

Ans. Given :

(i) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$, $\Delta H = -890.3$ kJ mol^{-1}

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5$ kJ mol^{-1}

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$, $\Delta H = -285.8$ kJ mol^{-1}

Aim : $C(s) + 2H_2(g) \longrightarrow CH_4(g)$, $\Delta H = ?$

Eqn. (ii) + 2 Eqn. (iii) –Eqn. (i) gives the required equation with

$\Delta H = -393 \cdot 5 + 2(-285 \cdot 8) - (-890.3)$ kJ mol^{-1} $= -74.8$ kJmol^{-1}.

Hence, (i) is the correct answer.

6.6 A reaction, $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(iv) possible at any temperature.

Ans. Here, $\Delta H = -$ve and $\Delta S = +$ve. $\Delta G = \Delta H - T\Delta S$. For the reaction to be spontaneous, ΔG should be –ve which will be so at any temperature, i.e., option (iv) is correct.

6.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

Ans. $q = +701$ J, $w = -394$ J, $\Delta U = ?$

By first law of thermodynamics

$\Delta U = q + w = +701$ J $+ (-394$ J$) = +307$ J

i.e., internal energy of the system increases by 307 J.

6.8 The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(\ell).$$

Ans. $\Delta n_g = (n_p - n_r)g = 2 - \frac{3}{2} = +\frac{1}{2}$ mol

$\Delta H = \Delta U + \Delta n_g RT$

$= -742.7$ kJmol^{-1} $+ (+1/2$ mol $)$

$(8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1} mol$^{-1})$ $(298$ K$)$

$= -742.7 + 1.2$ kJ mol^{-1} $= -741.5$ kJ mol^{-1}.

6.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

Ans. $q = n \times C \times \Delta T = \left(\frac{60 \text{ mol}}{27}\right)(24 \text{ J mol}^{-1} \text{ K}^{-1})(328 - 308)\text{K}$

$= 1066.7\text{J} = 1.07$ kJ.

6.10 Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at –10°C.

$\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C

$C_p[H_2O(\ell)] = 75.3$ J mol^{-1} K^{-1}

$C_p[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}.

Ans. Total ΔH = (1 mol water at 10°C ⟶ 1 mol of water at 0°C) + (1 mole of water at 0°C ⟶ 1mol ice at 0°C)+ (1 mole of ice at 0°C ⟶ 1 mol of ice at –10°C)

$$= C_p[H_2O.(l)] \times \Delta T + \frac{\Delta H_{freezing}}{T_f} + C_p[H_2O(s)] \times \Delta T$$

$(\Delta T = T_2 - T_1)$

$= (75.3 \text{ JK}^{-1}\text{ mol}^{-1})(0-10)\text{K} + (-6.03 \text{ kJ mol}^{-1})$

$+ (36.8 \text{ JK}^{-1}\text{ mol}^{-1})(-10\text{ K})$

$= -753 \text{ J mol}^{-1} - 6.03 \text{ kJ mol}^{-1} - 0.368 \text{ J mol}^{-1}$

$= -0.753 \text{kJ mol}^{-1} - 6.03 \text{ kJmol}^{-1} - 0.368 \text{ kJ mol}^{-1}$

$= -7.151 \text{ kJ mol}^{-1}$.

6.11 Enthalpy of combustion of carbon to CO_2 is – 393· 5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans. $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5$ kJ mol^{-1}

For CO_2, 1 mol = 44 g
Heat released when 44 g CO_2 is formed = 393.5 kJ
∴ Heat released when 35.2 g CO_2 is formed

$$= \frac{393.5 \times 35.2\,\text{kJ}}{44} = 314.8\,\text{kJ}$$

6.12 Enthalpies of formation of CO (g), CO_2 (g), N_2O (g) and N_2O_4 (g) are –110, –393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction :

$N_2O_4(g) + 3CO(g) \longrightarrow N_2O\,(g) + 3\,CO_2\,(g)$

Ans. $\Delta_f H = \Sigma\Delta_f H$ (Products) $-\Sigma\ \Delta_f H$ (Reactants)

$= (\Delta_f H\,(N_2O) + 3\,\Delta_f H\,(CO_2)]$
$\quad - [\Delta_f H\,(N_2O_4) + 3\,\Delta_f H\,(CO)]$
$= [81 + 3\,(-393)] - [9.7 + 3\,(-110)]$ kJ
$= -777.7$ kJ.

6.13 Given : N_2 (g) + $3H_2$ (g) → $2NH_3$ (g); $\Delta_r H^\ominus = -92.4$ kJ mol^{-1}. What is the standard enthalpy of formation of NH_3 gas ?

Ans. Reaction for the enthalpy of formation of NH_3 (g) is

$$\frac{1}{2}N_2(g) + 3/2\,H_2(g) \longrightarrow NH_3(g)$$

$\Delta_f H° = -92.4/2 = -46.2$ kJ mol^{-1}.

6.14 Calculate the standard enthalpy of formation of CH_3OH (*l*) from the following data :

(i) $CH_3OH\,(l) + \frac{3}{2}\,O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$;

$\Delta_r H^\ominus = -726$ kJ mol^{-1}

(ii) C (graphite) + O_2 (g) $\longrightarrow$ CO_2 (g) ;

$\Delta_c H^\ominus = -393$ kJ mol^{-1}

(iii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$;

$\Delta_f H^\ominus = -286$ kJ mol^{-1}.

Ans. Aim : $C\,(s) + 2\,H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CH_3OH\,(\ell),\ \Delta_f H° = ?$

Eqn. (ii) + 2 × Eqn. (iii) – Eqn. (i) gives the required eqn. with
$\Delta H = -393 + 2\,(-286) - (-726)$ kJ mol^{-1}
$= -239$ kJ mol^{-1}.

6.15 Calculate the enthalpy change for the process

CCl_4 (g) $\longrightarrow$ C (g) + 4Cl (g) and calculate bond enthalpy of C – Cl in CCl_4 (g)

$\Delta_{vap} H^\ominus$ (CCl_4) = 30.5 kJ mol^{-1}

$\Delta_f H^\ominus$ (CCl_4) = –135.5 kJ mol^{-1}

$\Delta_a H^\ominus$ (C) = 715.0 kJ mol^{-1} where $\Delta_a H^\ominus$ is enthalpy of atomisation

$\Delta_a H^\ominus$ (Cl_2) = 242 kJ mol^{-1}.

Ans. The given data imply as under :

(i) $CCl_4(\ell) \longrightarrow CCl_4(g)$, $\Delta H = 30.5$ kJ mol^{-1}
(ii) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(\ell)$, $\Delta H = -135.5$ kJ mol^{-1}
(iii) $C(s) \longrightarrow C(g)$, $\Delta H = 715.0$ kJ mol^{-1}
(iv) $Cl_2(g) \longrightarrow 2Cl(g)$, $\Delta H = 242$ kJ mol^{-1}

Aim : $CCl_4(g) \longrightarrow C(g) + 4Cl(g)$, $\Delta H = ?$

Eqn. (iii) + 2 × Eqn. (iv) – Eqn. (i) – Eqn. (ii) gives the required equation with
$\Delta H = 715.0 + 2\,(242) - 30.5 - (-135.5)$ kJmol^{-1}
$= 1304$ kJ mol^{-1}
Bond enthalpy of C-Cl in CCl_4 (average value)

$$= \frac{1304}{4} = 326\ \text{kJ mol}^{-1}.$$

6.16 For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans. $\Delta U = 0$ means that energy factor has no role to play. Hence, for the process to be spontaneous, entropy factor should favour the process, i.e. ΔS must be positive i.e. $\Delta S > 0$. Consider the example of two gases contained separately in two bulbs connected by a stop-cock, and isolated from the surroundings as an example of an isolated system. On opening the stop-cock, the two gases mix up, i.e., the system becomes more disordered. This implies that $\Delta S > 0$., but $\Delta U = 0$ for the process.

6.17 For the reaction at 298 K, 2A + B $\longrightarrow$ C
$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}.
At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

Ans. Let us first calculate the temperature at which the reaction will be in equilibrium, i.e., $\Delta G = 0$.
Now, $\Delta G = \Delta H - T\Delta S$ ∴ $0 = \Delta H - T\Delta S$ or $T = \Delta H / \Delta S = 400$ kJ mol^{-1} / 0.2kJ K^{-1} mol^{-1} = 2000 K
For reaction to be spontaneous, i.e., for ΔG to be –ve, T should be greater than 2000 K.

6.18 For the reaction, 2Cl (g) $\longrightarrow$ Cl_2 (g), what are the signs of ΔH and ΔS?

Ans. The given reaction represents the formation of bonds. Hence, energy is released, i.e.. ΔH is -ve. Further, 2 moles of atoms have greater randomness than 1 mole of molecules. Hence, randomness decreases, i.e.
ΔS is –ve.

6.19 For the reaction, 2A(g) + B(g) $\longrightarrow$ 2D(g),

$\Delta U^\ominus = -10.5$ kJ and $\Delta S^\ominus = -44.1$ JK^{-1} Calculate $\Delta G^\ominus$ for the reaction, and predict whether the reaction may occur spontaneously.

Ans. For the given reaction, $\Delta n_g = 2 - (3) = -1$

∴ $\Delta H° = \Delta U° + \Delta n_g RT$
$= -10.5$ kJ + (–1) (8.314 × 10^{-3} k J) (298)
$= -10.5 - 2.48 = -12.98$ kJ

$\Delta G° = \Delta H° - T\Delta S°$
$= -12{\cdot}98$ kJ – 298 (–44·1 × 10^{-3} kJ)
$= -12.98$ kJ + 13.14 kJ = 0.16 kJ

As $\Delta G°$ comes out to be +ve, the reaction will not occur spontaneously.

6.20 The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^\ominus$? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

Ans. $\Delta G° = -2.303\,RT \log K$
$= -2.303 \times 8.314$ JK^{-1} mol^{-1} × 300K × log 10
$= -5744.1$ J.

6.21 Comment on the thermodynamic stability of NO (g), given

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g);$$

$$\Delta_r H^{\ominus} = 90 \text{ kJ mol}^{-1}$$

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g);$$

$$\Delta_r H^{\ominus} = -74 \text{ kJ mol}^{-1}$$

Ans. As energy is absorbed in the first reaction, NO (g) is unstable. As energy is released in the second reaction, NO_2 (g) is stable. Thus, unstable NO (g) changes into the stable NO_2 (g).

6.22 Calculate the entropy change in surroundings when 1· 00 mol of H_2O (*l*) is formed under standard conditions: $\Delta_f H^{\ominus}$ = –286 kJ mol^{-1}.

Ans. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$

This means that when 1 mol of H_2O (l), is formed, 286 kJ of heat is released. This heat is absorbed by the surroundings, i.e.,$q_{surr} = +286 \text{ kJmol}^{-1}$.

$$\Delta S = q_{surr} / T = \frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$

$$= 0.9597 \text{ kJK}^{-1}\text{mol}^{-1} = 959.7 \text{ JK}^{-1}\text{mol}^{-1}.$$

Practice Questions

Very Short Answer Questions [1 Marks]

1. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)\ \Delta H = -242 \text{ kJ mol}^{-1}$.

   Bond energy of H_2 and O_2 are 436 kJ mol^{-1} and 500 kJ mol^{-1} respectively. What is bond energy of O – H bond.
2. Predict $\Delta H > \Delta U$ or ΔH is less than ΔU or $\Delta H = \Delta U$.
   (a) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$
   (b) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$.
3. State why heat changes in physical and chemical processes are indicated by enthalpy changes and not internal energy changes.
4. In the equation $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, what whould be the sign of work done?
5. What is the value of ΔG when ice and water are in equilibrium?
6. What is the importance of 'free energy' concept for chemical reaction?
7. An endothermic process, $A \rightarrow B$, proceeds to completion. What is sign of ΔS?
8. Does an aqueous solution of Mg^{2+} ions have a larger entropy before or after hydration of the ions?
9. Why is entropy of a solution higher than that of pure liquid?
10. The enthalpy change for the conversion of liquid water to steam is 40.8 kJ at 100°C. Calculate ΔS for the process.
    $= 0.1094 \text{ kJ mol}^{-1} \text{ K}^{-1}$.
11. Give an example of following energy conversions:
    (i) Radiation energy into chemical energy.
    (ii) Radiation energy into electrical energy.
12. Hydrogen iodide is put in a glass bulb which is sealed and is then heated to decompose hydrogen iodide into H_2 and I_2. What type of system does the reaction mixture represent.
13. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the change from the initial state to a final state were made by a different path, would ΔH be the same as that for the first path? would q too be the same?
14. If an equation for a reaction is multiplied by 2 and then reversed, how is the value of ΔH changes?
15. What property of enthalpy provides the basis of Hess's law?
16. For the reaction $2A + B \rightleftharpoons A_2B$, the $K_p = 2.3 \times 10^2$ at 25°C. Predict the sign of $\Delta G_r°$.
17. Can the absolute value of internal energy be determined ?
18. One mole of CO_2 at 300 K and 1 atm pressure is heated in a closed vessel so that temperature is 500 K and pressure is 5 atm. Then, it is cooled back to temperature of 300 K and pressure 1 atm. What is the change in internal energy of the gas ?
19. Water decomposes by absorbing 286·2 kJ of electrical energy per mole. When H_2 and O_2 combine to form one mole of H_2O, 286.2 kJ of heat is produced. Which law is proved ? What statement of the law follows from it ?
20. Neither q nor w is a state function, yet q + w is a state function. Explain why.
21. For the same increase in volume, why work done is more if the gas is allowed to expand reversibly at higher temperature ?
22. Why standard heat of formation of diamond is not zero though it is an element ?
23. Water can be lifted into the water tank at the top of the house with the help of a motor pump. Then why this change is not considered to be spontaneous ?
24. Rank the following in the order of increasing entropy :
    (a) 1 mole of H_2O (*l*) at 25 °C and 1 atm. pressure.
    (b) 2 mole of H_2O (s) at 0 °C and 1 atm. pressure.
    (c) 1 mole of H_2O (g) at 100 °C and 1 atm. pressure.
    (d) 1 mole of H_2O (*l*) at 0 °C and 1 atm. pressure.
25. Under what condition, the heat evolved or absorbed in a reaction is equal to its free energy change ?
26. The standard free energy of a reaction is found to be zero. What is its equilibrium constant ?
27. State second law of thermodynamics.
28. Place the following systems in order of increasing randomness :
    (a) 1 mol of a gas X
    (b) 1 mol of a solid X
    (c) 1 mol of a liquid X.
29. Which out of the following can be determined ? Absolute internal energy, absolute enthalpy, absolute entropy.
30. Is the bond energy of all the four C — H bonds in CH_4 molecule equal? If not then why ? How is the C—H bond energy then reported ?

31. Give an example of reaction where $\Delta H = \Delta U$
32. Addition of CCl_4 to water is spontaneous or not.
33. State Nernst Law of thermodynamics and its useful application.
34. What are the limitations of first law of thermodynamics?

Short Answer Questions [2 & 3 Marks]

1 What are the sign conventions for heat and work?

2. Prove that the change in internal energy is equal to the heat exchanged between the system and the surrounding.

3. Prove that the change in enthalpy is equal to the heat exchanged between the system and the surrounding at constant T and P.

4. 0.562 g of graphite kept in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure was burnt according to the equation

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

During the reaction, temperature rises from 298 K to 298.89 K. If the heat capacity of the calorimeter and its contents is 20.7 kJ/K. What is the enthalpy change for the above reaction at 298 K and 1 atm?

5. What would be the heat released when:
   (i) 0.25 mol of hydrochloric acid solution is neutralised by 0.25 mol of sodium hydroxide solution?
   (ii) 0.02 mol of sulphuric acid solution is mixed with 0.2 mol of potassium hydroxide solution?

6. Why is it important to give the states of the reactants and products when giving an equation for ΔH?

7. What is meant by the reference form of an element? What is the standard enthalpy of formation of an element in its reference form?

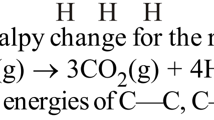
8. Calculate the heat of combustion of glucose from the following data:
   (i) $C(gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = -394\ kJ$
   (ii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g) \qquad \Delta H° = -286\ kJ$
   (iii) $6C(gr) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)\ \Delta H° = -1170\ kJ$

9. Determine the enthalpy of reaction for the hydrogenation of acetylene to form ethane:

$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$$

From the following data:
   (i) $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(1)\ \Delta H° = -2600\ kJ$
   (ii) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(1)\ \Delta H° = -3120\ kJ$
   (iii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(1) \qquad \Delta H° = -286\ kJ$

10. Propane has the structure



If standard enthalpy change for the reaction ($\Delta_r H°$) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ is -2.05×10^3 kJ/mol and bond energies of C—C, C—H, C═O and O—H are 347, 414, 741 and 464 respectively. Calculate the energy of oxygen-oxygen bond in O_2 molecule.

11. The reaction $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ has $\Delta_r S° = -217\ J\ K^{-1}\ mol^{-1}$ and $\Delta_r H° = -1202$ kJ mol.
Predict whether the reaction will be spontaneous or not.

12. Silane, SiH_4 burns in air. The products are solid SiO_2 and gaseous water.

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(g)$$

Given :

$\Delta_f G°$(kJ/mol:	– 805	– 228.6	52.3	0
Substance :	SiO_2	H_2O	SiH_4	O_2

Predict the spontaneity of the reaction.

13. For the reaction
$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$
$\Delta_r H° = +467.9$ kJ/mol and
$\Delta_r S° = +0.56$ kJ/mol K.
Calculate the temperature at which the $\Delta_r G°$ becomes zero. What will be the direction of reaction above this temperature?

14. What is the equilibrium constant K for the following reaction at 400 K?

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Given : $\Delta_r H° = 77.2$ kJ/mol
and $\Delta_r S° = 122\ JK^{-1}\ mol^{-1}$ at 400 K.

15. Under what conditions
(i) $\Delta H < \Delta E$ (ii) $\Delta H > \Delta E$?

16. Which of the following conditions predict spontaneity:
   (a) $\Delta H = +$ ve, $\Delta S = -$ ve, high temperature
   (b) $\Delta H = -$ ve, $\Delta S = +$ ve, low temperature
   (c) $\Delta H = +$ ve, $\Delta S = +$ ve, high temperature
   (d) $\Delta H = -$ve, $\Delta S = -$ ve, low temperature?

17. Calculate $\Delta H_f°$ for chloride ion from the following data:

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g); \qquad \Delta_f H° = -92.8\ kJ\ mol^{-1}$$

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq), \qquad \Delta_{diss} H° = -75.2\ kJ\ mol^{-1}$$

18. Separate out the following into extensive and intensive: Volume, Temperature, Pressure, Boiling point, Free energy

19. Predict whether following reaction will be exothermic or endothermic. Give reason for your answer

$$H–H(g) + Cl–Cl(g) \longrightarrow 2H–Cl(g)$$

20. State whether each of the following processes will increase or decrease the total energy content of the system
   (a) Heat transferred to the surroundings
   (b) Work done by the system
   (c) Work done on the system
   (d) Heat transferred to the system

21. What do you mean by a spontaneous process ? Explain your answer with a suitable examples.

22. Which of the following processes are accompanied by increase of entropy ?
   (a) Dissolution of iodine in a solvent,
   (b) HCl is added to $AgNO_3$ solution to form a ppt. of AgCl.
   (c) A partition is removed to allow gases to mix.
   (d) Formation of NH_3 from N_2 and H_2

23. Predict the sign of entropy change for each of the following changes of state :

(a) $Hg(l) \longrightarrow Hg(g)$

(b) $AgNO_3(s) \longrightarrow AgNO_3(aq)$

(c) $I_2(g) \longrightarrow I_2(s)$

(d) $C(graphite) \longrightarrow C(diamond)$

24. An exothermic reaction $A \longrightarrow B$ is spontaneous in the backward direction. What will be the sign of ΔS for the forward reaction ?

25. Predict in which of the following, entropy increases/decreases.

(i) A liquid crystallizes into a solid

(ii) Temperature of a crystalline solid is raised from 0K to 115 K

(iii) $2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)$

(iv) $H_2\,(g) \longrightarrow 2\,H\,(g)$

26. Explain why the entropy of a pure crystalline substance is zero at 0K ? State the law on which it is based. Give the application of this law ?

27. A chemist claims that the following reaction is feasible at 298K

$$SF_6(g) + 8HI(g) \longrightarrow H_2S(g) + 6HF(g) + 4I_2(s)$$

Verify his claim. Given that ΔG_f^o for $SF_6(g)$, $HI(g)$, $H_2S(g)$ and $HF(g)$ are – 991.61, 1.30, –33.01 and – 270.73 kJ mol^{-1} respectively.

28. Which of the following processes are accompanied by increase of entropy ?

(a) Stretching of rubber band,

(b) Boiling of an egg

(c) A deodrant is sprayed.

29. To what type of system the following belong ?

(i) Tree (ii) Pond (iii) Animals

(iv) Tea in a closed kettle

(v) Tea placed in thermos flask (vi) Tea placed in a cup

30. Comment on the following statements :

(a) An exothermic reaction is always thermodynamically spontaneous.

(b) The entropy of a substance increases in going from the liquid to the vapour state at any temperature.

(c) Reaction with $\Delta G° < 0$ always have an equilibrium constant greater than 1.

31. At a certain temperature 'T', the endothermic reaction $A \longrightarrow B$ proceeds virtually to the end. Determine

(i) sign of ΔS for this reaction (ii) sign of ΔG for the reaction $B \longrightarrow A$ at the temperature T, and (iii) the possibility of reaction $B \longrightarrow A$ proceeding at a low temperature.

32. Comment on the validity of the following statements, giving reasons :

(i) Thermodynamically, an exothermic reaction is sometimes not spontaneous,

(ii) The entropy of steam is more than that of water at its boiling point,

(iii) The equilibrium constant for a reaction is one or more if $\Delta_r G°$ for it is less than zero.

33. Give reasons for the following :

(a) Why the heat produced be different if same mass of diamond and graphite are burnt in oxygen?

(b) The dissolution of ammonium chloride in water is endothermic still it dissolves in water

(c) A real crystal has more entropy than an ideal crystal.

34. Calculate the value of log Kp for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C. The standard enthalpy of formation of $NH_3(g)$ is – 46 kJ mol^{-1} and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130, 192 JK^{-1} mol^{-1} respectively.

35. The heat of combustion of $H_2(g)$ at constant pressure and 300 K is – 280 kJ mol^{-1}. What will be heat of combustion at constant volume and at 300 K ?

36. The enthalpy of vapourisation of liquid diethyl ether, $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS^0 for the conversion of

(a) liquid to vapour, and

(b) vapour to liquid at 35.0°C.

Long Answer Questions [5 Marks]

1. Define the following terms :

(a) System

(b) Isothermal processes

(c) Adiabatic processes

(d) State variables/state functions

(e) Work

2. **(i)** Calculate the standard molar entropy change for the following reactions at 298 K.

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

(b) $Ca\,(s) + 2\,H_2O\,(l) \longrightarrow Ca(OH)_2\,(aq) + H_2\,(g)$

Given:

$S°_{Fe(s)} = 27.28$, $S°_{O_2(g)} = 205.14$, $S°\,Fe_2O_3\,(s) = 87.4$

$S°_{Ca(s)} = 41.42$, $S°_{H_2O(l)} = 69.9$,

$S°Ca_{(OH)_2(aq)} = 74.5$, $S°_{H_2(g)} = 130.68$,

(ii) Calculate the standard molar Gibbs energy of formation of CS_2, given that its standard enthalpy of formation is 89.7 kJ mol^{-1} and the standard molar entropies of graphite, S and CS_2 are 5.7, 31.8 and 151.3JK^{-1}mol^{-1} respectively.

3. **(i)** Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

(ii) Under what conditions will the reaction occur, if

(a) both ΔH and ΔS are positive

(a) both ΔH and ΔS are negative

4. Derive Gibbs – Helmholtz equation.

5. Calculate the enthalpy of formation of anhydrous aluminium chloride, Al_2Cl_6 from the following data:

(i) $2Al\,(s) + 6HCl\,(aq) \rightarrow Al_2Cl_6\,(aq.) + 3H_2(g)$; $\Delta H = -1004.0$ kJ

(ii) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; $\Delta H = -183.9$ kJ

(iii) $HCl\,(g) + (aq) \rightarrow HCl\,(aq)$; $\Delta H = -73.2$ kJ

(iv) $Al_2Cl_6(s) + (aq) \rightarrow Al_2Cl_6\,(aq)$; $\Delta H = -643$ kJ

6. For the reaction

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

at 25°C, the equilibrium constant is 7.0×10^{-84}.

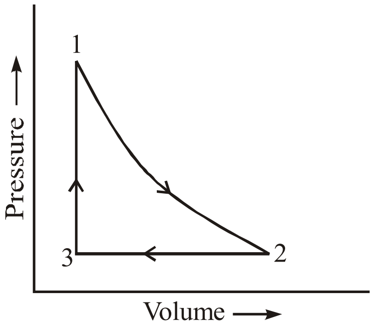
(i) Calculate the standard Gibbs energy formations of water at 25°C.

(ii) $\Delta_r\,H°_{H_2O} = -280$ kJ mol^{-1}. Calculate the entropy change for the reaction.

HOTS/Exemplar Questions

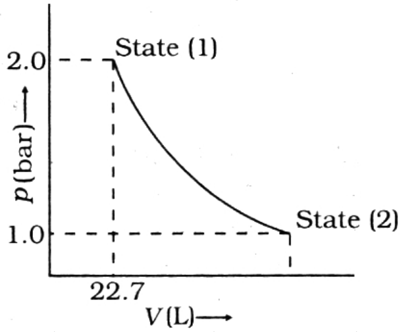
Very Short Answer Questions [1 Mark]

1. We are consuming a lot of electrical energy, solar energy etc in our routine basis. Do you, think that energy of the universe is continuously decreasing ? Name any other thermodynamic quantity which is continuously increasing or decreasing ? **[HOTS]**
2. One kg of graphite is burnt in a closed vessel. The same amount of the same sample is burnt in an open vessel. Will the heat evolved in the two cases be same? If not, in which case it would be greater? **[HOTS]**
3. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in fig. What will be the value of ΔH for the cycle as a whole? **[Examplar]**



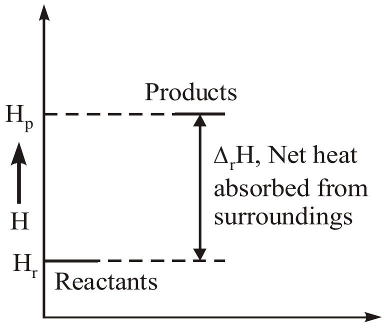
Short Answer Questions [2 & 3 Marks]

1. A chemist while studying the properties of gaseous $C_2Cl_2F_2$, a chlorofluorocarbon refrigerant, cooled 1.25 g sample at constant atmospheric pressure of 1.0 atm from 320 K to 293 K. During cooling, the sample volume decreased from 274 to 248 ml. Calculate ΔH and ΔU for the chlorofluorocarbon for this process.
   The value of molar heat capacity is 80.7 J mol^{-1} K^{-1}. **[HOTS]**
2. Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane. The heat of combustion of methane to CO_2 and water as gas is given by
   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + 809\ kJ$
   How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20000 kJ of energy per day to meet all its needs and that the methane content in the gobar gas is 80 percent by weight. **[HOTS]**
3. Why is it more convenient to predict the direction of reaction in terms of ΔG_{sys} instead of ΔS_{total}? Under what conditions can ΔG_{sys} be used to predict the spontaneity of a reaction? **[HOTS]**
4. Find out whether it is possible to reduce MgO using carbon at 298 K. If not, at what temperature, it becomes spontaneous for reaction.
   $$MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$$
   Given : $\Delta_r H° = +491.18\ kJ\ mol^{-1}$
   and $\Delta_r S° = +197.67\ JK^{-1}\ mol^{-1}$ at 298 K **[HOTS]**
5. 10 moles of an ideal gas expand isothermally and reversibly from a pressure of 5 atm to 1 atm at 300K. What is the largest mass that can be lifted through the height of 1 metre by this expansion? **[HOTS]**
6. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. Calculate the amount of work done for the expansion of gas from state (1) to state (2) at 298 K.



[HOTS]

7. Air contain 99% N_2 and O_2 gases. Then why don't they combine to form NO under the standard conditions? Given that the standard free energy of formation of NO(g) is 86.7 kJ mol^{-1}. **[HOTS]**
8. What is the difference in between bond energy of H–H bond and heat of formation of H atom. Illustrate with example. **[HOTS]**
9. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25°C. Lattice energy of NaCl = 777.8 kJ mol^{-1} and ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = –774.1 kJ mol^{-1}. **[HOTS]**
10. A swimmer coming out from a pool is covered with a film of water weighing about 80 g. How much heat must be supplied to evaporate this water? (Δ°_{vapH} for water = +40.79 kJmol^{-1}) **[HOTS]**
11. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not? **[Exemplar]**
12. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre? **[Exemplar]**
13. Enthalpy diagram for a particular reaction is given in Fig. (A). Is it possible to decide spontaneity of a reaction from given diagram.
    Explain.



[Exemplar]

Fig. (A)

14. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol–1. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water? **[Exemplar]**

15. The value of $\Delta_f H^{\ominus}$ for NH_3 is –91.8 kJ mol^{-1}. Calculate enthalpy change for the following reaction:
$2NH_3(g) \rightarrow N_2(g) + 3\,H_2(g)$ **[Exemplar]**

16. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ ... which represents enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$ ... etc. for intermediate reactions. **[Exemplar]**

17. The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H\,(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond? **[Exemplar]**

18. The molar enthalpy of vapourisation of acetone is less than that of water. Why?

19. Which quantity out of $\Delta_r G$ and $\Delta_r G$□ will be zero at equilibrium? **[Exemplar]**

20. Predict the change in internal energy for an isolated system at constant volume. **[Exemplar]**

21. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain. **[Exemplar]**

22. The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for 10 moles of an ideal gas. **[Exemplar]**

23. An ideal gas is allowed to expand against a constant pressure of 2 bar from 1 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case? [Given that 1 L bar = 100 J] **[Exemplar]**

24. Represent the potential energy / enthalpy change in the following processes graphically. **[Exemplar]**

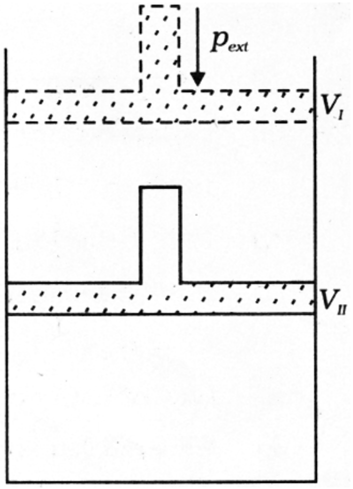
(a) Throwing a stone from the ground to roof.

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)\ \Delta_r H^{\ominus} = 92.32\text{kJ mol}^{-1}$

In which of the processes potential energy / enthalpy change is contributing factor to the spontaneity?

25. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps? **[Exemplar]**

26. What will be the work done on an ideal gas enclosed in cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. Explain graphically. **[Exemplar]**



[Exemplar]

27. The enthalpy of reaction for the reaction : **[Exemplar]**
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta_r H^{\ominus} = -572$ kJ mol^{-1}.
What will be standard enthalpy of formation of H_2O (l) ?

28. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1}). **[Exemplar]**

29. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction. **[Exemplar]**
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1}, 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

30. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also. **[Exemplar]**

Long Answer Questions [5 Marks]

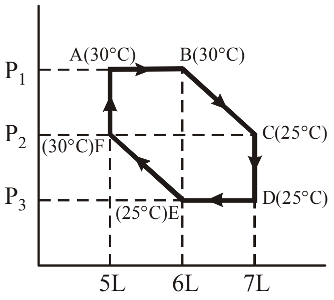
1. **(i)** Diborane is a potential rocket fuel which undergoes combustion according to the reaction
$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$
From the following data, calculate the enthalpy change for the combustion of diborane
$2B(s) + 3/2\,O_2(g) \longrightarrow B_2O_3(s)\ \Delta H = -1273\ \text{kJ mol}^{-1}$
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)\ \Delta H = -286\ \text{kJ mol}^{-1}$
$H_2O(\ell) \longrightarrow H_2O(g)\ \Delta H = 44\ \text{kJ mol}^{-1}$
$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)\ \Delta H = -36\ \text{kJ mol}^{-1}$

(ii) Calculate ΔH at 25°C for the process of dissolving 1.00 mol of KCl in a large excess of water. Does this process represent an ionization reaction ? Explain.

Given
$\Delta_f H°K^+ = -251.2$ kJ mol^{-1}
$\Delta_f H°Cl^- = -167.08$ kJ mol^{-1}
$\Delta_f KCl = -437.6$ kJ mol^{-1} **[HOTS]**

2. A system containing an ideal gas was subjected to a number of changes as shown in the P-V diagram below. Temperatures at different points are indicated in the diagram.

(i) Name the type of process at each step.
(ii) What will be the value of ΔU for the complete process ?
(iii) At which point, the number of moles of the gas will be maximum ?



[HOTS]

3. Predict the sign of entropy change in each of the following :

(i) H_2 (at 298 K, 1 atm) → H_2 (at 298 K, 10 atm)
(ii) H_2O (at 298 K, 1 atm) → H_2O (at 330 K, 1 atm)
(iii) $2\,NH_4NO_3\,(s) \rightarrow 2\,N_2\,(g) + 4\,H_2O\,(g) + O_2\,(g)$
(iv) Crystallization of copper sulphate from its saturated solution
(v) $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ **[HOTS]**

4. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s). **[Exemplar]**

5. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_v, V_f). With the help of a pV plot compare the work done in the above case with that carried at against a constant external pressure p_f. **[Exemplar]**

CHAPTER TEST

Time : *30 min.* **Max. Marks : *15***

Directions :
- ***(i) Attempt all questions***
- ***(ii) Questions 1 to 3 carry 1 mark each.***
- ***(iii) Questions 4 and 5 carry 2 marks each.***
- ***(iv) Question 6 carry 3 marks***
- ***(v) Question 7 carry 5 marks***

1. Is entropy an extensive or intensive property?

2. The standard free energy change of a reaction is found to be zero. What is its equilibrium constant?

3. A reversible reaction has ΔG° negative for forward reaction ? What would be the sign of ΔG° for backward reaction?

4. The bond dissociation energies of gaseous H_2, Cl_2, and HCl are 104 , 58, and 103 kcal/mol respectively. Calculate the energy of formation of HCl gas.

5. The reaction $CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O\,(l)$ was carried out at 27°C by taking one mole of each reactants. The equilibrium constant is 4. Calculate the standard free energy change for the reaction ($R = 8.314\ JK^{-1}mol^{-1}$).

6. Prove $\Delta G = -T\Delta S_{total}$

7. **(i)** At a certain temperature 'T', the endothermic reaction A → B proceeds virtually to an end. Determine
(a) sign of entropy change for this reaction
(b) sign of free energy change for the reaction B → A at high temperature.
(c) the possibility of reaction B → A proceeding at low temperature.

(ii) Predict whether entropy change is positive or negative in following processes:
(a) $N_2O_3 \longrightarrow N_2O(g) + O_2(g)$
(b) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$
(c) Dissolution of NaCl in water
(d) Heating of $CaCO_3$

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -242 \text{ kJ mol}^{-1}$

ΔH = Bond energy of reactants – Bond energy of products.

$$\Delta H = B_{H\text{-}H} + \frac{1}{2}B_{O=O} - 2\,B_{O\text{-}H} = -\,242 \text{ kJ}$$

$$= 436 + \frac{1}{2}(500) - 2B_{O\text{-}H}$$

$$-\,928 \text{ kJ} = -\,2B_{O\text{-}H};\ B_{O\text{-}H} = \frac{928}{2} = 464 \text{ kJ mol}^{-1}.$$

2. (a) $\Delta H = \Delta U$ because $\Delta n = 0$
(b) $\Delta H > \Delta U$ because $\Delta n = 1$
$[\Delta H = \Delta U + \Delta nRT.]$

3. Most of the processes are carried out in open container, i.e., at constant pressure. Therefore, enthalpy changes are indicated and not internal energy changes.

4. The sign of work done will be +ve i.e. work will be done on the system due to decrease in volume.

5. $\Delta G = 0$.

6. Free energy helps in determining spontaneity of the process.

7. ΔS is positive.

8. Mg^{2+} has more entropy before hydration of ions.

9. In solution, there is more disorderness than in pure liquid.

10. $\Delta S = \frac{\Delta H_{vap}}{T} = \frac{40.8}{373} = 0.1094 \text{ kJ mol}^{-1}\text{ K}^{-1}.$

11. (i) Photosynthesis
(ii) Photoelectric effect.

12. The reaction mixture represents a closed system as there is an exchange of energy between the system and the surrounding.

13. ΔH is the same, since it is a state function, but q will be different for the different paths.

14. When a thermochemical equation is multiplied by 2, the value of ΔH becomes double, i.e. $2\Delta H$. When a chemical equation is reversed, the value of ΔH is reversed in sign i.e. $-\,2\Delta H$.

15. (a) Enthalpy is a state function and (b) law of conservation of energy are the two basis of Hess's law. Hess's law enables us to predict the enthalpies of reactions that we cannot measure directly in the laboratory.

16. $K_p = 2.3 \times 10^2$ at 25°C. Predict the sign of $\Delta G_r°$.
We know that $\Delta G_r° = -\,2.303\ RT \log K_p$
If $K_p > 1$, then $\Delta G_r° < 0$
In this reaction, $K_p = 2.3 \times 10^2$ is greater than 1, therefore, $\Delta G_r°$ will have a negative sign.

17. No, because it is the sum of different types of energies some of which cannot be determined.

18. No change because internal energy is a state function and in this case system has returned to its original state.

19. Law of conservation of energy (or 1st law of thermodynamics). According to this law energy can neither be created or destroyed, although it may be converted from one form to another.

20. For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out.

21. For isothermal reversible expansion,
$w = -P_{int} \times \Delta V$. At higher temperature, internal pressure of the gas is more.

22. It is because standard state chosen for carbon is graphite and not diamond.

23. A spontaneous process is one which should continue by itself after initiation. But this is not so in the given case because water will go up so long as the pump is working.

24. (b) < (d) < (a) < (c).

25. As $\Delta G = \Delta H - T\Delta S$. Thus, $\Delta G = \Delta H$ only when either the reaction is carried out at 0 K or the reaction is not accompanied by any entropy change, i.e., $\Delta S = 0$.

26. $\Delta G° = -\,2.303\ RT \log K$. Hence, $\log K = 0$ or $K = I$.

27. The entropy of the universe increases in every spontaneous (natural) change. The entropy of the universe is continuously increasing.

28. 1 mol of solid X < 1 mol of liquid X < 1 mol of gas X.

29. Absolute entropy.

30. No because after breaking of C—H bonds one by one, the electronic environments change. The reported value is the average value of the bond dissociation energies of the four C—H bonds.

31. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ As $\Delta n_g = 0$

32. It is non-spontaneous.

33. The entropy of a perfectly crystalline solid approaches zero as the temperature approaches absolute zero. Thus with this one can calculate standard entropy changes of reactions.

34. It could not give information about the spontaneity of chemical reactions.

Short Answer Questions

1. The sign conventions for heat (q) are:
heat absorbed by the system is positive, $q > 0$
heat released by the system is negative, $q < 0$
The sign conventions for work (w) are:
work done on the system is positive, $W_{on} > 0$
work done by the system is negative, $W_{by} < 0$

2. $\Delta U = q + w$
(First law of thermodynamics)
q = energy supplied to the system as heat
w = work done on the system
If the work is a P – V work, then $w = P\Delta V$
Therefore, $\Delta U = q + P\,\Delta V$
If the system is closed (like bomb calorimeter), then $\Delta V = 0$
$\therefore \quad \Delta U = q_v$
Hence, the heat exchange between the system and the surrounding is equal to change in internal energy.

3. $\Delta H = \Delta U + P\Delta V$ (at constant P)

But $\Delta U = q + w$ (Ist law of thermodynamics)

or $\Delta U = q - P\,\Delta V$ ($\because w = -P\,\Delta V$)

$\therefore$ $\Delta H = q - P\,\Delta V + P\,\Delta V$

$\Delta H = q_p$

4. $\Delta H = \Delta U + \Delta n_g RT$

For the reaction $C(gr) + O_2(g) \rightarrow CO_2(g)$, $\Delta n_g = 0$

$\therefore$ $\Delta H = \Delta U = q_v$

$\Delta H = q_v = C_v(\Delta T)$

$= 20.7\ \text{kJ K}^{-1} \times 0.89\ \text{K} = 18.4\ \text{kJ}$

As the reaction is a combustion reaction (exothermic)

$\Delta H = -18.4$ kJ for the combustion of

0.562 g C (graphite)

For 1 mol C (graphite),

$$\Delta H = -18.4 \times \frac{12.0}{0.562}$$

$\Delta H = -392.88$ kJ/mol

The enthalpy of combustion of graphite is $-392.88\ \text{kJ mol}^{-1}$

5. (i) 0.25 mole HCl(aq) + 0.25 mole NaOH(aq)

The net reaction is

H^+ (0.25 mole) + OH^- (0.25 mole)

$\rightarrow H_2O$ (0.25 mole)

Therefore heat released = 57.1 × 0.25 kJ

= 14.3 kJ

(ii) 1 mole of H_2SO_4 contains 2 mole of H^+

$\therefore$ 0.02 mole of H_2SO_4 contains 0.04 mols of H^+

The net reaction is

H^+ (0.04 mole + OH^- (0.2 mole) $\rightarrow H_2O$(0.04 mole)

Therefore heat released would be

$0.04 \times 57.1 = 2.284$ kJ

6. It is important to specify the states (whether a gas, liquid, solid or aqueous) of the reactants and products while writing the thermochemical equation because the enthalpy change, ΔH depends on the state of the substances. Consider the reaction of hydrogen and oxygen to produce water. If the product is water vapour, 2 moles of H_2 burn to release 483.7 kJ of heat.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
$$\Delta H = -483.7\ \text{kJ}$$

On the other hand, if the product is liquid water, the heat released is 571.7 kJ

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$$
$$\Delta H = -571.7\ \text{kJ}$$

In this case, additional heat is released when water vapour condenses to liquid.

7. The reference form of an element is the stablest form (physical state and allotrope) of the elements under standard thermodynamics conditions. The reference form of oxygen at 298 K is $O_2(g)$, the reference form of carbon at 298K is graphite.

The standard enthalpy of formation ($\Delta_f H°$) of an element in its reference form is zero.

8. Our aim is to calculate the ΔH° of glucose for the reaction

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(1)$ $\Delta H° = ?$

Given :

$C(gr) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -394$ kJ (a)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1)$ $\Delta H° = -286$ kJ (b)

$6C(gr) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$

$\Delta H° = -1170$ kJ (c)

Step I : Multiplying equation (a) by 6 and equation (b) by 6, we have,

$6C(gr) + 6O_2(g) \rightarrow 6CO_2(g)$

$\Delta H° = 6 \times (-394)$ ...(1)

$= -2364$ kJ

$6H_2(g) + 3O_2(g) \rightarrow 6H_2O(1)$

$\Delta H° = 6 \times (-286)$ ...(2)

$= -1716$ kJ

Step II : Reverse equation (c),

$C_6H_{12}O_6(s) \rightarrow 6C(s) + 6H_2(g) + 3O_2(g)$ ...(3)

$\Delta H° = 1170$ kJ

Step III : Adding equations (1), (2) and (3)

$$6C(gr) + 6O_2(g) \longrightarrow 6CO_2(g)$$
$$\Delta H° = -2364\ \text{kJ}$$
$$\oplus \qquad \oplus$$
$$6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(1)$$
$$\Delta H° = -1716\ \text{kJ}$$
$$\oplus \qquad \oplus$$
$$C_6H_{12}O_6(s) \longrightarrow 6C(gr) + 6H_2(g) + 3O_2(g)$$
$$\Delta H° = +1170\ \text{kJ}$$

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(1)$$
$$\Delta_c H° = -2364 - 1716 + 1170$$
$$= -2910\ \text{kJ}$$

9. The equation for which we have to calculate ΔH° is

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_2(g)$ $\Delta H° = ?$

Step I : Multiplying equation (i) by $\frac{1}{2}$ and equation (iii) by 2

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(1)$$

$$\Delta H°_1 = -\frac{1}{2} \times -2600$$

$= -1300$ kJ ...(1)

$2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$

$\Delta H°_2 = 2 \times (-286)$

$= -572$ kJ ...(2)

Step II : Reversing equation (ii), then multiply the equation by $\frac{1}{2}$

$$2CO_2(g) + 3H_2O(1) \rightarrow C_2H_6(g) + \frac{7}{2}O_2(g)$$

$$\Delta H_3° = \frac{1}{2} \times 3120$$

$= +1560$ kJ ...(3)

Step III : Adding equations (1), (2) and (3), gives

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

$\Delta H° = \Delta H_1° + \Delta H_2° + \Delta H_3°$

$\Delta H° = -1300 - 572 + 1560$

$= -312$ kJ

10. $\Delta_r H° = \sum BE(\text{reactants}) - \sum BE\ (\text{products})$

$\Delta_r H° = [8\,BE(C—H) + 2\,BE(C—C) + 5\,BE(O=O)] - [6\,BE(C=O) + 8\,BE(O—H)]$

$-2.05 \times 10^3 = [8 \times 414 + 2 \times 347 + 5\,BE(O=O)] - [6 \times 741 + 8 \times 464]$

$-2050 = 4006 + 5\,BE\,(O=O) - 8158$

$5BE\,(O=O) = 2102$

$BE(O=O) = 420.4\ \text{kJ mol}^{-1}$

11. The criterion for spontaneity is that $\Delta S_{total} > 0$ and $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$.

Given : $\Delta S_{system} = -217\ \text{J K}^{-1}\ \text{mol}^{-1}$

As the reaction is exothermic, the heat evolved will increase the entropy of the surrounding.

$$\Delta S_{surr.} = -\Delta S_{sys} = \frac{-\Delta H_{sys}}{T}$$

$$= \frac{-(-1202 \times 10^3)}{298}$$

$\Delta S_{surr} = 4.03 \times 10^3\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\therefore \quad \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$= -217 + 4030$

$= 3813\ \text{J K}^{-1}\ \text{mol}^{-1}$

As $\Delta S_{total} > 0$, the reaction will be spontaneous.

12. To predict whether the reaction is spontaneous or not, we should first calculate $\Delta_r G°$. For the reaction

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(g)$$

$$\Delta_r G° = [\Delta_f G^o_{(SiO_2)} + 2\Delta_f G^o_{(H_2O)}]$$

$$-[\Delta_f G^o_{(SiH_4)} + 2\Delta_f G^o_{(O_2)}]$$

$\Delta_r G° = [-805 + 2(-228.6)] - [+52.3 + 2 \times 0]$ $\quad \Delta_r G° = [-805 - 457.2] - 52.3$

$\Delta_r G° = -1314.5\ \text{kJ/mol}$

The reaction would be spontaneous as $\Delta_r G°$ is negative.

13. We know the Gibbs energy equation is

$\Delta_r G° = \Delta_r H° - T\,\Delta_r S°$

Temperature at which the $\Delta_r G°$ become zero is given by

$$0 = \Delta_r H° - T\,\Delta_r S° \text{ and } T = \frac{\Delta_r H°}{\Delta_r S°}$$

$$T = \frac{467.9\ \text{kJ mol}^{-1}}{0.56\ \text{kJ mol}^{-1}\ \text{K}^{-1}}$$

$T = 835.5\ \text{K}$

Above this temperature, sign of $\Delta_r G°$ will be negative, $\Delta_r G° < 0$. Therefore, the forward direction will be favourable.

14. Step (1) is to calculate $\Delta_r G°$

$\Delta_r G° = \Delta_r H° - T\,\Delta_r S°$

$= (77.2\ \text{kJ mol}^{-1}) - 400\ \text{K} \times (122 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})$

$\Delta_r G° = (77.2 - 48.8)\ \text{kJ mol}^{-1}$

$\Delta_r G° = 28.4\ \text{kJ mol}^{-1}$

Step (2) is to calculate K

$$\log\ K = \frac{-\Delta_r G°}{2.303\,RT}$$

$$= \frac{-28.4\ \text{kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1} \times 400\text{K}}$$

$\log K = -3.708$

$K = \text{antilog}\ (\bar{4}.292)$

$K = 1.96 \times 10^{-4}$

15. We know that

$\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \Delta n_g RT$

Where Δn_g represents difference between the gaseous moles of products and reactants.

(i) When Δn_g is a – ve quantity i.e., reaction in which there is decrease in the number of moles of the gaseous components:

$\Delta H = \Delta E$ + (negative quantity) × RT so that $\Delta H < \Delta E$

e.g. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

$$\Delta n_g \left(1 - 1\frac{1}{2}\right) = -\frac{1}{2}$$

(ii) When Δn_g is a + ve quantity i.e. the reaction proceeds by increase in the number of mole of the gaseous components?

$\Delta H = \Delta E$ + (+ ve quantity) + RT so that

$\Delta H > \Delta E$

e.g. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

$\Delta n_g = (1 + 3) - 2 = 2.$

16. (a) ΔH = + ve, ΔS = – ve, high temperature

$\Delta G = (+) - T(-) = +$ ve

Non-spontaneous at all temperatures.

(b) ΔH = – ve, ΔS = + ve, low temperature

$\Delta G = (-) - T\,(+) = -$ ve

Spontaneous at all temperature.

(c) ΔH = + ve, ΔS = + ve, high temperature

$\Delta G = (+) - T\,(+)$ At high temperature ($T\Delta S > \Delta H$), ΔG = – ve and therefore reaction will be spontaneous.

(d) ΔH = – ve, ΔS = – ve, low temperature

$\Delta G = (-) - T\,(-)$; at low temperature

($T\Delta S < \Delta H$)

ΔG = – ve and therefore reaction will be spontaneous.

17. From the second reaction,

$\Delta_r H° = \{\Delta_f H°\,[H_3O^+(aq)] + \Delta_f H°\,[Cl^-(aq)]\} - \Delta_f H°\,(HCl)$

But enthalpy of formation of H^+ ion in dilute aqueous solution is taken as zero, i.e.,

$\Delta_f H°[H_3O^+(aq)] = 0$

Also from the first reaction,

$\Delta_f H°\,(HCl) = -92 \cdot 8\ \text{kJ mol}^{-1}$

$-75{\cdot}2 = 0 + \Delta_f H°[Cl^-(aq)] - (-92{\cdot}8)$

or $\quad \Delta_f H°[Cl^-(aq)] = -75.2 - 92.8 = -168.0\ \text{kJ mol}^{-1}$.

18. The properties which depend upon the quantity of the substance or substances present in the system. The properties which are independent of the quantity of the substance present in the system volume and free energy are extensive, others are intensive.

19. This reaction is accompanied by decrease of randomness, i.e., decrease of entropy. For the reaction to be spontaneous total entropy change should be negative. A reaction would be exothermic with respect to the system if it adds entropy to the surroundings and endothermic if it reduces entropy of surrounding.

$\Delta S_{surr} > 0$ – exothermic $\Delta S_{surr} < 0$ – endothermic.

20. (a) decrease (b) decrease
(c) increase (d) increase

21. Process which takes place by itself or by some initiation. Example- water flowing down hill is a spontaneous process but the reverse is a non-spontaneous process. Burning of coal has to be initiated by igniting some coals to fire but once ignited it will continue burning even if the igniting flame is removed.

22. (a) When solid iodine is dissolved in a suitable solvent it forms iodine solution. Thus entropy increases.

(b) $HCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + HNO_3(aq)$
Formation of solid ppt. (AgCl) entropy decreases.

(c) When a partition is removed to allow intermixing of gases. The volume increases and hence entropy also.
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(d) As per above equation total number of moles of gaseous species decreases. Thus entropy decreases.

23. (a) ΔS = +ve (b) ΔS = +ve
(c) ΔS = –ve (d) S = –ve.

24. Backward reaction will be endothermic. Thus, energy factor opposes the backward reaction. As backward reaction is spontaneous, randomness factor must favour, i.e., ΔS will be + ve for backward reaction or it will be –ve for forward reaction.

25. (i) Decreases because a solid has ordered arrangement of constituent particles.

(ii) Increases because at 0K, there is a perfect order of constituent particles. As temperature is increased, the particles start vibrating about their equilibrium position. Hence, a disorder sets in.

(iii) Increases because the reactant is solid whereas products have gaseous substance.

(iv) Increases because the products have larger (double) number of particles.

26. At 0K, there is a perfectly ordered arrangement of the constituent particles of a pure crystalline substance and there is no disorder at all. Hence, its entropy is taken as zero. This statement is based on the third law of thermodynamics. The law is applied to find the absolute entropy of a substance in any state at any temperature.

27.
$$\begin{aligned}\Delta G &= [\Delta G_f(H_2S) + 6\Delta G_f(HF) + 4\Delta G_f(I_2)] - [\Delta G_f(SF_6) + 8\Delta G_f(HI)]\\ &= [(-33.01) + 6(-270.73) + 4(0)] - [(-991.61) + 8(1.30)] = (-1659.39) - (-981.21)\\ &= -676.18 \text{ kJ mol}^{-1}\end{aligned}$$

As ΔG is coming out to be –ve , the reaction is feasible. Hence chemist's claim is true.

28. (b) and (c).

29. (i) Open system (ii) Open system
(iii) Open system (iv) Closed system
(v) Isolated system (vi) Open system

30. (a) An exothermic reaction is not always spontaneous. This is because if ΔS is –ve and $T\Delta S > \Delta H$ in magnitude, then according to the equation $\Delta G = \Delta H - T\Delta S$, ΔG will be +ve and the process will be non-spontaneous.

(b) At any temperature, the molecules in the vapour state have greater freedom of motion because of lesser intermolecular forces of attraction than in the liquid state.

(c) $-\Delta G° = RT \ln K$. Thus, if $\Delta G°$ is less than zero, i.e., it is –ve, then ln K will be +ve and hence K will be greater than 1.

31. (i) As we know that $\Delta G = \Delta H - T\Delta S$. For endothermic reactions ΔH = +ve. Thus for ΔG = –ve, ΔS must be positive.

(ii) For $A \longrightarrow B$, ΔG is –ve, therefore, for
$B \longrightarrow A$, ΔG will be +ve.

(iii) For $B \longrightarrow A$, ΔH = –ve and ΔS is also –ve, i.e., ΔS opposes the process but at low temp., $T\Delta S$ may be so low that ΔH is greater in magnitude than $T\Delta S$ and the process will be spontaneous.

32. (i) Yes, the given statement is true. This is because $\Delta G = \Delta H - T\Delta S$. For exothermic reaction, ΔH is –ve. If $T\Delta S$ is +ve (i.e., entropy factor opposes the process) and $T\Delta S > \Delta H$ in magnitude, ΔG will be +ve and process will not be spontaneous.

(ii) Yes, the given statement is true. This is because at the same temperature, gaseous state is more disordered than the liquid state.

(iii) $-\Delta G° = RT \ln K$. Thus, if $\Delta G°$ is less than zero, i.e., it is –ve, then ln K will be +ve and hence K will be greater than 1.

33. (a) The heat evolved is different because they have different crystal structure.

(b) On dissolution, entropy increases, i.e., ΔS is +ve. Though here ΔH is +ve but if $T\Delta S > \Delta H$, then according to the equation, $\Delta G = \Delta H - T\Delta S$, ΔG will be –ve. Hence, the process is spontaneous,

(c) A real crystal has some disorder due to presence of defects whereas ideal crystal has no disorder. Hence,a real crystal has more entropy than ideal crystal.

34.
$$\begin{aligned}\Delta G°_f(NH_3) &= \Delta H° - T\Delta S°\\ &= -46000 - (298 \times 192) \text{ J mol}^{-1}\\ &= -103.2 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G°_f(N_2) &= \Delta H° - T\Delta S°\\ &= 0 - (298 \times 191)\\ &= -56.9 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G°_f(H_2) &= \Delta H° - T\Delta S°\\ &= 0 - (298 \times 130)\\ &= -38.74 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta G° \text{ for the reaction} = 2 \times \Delta G°_f(NH_3) - [\Delta G°_f(N_2) + 3(\Delta G°_f(H_2)]$$

$= -206.4 + 56.9 + 116.2$
$= -33.28\ \text{kJ mol}^{-1}$

$-\Delta G° = 2.303\ RT \log K_p$
$33.28 = 2.303 \times (8.314 \times 298) \log K_p$
or $\log K_p = 5.83 \times 10^{-3}$

35. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\,(l)\ \Delta H = -280\ \text{kJ mol}^{-1}$

$\Delta H = \Delta U + \Delta n RT,\ \Delta n = 0 - \frac{3}{2} = -\frac{3}{2},$

$\Delta H = \Delta U - \frac{3}{2} \times 8.314 \times 300$

$-280\ \text{kJ} = \Delta U - \frac{74826}{20} \times \frac{1}{1000}\ \text{kJ}$

$\Rightarrow\ \Delta U = -276.2587\ \text{kJ}.$

36. $\Delta H_{\text{vaporisation}} = 26.0\ \text{kJ mol}^{-1}.$
$T_b = 35°C$
$= 35 + 273\ K = 308\ K$
$\Delta H_{\text{vap}} = 26000\ \text{J mol}^{-1}$
$\Delta S_{\text{vaporisation}} = \Delta H_{\text{vap}} / T_b = 26000\ \text{J mol}^{-1} / 308\ K$
$= 84.4\ \text{JK}^{-1}\ \text{mol}^{-1}$
$\Delta H_{\text{condensation}}\ (\text{vapour} \longrightarrow \text{liquid}) = -\Delta H_{\text{vap}}$
$= -26.0\ \text{kJ mol}^{-1} = -26000\ \text{J mol}^{-1},$
$\Delta S_{\text{condensation}} = -26000\ \text{J mol}^{-1} / 308K$
$= -84.4\text{JK}^{-1}\text{mol}^{-1}$

Long Answer Questions

1. (a) It is that part of the universe which is under observation.

(b) Process in which temperature remains constant throughout the process is known as isothermal process. When such a process occurs, heat can flow from the system to the surrounding and vice-versa.

(c) Adiabatic process is a process which is carried out in such a manner that no heat can flow from the system to the surrounding or vice-versa.

(d) Functions or variable which depend on the initial and the final state of the system.

(e) Work is said to have been done whenever the point of application of a force is displaced in the direction of force.

2. **(i)** (a) $\Delta S° = S°\,(\text{Products}) - S°\,(\text{Reactants})$
$= [2 \times S°\,(Fe_2O_3)\,(s)] - [4 \times S°\,Fe\,(s) + 3 \times S°\,O_2\,(g)]$
$= (2 \times 87.4) - (4 \times 27.28 + 3 \times 205.14)\text{JK}^{-1}\ \text{mol}^{-1}$
$= 174.8 - (109.12 + 615.42)\ \text{JK}^{-1}\ \text{mol}^{-1}$
$= -549.74\ \text{JK}^{-1}\ \text{mo1}^{-1}$

(b) $\Delta S° = \left[S°Ca(OH)_2(aq) + S°H_2(g)\right]$
$-\left[S°Ca(s) + 2 \times S°H_2O(l)\right]$
$= [74.5 + 130.68] - [41.42 + 2 \times 69.9] = 205.18 - 181.22 =$
$23.96\ \text{JK}^{-1}\ \text{mol}^{-1}$

(ii) $C + 2S \longrightarrow CS_2$
$\Delta S° = [S°CS_2 - (S°C + 2\ S°S]$
$= 151.3 - (5.7 + 2 \times 31.8) = 82\ \text{JK}^{-1}\ \text{mol}^{-1}$
$= 0.082\ \text{kJ K}^{-1}\ \text{mol}^{-1}$
$\Delta G° = \Delta H° - T\Delta S° = 89.7\ \text{kJ mol}^{-1}$
$-298 \times (0.082\ \text{kJ K}^{-1}\text{mol}^{-1}) = 65.27\ \text{kJ mol}^{-1}.$

3. **(i)** substance has perfectly ordered arrangement of its constituent particles only at absolute zero. When the element formed from itself. This means no heat change. Thus, $\Delta_f H = 0$

(ii) (a) If both ΔH and ΔS are positive ΔG can be –ve only TΔS > ΔH in magnitude.
Thus the temperature should be high.

(b) If both ΔH and ΔS are negative ΔG can be negative only TΔS < ΔH is magnitude. Thus the value of T should be low.

4. Gibbs – Helmholtz equation is
$\Delta G = \Delta H - T\Delta S$
where ΔG = Change in free energy
ΔH = Change in enthalpy
T = Kelvin temperature
ΔS = Change in entropy

Derivation : Let us consider a reactions being carried out at constant temperature, T and constant pressure, P.

Let G_R = Free energy of reactants
H_R = Enthalpy of reactants
S_R = Entropy of reactants
G_P = Free energy of products
H_P = Enthalpy of products
S_P = Entropy of products.

We know that, $G = H - T_S$
For reactants, $G_R = H_R - TS_R$
For products, $G_P = H_P - TS_P$
$\Delta G = G_P - G_R$
$= (H_P - TS_P) - (H_R - TS_R)$
$= H_P - TS_P - H_R + TS_R$
$= (H_P - H_R) - T(S_P - S_R)$
$\Delta G = \Delta H - T\Delta S$
which is Gibbs –Helmholtz equation.

5. The formation of Al_2Cl_6 from its elements may be represented as:

$$2Al\,(s) + 3Cl_2\,(g) \rightarrow Al_2Cl_6\,(s)$$

Multiply Eq. (ii) by 3 and Eq. (iii) by 6 and adding,
(ii) × 3, $3H_2(g) + 3\,Cl_2\,(g) \rightarrow 6HCl\,(g);$
$\Delta H = -551.7\ \text{kJ}$
(iii) × 6, $6HCl(g) + (aq) \rightarrow 6HCl\,(aq);$
$\Delta H = -439.2\ \text{kJ}$
(v) $3H_2\,(g) + 3Cl_2\,(g) + (aq) \rightarrow 6HCl\,(aq);$
$\Delta H = -990.9\ \text{kJ}$

Add Eq. (i) to Eq. (v),
(i) $2Al\,(s) + 6HCl\,(aq) \rightarrow Al_2Cl_6\,(aq) + 3H_2(g);$
$\Delta H = -1004.0\ \text{kJ}$
Add (vi) $2Al\,(s) + 3Cl_2(g) + (aq);$
$\rightarrow Al_2Cl_6\,(aq);$
$\Delta H = -1994.9\ \text{kJ}$

Subtract Eq. (iv) from Eq. (vi)
(iv) $Al_2Cl_6\,(s) + aq \rightarrow Al_2Cl_6\,(aq);$
$\Delta H = -643\ \text{kJ}$
Subtract $2Al\,(s) + 3Cl_2(g) \rightarrow Al_2Cl_6\,(s);$
$\Delta H = -1351.9\ \text{kJ}$

Thus, enthalpy of formation or anhydrous $Al_2Cl_6 = -1351.9\ \text{kJ}.$

6. Using equation $\Delta_r G° = -2.303\ RT \log K_p$
(i) $\Delta_r G° = -2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$
$\times 298\ K \times \log 7.0 \times 10^{-84}$

$$\Delta_r G° = -2.303 \times 8.314 \times 298 \times (-83.15)\ \text{J mol}^{-1}$$

$$\Delta_r G° = 474441\ \text{J mol}^{-1} = 474.44\ \text{kJ mol}^{-1}$$

For the reaction $2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$

$$\Delta_r G° = [2\Delta_r G°_{H_2} + \Delta_f G°_{O_2}] - 2\,\Delta_f G°_{H_2O}$$

$$474.44 = (0 + 0) - 2\Delta_f G°_{H_2O}$$

$$\therefore\ \Delta_f G°_{H_2O} = -\frac{474.44}{2} = -237.22\ \text{kJ mol}^{-1}$$

(ii) $\Delta_r H° = [2\,\Delta_f H°_{H_2} + \Delta_f H°_{O_2}] - 2\Delta_f H°_{H_2O}$

$$\Delta_r H° = (0 + 0) - 2\,(-286)$$

$$\Delta_r H° = 572\ \text{kJ mol}^{-1}$$

Using equation $\Delta_r G° = \Delta_r H° - T\,\Delta_r S°$

we calculate $\Delta_r S°$

$$\Delta_r S° = \frac{\Delta_r H° - \Delta_r G°}{T}$$

$$\Delta_r S° = \frac{(572\ \text{kJ mol}^{-1}) - (474.44\ \text{kJ mol}^{-1})}{298\ \text{K}}$$

$$\Delta_r S° = 0.327\ \text{kJ mol}^{-1}\ \text{K}^{-1}$$

$$\Delta_r S° = 327\ \text{J mol}^{-1}\ \text{K}^{-1}$$

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. No, energy of the universe remains constant according to first law of thermodynamics. Entropy of the universe is continuously increasing.
2. Same in both cases because $\Delta n_g = 0$.
3. ΔH (cycle) = 0.

Short Answer Questions

1. $q = \Delta U = -C\Delta T$

$$q = -80.7\ \text{J mol}^{-1}\ \text{K}^{-1} \times 27\ \text{K} = -2178.9\ \text{J mol}^{-1}$$

$$\Delta U = -2178.9\ \text{J mol}^{-1} \times \frac{1.25\text{g}}{133\text{g mol}^{-1}}$$

$$\Delta U = -20.48\ \text{J}$$

$$\Delta H = \Delta U + P\Delta V$$

$$P\Delta V = 1\ \text{atm} \times (274 - 248) \times 10^{-3}\ \text{L} = 0.026\ \text{L atm} = 0.026 \times 101\ \text{J} = 2.626\ \text{J}$$

$$\therefore\ \Delta H = -20.48\ \text{J} - 2.626\ \text{J}$$

$$\Delta H = -23.11\ \text{J}$$

2. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + 809\ \text{kJ}$

$\quad 16\text{g}$

Total energy required per day

$$= 100 \times 20{,}000 = 2 \times 10^6\ \text{kJ}$$

809 kJ of energy is produced by burning 16g CH_4

∴ 2×10^6 kJ of energy is produced by

$$\text{burning } \frac{16\text{g} \times 2 \times 10^6\ \text{kJ}}{809\ \text{kJ}}$$

$$= 3.955 \times 10^4\text{g}$$

$$= 39.55\ \text{kg of } CH_4$$

Therefore, corresponding amount of gobar gas produced per day

$$= \frac{39.55}{80} \times 100 = 49.44\ \text{kg}$$

3. The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe; $\Delta S_{total} > 0$. In order to determine the sign of ΔS_{total} for a reaction, we would need to calculate both ΔS_{sys} and ΔS_{surr}. However, we usually concerned with what happens in a particular system. Secondly, calculation of ΔS_{surr} is quite difficult. Therefore, it is convenient to predict the direction of reaction in terms of ΔG_{sys} and we can ignore the surrounding. ΔG_{sys} can be used to predict the spontaneity of a reaction under the conditions of constant temperature and pressure.

4. To find whether the reaction is spontaneous or not at 298 K we calculate $\Delta_r G°$ for the reaction using

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$

$$\Delta_r G° = (491.18\ \text{kJ mol}^{-1}) - (298\ \text{K})(197.67 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})$$

$$\Delta_r G° = (491.18 - 58.91)\ \text{kJ mol}^{-1})$$

$$\Delta_r G° = 432.27\ \text{kJ mol}^{-1}$$

As $\Delta_r G° > 0$, the reaction is non-spontaneous at 298 K.

Temperature at which $\Delta_r G° = 0$ is given by

$$T = \frac{\Delta_r H°}{\Delta_r S°} = \frac{491.18\ \text{kJ mol}^{-1}}{197.67 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}}$$

$$T = 2485\ \text{K}$$

The reaction will be spontaneous above 2485 K.

5. $W_{exp} = -2.303nRT \log \dfrac{P_1}{P_2}$

$$= -2.303 \times (10\ \text{mol}) \times (8.314) \times (300\text{K}) \log 5/1$$

$$= -40.15 \times 10^3\ \text{J}$$

If 'M' is the mass that can be lifted by this work, through the height of 1 metre,

then work done = M × g × h 'g' acceleration due to gravity = 9.81m/s²

$$40.15 \times 10^3 = M \times 9.81\ \text{ms}^{-2} \times 1\text{m}$$

$$\text{or } M = \frac{40.15 \times 10^3\ \text{kg m}^2\text{s}^{-2}}{9.81 \times 1\ \text{m}^2\text{s}^{-2}} = 4092.76\ \text{kg}$$

6. It is clear from the figure that the process has been carried out in infinite steps, hence it is isothermal reversible expansion.

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

$$\text{But, } p_1V_1 = p_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$$

$\therefore \quad w = -2.303nRT \log \frac{p_1}{p_2}$

$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K}^{-1} \times \log 2$

$= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J} = -1717.46 \text{ J}$

7. Standard free energy of formation ($\Delta G°_f$) for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ is positive (equal to +86.7 kJ mol^{-1}). Hence, the reaction is non-spontaneous under the standard conditions.

8. Bond energy of H–H bond i.e., $H_2 \longrightarrow 2H; \Delta H = B.E$ and heat of formation of H atom

$\frac{1}{2}H_2 \longrightarrow H; \ \Delta H = \Delta H_f$

$\therefore$ B.E. of H–H = $2 \times \Delta H_{\text{formation of H atom}}$.

9. Using the relation,

$\Delta H_{\text{dissolution}}$ = Lattice energy + Hydration energy, we find

For NaCl, $\quad \Delta H_{\text{dissolution}} = (777.8 - 774.1) \text{ kJ mol}^{-1}$

$= 3.7 \text{ kJ mol}^{-1}$

Again, $\Delta G = \Delta H - T\Delta S$

$\therefore \quad \Delta G = (3.7 - 298 \times 0.043) \text{ kJ mol}^{-1}$

$(3.7 - 12.814) \text{ kJ mol}^{-1} = -9.114 \text{ kJ mol}^{-1}$.

10. The process of evaporation can be represented as

$$\underset{\text{(Liquid)}}{80g\ H_2O} \xrightarrow{\text{Vaporization}} \underset{\text{(Vapour)}}{80g\ H_2O}$$

Now $\Delta_{vap}H^0$ for water = + 40.79 kJ mol^{-1}

Molar mass of water = 18 g mol^{-1}

Number of moles in 80 g of water (*n*) $= \frac{80g}{18g\ mol^{-1}} = 4.44$ mol

$\therefore$ Heat supplied (q) = $n \times \Delta_{vap} H^0$

$= (4.44 \text{ mol}) \times (40.79 \text{ kJ mol}^{-1}) = 1.81 \times 10^2 \text{ kJ}$

11. It is spontaneous process. Although enthalpy change is zero but randomness or disorder (i.e., ΔS) increase. Therefore, in equation $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. Hence, ΔG will be negative.

12. $(-w) = p_{ext}(V_2 - V_1)\ 0 \times (5 - 1) = 0$

For isothermal expansion q = 0

By first law of thermodynamics

$q = \Delta U + (-w)$

$\Rightarrow \quad 0 = \Delta U + 0$ so $\Delta U = 0$

13. No.

Enthalpy is one of the contributory factors in deciding spontaneity but it is not the only factor. One must look for contribution of another factor i.e., entropy also, for getting the correct result.

14. +81.58 kJ, $\Delta_{vap}H^{\ominus} = +40.79 \text{ kJ mol}^{-1}$

15. $\Delta_r H^{\ominus} = +91.8 \text{ kJ mol}^{-1}$

16. $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots$

17. $\frac{1665}{4} \text{ kJ mol}^{-1} = 416.2 \text{ kJ mol}^{-1}$

18. Because of strong hydrogen bonding in water, its enthalpy of vapourisation is more.

19. $\Delta_r G$ is always be zero.

$\Delta_r G^{\ominus}$ is zero for K = 1 because $\Delta G^{\ominus} = -RT \ln K$, $\Delta G^{\ominus}$ will be non zero for other values of K.

20. For an isolated system, there is no transfer of energy as heat or as work i.e., w = 0 and q = 0. According to the first law of thermodynamics.

$\Delta U = q + w$

$= 0 + 0 = 0$

$\therefore \quad \Delta U = 0$

21. **As constant volume**

By first law of thermodynamics:

$q = \Delta U + (-w)$

$(-w) = p\Delta V$

$\therefore \quad q = \Delta U + p\Delta V$

$\Delta V = 0$, since volume is constant

$\therefore \quad q_v = \Delta U + 0$

$\Rightarrow \quad q_v = \Delta U$ = change in internal energy

At constnt pressure

$q_p = \Delta U + p\Delta V$

But, $\Delta U + p\Delta V = \Delta H$

$\therefore \quad q_p = \Delta H$ = change in enthalpy

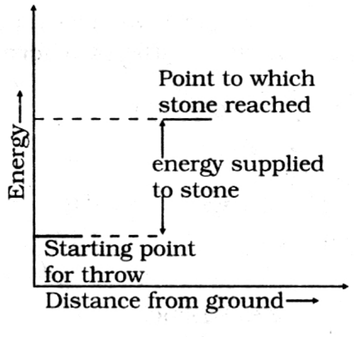
So, at a constant volume and at constant pressure net change is a state function because it is equal to change in internal energy and change in enthalpy respectively which are state functions.

22. $C_p - C_V = nR = 10 \times 4.184$ J

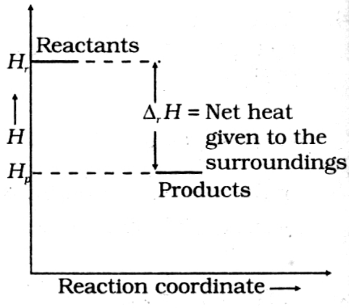
23. $w = p_{ex}(V_f - V_i) = -2 \times 40 = -80$ L bar = – 8 kJ

The negative sign shows that work is done by the system on the surrounding. Work done will be more in the reversible expansion because internal pressure and external pressure are almost same at every step.

24.

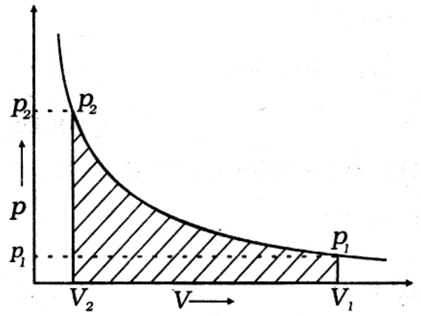


(a)

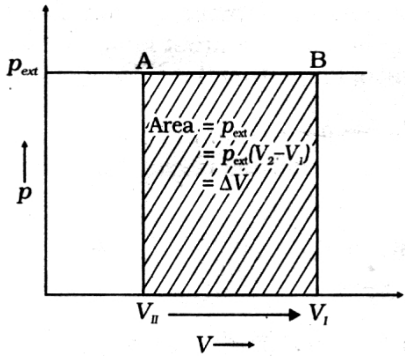


(b)

25. The work done can be calculated with the help of p–V plot. A p–V plot of the work of compression which is carried out by change in pressure in infinite steps, is given in Fig. Shaded area represents the work done on the gas.



26. Work done on an ideal gas can be calculated from p-V graph shown in Fig. Work done is equal to the shaded area ABV_IV_{II}.



27. According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $H_2O(l)$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l).$$

or the standard enthalpy of formation of $H_2O(l)$ will be half of the enthalpy of the given equation i.e., $\Delta_r H^\ominus$ is also halved.

$$\Delta_f H^\ominus_{H_2O(l)} = \frac{1}{2} \times \Delta_r H^\ominus = \frac{-572 \text{ kJ mol}^{-1}}{2} = -286 \text{ kJ/mol.}$$

28. $q_p = \Delta H = -30.5 \text{ kJ mol}^{-1}$

∴ Heat required for vapourisation of 284 g of CCl_4

$$= \frac{284 \text{ g}}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ mol}^{-1} = 56.2 \text{ kJ}$$

29. $\Delta_r H^\ominus$ = Bond energy of H_2 + Bond energy of Br_2 – 2 × Bond energy of HBr

$= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$

$\Rightarrow \Delta_r H^\ominus = -109 \text{ kJ mol}^{-1}$

30. Molar enthalpy change of graphite

= enthalpy change for 1 g carbon × molar mass of carbon

$= -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$

∴ $\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$

Negativ value of ΔH ⇒ exothermic reaction.

Long Answer Questions

1. **(i)** Given $2B(s) + 3/2\, O_2(g) \longrightarrow B_2O_3(s)$

$\Delta H = -1273 \text{ kJ mol}^{-1}$ …(i)

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell)$

$\Delta H = -286 \text{ kJ mol}^{-1}$ …(ii)

$H_2O(\ell) \longrightarrow H_2O(g)$

$\Delta H = 44 \text{ kJmol}^{-1}$ …(iii)

$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$

$\Delta H = -36 \text{ kJ mol}^{-1}$ …(iv)

Aim equation is

$B_2H_6(g) + 3H_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$

The following operation has to be done to reach at the aim equation .

Eqn (i) + 3 × Eqn(ii) + 3 × Eqn (iii) – Eqn (iv)

$\Delta H = -1273 + \{3 \times (-286)\} + \{3 \times (44)\} - (-36) = -1963 \text{ kJmol}^{-1}$

(ii) Aim : $KCl(s) + aq \longrightarrow K^+(aq) + Cl^-(aq)$, $\Delta H^\circ = ?$

$\Delta H^\circ = \{[\Delta_f H^\circ K^+(aq)] + \Delta_f H^\circ [Cl^-(aq)]\} - \Delta_f H^\circ (KCl)$

$= -251.2 + (-167.08) - (-437.6) \text{ kJmol}^{-1}$

$= +19.32 \text{ kJ mol}^{-1}$

No, the given process does not represent an ionization process, because KCl is an ionic solid and is already in the ionized form. The given process represents dissolution process.

2. (i) AB = isothermal and isobaric expansion

BC = adiabatic expansion (temperature falls)

CD = isochoric and isothermal

DE = isothermal and isobaric compression

EF = adiabatic compression (temperature rises)

FA = isothermal and isochoric.

(ii) As complete process is cyclic, therefore, ΔU = 0.

(iii) Process AB is accompanied by increase of volume due to increase in the number of moles. Process BC is accompanied by increase in volume due to fall of temperature. Process CD is accompanied by fall of pressure due to decrease in the number of moles. Process DE is due to decrease in the number of moles. In process EF, there will be no change in the number of moles. Process FA is accompanied by increase of pressure due to higher number of moles at A. But as already explained, at B number of moles is greater than that at A. Hence, the number of moles is maximum at point B.

3. Entropy is a measure of randomness or disorder of a system. If randomness increases, entropy increases.

(i) Gas at lower pressure has greater randomness than at high pressure (compressed gas) at the same temperature. Hence entropy decreases, i.e., ΔS is –ve.

(ii) Molecules at higher temperature have greater randomness at the same pressure. Hence, ΔS is +ve.

(iii) Gaseous molecules have greater randomness than the solid. Hence, ΔS is +ve.

(iv) $CuSO_4$ crystals have ordered arrangement whereas ions in the solution have greater randomness. Hence, ΔS is –ve.

(v) There are 3 moles of two different gaseous reactants which have greater randomness than 2 moles of the only gaseous product, SO_3. Hence, randomness decreases, i.e., ΔS is –ve.

4.
- $Na(s)+\frac{1}{2}Cl_2(g)\rightarrow Na^+(g)+Cl^-(g);\ \Delta_{lattice}H^{\ominus}$
- Born - Haber Cycle
- Steps to measure lattice enthalpy from Born - Haber cycle
- Sublimation of sodium metal

(1) $Na(s)\rightarrow Na(g)$; $\Delta_{sub}H$

(2) Ionisation of sodium atoms

$Na(g)\rightarrow Na^+(g)+e^-(g)$; Δ_rH i.e., Ionisation enthalpy

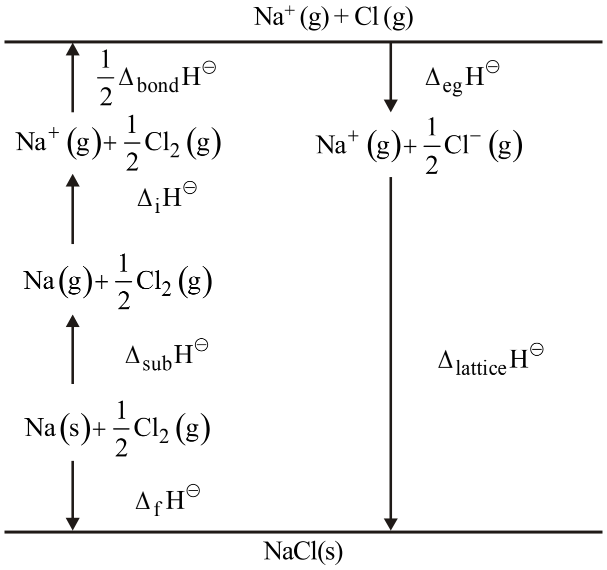
(3) Dissociation of chlorine molecule

$\frac{1}{2}Cl_2(g)\rightarrow Cl(g);\ \frac{1}{2}\Delta_{bond}H$

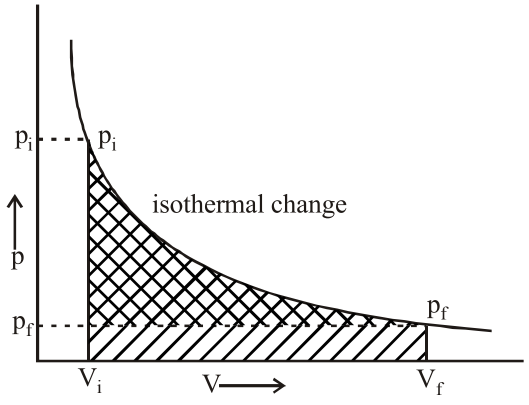
i.e., One-half of bond dissociation enthalpy

(4) $Cl(g)+e^-(g)\rightarrow Cl^-(g)$; $\Delta_{eg}H$

i.e., electron gain enthalpy



5.



(i) Reversible work is represented by the combined ▩ area and ▨.

(ii) Work against constant pressure., p_f is represented by the area ▨ work (i) > work (ii)

CHAPTER TEST

1. Extensive

2. log K = 0 means K = 1.

3. It would be still negative.

4. $H-H+Cl-Cl\longrightarrow 2\,H-Cl$

$\Delta H_f = \Sigma$ B.E (reactants) – Σ B.E (products)

$= (104+58)-2(103) = 162-206 = -44$ kcal/mol

5. $\Delta G° = -2.303\ RT\log K$

Given K = 4 hence log K = 0.6021

For standard condition, temperature is 25°C = 298 K

Hence $\Delta G° = -(2.303\times 8.314\times 298\times 0.6021)$

$= -3435\ J\ mol^{-1} = -3.435\ kJ\ mol^{-1}$

6. For a non-isolated system the total entropy change is given by

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$ ...(i)

Consider a process where heat is lost by the surrounding, then by definition of entropy change

$\Delta S_{surrounding} = -q_p/T$ ...(ii)

Further at constant pressure $q_p = H$ and substituting in eqn (ii) we get

$\Delta S_{surrounding} = -\Delta H/T$. This value is substituted in eqn (i), hence we get

$\Delta S_{total} = \Delta S_{system} - \Delta H/T$ ...(iv)

Using the symbol ΔS in place of ΔS_{system} in above equation

$\Delta S_{total} = \Delta S_{system} - \Delta H/T$ ...(v)

Multiply through eqn (v) by T, we get

$T\,\Delta S_{total} = T\Delta S_{system} - \Delta H$ ...(vi)

We know that $\Delta G = \Delta H - T\Delta S$, thus eqn (vi) becomes

$T\,\Delta S_{total} = -\Delta G$

or $\Delta G = -T\,\Delta S_{total}$

7. **(i)**

(a) ΔS is + ve

As the reaction is endothermic thus entropy increases, with temperature.

(b) G is + ve

As ΔH = – ve and ΔS = – ve hence ΔG at a high temperature T will be + ve.

(c) $B\rightarrow A$, ΔH = –ve and ΔS = –ve but at low temperature, TΔS will be so low that ΔH is greater in magnitude than TΔS and the process will become spontaneous.

(ii) (a) + ve (b) –ve (c) + ve (d) + ve

7

Chapter

Equilibrium

INTRODUCTION

Equilibrium can be established for both physical and chemical processes. The reaction may be fast or slow depending on the experimental conditions and the nature of reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of reactants goes on decreasing while those of products goes on increasing but after sometime a stage is reached where there is no change in the concentrations of either reactants or products is observed. This stage of the system is known as dynamic equilibrium and at this stage the rates of forward and backward reactions become equal.

Equilibrium mixture : The mixture of reactants and products in the equilibrium state is called an equilibrium mixtures.

Based on the extent to which the reaction proceed to reach the state of equilibrium. These may be classified in three groups :

(a) The reactions which proceed almost completion the concentration of the reactions left are negligible.

(b) The reactions in which most of the reactants remains unchanged, i.e, only smalls amounts of products are formed.

(c) The reactions in which the concentrations of both the reactants and products are comparable when the system is in equilibrium.

PHYSICAL EQUILIBRIUM

The most familiar examples of physical equilibrium are phase transformation processes, eg : solid - liquid; liquid - gas and gas - solid

(i) **Solid - liquid equilibrium :** Ex :

Ice $\rightleftharpoons$ water (in an insulated flask)

i.e. $H_2O(s) \rightleftharpoons H_2O(l)$ (at 273 K)

At equilibrium

Rate of melting $\rightleftharpoons$ Rate of freezing

At its (melting point) and at 1 atm (1.013 bar) pressure the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.

(ii) **Liquid-vapour equilibrium :** Ex :

$H_2O\,(l) \rightleftharpoons H_2O$ (vap)

at equilibrium,

rate of evaporation = rate of condensation. The vapour pressure is constant at a given temperature.

(iii) **Solid - gas equilibrium :** Ex :

I_2 (solid) $\rightleftharpoons$ I_2 (vapour)

camphor (solid) $\rightleftharpoons$ camphor (vap)

$NH_4Cl\,(s) \rightleftharpoons NH_4Cl$ (vap)

at equilibrium

Rate of sublimation = Rate of condensation

(iv) **Equilibrium involving dissolution of solid or gases in liquid**

(a) For dissolution of solids in liquids, the solubility is constant at a given temperature. In a saturated solution, a dynamic equilibrium exists as :

solute(solution) $\rightleftharpoons$ solute (solid)

and, at equilibrium

rate of dissolution = rate of crystallisation of solute

(b) For dissolution of gases in liquid, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

There is an equilibrium between molecules in gaseous state and molecules dissolved in the liquid under pressure, i.e.

$$\text{Gas (g)} \rightleftharpoons \text{Gas (solution)}$$

This equilibrium is governed by **Henry's law.** It states that "*the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent. This amount decreases with the increase in temperature*."

General Characteristics of Equilibria Involving Physical Process

(a) Equilibrium is possible only in a closed system at a given temperature.
(b) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
(c) All measurable properties of the system remain constant.
(d) When equilibrium is attained for a physical process, it is characterised by constant value of one of the parameters at a given temperature.

CHEMICAL EQUILIBRIUM IS DYNAMIC

Chemical equilibrium in a reversible reaction is a state at which both backward and forward reaction occur at the same speed i.e., the stage of the reversible reaction at which the concentrations of the reactants and products do not change with the time.

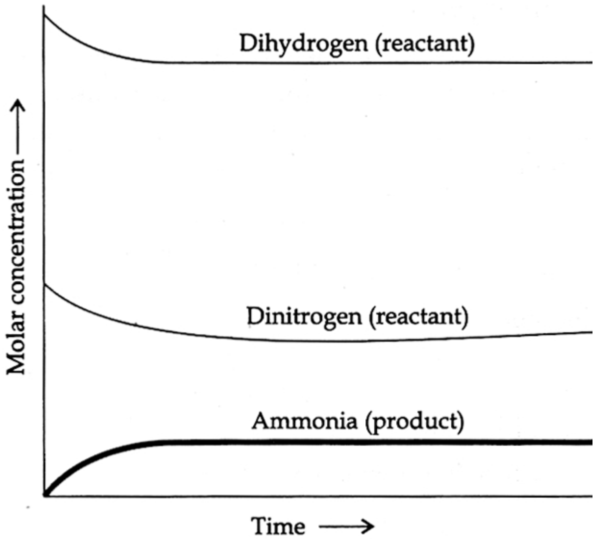
In order to understand the dynamic nature of chemical equilibrium, synthesis of ammonia is carried out by Haber's process. Haber started his experiment with the known amount of N_2 and H_2 at high temperature and pressure. At regular interval of time he determined the amount of ammonia present.

He also found out concentration of unreacted N_2 and H_2. After certain time he found that the composition of mixture remains the same even though some of the reactants are still present. This constancy indicate the attainment of equilibrium.

In general for a reversible reaction the chemical equilibria can be shown by

$$A + B \rightleftharpoons C + D$$

After certain time the two reactions occur at the same rate and the system reaches a state of equilibrium. This can be shown by the given figure.



Depiction of equilibrium for the reaction

Equilibrium can be attained from both sides, whether we start reaction by taking, $H_2(g)$ and $N_2(g)$ and get $NH_3(g)$ or by taking $NH_3(g)$ and decomposing it into $N_2(g)$ and $H_2(g)$.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

LAW OF CHEMICAL EQUILIBRIUM

This rule is applicable only for Reversible reactions. According to this law. "*At a given temperature, the rate of reaction at a particular instant is proportional to the product of the active masses of the reactants.*"
A simple reversible reaction in equilibrium state.

$$A + B \rightleftharpoons C + D$$

At equilibrium state, Rate of forward reaction = Rate of backward reaction.

$$k_f[A][B] = k_b[C][D]$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

At constant temperature, k_f and k_b are constants. Therefore, substituting $\frac{k_f}{k_b}$ by another constant K we get,

$$K = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

K is known as equilibrium constant. It has a constant value for a given reaction at a specific temperature.

Note : Active mass is the number of moles / litre of the substance. It is represented by putting the chemical formula of substance is square brackets.

Now consider a more general reversible reaction.

$$\ell A + mB \rightleftharpoons xC + yD$$

The equilibrium constant, K, may be written as

$$K = \frac{[C]^x [D]^y}{[A]^\ell [B]^m}$$

The Concentration ratio of the products and reactants is also termed as concentration quotient and is represented by " Q". Hence at equilibrium.

$$K = Q = \frac{[C]^x [D]^y}{[A]^\ell [B]^m}$$

This mathematical expression is known as law of **chemical equilibrium**. It may be defined as *the ratio of the active masses of the products to that of the active masses of the reactants each raised to the power equal to its stoichiometric coefficient as represented in a balanced chemical reaction at a constant temperature.*

Illustration 1 :

The equilibrium constant of a reaction is 20.0. At equilibrium, the rate constant of forward reaction is 10.0. Find the rate constant for backward reaction.

Sol. $K_c = 20 \quad K_f = 10, K_b = ?$

$$K_c = \frac{K_f}{K_b} \quad ; \quad 20 = \frac{10}{K_b}$$

$$\therefore K_b = \frac{10}{20} = 0.5$$

HOMOGENEOUS EQUILIBRIUM

When equilibrium reaction has all its reactants and products in the same phase, it is known as homogeneous equilibrium system. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Equilibrium Constant in Gaseous System

If the equilibrium involves gaseous species, then the concentration in the concentration quotient may be represented by partial pressure because at a given temperature the partial pressure of a gaseous component is proportional to its concentration.

For ideal gas equation $PV = nRT$

$$P = \frac{n}{V}RT$$

$\frac{n}{V}$ is concentration expressed in mol/m^3

If concentration C is in mol/litre P is in bar then $P = cRT$,

At constant temperature $P \propto [gas]$

For reaction in equilibrium $H_2(g) + I_2(g) \rightarrow 2HI(g)$

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \; ; \; K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$$

$$P_{HI} = [HI(g)]RT\ ;\ P_{I_2} = [I_2(g)]RT\ ;\ P_{H_2} = [H_2(g)]RT$$

Therefore, $$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$K_p = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = K_c$$

$$K_p = K_c$$

In case of the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{[NH_3(g)]^2[RT]^2}{[N_2(g)]RT[H_2(g)]^3(RT)^3}$$

$$= \frac{[NH_3(g)]^2[RT]^{-2}}{[N_2(g)][H_2(g)]^3} = K_c(RT)^{-2}$$

or $K_p = K_c\,(RT)^{-2}$

So, For a general reaction $K_p = K_c\,(RT)^{\Delta n}$

Where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants in the balanced chemical equation)

- when $\Delta n = 0,\ K_p = K_c$
- when $\Delta n > 0,\ K_p > K_c$
- when $\Delta n < 0,\ K_p < K_c$

Illustration 2 :

At 1000K, the value of K_p for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 20R, then find K_c.

Sol. $K_p = 20R$ (given)

for the reaction $\Delta n = (2 - 1) = 1$

$K_p = K_c\,(RT)^{\Delta n}$

$20\,R = K_c\,(RT)^1$

$$\therefore\ K_c = \frac{20\,R}{R \times 1000} = 0.02$$

HETEROGENEOUS EQUILIBRIUM

When an equilibrium reaction has its reactants and products in different phases, it is termed as heterogeneous equilibrium. For example,

$$3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Let us consider another important example of heterogeneous chemical equilibrium

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

On the basis of stiochiometric equation,

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since [$CaCO_3$(s) and CaO(s)] are both constant.

$\therefore$ $$K_c' = [CO_2(g)]$$

$$K_p = P_{CO_2}$$

This shows that at a particular temperature here is a constant concentration or pressure of CO_2 in equilibrium with CaO(s) and $CaCO_3$. The concentration of pure solid and liquid i.e, active mass of solid and liquid is taken as unity.

Characteristics of Equilibrium Constant:

(a) At a given temperature, the equilibrium constant for a particular reaction has a definite value.

(b) It is independent of the initial concentration of the reactants and the direction from which equilibrium is attained.

(c) If the reaction is reversed, the value of equilibrium constant is also inversed.

(d) If the chemical equation is divided by 2, the value of equilibrium constant for the new equation is square root of the previous value of K.

$$K_2 = \sqrt{K_1}$$

(e) If the equation (having equilibrium constant K_c) is written in two steps (having equilibrium constants K'_1 and K_2'' respectively) then $K_c = K_1' \, K_2''$.

(f) Addition of catalyst to the reaction does not affect the value of equilibrium constant.

(g) If equilibrium constant is expressed in terms of concentration, it has different units for different reactions.

(h) If the number of moles of the product is the same as the number of moles of reactants then K has no units.

(i) If the number of moles of the products is not the same as that of reactant K will have certain unit depending upon the changes in the number of moles.

APPLICATION OF EQUILIBRIUM CONSTANT

Predicting the Extent of a Reaction

1. The magnitude of equilibrium constant is helpful in predicting the relative amount of the reactants and the products of a reversible reaction.

   If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion.

   If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely.

Predicting the Direction of a Reaction

(i) If K_c is in the range of 10^{-3} to 10^3 appreciable concentration of both reactants and products are present.

(ii) From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place.

For this purpose we calculate reaction quotient Q. The reaction Quotient, Q is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values.

For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = [C]^c [D]^d / [A]^a [B]^b$$

Then

If $Q_c > K_c$ the net reaction will proceed in the reverse direction

If $Q_c < K_c$ the reaction will proceed in the forward direction

If $Q_c = K_c$ the reaction mixture is already at equilibrium.

Calculating equilibrium concentrations

By knowing the value of equilibrium constant. Concentration of reactants and products can be calculated.

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K, REACTION QUOTIENT Q AND GIBBS ENERGY G :

A mathematical expression of thermodynamic view of equilibrium can be described by the equation.

$$\Delta G = \Delta G^{\ominus} + RT \ln Q$$

where $G^{\ominus}$ is standard Gibbs energy,

At equilibrium when $\Delta G = 0$ and $Q = K_c$

$$\Delta G = \Delta G^{\ominus} + RT \ln K = 0$$

$$\Delta G^{\ominus} = -RT \ln K$$

$$\ln K = \frac{-\Delta G^{\ominus}}{RT}$$

Taking antilog both sides $K = e^{-\Delta G^{\ominus}/RT}$

Three cases may arise :

(i) $\Delta G^\circ = 0$ then $K_c = 1$

(ii $\Delta G^\circ > 0$ i.e. + ve then $K_c < 1$

In this case reverse reaction is feasible i.e., less concentration of products at equilibrium state.

(iii) $\Delta G^\circ < 0$ i.e., –ve then $K_c > 1$

In this case forward reaction is feasible i.e., large concentration of products at equilibrium state.

In short, Free energy change, equilibrium constant and concentration of reactants and products are related as :

$\Delta G^\circ = 0$	$K_c = 1$	Reactants = Products
$\Delta G^\circ > 0$	$K_c < 1$	Reactants > Products
$\Delta G^\circ < 0$	$K_c > 1$	Reactants < Products

LE CHATELIER'S PRINCIPLE

According to this principle, "*If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shift in a direction that tends to undo the effect of the change*".

Effect of Change in Concentration

In a chemical equilibrium, increasing the concentration of the reactants result in shifting the equilibrium in favour of products (i.e., equilibrium shift in forward direction). Increasing concentration of the products results in shifting the equilibrium in favour of reactants (i.e., in the backward direction).

Concentration	**Equilibrium shift**
Concentration of reactant ↑	Forward direction
Concentration of product ↑	Backward direction

Effect of Change in Pressure

According to Le Chatelier's principal if the pressure is increased reaction will take place in that direction, which will bring lowering of pressure or lowering in number of mole.

(i) Increase of pressure shifts the equilibrium in that direction where number of moles decreases. ($\Delta n < 0$)
eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta n = 2 - 4 = -2$
i.e., on ↑ pressure equilibrium shift in forward direction.

(ii) Decrease of pressure shifts the equilibrium in that direction where number of mole increase. ($\Delta n > 0$)
eg. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\Delta n = 2 - 1 = +ve$
i.e., ↓ in pressure equilibrium shift in forward direction

(iii) Change of pressure has no effect if $\Delta n = 0$
eg. $H_2 + I_2 \rightleftharpoons 2HI$ $\Delta n = 2 - 2 = 0$

Change in Temperature

(i) **For endothermic reaction :** If we increase the temperature, equilibrium shift in forward direction which proceed with absorption of heat.

(ii) **For exothermic reaction :** If we increase the temperature, the equilibrium shifts in backward direction which proceed with evolution of the heat.

Role of Catalyst

Positive catalyst increases the rate of both the forward and backward reaction equally so the equilibrium will be attained in less time. Negative catalyst decreases the rate of both forward and backward reaction so equilibrium will be attained in more time.

Effect of Addition of Inert Gas

(i) **At constant volume :**

No effect, what so ever is the value of Δn

(ii) **At constant pressure :**

Addition of inert gas favours forward reaction when $\Delta n > 0$

Addition of inert gas favours backward reaction when $\Delta n < 0$

Addition of inert gas has no effect when $\Delta n = 0$

Effect of Temperature, Pressure, Concentration and Addition of Inert Gas on Equilibrium

	Effect of increase in pressure	**Effect of increase in concentration of reactant**	**Effect of increase in temperature**	**Effect of addition of inert gas**
$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x$	Forward	Forward	Backward	Backward
$2NH_3 \rightleftharpoons N_2 + 3H_2 - 93.0kJ$	Backward	Forward	Forward	Forward
$N_2O_4 \rightleftharpoons 2NO_2 - 62\ kJ$	Backward	Forward	Forward	Forward
$N_2 + O_2 \rightleftharpoons 2NO + 180\ kJ$	No effect	Forward	Backward	No.effect
$PCl_5 \rightleftharpoons PCl_3 + Cl_2 - x\ kJ$	Backward	Forward	Forward	Forward
$H_2 + I_2 \rightleftharpoons 2HI - 12.4\ kJ$	No effect	Forward	Forward	No.effect

Illustration 3 :

If pressure is increased in the following reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -22.4$ k Cal then what will be the effect on equilibrium ?

Sol. On increasing pressure in the reaction, equilibrium will shift towards the direction where volume gets decreased i.e;, towards forward (right) direction.

Illustration 4 :

Which conditions will be helpful for obtaining maximum yield of SO_3 according to Le Chatelier principle ?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ (\Delta H = -0.95\ \text{k Cal.})$$

Sol. Since the reaction is exothermic, low temperature and since Δn is negative, high pressure will favour formation of SO_3. High concentrations of the reactants, SO_2 and O_2 will favour formation of SO_3

Example of Effect of Change in Concentration from Daily Life

(i) The sweating on humid day is more because surrounding air has large amount of water vapours and our body cannot lose water as water vapour.

(ii) **Transport of oxygen by haemoglobin in blood :** The equilibrium between haemoglobin (Hb) in the red corpuscles of our blood and oxygen in the lung is given as

$$Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)\ \text{Oxyhaemoglobin.}$$

(iii) When it reaches the tissues where partial pressure of oxygen is low, the oxyhaemoglobin loses the oxygen i.e. backward reaction favours. When blood (Hb) returns to lungs,where partial pressure of oxygen is high, more oxyghaemoglobin is formed.

IONIC EQUILIBRIUM

Introduction

Those compounds which can conduct electricity either in fused state or in solution state in any solvent are called *Electrolytes*.

Compounds which contain ions in pure solid state and can conduct electricity in the pure liquid state are called *True electrolytes* e.g. NaCl, KCl etc.

Compounds which do not conduct electricity in fused state but their solution can conduct electricity are called *potential electrolytes* e.g. HCl, CH_3COOH, NaOH, NH_4OH etc.

There are two types of electrolytes

(i) Strong Electrolytes : Compounds which completely ionise in aqueous solution and are good conductors of electricity e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, CH_3COONa, NH_4Cl etc. ($\alpha = 100\%$)

(ii) Weak Electrolytes : Compounds which ionise partially in aqueous solution and are poor conductors of electricity e.g. CH_3COOH, HCN, NH_4OH, $Al(OH)_3$ etc. ($\alpha < 100\%$)

Those compounds which do not conduct electricity either in fused state or their solution are called Non-electrolytes.

CONCEPTS OF ACIDS AND BASES

Arrhenius Concept

According to this concept an acid is a substance which ionise in aqueous solution to give hydrogen ions (H^+) whereas base is a substance which ionise in aqueous solution to give hydroxyl ions (OH^-).

The acids which dissociates completely in aqueous solution are termed as strong acids for example, HCl, HNO_3, H_2SO_4, etc. The acids which ionise to a small extent in their aqueous solution are called weak acids for example, acetic acid, oxalic acid, phosphoric acid, carbonic acid, boric acid, etc.

Similarly, substances which are completely ionised in water to give OH^- ions are called strong bases for example, NaOH, KOH, etc. While substances which, dissociate to a small extent in aqueous solution are called weak bases for example, NH_4OH, $Mg(OH)_2$, $Al(OH)_3$, etc.

Bronsted-Lowry Concept

According to this theory an acid is a substance which can donate a proton (H^+) while a base is a substance which accepts proton. In short acid is proton donor whereas base is proton acceptor.

loses proton

$$\underset{\text{acid 1}}{HCl(aq)} + \underset{\text{base 2}}{H_2O\,(1)} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+(aq)} + \underset{\text{base 1}}{Cl^-(aq)}$$

adds proton

Amphoteric Substance:

The species which are capable of functioning as both an acid as well as a base are called amphoteric or amphiprotic species for example, H_2O, HCO_3^-, etc.

$$\underset{\text{Acid}}{HCO_3^-\ (aq)} + \underset{\text{Base}}{NH_3(aq)} \rightleftharpoons NH_4^+\ (aq) + CO_3^{2-}\ (aq)$$

$$\underset{\text{Base}}{HCO_3^-(aq)} + \underset{\text{Acid}}{HCl(aq)} \rightleftharpoons H_2CO_3(aq) + Cl^-(aq)$$

Conjugate acid-base Pair:

Consider an acid-base reaction

$$\underset{[\text{Acid}]}{HCO_3^-\ (aq)} + \underset{[\text{Base}]}{NH_3(aq)} \rightleftharpoons \underset{[\text{Acid}]}{NH_4^+\ (aq)} + \underset{[\text{Base}]}{CO_3^{2-}\ (aq)}$$

When an acid (HCO_3^-) donates its proton, it changes to a base (CO_3^{2-}). Likewise, the base NH_3 accepts a proton (acts as a base for the forward reaction) and forms NH_4^+ ion. Therefore, the base developed from an acid is called conjugate base of the acid. Similarly, the acid formed from a base is termed as Conjugate acid of the base.

The conjugate acid differs from the conjugate base by one proton and vice-versa. These are called as conjugated acid-base pair. For example,

$$\text{Acid} \rightleftharpoons \text{Conjugate base} + H^+$$
$$\text{Base} + H^+ \rightleftharpoons \text{Conjugate acid}$$

Bronsted and Lowry stated that the strength of an acid depends upon its tendency to release a proton and the strengths of base depends upon its tendency to accept a proton.

The conjugate acid of a strong base is weak and conversely the conjugate acid of the weak base is strong.

Lewis Concept of Acids and Bases

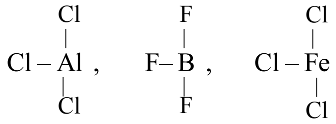
According to Lewis concept an acid is a substance (ion, atom or molecule) which is capable of accepting a pair of electrons whereas base is a substance (ion or molecule) which is capable of donating a pair of electrons.

$$\underset{\text{Lewis base}}{H_3N:} + \underset{\text{Lewis acid}}{BF_3} \longrightarrow \left[\underset{\text{Ammonia}}{H_3N} \longrightarrow \underset{\text{boron trifloride}}{BF_3}\right]$$

According to lewis concept, only those species function as lewis bases which are either negatively charged species or neutral species having at least one lone pair of electron. For example, $\bar{C}N, \bar{O}H, \bar{C}l, R-\underset{..}{\ddot{O}}-H, R-\ddot{N}H_2$, etc.

Lewis acids are

- Simple cations : Cations being deficient of electrons act as lewis acids. e.g. H^+, Ag^+ ion, etc
- Molecules having central atom with incomplete octet : e.g.



$$Cl-\underset{Cl}{\overset{Cl}{Al}}\ ,\quad F-\underset{F}{\overset{F}{B}}\ ,\quad Cl-\underset{Cl}{\overset{Cl}{Fe}}$$

- Molecule having unsaturation between hetro atoms: For example, CO_2 , SO_2, etc.
- Molecules in which central atom has empty d-orbital. eg., SiF_4 , PF_5 , etc.

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

IONIZATION OF ACIDS AND BASES

Acids and bases can be classified as strong or weak depending on the extent to which they ionize. Strong acids and bases ionize to a large extent to form many hydrogen or hydroxide ions. wWeak acids or bases ionize to a small extent to form few hydrogen or hydroxide ions. An example of a weak acids is acetic acid. Strong and weak acids are defined by the ease with which they lose (or donate) hydrogen ions (protons). A strong acid, when placed in water, will almost fully ionize/ dissociated straight away, producing H^+ (aq) ions from water. A weak acid will, however only partially dissociate into ions, leaving a high percentage of unreacted molecules in the solution.

IONIC PRODUCT OF WATER

Water is a weak electrolyte, which gets ionised into H^+ and OH^- to a very less extent.

$$H_2O \rightleftharpoons H^+ + OH^-$$

According to law of mass action,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Here K is called *ionisation constant of water*.

Therefore, $K[H_2O] = [H^+][OH^-]$

$K_w = [H^+][OH^-]$ Here $K_w = K[H_2O]$

K_w is called ionic product of water.

In pure water, $[H^+] = [OH^-]$

10^{-7} 10^{-7}

Value of ionic product of water K_W is 1.0 × 10^{-14} at 25° C

Value of K_w depends on temperature. Value of K_w increases with increase in temperature and decreases with decrease in temperature.

Since this shows the product of the concentration of H^+ and OH^-, this is known as *ionic product of water*.

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations :

Acidic : $[H_3O^+] > [OH^-]$

Neutral : $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

pH Scale

Sorensen [1909] introduced a new scale to correlate [H_3O^+] ion concentration in aqueous solutions of acids and bases and termed it pH scale. pH is defined as the negative logarithm of the [H_3O^+] concentration in moles per litre Mathematically, it is expressed as

$$pH = -\log\left[H_3O^+\right] \text{ or } pH = \log \frac{1}{\left[H_3O^+\right]}$$

Similarly, $pOH = -\log [\,OH^-\,]$

$pH < 7$ for acidic solution

$pH > 7$ for basic solution

$pH = 7$ for neutral solution

As $K_w = [H^+]\,[OH^-] = 10^{-14}$

taking logarithm on both sides.

$$-\log K_w = -\log\left[[H^+]\,[OH^-]\right] = -\log 10^{-14}$$

$$-\log K_w = -\log [H^+] - \log [OH^-] = 14 \log 10$$

$$-\log [H^+] = pH$$

$$-\log [OH^-] = pOH$$

$$-\log K_w = pK_w$$

$$\therefore \quad pK_w = pH + pOH = 14$$

pH = 0 means [H_3O^+] is 1M.

If pH lies between 0 and 2, the solution is strongly acidic whereas pH between 2 and 4 is moderately acidic.

If pH lies in between 4 to 7, it is weakly acidic.

if pH between 7 and 10, 10 and 12 and12 and 14 represent weakly basic, moderately basic and strongly basic respectively.

pH Range of Some Important Substances

Substance	pH range	Substance	pH range
Tears	7.4	Vinegar	2.4 – 3.4
Blood plasma	7.3 – 7.42	Soft drinks	2.0 – 4.0
Human saliva	6.5 – 7.5	Gastric Juice	1.0 – 3.0
Human Urine	4.8 – 8.4	Boiling water	6.56

Illustration 5 :

At 25°C, the $[H^+]$ of an acidic solution is 10^{-5}. Find out its pH.

Sol. $pH = -\log [H^+] = -\log 10^{-5} = +5 \log 10 = 5$

Illustration 6 :

At 25°C, the $[OH^-]$ is 10^{-9}. Find out the value of pH of the solution.

Sol. $pH + pOH = 14$

$$[H^+]\,[OH^-] = 10^{-14}$$

$$[H^+] = \frac{10^{-14}}{10^{-9}} = 10^{-5}$$

$$pH = -\log [H^+] = -\log [10^{-5}] = +5 \log 10 = 5$$

Ionization Constant of Weak Acids

Let us consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by

$$\underset{\substack{C \\ \text{Initial concentration}}}{HX(aq)} + H_2O(l) \rightleftharpoons \underset{0}{H_3O^+(aq)} + \underset{0}{X^-(aq)}$$

Let α be the extent of ionization

Change
$-c\alpha \quad +c\alpha \quad + \quad c\alpha$

Equilibrium Concentration (M)

$c - c\alpha \quad c\alpha \quad c\alpha$

Here, c = initial concentration of the undissociated acid.

HX at time, t = 0

α = extent upto which HX is ionized into ions.

$$K_a = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

K_a is called the dissociation or ionization constant of acid HX. In terms of molar concentration

$$K_a = \frac{\left[H^+\right]\left[X^-\right]}{[HX]}$$

Ionization of Weak Bases

The ionization of base MOH can be represented as.

$$MOH\,(aq) \rightleftharpoons M^+\,(aq) + OH^-\,(aq)$$

The ionization constant of base can be denoted by

$$K_b = \frac{\left[M^+\right]\left[OH^-\right]}{[MOH]}$$

If c = initial concentration of base

α = degree of ionization of base

$$K_b = \frac{c\alpha^2}{c(1-\alpha)}$$

Relation between K_a and K_b

Let us take an example of a weak acid which ionises in aqueous solution

$$\underset{\text{Base}}{HA} + H_2O \rightleftharpoons H_3O^+(aq) + \underset{(\text{conjugate base})}{A^-(aq)}$$

$$K_a = \frac{[H_3O]^+\left[A^-\right]}{[HA]} \qquad \ldots(i)$$

Dissociation of a weak base (conjugate base) in water can be written as

$$\underset{\text{Base}}{A^-} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{HA + OH^-}$$

$$K_b = \frac{[HA]\left[OH^-\right]}{\left[A^-\right]} \qquad \ldots(ii)$$

Multiplying eq. (i) and (ii)

$$K_a \times K_b = \frac{[H_3O]^+\left[A^-\right]}{[HA]} \times \frac{[HA]\left[OH^-\right]}{\left[A^-\right]}$$

$$= [H_3O^+]\,[OH^-] = K_w$$

$$\boxed{K_a \times K_b = K_w}$$

If we take negative logarithm on both sides of the equation.

$$pK_a + pK_b = pK_w = 14 \text{ (at 298 K)}$$

Polybasic acids : These acids undergo complete ionisation in several steps; the number of steps is equal to the number of replaceable hydrogen atoms in the molecule of the acid. Thus there will be as many ionisation constants of the acid as the number of replaceable hydrogen atoms. The value of ionisation constant of each step is definite and constant. For example, orthophosphoric acid (H_3PO_4) is completely ionised in three steps :

$$H_3PO_4 \xrightleftharpoons{K_1} H^+ + H_2PO_4^-$$

$$H_2PO_4^- \xrightleftharpoons{K_2} H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \xrightleftharpoons{K_3} H^+ + PO_4^{3-}$$

The relative value of these constants is as below :

$$K_1 > K_2 > K_3$$

The overall dissociation constant (K) is given by the following relation.

$$K = K_1 \times K_2 \times K_3$$

Factors that Affect Acid Strength

There are several factors that can affect acid strength, and the importance of the factor can be variable. However, some trends are notable.

(i) **Bond strength :** The strength of the bond between the acidic proton and the rest of the molecule will have an effect on acidity. The weaker the bond, the more acidic and acid will be generally.

(ii) **Bond Polarity :** The polarity of a bond is the distribution of the electrons between the two bonded atoms. If the electrons are fairly equally distributed, the bond is not very polar. As the electron distribution gets weighted towards one atom, the bond becomes more polar. A highly polar bond between an acidic hydrogen and another atom tends to make it more easy for the proton to leave the molecule than would happen for a non-polar bond.

COMMON ION EFFECT

It states that *if to the solution of a weak electrolyte, a solution of strong electrolyte is added which furnishes an ion common to that furnished by the weak electrolyte, the ionization of the weak electrolyte is suppressed*. For example, NH_4OH is a weak electrolyte and ionizes to a small extent.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

When a strong electrolyte furnishing NH_4^+ or OH^- ion is added (e.g., NH_4Cl, NaOH etc.) to NH_4OH solution, the above equilibrium will be shifted to the left because of high concentration of the common ion and thus the ionisation of NH_4OH is further suppressed. Similarly, the ionisation of CH_3COOH is suppressed by the addition of CH_3COONa or HCl. Thus in short, *the suppression of ionization of a weak acid or a weak base by adding one of its own ions is known as* **common ion effect.**

Applications of common ion effect :

(a) H_2S is used in presence of HCl as a group reagent for the analysis of second group in qualitative analysis. HNO_3 cannot be used because it oxidises H_2S to sulphur.

(b) NH_4OH and NH_4Cl are used as group reagent for the analysis of third group.

(c) Purification of common salt by passing HCl gas in a saturated solution of NaCl.

(d) Soap is precipitated from its solution by adding some NaCl.

SALT HYDROLYSIS

Salt hydrolysis is defined as **" a process in which a salt reacts with water to produce either acidic or basic or neutral solution."**

(i) Salts of Strong Acid and Strong Base

e.g., NaCl, KNO_3 , Na_2SO_4 , $KClO_4$, etc. Such salts on hydrolysis produce equally strong acids and bases. Thus, their solutions are almost neutral with pH = 7.

(ii) Salts of Weak Acid and Strong Base

e.g., Na_2CO_3 , KCN, CH_3COONa , K_2CO_3 , etc. Hydrolysis of these salts produce weak acid and strong base and thus their aqueous solutions are basic (pH > 7).

$$K_h = \frac{K_w}{K_a};$$

$$\text{Degree of hydrolysis, } h = \frac{\sqrt{K_h}}{C} = \sqrt{\frac{K_w}{K_a C}}$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C \text{ or } -\frac{1}{2}[\log K_w + \log K_a - \log C]$$

Here K_h is hydrolysis constant of salt K_w and K_a are ionisation constants of water and weak acid respectively. C is the concentration of salt in mole/litre.

(iii) **Salt of strong acid and weak base.** e.g., NH_4Cl , $CuSO_4$, NH_4NO_3 , $AlCl_3$, etc. These produce strong acid and weak base on hydrolysis resulting in acidic nature of solution (pH < 7).

$$K_h = \frac{K_w}{K_b}; \; h = \sqrt{\frac{K_w}{K_b C}}$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C \text{ or } -\frac{1}{2}[\log K_w - \log K_b + \log C]$$

(iv) **Salts of weak acids and weak base** e.g., $(NH_4)_2CO_3$, $CH_3COO^-NH_4^+$, $AlPO_4$ etc. Their hydrolysis give weak acids and weak base.

$$K_h = \frac{K_w}{K_a K_b};$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b \text{ or } -\frac{1}{2} \log K_a + \log K_w - \log K_b]$$

BUFFER SOLUTION

Buffer solution is defined as the solution which resists the change in hydrogen ion concentration on the addition of small amount of acid or base.

Buffer solutions are of two types :

(i) Acidic buffer : It is obtained by mixing equimolar quantities of a weak acid and its salt with strong base e.g.

(a) $CH_3COOH + CH_3COONa$ (b) $HCOOH + HCOOK$

The pH value of acidic buffer is usually less than 7.

(ii) Basic buffer : It contains equimolar quantities of weak base and its salt with strong acid. For example,

(a) $NH_4OH + NH_4Cl$ (b) $C_6H_5NH_2 + C_6H_5\overset{+}{N}H_3Cl^-$

Buffer Action

The ability of buffer solution to resist the change in its pH value on additon of small amount of strong acid or strong base is called buffer action.

The pH of buffer solutions can be calculated applying *Henderson's equation*. For pH of acidic buffer solution

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

For pH of basic buffer Solution ;

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$pH = 14 - pK_b - \log \frac{[Salt]}{[Base]}$$

Some examples of common Buffer solutions.

Buffer Solution	Range of pH
$CH_3COOH + CH_3COONa$	4.74
$HCOOH + HCOOK$	$3.70 - 5.6$
Citric acid + Sod. citrate	$1.0 - 5.0$
Phthalic acid + pot. hydrogen phthalate	$2.2 - 3.8$
$KH_2PO_4 + K_2HPO_4$	$5.8 - 8.0$
$NH_4OH + NH_4Cl$	9.25
$H_3BO_3 + Na_2B_4O_7$ (Borax)	$9.2 - 11.0$
$H_2CO_3 + NaHCO_3$	7.4

SOLUBILITY & SOLUBILITY PRODUCT

Solubility :

Every substance has a definite solubility in a particular solvent at a particular temperature. It is generally defined as the concentration of the solute in its saturated solution in the solvent employed at a given temperature. It is generally expressed as the amount of the solute (in grams) in one litre of the solution. However, in problems, solubility is expressed in moles per litre.

$$\text{Solubility of a solute in moles/litre} = \frac{\text{Solubility of solute in gram/litre}}{\text{Mol. wt. of the solute}}$$

Solubility of sparingly soluble salt in acids or bases :

There are many salts of weak acids or weak bases which are almost insoluble in water but their solubility increases with decreasing pH. The salts containing carbonates, phosphates, fluorides, acetates etc. are soluble at low pH. The salts of weak bases similarly dissolve at higher pH (low acidity). CaF_2 is insoluble in water but it goes into solution when some acid is added.

Solubility Product (K_{sp}) :

Solubility product of a sparingly soluble electrolyte is equal to the product of ionic concentrations in a saturated solution at a given temperature.

Let solubility of a compound A_xB_y be S mol lit^{-1}. It means that if more than S moles are dissolved in solvent(one litre) only S moles will be soluble, rest will be insoluble and following equilibrium is established.

$$\underset{\substack{\text{Insoluble}\\ \text{Solute}}}{AB} \rightleftharpoons \underset{\text{unionised solut}}{AB} \rightleftharpoons \underset{\substack{\text{Ions}\\ \text{(saturated solution)}}}{A^+ + B^-}$$

K_{sp} increases with increase in temperature

(i) In a saturated solution $K_{sp} = [A^+][B^-]$

(ii) In an unsaturated solution of AB, $K_{sp} > [A^+][B^-]$ i.e., more solute can be dissolved.

(iii) In a super saturated solution, $K_{sp} < [A^+]\,[B^-]$ i.e precipitation will start to occur.

Ionisation of compound A_xB_y may be shown as

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Let solubility of compound A_xB_y is s mol lit^{-1}, then

$$\begin{array}{lcll} A_xB_y & \rightleftharpoons & xA^{y+} + & yB^{x-} \\ s & & xs & ys \\ K_{sp} & = & (xs)^x & (ys)^y \\ K_{sp} & = & X^xY^y & S^{x+y} \end{array}$$

(a) For AB type (in case of AgCl, $PbSO_4$, $BaSO_4$), $K_{sp} = s^2$

(b) For AB_2 or A_2B type (in case of $PbCl_2$, $CaCl_2$, Na_2SO_4, $Pb(NO_3)_2$),
$K_{sp} = 4s^3$

(c) For A_3B or AB_3 type [$AlCl_3$, $FeCl_3$, Na_3PO_4)],
$K_{sp} = 27s^4$

(d) For A_3B_2 or A_2B_3 type [$Al_2(SO_4)_3$, $Ba_3(PO_4)_2$]
$K_{sp} = 108\,s^5$

Common Ion Effect on Solubility of Ionic Salt

The reduction in solubility of an ionic precipitate when a soluble compound that has one of the ions of precipitate is added to the solution in equilibrium with the precipitate is called common ion effect.

The common ion states that if concentration of any ion is increased. Then according to Le-Chatelier's principle the ions which are present in the excess should combine with the oppositely charged ions. Some amount of the salt will be precipitated out until the ionic product is equal to the solubility product. Similarly if the concentration of any one ion is decreased then more salt will be dissolved in order to increase the concentration of both the ions.

We use common ion effect for the complete precipitation of any particular ion as its sparingly soluble salt which has a low value of solubility product for gravimetric estimation. Therefore silver ion can be precipitated as silver chloride and ferric ion as hydroxide.

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. In this case we have to satisfy two equilibria simultaneously i.e.,

$$K_{sp} = [M^+]\,[X^-],$$

$$HX\,(aq) \rightleftharpoons H^+\,(aq) + X^-\,(aq);$$

$$K_a = \frac{\left[H^+(aq)\right]\left[X^-(aq)\right]}{\left[HX(aq)\right]}$$

$$[X^-]\,/\,[HX] = K_a\,/\,[H^+]$$

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [X^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

Now, again taking inverse, we get

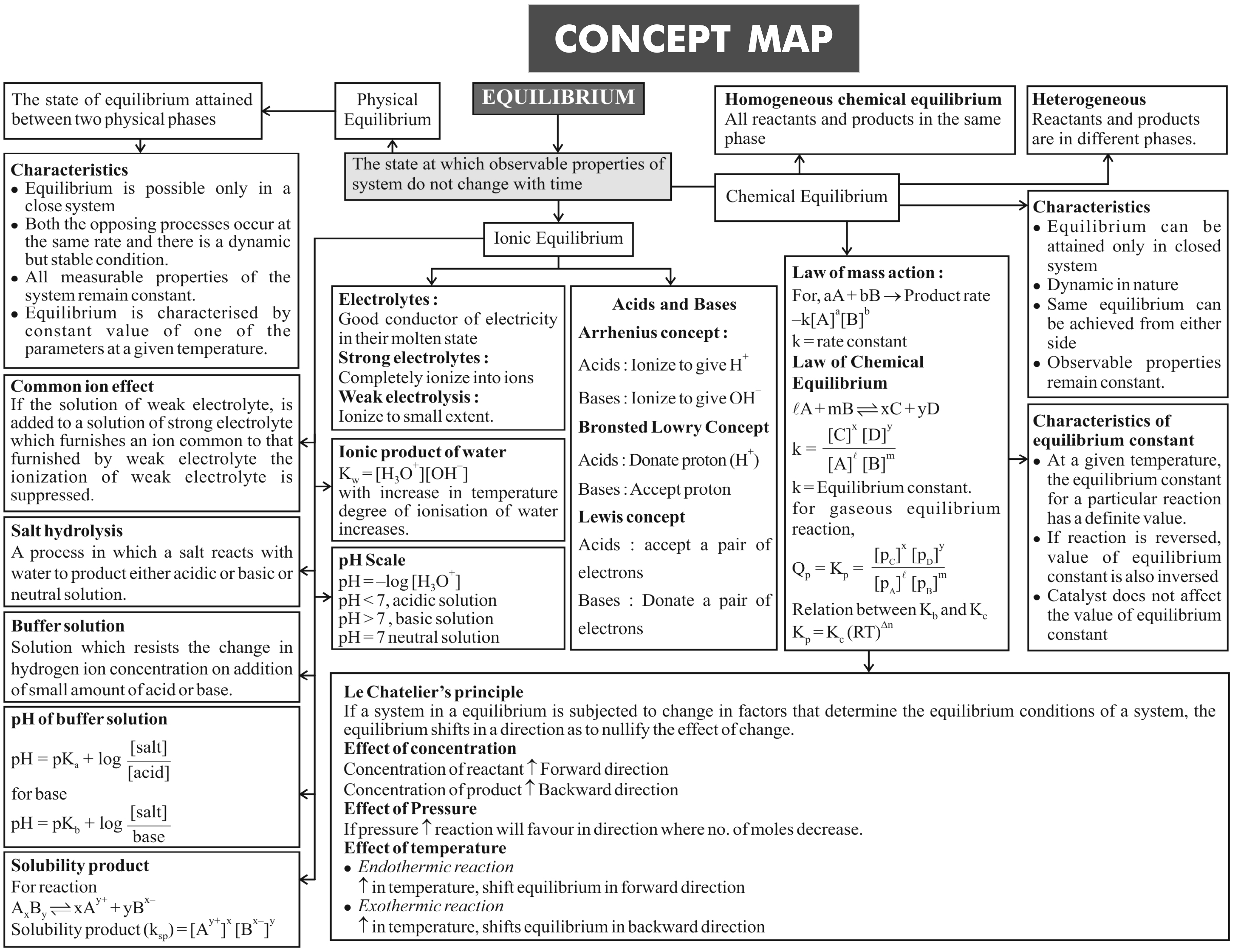
$[X^-]\,/\,\{[X^-] + [HX]\} = f = K_a\,/\,\{(K_a + [H^+]\}$ and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

$$K_{sp} = [S]\,[S] = S^2\,\{K_a\,/\,(K_a + [H^+])\}\text{ and}$$

$$S = \{K_{sp}\,([H^+] + K_a)\,/\,K_a\}^{1/2}$$

Thus solubility S increases with increase in $[H^+]$ or decrease in pH.

CONCEPT MAP



EQUILIBRIUM

The state at which observable properties of system do not change with time

Physical Equilibrium

The state of equilibrium attained between two physical phases

Characteristics
- Equilibrium is possible only in a close system
- Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- All measurable properties of the system remain constant.
- Equilibrium is characterised by constant value of one of the parameters at a given temperature.

Chemical Equilibrium

Homogeneous chemical equilibrium
All reactants and products in the same phase

Heterogeneous
Reactants and products are in different phases.

Characteristics
- Equilibrium can be attained only in closed system
- Dynamic in nature
- Same equilibrium can be achieved from either side
- Observable properties remain constant.

Law of mass action :
For, $aA + bB \rightarrow$ Product rate $-k[A]^a[B]^b$
k = rate constant

Law of Chemical Equilibrium
$\ell A + mB \rightleftharpoons xC + yD$

$$k = \frac{[C]^x\,[D]^y}{[A]^\ell\,[B]^m}$$

k = Equilibrium constant.
for gaseous equilibrium reaction,

$$Q_p = K_p = \frac{[p_C]^x\,[p_D]^y}{[p_A]^\ell\,[p_B]^m}$$

Relation between K_b and K_c
$K_p = K_c\,(RT)^{\Delta n}$

Characteristics of equilibrium constant
- At a given temperature, the equilibrium constant for a particular reaction has a definite value.
- If reaction is reversed, value of equilibrium constant is also inversed
- Catalyst does not affect the value of equilibrium constant

Le Chatelier's principle
If a system in a equilibrium is subjected to change in factors that determine the equilibrium conditions of a system, the equilibrium shifts in a direction as to nullify the effect of change.

Effect of concentration
Concentration of reactant ↑ Forward direction
Concentration of product ↑ Backward direction

Effect of Pressure
If pressure ↑ reaction will favour in direction where no. of moles decrease.

Effect of temperature
- *Endothermic reaction*
  ↑ in temperature, shift equilibrium in forward direction
- *Exothermic reaction*
  ↑ in temperature, shifts equilibrium in backward direction

Ionic Equilibrium

Electrolytes :
Good conductor of electricity in their molten state
Strong electrolytes :
Completely ionize into ions
Weak electrolysis :
Ionize to small extent.

Acids and Bases

Arrhenius concept :
Acids : Ionize to give H^+
Bases : Ionize to give OH^-

Bronsted Lowry Concept
Acids : Donate proton (H^+)
Bases : Accept proton

Lewis concept
Acids : accept a pair of electrons
Bases : Donate a pair of electrons

Ionic product of water
$K_w = [H_3O^+][OH^-]$
with increase in temperature degree of ionisation of water increases.

pH Scale
$pH = -\log [H_3O^+]$
$pH < 7$, acidic solution
$pH > 7$, basic solution
$pH = 7$ neutral solution

Common ion effect
If the solution of weak electrolyte, is added to a solution of strong electrolyte which furnishes an ion common to that furnished by weak electrolyte the ionization of weak electrolyte is suppressed.

Salt hydrolysis
A process in which a salt reacts with water to product either acidic or basic or neutral solution.

Buffer solution
Solution which resists the change in hydrogen ion concentration on addition of small amount of acid or base.

pH of buffer solution

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

for base

$$pH = pK_b + \log \frac{[salt]}{base}$$

Solubility product
For reaction
$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$
Solubility product $(k_{sp}) = [A^{y+}]^x\,[B^{x-}]^y$

Textbook Exercises

7.1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

(a) What is the initial effect of the change on vapour pressure ?

(b) How do rates of evaporation and condensation change initially ?

(c) What happens when equilibrium is restored finally and what will be the final vapour pressure ?

Ans. (a) Initially, the vapour pressure will decrease.

(b) The rate of evaporation remains constant at constant temperature in a closed vessel. However, the rate of condensation will be low initially because there are fewer molecules per unit volume in the vapour phase and hence the number of collisions per unit time with the liquid surface decreases.

(c) When equilibrium is restored, rate of evaporation = rate of condensation. The final vapour pressure will be same as it was initially.

7.2 What is K_c for the following equilibrium when the equilibrium concentration of each substance is : $[SO_2] = 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90M$?

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Ans.
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.90M)^2}{(0.60M)^2(0.82M)}$$

$$= 12.229M^{-1} \text{ or } 12.229 L\, mol^{-1}$$

7.3 At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of Iodine atoms

$I_2(g) \rightleftharpoons 2I(g)$. Calculate K_p for the equilibrium.

Ans. Partial pressure of I atoms $(P_I) = 40/100 \times 10^5 \text{ Pa} = 0.4 \times 10^5 \text{ Pa}$

Partial pressure of

$$I_2(P_{I_2}) = \frac{60}{100} \times 10^5 \text{ Pa} = 0.6 \times 10^5 \text{ Pa}$$

$$\therefore K_p = \frac{P_I^2}{P_{I_2}} = \frac{(0.4 \times 10^5)^2}{0.60 \times 10^5} = 2.67 \times 10^4 \text{ Pa}$$

7.4 Write the expression for the equilibrium constant, K_c for each of the following reactions :

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

Ans. (i)
$$K_c = \frac{[NO(g)]^2[Cl_2(g)]}{[NOC1(g)]^2}$$

(ii)
$$K_c = \frac{[CuO(s)]^2[NO_2(g)]^4[O_2(g)]}{[Cu(NO_3)_2(s)]^2}$$

$$= [NO_2(g)]^4[O_2(g)]$$

(iii)
$$K_c = \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)][H_2O](\ell)]}$$

$$K_c = \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]}$$

(iv)
$$K_c = \frac{[Fe(OH)_3(s)]}{[Fe^{3+}(aq)][OH^-(aq)]^3}$$

$$= \frac{1}{[Fe^{3+}(aq)][OH^-(aq)]^3}$$

(v)
$$K_c = \frac{[IF_5]^2}{[I_2(s)][F_2]^5} = \frac{[IF_5]^2}{[F_2]^5}$$

7.5 Find out the value of K_c for each of the following equilibria from the value of K_p

(a) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $K_p = 1.8 \times 10^{-2}$ at 500 K

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_p = 167$ at 1073K.

Ans. (a) $\Delta n_g = 3 - 2 = 1, K_p = K_c(RT)$

or $K_c = K_p / RT = (1.8 \times 10^{-2}) / (0.0831 \times 500)$

$(R = 0.0831 \text{ bar litre mol}^{-1} K^{-1})$

$= 4.33 \times 10^{-4}$

(b)
$$\Delta n_g = 1, K_c = K_p/RT = \frac{167}{.0831 \times 1073} = 1.87$$

7.6 For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction ?

Ans. For the reverse reaction
$$K'_c = 1/K_c = \frac{1}{6.3 \times 10^{14}}$$

$$= 1.587 \times 10^{-15}$$

7.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

Ans. [Pure liquid] or [Pure solid]

$$= \frac{\text{No.of moles}}{\text{Volume in L}} = \frac{\text{Mass / Mol.mass}}{\text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Mol. mass}} = \frac{\text{Density}}{\text{Mol. mass}}$$

As density of a pure liquid or pure solid is constant at constant temperature and molecular mass is also constant, therefore, their molar concentrations are constant and thus not included into the equilibrium constant.

7.8 Reaction between N_2 and O_2 takes place as follows :

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

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$. Determine the composition of equilibrium mixture.

Ans.

	$2N_2(g)$ +	$O_2(g) \rightleftharpoons$	$2N_2O(g)$
Initial	0.482 mol	0.933mol	
At eqm.	0.482 – x	0.933 –x/2	x
Molar	$\frac{0.482-x}{10}$	$\frac{0.933-x/2}{10}$	$\frac{x}{10}$

As $K_c = 2.0 \times 10^{-37}$ is very small, this means that the amount of N_2 and O_2 reacted (x) is very very small and can be neglected. Hence, at equilibrium, we have

$[N_2] = 0.0482 \text{ mol L}^{-1}$,

$[O_2] = 0.0933 \text{ mol L}^{-1}$, $[N_2O] = 0.1\,x$

$$K_c = \frac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37}$$

On solving, this gives $x = 6.57 \times 10^{-20}$

$[N_2O] = 0.1\,x = 6.57 \times 10^{-21} \text{ mol L}^{-1}$

7.9 Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

Ans. 0. 0518 mol of NOBr is formed from 0. 087 mol of NO and 0. 0437 mol of Br_2.

At equilibrium, amount of NO = 0. 087 – 0. 0518 = 0. 0352 mol

Amount of Br_2 = 0. 0437 – 0. 0259 = 0. 0178 mol.

7.10 At 450 K, $K_p = 2.0 \times 10^{10}$ bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_c at this temperature ?

Ans. For the given reaction, $\Delta n_g = 2 - 3 = -1$

$K_p = K_c(RT)^{\Delta n}$ or $K_c = K_p(RT)^{-\Delta n} = K_p(RT)$

$= (2.0 \times 10^{10} \text{ bar}^{-1})(0.0831 \text{ L bar K}^{-1}\text{mol}^{-1})(450\text{K})$

$= 74.8 \times 10^{10} \text{ L mol}^{-1} = 7.48 \times 10^{11} \text{ L mol}^{-1}$

7.11 A sample of HI (g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium ?

Ans.

	2HI (g) $\rightleftharpoons$	$H_2(g)$ +	$I_2(g)$
Initial pressure	0. 2 atm	0	0
At eqm.	0. 04 atm	0.16 /2 atm = 0. 08 atm	0. 16/2atm = 0. 08 atm

(Decrease in the pressure of HI = 0. 2 – 0. 04 = 0. 16 atm.)

$$\therefore\ K_p = \frac{p_{H_2} \times p_{I_2}}{p^2_{HI}} = \frac{0.08 \text{ atm} \times 0.08 \text{ atm}}{(0.04 \text{ atm})^2} = 4.0$$

7.12 A mixture of 1. 57 mol of N_2, 1. 92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium ? If not, what is the direction of the net reaction ?

Ans. Given reaction is:

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

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(8.13/20 \text{mol L}^{-1})^2}{(1.57/20 \text{ mol L}^{-1})(1.92/20 \text{ mol L}^{-1})^3} = 2394.20$$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.

As $Q_c > K_c$, the net reaction will be in the backward direction.

7.13 The equilibrium constant expression for a gas reaction is.

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Ans. $4\,NO(g) + 6\,H_2O(g) \longrightarrow 4\,NH_3(g) + 5\,O_2(g)$

7.14 One mole of H_2O and one mole of CO are taken in 10 litre vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Ans. At equilibrium,

$[H_2O] = (1 - 0.40)/10 \text{ mol L}^{-1} = 0.06 \text{ mol L}^{-1}$

$[CO] = 0.06 \text{ mol L}^{-1}$,

$[H_2] = 0.04 \text{ mol L}^{-1}$

$[CO_2] = 0.04 \text{ mol L}^{-1}$

$$K = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.444$$

7.15 At 700 K, equilibrium constant for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of HI (g) is present at equilibrium at 700 K, what are the concentration of H_2 (g) and I_2 (g) assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K?

Ans. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, K = 1/54.8

At equilibrium, $[HI] = 0.5 \text{ mol L}^{-1}$,

$[H_2] = [I_2] = x \text{ mol L}^{-1}$

$$\therefore\ K = \frac{x \times x}{(0.5)^2} = 1/54.8 \text{ (Given).}$$

This gives x = 0. 068, i. e., $[H_2] = [I_2] = 0.068 \text{ mol L}^{-1}$.

7.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$$\mathbf{2\,ICl(g) \rightleftharpoons I_2(g) + Cl_2(g),\ K_c = 0.14}$$

Ans. Suppose at equilibrium, $[I_2] = [Cl_2] = x \text{ mol L}^{-1}$. Then

$$2ICl \rightleftharpoons I_2(g) + Cl_2(g)$$

Initial conc. 0.78M	0	0
At eqm. 0.78 − 2x	x	x

$$K_c = \frac{[I_2][Cl_2]}{[ICl_2]^2} \quad \therefore \quad 0.14 = \frac{(x)(x)}{(0.78-2x)^2}$$

or $x^2 = 0.14\,(0.78 - 2x)^2$

or $x/(0.78 - 2x) = \sqrt{0.14} = 0{\cdot}374$

or $x = 0.292 - 0.748\,x$

or $1.748x = 0.292$ or $x = 0.166$

Hence, at equilibrium, $[I_2] = [Cl_2] = 0.166$ M, $[ICl] = 0.78 - (2 \times 0.166\text{ M}) = 0.448$ M

7.17 K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6, when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium ?

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Ans.

	$C_2H_6(g) \rightleftharpoons$	$C_2H_4(g)$ +	$H_2(g)$
Initial pressure	4.0 atm	0	0
At. eqm.	4 − p	p	p

$$K_p = \frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}}$$

$\therefore$ $0.04 = p^2/(4 - p)$ or $p^2 = 0.16 - 0.04\,p$

or $p^2 + 0.04p - 0.16 = 0$

$$\therefore p = \frac{-0.04 \pm \sqrt{0.0016 - 4(-0.16)}}{2} = \frac{-0.04 \pm 0.80}{2}$$

Taking positive value, $p = 0.76/2 = 0.38$

$\therefore$ $[C_2H_6]_{eq} = [4 - 0.38]$ atm $= +3.62$ atm

7.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as

$$CH_3COOH\,(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5\,(\ell) + H_2O\,(\ell)$$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (Note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached ?

Ans. (i) $$Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

(ii)

	CH_3COOH +	$C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial	1.00 mol	0.180 mol		
At eqm.	1 − 0.171 = 0.829 mol	0.180 − 0.171 = 0.009 mol	0.171 mol	0.171 mol

Let V be the volume of reaction vessel.

Molar conc.	0.829/V	0.009/V	0.171/V	0.171/V

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(0.171/V)(0.171/V)}{(0.829/V)(0.009/V)} = 3.94$$

(iii)

	CH_3COOH +	$C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial	1.000 mol	0.500 mol		
After time't'	1 − 0.214 = 0.786 mol	0.500 − 0.214 = 0.286 mol	0.214 mol	0·214 mol

Let V be the volume of reaction vessel.

$$\text{Reaction quotient } (Q_c) = \frac{(0.214/V)(0.214/V)}{(0.786/V)(0.286/V)} = 0.203$$

As $Q_c \neq K_c$, equilibrium has not been attained.

7.19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Ans.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
At eqn.	0.5×10^{-1} mol L^{-1}	x mol L^{-1}	x mol L^{-1}

$$K_c = \frac{x^2}{(0.5 \times 10^{-1})} = 8.3 \times 10^{-3} \text{ (Given)}$$

or $x^2 = (8.3 \times 10^{-3})(0.5 \times 10^{-1}) = 4.15 \times 10^{-4}$

or $x = \sqrt{4.15 \times 10^{-4}} = 2.03 \times 10^{-2}\text{ M} = 0.02\text{ M}$

7.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$;

K_p = 0.265 atm at 1050 K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are : p_{CO} = 1.4 atm and p_{CO_2} = 0.80 atm?

Ans. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

Initial pressures 1.4 atm 0.80 atm.

$$Q_p = \frac{P_{CO_2}}{P_{CO}} = \frac{0.80}{1.4} = 0.571$$

As $Q_p > K_p$, reaction will move in the backward direction, i.e. pressure of CO_2 will decrease and that of CO will increase to attain equilibrium. Hence, if P is decrease in pressure of CO_2, increase in pressure of CO = P

At equilibrium, $P_{CO_2} = (0.80 - P)$ atm,

$P_{CO} = (1.4 + P)$ atm

$$K_p = \frac{P_{co_2}}{P_{co}} \therefore 0.265 = \frac{0.80 - P}{1.4 + P}$$

or $0.265(1.4 + P) = 0.80 - P$

or $0.371 + 0.265P = 0.80 - P$

or $1.265P = 0.429$ or $P = 0.339$ at equilibrium.

$\therefore$ $P_{CO} = 1.4 + 0.339 = 1.739$ atm

and $P_{CO_2} = 0.80 - 0.339 = 0.461$ atm

7.21 Equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

Ans. $$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

As $Q_c \neq K_c$ reaction is not in equilibrium.

As $Q_c < K_c$ reaction will proceed in the forward direction.

7.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ for which $K_c = 32$ at 500K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

Ans. $2BrCl \rightleftharpoons Br_2 + Cl_2$

Initial 3.30×10^{-3} mol L^{-1}

At eqbm. $(3.30 \times 10^{-3} - x)$ $x/2$ $x/2$

$$K_c = \frac{(x/2)(x/2)}{(3.30 \times 10^{-3} - x)^2} = 32 \text{ (Given)}$$

$$\therefore \frac{x/2}{(3.30 \times 10^{-3} - x)} = \sqrt{32}$$

or $x/2 = 5.66 \times (3.30 \times 10^{-3} - x)$

$x = 11.32(3.30 \times 10^{-3} - x)$

or $12.32x = 11.32(3.30 \times 10^{-3})$ or $x = 3.03 \times 10^{-3}$

at eqn. $[BrCl] = (3.30 \times 10^{-3} - 3.0 \times 10^{-3})$

$= 0.30 \times 10^{-3} = 3.03 \times 10^{-4}$ mol L^{-1}

7.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass,

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$.

Calculate K_c for this reaction at the above temperature.

Ans. If total mass of mixture of CO and CO_2 is 100 g, then CO = 90.55g and $CO_2 = 100 - 90.55 = 9.45$ g.

Number of moles of CO = $90 \cdot 55/28 = 3.234$

Number of moles of $CO_2 = 9.45/44 = 0.215$

$p_{CO} = 3.234/(3.234 + 0.215) \times 1$ atm

$= 0.938$ atm

$p_{CO_2} = 0.215/(3.234 + 0.215) \times 1$ atm $= 0.062$ atm

$$K_p = \frac{p^2{}_{CO}}{p_{CO_2}} = \frac{(0.938)^2}{0.062} = 14.19$$

$\Delta n_g = 2 - 1 = 1$

$\therefore$ $K_p = K_c(RT)$

or $K_c = K_p/RT = 14.19/(0.0821 \times 1127) = 0.153$.

7.24 Calculate (a) $\Delta G^{\ominus}$ and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

where $\Delta G^{\ominus}(NO_2) = 52.0$ kJ/mol,

$\Delta G^{\ominus}(NO) = 87.0$ kJ/mol,

$\Delta_f G^{\ominus}(O_2) = 0$ kJ/mol.

Ans. (a) $\Delta_r G° = \Sigma_f G°\text{ (Products)} — \Sigma_f G°\text{ (Reactants)}$

$= \Delta_f G°(NO_2) - [\{\Delta_f G°(NO) + ½\Delta_f G°(O_2)\}]$

$= 52.0 - (87.0 + ½ \times 0) = -35.0$ kJ mol^{-1}

(b) $-\Delta G° = 2.303\, RT \log K$.

Hence, $-(-35000) = 2.303 \times 8.314 \times 298 \times \log K$

or $\log K = 6.1341$ or $K = 1.361 \times 10^6$

7.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Ans. Applying Le Chatelier's principle, on decreasing the pressure, moles of reaction products will

(a) increase

(b) decrease

(c) remain same ($\because n_p = n_r$ gaseous)

7.26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction?

(i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(ii) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

Ans. Reactions affected will be those in which $(n_p \neq n_r)$ (gaseous). Hence, reactions (i), (iii), (iv), (v) and (vi)will be affected. By applying Le Chatelier's principle, we can predict the direction.

(i') $n_p = 2$, $n_r = 1$ i.e., $n_p > n_r$ reaction will proceed in the backward direction

(ii) $n_p = 3, n_r = 3$ i.e. $n_p = n_r$ reaction will not be affected by pressure.

(iii) $n_p = 2, n_r = 1$, i.e.., $n_p > n_r$ reaction will proceed in the backward direction.

(iv) $n_p = 1, n_r = 3$ i.e., $n_p < n_r$ reaction will proceed in the forward direction.

(v) $n_p = 1, n_r = 0$ i.e., $n_p > n_r$. reaction will proceed in the backward direction.

(vi) $n_p = 10, n_r = 9$, i.e., $n_p > n_r$ reaction will proceed in the backward direction.

7.27 The equilibrium constant for the following reaction is 1.6 × 10^5 at 1024 K

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

Ans. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), K = 1/(1.6 \times 10^5)$

Initial 10 bar

At eqm. 10 – p p/2 p/2.

$$K_p = \frac{(p/2)(p/2)}{(10-p)^2} = \frac{1}{1.6\times10^5}$$

$$\text{or } \frac{p^2}{4(10-p)^2} = \frac{1}{1.6\times10^5}$$

Taking square root of both sides, we get

$$\frac{p}{2(10-p)} = \frac{1}{(4.0\times10^2)}$$

or $4\times10^2 p = 2(10-p)$ or $402p = 20$ or

$p = 20/402 = 4.97\times10^{-2}$ bar

Hence, at equilibrium $P_{H_2} = P_{Br_2} = P/2$

$= 2.48\times10^{-2}$ bar,

$P_{HBr} = 10 - p \approx 10$ bar

7.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

(a) Write an expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

(i) increasing the pressure ?

(ii) increasing the temperature ?

(iii) using a catalyst ?

Ans. (a) $$K_p = \frac{p_{CO}\times(p_{H_2})^3}{p_{CH_4}\times p_{H_2O}}$$

(b) (i) By Le Chatelier's principle, equilibrium will shift in the backward direction, and value of K_p decreases.

(ii) By Le Chatelier's principle, equilibrium will shift in the forward direction, and value of K_p increases

(iii) Equilibrium composition will not be disturbed but equilibrium will be attained quickly and value of K_p remains unaffected.

7.29 Describe the effect of :

(a) addition of H_2

(b) addition of CH_3OH

(c) removal of CO

(d) removal of CH_3OH, on the equilibrium of the reaction:

$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

Ans. (a) Equilibrium will shift in the forward direction.

(b) Equilibrium will shift in the backward direction.

(c) Equilibrium will shift in the backward direction.

(d) Equilibrium will shift in the forward direction.

7.30 At 473 K, equilibrium constant, K_c, for decomposition of phosphorus pentachloride,

PCl_5 is 8.3 × 10^{-3}. If decomposition is depicted as :

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g), \Delta_rH^\ominus = 124.0\ kJ\ mol^{-1}$

(a) write an expression for K_c for the reaction ?

(b) what is the value of K_c for the reverse reaction at the same temperature ?

(c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

Ans. (a) $$K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

(b) $$K' = 1/K_c = \frac{1}{8.3\times10^{-3}} = 120.48$$

(c) (i) No effect as K_c is constant at constant temperature.

(ii) No effect

(iii) As given reaction is endothermic, on increasing the temperature k_f will increase as $K_c = k_f/k_b$ hence K_c will increase with increase of temperature.

7.31 Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g).$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = P_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium ? $K_P = 10.1$ at 400°C.

Ans. Suppose the partial pressure of H_2 at equilibrium = p bar

	$CO(g)$ +	$H_2O(g) \rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
Initial pressure	4.0 bar	4.0 bar		
At eqm.	(4 – p)	(4 – p)	p	p

$K_p = p^2/(4-p)^2 = 10.1$ (Given)

$\therefore\ p/(4-p) = \sqrt{10.1} = 3.178$

or $p = 3.042$ bar

7.32 Predict which of the following reaction will have appreciable concentration of reactants and products:

(a) $Cl_2(g) \rightleftharpoons 2Cl(g), K_c = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g),$

$K_c = 3.7 \times 10^8$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g),$

$K_c = 1.8$

Ans. For reaction (c), as K_c is neither high nor very low, reactants and products will be present in comparable amounts. In reaction (a) K_c is very small and in reaction (b) K_c is very large.

7.33 The value of K_c for the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is $1\cdot 6 \times 10^{-2}$, what is the concentration of O_3 ?

Ans. $K_c = \dfrac{[O_3]^2}{[O_2]^3}$

$\therefore\ 2.0 \times 10^{-50} = \dfrac{[O_3]^2}{(1.6\times10^{-2})^3}$

or $[O_3]^2 = (2.0\times10^{-50})(1.6\times10^{-2})^3$
$= 8\cdot 192\times10^{-56}$

or $[O_3] = 2\cdot 86\times10^{-28}\,M$

7.34 The reaction, $CO\,(g) + 3H_2(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g)$, is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c, for the reaction at the given temperature is 3.90.

Ans. $K_c = \dfrac{[CH_4][H_2O]}{[CO][H_2]^3}$

$\therefore\ 3.90 = \dfrac{[CH_4][0.02]}{(0.30)\,(0.10)^3}$

(Molar conc. = No. of moles because vol. of flask = 1L)

or $[CH_4] = 0.0585\,M = 5.85 \times 10^{-2}\,M$

7.35 What is meant by the conjugate acid–base pair ? Find the conjugate acid/base for the following species: HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-} and S^{2-}

Ans. An acid-base pair which differ by a proton is called conjugate acid base pair. NO_2^-, HCN, ClO_4^-, HF, H_2O (acid) or O^{2-} (base), HCO_3^- and HS^-.

7.36 Which of the following are Lewis acids ? H_2O, BF_3, H^+, NH_4^+.

Ans. BF_3, H^+ and NH_4^+ are Lewis acids as they can accept a lone pair of electrons (Remember that all cations are Lewis acids).

7.37 What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3^-?

Ans. Bronsted acid = Conjugate base + H^+

or Conjugate base = Bronsted acid – H^+.

$\therefore$ Conjugate bases of the given acids will be F^-, HSO_4^-, CO_3^{2-}.

7.38 Write the conjugate acids for the following Bronsted bases: NH_2^-, NH_3 and $HCOO^-$

Ans. NH_3, NH_4^+ and HCOOH.

7.39 The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

Ans. Conjugate acids: H_3O^+, H_2CO_3, H_2SO_4 and NH_4^+

Conjugate bases: OH^-, CO_3^{2-}, SO_4^{2-} and NH_2^-.

7.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base:

(a) OH^- **(b) F^-**

(c) H^+ **(d) BCl_3**

Ans. (a) OH^- can donate electron pair. Hence, it is a Lewis base.

(b) F^- can donate electron pair. Hence, it is a Lewis base.

(c) H^+ can accept electron pair. Hence, it is a Lewis acid.

(d) BCl_3 is deficient in electrons as its octet is incomplete. Hence, it can accept electron pair and is, therefore, a Lewis acid.

7.41 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH ?

Ans. $pH = -\log[H^+] = -\log(3.8\times10^{-3})$
$= -\log 3.8 + 3 = 3 - 0.5797 = 2.4203 = 2.42$

7.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it

Ans. $pH = -\log[H^+]$ or $\log[H^+] = -pH$
$[H^+] = \text{antilog}\,[-pH] = \text{antilog}\,(-3.76)$
$\therefore\ = 1.737\times10^{-4}M$
$= 1\cdot 74 \times 10^{-4}\,M$

7.43 The ionization constants of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constant of the corresponding conjugate base.

Ans. For F^-, $K_b = K_w / K_a = 10^{-14}/(6.8\times10^{-4})$
$= 1.47\times10^{-11} \approx 1.5\times10^{-11}$.
For $HCOO^-$, $K_b = 10^{-14}/(1.8\times10^{-4}) = 5.6\times10^{-11}$
For CN^-, $K_b = 10^{-14}/(4.8\times10^{-9}) = 2.08\times10^{-6}$

7.44 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

Ans.

	$C_6H_5OH \rightleftharpoons$	$C_6H_5O^-$ +	H^+
Initial conc.	0.05 M	0	0
After dissociation.	$0.05 - x$	x	x

$\therefore\ K_a = (x)(x)/0.05 - x = 1\cdot0\times10^{-10}$ (Given)

or $x^2 / 0.05 = 1.0\times10^{-10}$

or $x^2 = 5\times10^{-12}$

or $x = 2.23\times10^{-6}M$

In presence of 0.01M C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$[C_6H_5OH] = 0.05 - y \approx 0.05$,

$[C_6H_5O^-] = 0.01 + y \approx 0.01\,M$, $[H^+] = yM$

$K_a = (0.01)(y)/0.05 = 1.0\times10^{-10}$ (Given)

or $y = 5\times10^{-10}$

$$\alpha = \frac{y}{c} = \frac{5\times10^{-10}}{5\times10^{-2}} = 10^{-8}$$

7.45 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ions in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also ? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

Ans. To calculate $[HS^{-1}]$

	$H_2S \rightleftharpoons$	H^+ +	HS^-
Initial conc	0.1M	0	0
After dissociation	$0.1 - x$ $=0.1$	x	x

$K_a = (x)(x)/0.1 = 9.1\times10^{-8}$ or $x^2 = 9.1\times10^{-9}$

or $x = 9.54 \times 10^{-5}$.

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium $[H_2S] = 0.1 - y \approx 0.1$,

$[H^+] = 0.1 + y \approx 0.1$, $[HS^-] = yM$

$K_a = (0.1 \times y) / 0.1 = 9.1 \times 10^{-8}$ (Given)

or $y = 9.1 \times 10^{-8} M$

To calculate $[S^{2-}]$

$$H_2S \overset{K_{a_1}}{\rightleftharpoons} H^+ + HS^{-1}; HS^{-1} \overset{K_{a_2}}{\rightleftharpoons} H^+ + S^{2-}$$

For the overall reaction,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13}$$

$$= 1.092 \times 10^{-20}$$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

In the absence of 0.1 M HCl, $[H^+] = 2[S^{2-}]$

Hence, if $[S^{2-}] = x$, $[H^+] = 2x$

$(2x)^2 x / 0.1 = 1.092 \times 10^{-20}$

or $4x^3 = 1.092 \times 10^{-21}$

or $x^3 = 273 \times 10^{-24}$

$x = 6.487 \times 10^{-8}$ M

In presence of 0·1 M HCl,

suppose $[S^{2-}] = y$,

then $[H_2S] = 0.1 - y \approx 0.1$ M,

$[H^+] = 0.1 + y \approx 0.1M$

$K_a = (0.1)^2 \times y / 0.1 = 1.09 \times 10^{-20}$

or $y = 1.09 \times 10^{-19}M$.

7.46 The ionization constant of acetic acid is 1. 74 × 10^{-5}. Calculate the degree of dissociation of acetic acid in its 0. 05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

Ans. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

As $[CH_3COO^-] = [H^+]$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

or $[H^+] = \sqrt{K_a[CH_3COOH]}$

$$= \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} M$$

$[CH_3COO^-] = [H^+] = 9.33 \times 10^{-4}$ M

$pH = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$

7.47 It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a

Ans. $HA \rightleftharpoons H^+ + A^{-1}$

Here $[H^+] = [A^-]$

$pH = -\log[H^+]$ or $\log[H^+] = -pH = -4.15$

Taking antilog

$[H^+] = 7.08 \times 10^{-5}$ M

$[A^{-1}] = [H^+] = 7.08 \times 10^{-5}M$

$$K_a = \frac{[H^+][A^{-1}]}{[HA]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}}$$

$$= 5.012 \times 10^{-7}$$

$pK_a = -\log K_a = -\log(5.012 \times 10^{-7}) = 7 - 0.7000 = 6.30$

7.48 Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl **(b) 0.005 M NaOH**

(c) 0.002 M HBr **(d) 0.002 M KOH**

Ans. (a) $HCl + aq \longrightarrow H^+ + Cl^{-1}$,

$\therefore [H^+] = [HCl] = 3 \times 10^{-3}$ M,

$pH = -\log(3 \times 10^{-3}) = 2.52$

(b) $NaOH + (aq) \longrightarrow Na^+ + OH^-$

$[OH^-] = [NaOH]$

$\therefore [OH^{-1}] = 5 \times 10^{-3}$ M,

$[H^+] = 10^{-14} / (5 \times 10^{-3})$

$= 2 \times 10^{-12}$ M

$pH = -\log(2 \times 10^{-12}) = 11.699$

(c) $HBr + aq \longrightarrow H^+ + Br^{-1}$,

$[H^+] = [HBr]$

$\therefore [H^+] = 2 \times 10^{-3}$ M,

$pH = -\log(2 \times 10^{-3}) = 2.699$

(d) $KOH + aq \longrightarrow K^+ + OH^{-1}$,

$[OH^-] = [KOH]$

$\therefore [OH^{-1}] = 2 \times 10^{-3}$ M, $[H^+]$

$= 10^{-14}/(2 \times 10^{-3}) = 5 \times 10^{-12}$

$pH = -\log(5 \times 10^{-12}) = 11.30$

7.49 Calculate the pH of the following solutions:

(a) 2g of TlOH dissolved in water to give 2 litre of solution

(b) 0. 3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution

(c) 0. 3 g of NaOH dissolved in water to give 200 mL of solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

Ans. (a) Molar conc. of TlOH

$= 2g / (204 + 16 + 1)\ g\ mol^{-1} \times 1 / 2L$

$= 4.52 \times 10^{-3}$ M

$[OH^-] = [TlOH] = 4.52 \times 10^{-3}$ M

$[H^+] = 10^{-14}/(4{\cdot}52 \times 10^{-3}) = 2.21 \times 10^{-12}$ M

$pH = -\log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.655$

(b) Molar conc. of $Ca(OH)_2$

$= 0.3 / [(40 + 34)g\ mol^{-1}] \times 1 / 0.5$ L

$= 8.10 \times 10^{-3}$ M

$Ca(OH)_2 \longrightarrow Ca^{2+} + 2\ OH^{-1}$

$[OH^-] = 2[Ca(OH)_2] = 2 \times (8.10 \times 10^{-3})M$

$= 16.2 \times 10^{-3}M$

$pOH = -\log(16.2 \times 10^{-3}) = 3 - 1.2101 = 1.79$

$pH = 14 - 1.79 = 12.21$

(c) Molar conc. of NaOH

$= 0.3g / 40g\ mol^{-1} \times 1/0.2L$

$= 3.75 \times 10^{-2}$ M

$pOH = -\log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.426$

$pH = 14 - 1.426 = 12.57$

(d) $M_1V_1 = M_2V_2$

$\therefore 13.6M \times 1\ mL = M_2 \times 1000\ mL$

$\therefore M_2 = 1.36 \times 10^{-2}$ M

$[H^+] = [HCl] = 1.36 \times 10^{-2}$ M,

$pH = -\log(1.36 \times 10^{-2}) = 2 - 0.1335 = 1.8665$

7.50 The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a bromoacetic acid.

Ans. $CH_2(Br)COOH \rightleftharpoons CH_2(Br)COO^{-1} + H^+$

Initial conc. $\quad C \quad 0 \quad 0$

Conc. at eqm. $\quad C - C\alpha \quad C\alpha \quad C\alpha$

Here α is the degree of ionisation of bromo acetic acid

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$= 0.1 \times (0{\cdot}132)^2 = 1.74 \times 10^{-3}$

$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$

$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} M$

$pH = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$

7.51 The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b

Ans. $Cod + H_2O \rightleftharpoons CodH^+ + OH^{-1}$

$pH = 9.95 \therefore pOH = 14 - 9.95 = 4.05,$

$[pH + pOH = 14]$

i. e., $-\log[OH^-] = 4.05$

or $\log[OH^-] = -4.05 = -5.95$

or $[OH^-] = 8.913 \times 10^{-5}$

$$K_b = \frac{[CodH^+][OH]}{[Cod]} = \frac{[OH^-]^2}{[Cod]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}}$$

[at equilibrium $[Cod\,H^+] = [OH^-]$

$pK_b = -\log(1.588 \times 10^{-6}) = -\log 1.59 + 6 \log 10$

$= 6 - \log 1.59 = 5.80$

7.52 What is the pH of 0.001 M aniline solution ? The ionization constant of aniline is 4.27×10^{-10} Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

Ans. (i) $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3{}^+ + OH^-$

$$K_a = \frac{[C_6H_5NH_3{}^+][OH^-]}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$\therefore$ at equilibrium $[C_6H_5NH_3^+] = [OH^-]$

$[OH^-] = \sqrt{K_a[C_6H_5NH_2]}$

$= \sqrt{(4.27 \times 10^{-10})(10^{-3})} = 6.534 \times 10^{-7} M$

$pOH = -\log(6.534 \times 10^{-7}) = 7 - 0.8152 = 6.18$

$pH = 14 - 6{\cdot}18 = 7{\cdot}82$

(ii) Also $\quad C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3{}^+ + OH^-$

Initial $\quad C$

At. eqm. $\quad C - C\alpha \quad C\alpha \quad C\alpha$

$K_b = (C\alpha)(C\alpha) / C(1-\alpha) = (C\alpha^2) / (1-\alpha)$

$\therefore \alpha^2 = K_b / C = 4.27 \times 10^{-10} / 10^{-3}$

$(\because \alpha <<< 1, \text{i.e., } 1 - \alpha \approx 1)$

$\alpha = 6.53 \times 10^{-4}$

(iii) $pK_b + pK_a = 14$ (for a pair of conjugate acid and base)

$pK_b = -\log(4.27 \times 10^{-10}) = 10 - 0.62 = 9.37$

$pK_a = 14 - 9.37 = 4.63$

$-\log K_a = 4.62$ or $\log K_a = -4.62$

or $K_a = \text{Antilog } -4.62 = 2.399 \times 10^{-5} \approx 2{\cdot}4 \times 10^{-5}$

7.53 Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4. 74. How is the degree of dissociation affected when its solution also contains (a) 0. 01 M (b) 0. 1M in HCl?

Ans. $pK_a = 4.74$, i. e., $-\log K_a = 4.74$

or $\quad \log K_a = -4.74$

Taking Antilog $k_a = \text{Antilog}(-4.74)$

$\therefore K_a = 1.82 \times 10^{-5}$

$\alpha^2 = K_a/C = (1.82 \times 10^{-5}) / (5 \times 10^{-2}) = 1.908 \times 10^{-2}$

In presence of HCl, due to high concentration of H^+ ion, dissociation equilibrium will shift backward, i.e. dissociation of acetic acid will decrease,

(a) In presence of 0. 01 M HCl, if x is the amount dissociated, then

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Initial $\quad 0.05\,M$

After disso. $\quad 0.05 - x \quad x \quad 0.01 + x$

$= 0.05 \quad = 0.01\,M$

(0. 01 M H^+ ions are obtained from 0. 01 M HCl)

$(\because x << 0.01 \quad \therefore 0.01 + x \approx 0.01)$

$$\therefore K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$\therefore \alpha = (1.82 \times 10^{-5}) / 10^{-2} = 1.82 \times 10^{-3}$

$$\left(\text{since } \alpha = \frac{\text{Amount dissociated}}{\text{amount taken}}\right)$$

(b) In the presence of 0.1 M HCl, if y is the amount of acetic acid dissociated, then at equilibrium

$[CH_3COOH] = 0.05 - y \approx 0.05\,M$

$[CH_3COO^-] = y, [H^+] = 0.1M + y = 0.1M$

$K_a = (0.1) / 0.05$ or $y / 0.05 = K_a / 0.1$

$\therefore \alpha = (1.82 \times 10^{-5}) / 10^{-1} = 1.82 \times 10^{-4}$, i. e. $\alpha = 1.82 \times 10^{-4}$

7.54 The ionisation constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M NaOH ?

Ans. $\alpha^2 = K_b / C = (5.4 \times 10^{-4}) / (2 \times 10^{-2}) = 0.027; \alpha = 0.164$

In presence of 0. 1 M NaOH, if x is the amount of dimethyl amine dissociated,

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2{}^+ + OH^-$

Initial $\quad C \quad 0 \quad 0$

After disso. $\quad C(1-\alpha) \quad C\alpha \quad C\alpha$

$\approx 0.1 \; ([OH^-] = 0.1)$

$$K_b = \frac{C\alpha}{C} 0.1$$

$K_b = \alpha \times 0.1 \qquad \left[\alpha = \dfrac{5.4 \times 10^{-4}}{0.1} \text{ (\% ionization} = 0.54)\right]$

$= 5.4 \times 10^{-3} = 0.0054$

7.55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a) Human muscle–fluid, 6. 83

(b) Human stomach fluid, 1. 2

(c) Human blood, 7. 38

(d) Human saliva, 6·4

Ans. (a) $\log[H^+] = pH = -6.83$

$\therefore [H^+] = \text{Antilog} - 6.83 = 1.479 \times 10^{-7} M$

(b) $\log[H^+] = -pH = -1.2$

$\therefore [H^+] = \text{Antilog} -1.2 = 6.31 \times 10^{-2} M$

(c) $\log[H^+] = -pH = -7.38$

$\therefore [H^+] = \text{Antilog} -7.38 = 4.169 \times 10^{-8} M$

(d) $\log[H^+] = -pH = -6.4$

$\therefore [H^+] = \text{Antilog} - 6.4 = 3.981 \times 10^{-7} M$

7.56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5·0, 4.2, 2.2 and 7·8 respectively. Calculate corresponding hydrogen ion concentration in each.

Ans. Milk → $-\log[H^+] = pH = -6.8$
$\therefore$ $[H^+] = \text{Antilog}(-6.8) = 1.58 \times 10^{-7}$ M
Black coffee → $-\log[H^+] = pH = -5.0 =$
$\therefore$ $[H^+] = 10^{-5}$ M
Tomato juice → $-\log[H^+] = pH = -4.2$
$\therefore$ $[H^+] = \text{Antilog}(-4.2) = 6.31 \times 10^{-5}$M
Lemon juice → $-\log[H^+] = pH = -2.2$
$\therefore$ $[H^+] = \text{Antilog}(-2.2) = 6.31 \times 10^{-3}$ M
Egg white → $-\log[H^+] = pH = -7.8$
$\therefore$ $[H^+] = \text{Antilog}(-7.8) = 1.5 \times 10^{-8}$ M

7.57 If 0. 561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentration of potassium, hydrogen and hydroxyl ions. What is its pH ?

Ans. $[KOH] = 0.561 / 56 \times 1000 / 200 = 0.05$M
As $KOH \longrightarrow K^+ + OH^{-1}$,
$[K^+] = [OH^-] = 0.05$ M
$[H^+] = K_w / [OH^-] = 10^{-14} / 0.05 = 10^{-14}/(5 \times 10^{-2})$
$= 2.0 \times 10^{-13}$ M.
$pH = -\log 2 \times 10^{-13}$
$= 13 - \log 2 = 12.69$

7.58 The solubility of $Sr(OH)_2$ at 298K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

Ans. Molar mass of $Sr(OH)_2 = 87.6 + 34 = 121.6$ g mol^{-1}
Solubility of $Sr(OH)_2$ in moles L^{-1}
$= 19.23$ gL^{-1} / 121.6 g mol^{-1} = 0.1581 M
Assuming complete dissociation,
$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$
$\therefore$ $[Sr^{2+}] = 0.1581$M, $[OH^-] = 2 \times 0.1581 = 0.3162$M, pOH = $-\log 0.3162 = 0.5$,
$\therefore$ pH = 14 – 0. 5 = 13.5

7.59 The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

Ans. Assuming α to be very small, applying formula directly, we have

$$\alpha = \sqrt{K_a / c} = \sqrt{(1.32 \times 10^{-5}) / 0.05} = 1.62 \times 10^{-2}$$

$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$

In presence of HCl, equilibrium will shift in the backward direction, i.e. concentration of CH_3CH_2COOH will increase hence amount of dissociation will be less. If 'c' is the initial concentration and 'x' is the amount now dissociated, then at equilibrium

$[CH_3CH_2COOH] = C(1-x)$
$[CH_3CH_2COO^-] = Cx$, $[H^+] = C\alpha \approx 0.01 + x \approx 0.01$

$$\frac{Cx \times 0.01}{C(1-x)} = x \times 0.01 = 1.32 \times 10^{-5}$$

$x = 1.32 \times 10^{-3}$.

7.60 The pH of 0. 1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Ans. $HCNO \rightleftharpoons H^+ + CNO^-$
pH = 2.34 means
$-\log[H^+] = 2.34$
or $\log[H^+] = -2.34 = -3.66$
or $[H^+] = \text{Antilog} - 3.66 = 4.57 \times 10^{-3}$M
$[CNO^-] = [H^+] = 4.57 \times 10^{-3}$ M

$$K_a = \frac{(4.57 \times 10^{-2})^2}{0.1} = 2.09 \times 10^{-4}$$

$$\alpha = \sqrt{K_a / c} = \sqrt{(2.09 \times 10^{-4} / 0.1)} = 0.0457$$

7.61 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

Ans. Sodium nitrite is a salt of weak acid, strong base. Hence,
$K_h = K_w/K_a = 10^{-14}/(4{\cdot}5 \times 10^{-4}) = 2.22 \times 10^{-11}$

$$h = \sqrt{K_h / c} = \sqrt{(2.22 \times 10^{-11} / 0.04)}$$

$$= \sqrt{5.5 \times 10^{-10}} = 2.36 \times 10^{-5}$$

	$NO_2^- + H_2O \rightleftharpoons$	HNO_2	$+ \; OH^-$
Initial	C		
After hydrolysis	C(1–h)	Ch	Ch

$[OH^-] = Ch = 0.04 \times 2.36 \times 10^{-5} = 9.38 \times 10^{-7}$
$pOH = -\log(9.38 \times 10^{-7}) = 7 - 0.9722 = 6.03$
$pH = 14 - pOH = 14 - 6.03 = 7.97$.

7.62 0. 02 M solution of pyridinium hydrochloride has pH = 3·44. Calculate the ionization constant of pyridine.

Ans. pH = 3.44, i. e., $\log[H^+] = -3.44 = -4.56$
Taking Antilog
$\therefore$ $[H^+] = 3.63 \times 10^{-4}$

$$C_5H_5N^+HCl^- + aq \rightleftharpoons C_5H_5\overset{+}{N}\overset{-}{Cl} + H^+$$

$$K_a = \frac{[C_5N_5N^+Cl^-][H^+]}{[C_5H_5N^+HCl^-]}$$

$$= \frac{(3.63 \times 10^{-4})(3.63 \times 10^{-4})}{2 \times 10^{-2}} = 6.59 \times 10^{-6}$$

$pK_a = -\log(6.59 \times 10^{-6}) = 6 - 0.8187 = 5.18$
$pK_b + pK_b = 14$ $\therefore$ $pK_b = 14 - 5.18 = 8.82$
$-\log K_b = 8.82$ or $\log K_b = -8.82$ $\therefore$ $K_b, = 1.514 \times 10^{-9}$

7.63 Predict if the solutions of the following salts are neutral, acidic or bisic:
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

Ans. NaCN, $NaNO_2$, KF solutions are basic, as they are salts of strong base and weak acid. NaCl and KBr solutions are neutral, as they are salts of strong acid, strong base. NH_4NO_3 solution is acidic, as it is a salt of strong acid, weak base.

7.64 The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1M sodium salt solution ?

Ans. $ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$

$$K_a = \frac{[ClCH_2COO^-][H^+]}{[ClCH_2COOH]} = \frac{[H^+]^2}{C}$$

at equilibrium, $[ClCH_2COO^-] = [H^+]$

$[H^+] = \sqrt{K_a \times c} = \sqrt{1.35 \times 10^{-3} \times 0.1} = 1.16 \times 10^{-2}$

$pH = -\log(1.16 \times 10^{-2}) = 2 - 0.06 = 1.94$

Sodium salt of chloroacetic acid is a salt of strong base and weak acid. Hence,

$pH = -1/2\ [\log K_w + \log K_a - \log c]$

$\therefore\ pH = -½\ [\log 10^{-14} + \log 1.35{\times}10^{-3} - \log 0.1] = -½\ [-14 + (-3 + 0.1303) - (-1)] = 7 + 1.44 - 0.5 = 7.94$

7.65 The ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Ans. As $[H^+][OH^-] = K_W$

For neutral water $[H^+] = [OH^-]$

$\therefore\ [H^+]^2 = 2.7 \times 10^{-14}$

or $\sqrt{[H^+]^2} = \sqrt{2.7 \times 10^{-14}}$

$\therefore\ [H^+] = 1.643 \times 10^{-7}$

$pH = -\log[H^+] = -\log(1.643 \times 10^{-7}) = 7 - 0.2156 = 6.78$

7.66 Calculate the pH of the resultant mixtures

(a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl

(b) 10 mL of 0. 01 M H_2SO_4 + 10 mL of 0. 01 M $Ca(OH)_2$

(c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

Ans. (a) 10 mL of 0.2 M $Ca(OH)_2$ = 10 × 0.2 millimoles = 2 millimoles of $Ca(OH)_2$

25 mL of 0.1 M HCl = 25 × 0.1 millimoles = 2.5 millimoles of HCl

$Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O$

$\because$ 1 millimole of $Ca(OH)_2$ reacts with 2 millimoles of HCl

$\therefore$ 2.5 millimoles of HCl will react with 1.25 millimoles of $Ca(OH)_2$

$\therefore$ $Ca(OH)_2$ left = 2 – 1.25 = 0.75 millimoles (HCl is the limiting reactant)

Total volume of the solution = 10 + 25 mL= 35 mL

$\therefore$ Molarity of $Ca(OH)_2$ in the mixture solution = 0. 75/35 M = 0. 0214 M

$[OH^-] = 2 \times 0.0214M = 0.0428\ M$

$= 4.28 \times 10^{-2}$

$pOH = -\log(4.28 \times 10^{-2}) = 2 - 0.6314 = 1.3686 \approx 1.37$

$pH = 14 - 1.37 = 12.63$

(b) 10 mL of 0.01 M H_2SO_4 = 10 × 0.01 millimole = 0. 1 millimole

10 mL of 0. 01 M $Ca(OH)_2$ = 10 × 0. 01 millimole = 0. 1 millimole

$Ca(OH)_2 + H_2SO_4 \rightleftharpoons CaSO_4 + 2\,H_2O$

1 mole of $Ca(OH)_2$ reacts with 1 mole of H_2SO_4

$\therefore$ 0.1 millimole of $Ca(OH)_2$ will react completely with 0.1 millimole of H_2SO_4. Hence, solution will be neutral with pH = 7. 0

(c) 10 mL of 0.1 M H_2SO_4 = 1 millimole

10 mL of 0. 1 M KOH = 1 millimole

$2\,KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2\,H_2O$

1 millimole of KOH will react with 0·5 millimole of H_2SO_4

$\therefore$ H_2SO_4 left = 1–0.5 = 0.5 millimole

Volume of reaction mixture = 10 + 10 = 20 mL

$\therefore$ Molarity of H_2SO_4 in the mixture solution

$$= \frac{0.5}{20} = 2.5 \times 10^{-2}$$

$[H^+] = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2}$

$pH = -\log(5 \times 10^{-2}) = 2 - 0.6989 = 1.3011$

7.67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given in table 7.9. Determine also molarities of individual ions.

Ans. 1. $\underset{}{Ag_2CrO_4} \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}},\ K_{sp} = (2s)^2(s) = 4s^3$

$\therefore\ s^3 = K_{sp}/4$

$= (1.1 \times 10^{-12})/4 = 0.275 \times 10^{-12}$

$s = 6.5 \times 10^{-5}\,mol\,L^{-1}$

$[Ag^+] = 2 \times 6.5 \times 10^{-5} = 13.0 \times 10^{-5}M$

$= 1.30 \times 10^{-4}M$

$[CrO_4^{2-}] = 6.5 \times 10^{-5}M$

For $BaCrO_4$

2. $BaCrO_4(s) \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{s}{CrO_4^{-2}}$

$K_{sp} = s^2 = 1.2 \times 10^{-10},\ \therefore s = \sqrt{1.2 \times 10^{-10}}$

$= 1.1 \times 10^{-5}M = [Ba^{2+}] = [CrO_4^{-2}]$

For $Fe(OH)_3$

3. $Fe(OH)_3 \rightleftharpoons \underset{s}{Fe^{3+}} + \underset{3s}{3OH^{-1}}$

$K_{sp} = s \times (3s)^3 = 27\,s^4$

$\therefore\ s = 4\sqrt{(K_{sp}/27)} = 4\sqrt{(1 \times 10^{-38}/27)}$

Taking log

$$\log s = \log\left(\frac{1 \times 10^{-38}}{27}\right)^{1/4}$$

$$= \frac{1}{4}[\log 10^{-38} - \log 27] = \frac{1}{4}[-38 - \log 27]$$

$$= \frac{1}{4}[-38 - 1.43136] = \frac{1}{4}[-39.43] = -9.8578$$

$\therefore\ \log s = -9.8578$

Taking Antilog $s = 1.35 \times 10^{-10}$

Hence $[Fe^{3+}] = 1.35 \times 10^{-10}\,M$;

$[OH^{-1}] = 3 \times 1.35 \times 10^{-10} = 4.04 \times 10^{-10}M$

4. For $PbCl_2$ $\underset{s}{PbCl_2} \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2Cl^-}$

$K_{sp} = 4s^3$

$\therefore\ s = 3\sqrt{(K_{sp}/4)} = 3\sqrt{(1.6 \times 10^{-5}/4)}$

$S = 1.59 \times 10^{-2}$

Hence $[Pb^{2+}] = 1.59 \times 10^{-2}M$;

$[Cl^-] = 2 \times 1.59 \times 10^{-2} = 3.18 \times 10^{-2}\,M$

5. For Hg_2I_2 $Hg_2I_2 \rightleftharpoons \underset{s}{Hg_2^{2+}} + \underset{2s}{2I^-}$

$K_{sp} = 4s^3$ solve as above, we get

$s = 2.24 \times 10^{-8}M = [Hg_2^{2+}]$

and $2 \times 2.24 \times 10^{-8} = 4.48 \times 10^{-8}M = [I^-]$

7.68 The solubility product constants of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Ans. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$,

$\quad\quad\quad\quad\quad\quad 2S \quad S$

$K_{sp} = (2s)^2(s) = 4\,s^3, .\because .\, s^3 = K_{sp}/4$

$\therefore \quad s = 6.5 \times 10^{-5}$

$AgBr \rightleftharpoons Ag^+ + Br^-$

$\quad\quad\quad\quad s \quad s$

$K_{sp} = s^2 = 5 \times 10^{-13}$

$\therefore \quad s = \sqrt{5 \times 10^{-13}} = 7.07 \times 10^{-7}$

$\therefore$ ratio of $[Ag_2CrO_4] : [AgBr] = 6.5 \times 10^{-5} : 7.07 \times 10^{-7}$ $= 91.9$

Silver chromate is more soluble than silver bromide.

7.69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? For cupric iodate, $K_{sp} = 7.4 \times 10^{-8}$.

Ans. $2\,NaIO_3 + CuClO_4 \rightleftharpoons Na_2ClO_4 + Cu(IO_3)_2$

After mixing, $[NaIO_3] = [IO_3^-] = (2 \times 10^{-3})/2 = 10^{-3}$ M

$[CuClO_4] = [Cu^{2+}] = (2 \times 10^{-3})/2 = 10^{-3}$ M

Ionic product of $Cu(IO_3)_2 = [Cu^{2+}]\,[IO_3^-]^2$

$= (10^{-3})\,(10^{-3})^2 = 10^{-9}$

As ionic product is less than K_{sp}, no precipitation will occur.

7.70 The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3·19 compared to its solubility in pure water ?

Ans. $C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$

Solubility in water. Suppose solubility in water = x mol L^{-1}. Then $[C_6H_5COO^-] = [Ag^+] = x$ mol L^{-1}.

$\therefore\ x^2 = K_{sp}$ or $x = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7}$ mol L^{-1}

Solubility in buffer of pH = 3.19

pH = 3· 19 means $-\log\,[H^+] = 3.19$

or $\log\,[H^+] = -3.19 = \bar{4}.81$

or $\log\ [H^+] = 6.457 \times 10^{-4}$

$C_6H_5COO^-$ ions now combine with the H^+ ions to form benzoic acid but $[H^+]$ remains almost constant because we have buffer solution. Now

$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$.

$$K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$$

$$\text{or} \quad \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{[H^+]}{K_a} = \frac{6.457 \times 10^{-4}}{6.46 \times 10^{-5}} = 10 \quad \ldots(i)$$

Suppose solubility in the buffer solution is y mol L^{-1}. Then as most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionized), we have

$y = [Ag^+] = [C_6H_5COO^-] + [C_6H_5COOH]$

$= [C_6H_5COO^-] + 10\,[C_6H_5COO^-]$

$= 11\,[C_6H_5COO^-]$ (using eqn. (i))

$[C_6H_5COO^-] = y/11$

$\therefore \quad K_{sp} = [C_6H_5COO^-]\,[Ag^+]$

i. e., $2.5 \times 10^{-3} = y/11 \times y$ or $y^2 = 2.75 \times 10^{-12}$

or $y = 1.66 \times 10^{-6}$

$$\therefore\ y/x = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$$

Silver benzoate is 3.32 times more soluble in buffer of pH 3.19 then in pure water.

7.71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? For iron sulphide,

$K_{sp} = 6.3 \times 10^{-18}$.

Ans. Suppose the concentration of each of $FeSO_4$ and Na_2S is x mol L^{-1}. Then after mixing equal volumes,

$[FeSO_4] = [Na_2S] = x/2$ M, i. e., $[Fe^{2+}] = [S^{2-}] = x/2$ M

K_{sp} for FeS $= [Fe^{2+}][S^{2-}]$, i. e., $6.3 \times 10^{-18} = (x/2) \times (x/2)$

or $x^2 = 25{\cdot}2 \times 10^{-18}$, or $x = 5.01 \times 10^{-9}$M.

7.72 What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}.)

Ans. $CaSO_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq)$

If s is the solubility of $CaSO_4$ in moles L^{-1}, then

$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = s^2$

or. $s = (K_{sp})^{1/2} = 3.02 \times 10^{-3}$ mol L^{-1}

$= 3.02 \times 10^{-3} \times 136$g $L^{-1} = 0.4107$ gL^{-1}

(Molar mass of $CaSO_4$ = 136g mol^{-1})

Thus, for dissolving 0.4107 g, water required = 1 L

$\therefore$ For dissolving 1 g, water required = 1/(0. 411) L = 2.43 L.

7.73 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19}m. If 10 mL of this solution is added to 5 mL of 0.04 M solution of the following $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. In which solutions precipitation will take place ?

Ans. Precipitation will take place in the solution for which ionic product is greater than solubility product. As 10 mL of solution containing S^{2-} ion is mixed with 5 mL of metal salt solution, after mixing

$[S^{2-}] = 1.0 \times 10^{-19} \times (10/15) = 6.67 \times 10^{-20}$,

$[Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}] = (5/15) \times 0.04 = 1.33 \times 10^{-2}$ M

$\therefore$ Ionic product for each of these will be $= [M^{2+}]\,[S^{2-}] = (1.33 \times 10^{-2})\,(6.67 \times 10^{-20}) = 8.87 \times 10^{-22}$

As this is greater than the solubility product of ZnS and CdS, therefore, $ZnCl_2$ and $CdCl_2$ solutions be precipitated.

Practice Questions

Very Short Answer Questions [1 Mark]

1. In a reaction $a + b \rightleftharpoons c + d$ will addition of c to the system change the value of K?

2. In a reaction $a + b \rightleftharpoons c + d$ the change in enthalpy is –10 kcal. If heat is added to the system in which direction the reaction would proceed?

3. The equilibrium constants for HCN and HAc are 4.0×10^{-10} and 1.9×10^{-5} mole/L respectively. Which acid is stronger?

4. A certain metal sulphide MS, has a solubility product 1.3×10^{-18} mole^2/l^2. What must be $[S^{-2}]$ be in a 0.10M solution of M^{2+} when MS just starts to precipitate.

5. What is meant by the statement 'Equilibrium is dynamic in nature'?

6. At what temperature the solid and liquid are in equilibrium under 1 atm. pressure ?

7. What is the effect of temperature on solubility of gases in liquids ?

8. $A + B \rightleftharpoons AB;\ K = 1 \times 10^{2}$
$E + F \rightleftharpoons EF;\ K = 1 \times 10^{-3}$
Out of AB and EF, which one is more stable AB or EF ?

9. Which will have CO_2 to more extent, hot cold drink bottle or chilled cold drink bottle, why ?

10. Mention the conditions of temperature and pressure when gas will dissolve in liquid to maximum extent with decrease in volume and absorption of heat.

11. What is difference between strong electrolyte and weak electrolyte ?

12. Under what conditions a weak electrolyte can have high degree of ionisation ?

13. What is the effect of temperature on degree of dissociation ?

14. In qualitative analysis, on what basis cations are grouped ?

15. What is the effect of temperature on solubility product (K_{sp}) ?

16. Why is Lewis concept more useful than Bronsted-Lowry concept?

17. Is it possible to get precipitate of $Fe(OH)_3$ at pH = 2 ? Give reason.

18. What is the expression for K_{sp} of Ag_2CrO_4?

19. pK_a values of acids A, B, C, D are 1.5, 3.5, 2.0 and 5.0. Which of them is strongest acid ?

20. Give two applications of buffer solution.

21. Write an equation to show that NH_3 is an Arrhenius base.

22. Write two equations to show the amphiprotic (acid as well as base) property of water.

23. Which of the following is strongest Lewis acid ? CCl_4, $AlCl_3$, NCl_3, OCl_2.

24. Give an example of gas –liquid equilibrium in everyday life.

25. What is neutralization according to Lewis concept?

26. All Bronsted acids are not Lewis acids. Explain.

27. Which of the following is strongest conjugate base? CH_3^-, NH_2^-, OH^-, F^-.

28. What happens to ionic product of water if temperature is increased?

29. Write the expression for equilibrium constant K_p, for the reaction.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

30. The equilibrium constant for a gas phase reaction is

$$K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

Write the balanced chemical equation corres- ponding to this expression.

31. In a gaseous reaction $a + b \rightleftharpoons c + 2d$, 3 mol of inert gas is introduced into the vessel at constant pressure. What will be its effect on equilibrium?

32. How are the pK's of the conjugate acid and base are related to each other?

33. Which of the following salt will not be hydrolysed?
$NaNO_3$, CH_3COONa

34. On what factor the choice of an indicator in acid-base titration depends?

35. Name the buffer present in blood.

Short Answer Questions [2 & 3 Marks]

1. For the reaction $2a \rightleftharpoons c + d$, the equilibrium constant is 1.0×10^{-3}. At equilibrium, the concentrations observed were $[c] = 1.2 \times 10^{-3}$ M, $[d] = 3.8 \times 10^{-6}$ M.
What was [a] at equilibrium?

2. For the reaction $d + 2e \rightarrow f$, the initial concentrations of 'd' and 'e' were 0.2 and 1.2 mole / litre. At equilibrium, the concentration of 'f' was found to be 0.1 mole / litre. What is 'K' for the reaction?

3. Calculate the molar concentration of an acetic acid solution which is 2% ionized? ($K_a = 1.8 \times 10^{-5}$)

4. (i) Why in detection of cations, group IV metals are not precipitated in group II radicals?
(ii) Why do we pass H_2S gas in acidic medium in group 2?

5. Which has the greater molarity in water, AgCl or $Mg(OH)_2$
(K_{sp} (AgCl) $= 1.8 \times 10^{-10}$,
$K_{sp}Mg(OH)_2 = 1.2 \times 10^{-11}$)

6. On the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)\ \Delta H = +93.6$ kJ. Tell us what would be effect of
(a) temperature
(b) pressure

7. Calculate the pH of the solution produced when an aqueous solution of pH = 5 is mixed with equal volume of an aqueous solution of pH = 3.

8. How much CH_3COONa should be added to 1 litre of 0.1M CH_3COOH to make a buffer of pH = 4.0?
$K_a = 1.8 \times 10^{-5}$.

9. What is the pH of a 0. 50 M solution of Na_2CO_3?
($K_b = 1.8 \times 10^{-4}$)

10. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride?

11. Ionisation constant of a weak base MOH, is given by the expression $K_b = \dfrac{[M^+][OH^-]}{[MOH]}$

Values of ionisation constant of some weak bases at a particular temperature are given below:

Base	K_b
Dimethylamine	5.4×10^{-4}
Urea	1.3×10^{-14}
Pyridine	1.77×10^{-9}
Ammonia	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionisation at equilibrium. Which of the above base is the strongest?

12. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

13. Following data is given for the reaction : $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$$\Delta_f U^{\ominus}\,[CaO(s)] = -635.1\ \text{kJ mol}^{-1}$$

$$\Delta_f U^{\ominus}\,[CO_2(g)] = -393.5\ \text{kJ mol}^{-1}$$

$$\Delta_f U^{\ominus}\,[CaCO_3(s)] = -1206.9\ \text{kJ, mol}^{-1}$$

Predict the effect of temperature on the equilibrium constant of the above reaction.

14. Which of the following reactions involve homogeneous equilibria and which involve heterogeneous equilibria?

(i) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$

(ii) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(iii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iv) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

15. Given :

(i) $Cu(g) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

$$K = \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2} = 2.0 \times 10^{15}$$

(ii) $Cu(s) + Zn^{2+}_{(aq)} \rightleftharpoons Cu^{2+}(aq) + Zn(s)$

$$K = \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} = 2.0 \times 10^{-19}$$

Arrange the three metals in order of increasing reactivity.

16. One mole of H_2O and one mole of CO are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation

$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$

Calculate the equilibrium constant for the reaction.

17. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

18. For the reaction,

$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$, at 1173 K, the magnitude of the equilibrium constant, K_c is 3.6. For each of the following composition, decide whether the reaction mixture is at equilibrium. If it is not, decide to which direction the reaction should go

(i) $[CH_4] = 1.07$ M $[H_2S] = 1.20$ M, $[CS_2] = 0.90$ M, $[H_2] = 1.78$ M

(ii) $[CH_4] = 1.45$ M, $[H_2S] = 1.29$ M, $[CS_2] = 1.25$ M, $[H_2] = 1.75$ M

19. At a certain temperature and a total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate the K_p for the equilibrium.

20. What is the effect of catalyst on

(i) the rate constant

(ii) the equilibrium constant?

21. In a reaction

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$\Delta_r H° = -91.0$ kJ/mol. Concentration of hydrogen, carbon monoxide and methanol becomes constant at equilibrium. What will happen if:

(i) volume of the reaction vessel in which the reactants and products are contained is suddenly reduced to half,

(ii) the partial pressure of hydrogen is suddenly doubled,

(iii) an inert gas is added to the system?

22. The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act as both Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

23. At 298 K, a 0.1 M solutions of a weak acid, HA is 1.34 percent ionised. What is the ionization constant, K_a for an acid?

24. Calculate the concentrations of hydrogen ion and hydroxide ion at 25° C in

(i) 0.15 M HNO_3 and

(ii) 0.01 M $Ca(OH)_2$

25. The ionization constants of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

26. The solubility of $Sr(OH)_2$ at 298 K is 19.239/L of solutions. Calculate the concentration of strontium and hydroxyl ions and the pH of the solution.

27. What is the pH of 0.001 M aniline solution. The ionization constant of the base is 4.27×10^{-10}. Calculate the degree of ionization of aniline in the solution. Also, calculate the ionization constant of the conjugate acid of aniline.

28. A 2.461 g sample of solid sodium acetate is dissolved in enough water to make 50.00 mL of solution. To the sodium acetate solution, 100 mL of 0.120 M HCl is added. What is the pH of the resulting solution.

(K_a for $CH_3COOH = 1.8 \times 10^{-5}$)

29. 25.0 cm^3 of 0.001 M $AgNO_3$ solution is mixed with 75.0 cm^3 of 0.001 M Na_2CO_3 solution. Will it lead to the precipitation of Ag_2CO_3?

K_{sp} of Ag_2CO_3 is 6.2×10^{-12} at 298 K

30. Vapour pressure of water, acetone and ethanol at 293 K are 2.34, 12.3 and 5.85 kPa respectively. Which of these has the lowest and the highest boiling point? At 293 K which of these evaporates least in a sealed container before equilibrium is reached?

31. All Arrhenius bases are not Bronsted bases but it is true in case of acids. Justify.

32. All Bronsted bases are also Lewis bases but all Lewis acids are not Bronsted acids. Justify.

33 $A \rightleftharpoons B \quad K_1 = 1$
$B \rightleftharpoons C \quad K_2 = 2$
$C \rightleftharpoons D \quad K_3 = 3$
$D \rightleftharpoons E \quad K_4 = 4$
What is value of K for $A \rightleftharpoons E$?

Long Answer Questions [5 Marks]

1. (i) How much volume of 0.1 M acetic acid should be added to 50 ml of 0.2M sodium acetate solution if we want to prepare a buffer solution of pH = 4.91 . Given pK_a for acetic acid is 4.76.
(ii) Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 500K is numerically equal to three times the value of K_p.

2. (i) What is the pH of a solution that contains 0. 10 M HCl and 0.10 M CH_3COOH? For acetic acid, $K_a = 1.8 \times 10^{-5}$.
(ii) What are the concentrations of all the species present in a 0. 50 M solution of acetic acid. For CH_3COOH $K_a = 1.8 \times 10^{-5}$.

3. Carbonic acid, H_2CO_3, is a weak diprotic acid formed by the reaction of carbon dioxide with water, For this acid, $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 5.6 \times 10^{-11}$. What are the equilibrium concentrations of each species in a 0. 10 M solution of carbonic acid?

4. Reaction between nitrogen and oxygen takes place as following:

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

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$. Determine the composition of the reaction mixture.

5. How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solution of pH 8.65 and 10?
[$pK_b = 4.75$]

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. The equilibrium constant of a reaction is 2×10^{-3} at 25°C and 2×10^{-2} at 50°C. Is the reaction exothermic or endothermic? **[HOTS]**

2. On the basis of the equation pH = –log [H^+], the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason. **[Exemplar]**

Short Answer Questions [2 & 3 Marks]

1. Will there be any change in ionic product of water when temperature is increased? Explain. **[HOTS]**

2. Consider the dissociation of nitrosyl bromide **[HOTS]**

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

The equilibrium constant, K_P, for the reaction is 0.0225 at 350°C. If a mixture contains 0.50 atm NOBr, 0.40 atm NO and 0.20 atm Br_2, will there be any net reaction? If so in which direction? **[HOTS]**

3. Some solid NH_4HS is placed in a flask containing 0.5 moles of NH_3. What would be the pressure of $NH_3(g)$ and $H_2S(g)$ when equilibrium is reached ? **[HOTS]**

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g); \; K_p = 0.11$$

4. Two sparingly soluble salts AB and XY_2 have the same solubility product. Which salt will be more soluble? Explain. **[HOTS]**

5. Ammonium hydrogen sulphide (NH_4HS) dissociates as follows **[HOTS]**

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

If the observed pressure of mixture is 1.12 atm. at 106°C. Find out the value of K_P for it.

6. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4. **[Exemplar]**

7. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively. **[Exemplar]**

8. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u). **[Exemplar]**

Long Answer Questions [5 Marks]

1. How can we apply Le-chatelier's principle in understanding the origin of tooth decay? How does fluoride help in preventing tooth decay? **[HOTS]**

2. 1 mole of H_2, two moles of I_2 and three moles of HI are injected in a 1 litre flask, what will be concentrations of H_2, I_2 and HI at equilibrium at 490°C ? The equilibrium constant for the reaction at 490°C is 45.9. **[HOTS]**

3. Write the relation between ΔG and Q and define the meaning of each term and answer the following : **[Exemplar]**
(i) Why a reaction proceeds forward when Q < K and no net reaction occurs when Q = K.
(ii) Explain the effect of increase in pressure in terms of reaction quotient Q, for the reaction :
$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

CHAPTER TEST

Time : *30 min.* **Max. Marks :** *15*

Directions :

(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. Under what condition, a reversible process becomes irreversible?

2. How can we predict whether a precipitate will be formed or not on mixing two solutions?

3. What happens when pressure is applied to ice?

4. Two moles of HI when heated at 700K in a sealed tube until equilibrium is reached were found to be 22% dissociated. Calculate K_c for the dissociation.

5. Explain Na_2CO_3 is alkaline while $CuSO_4$ is acidic.

6. Two moles of PCl_5 were heated to 327°C in a closed 2 L vessel and when equilibrium was achieved, PCl_5 was found to be 40% dissociated. Calculate the equilibrium constants K_p and K_c for this reaction.

7. (i) Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10M Mg^{2+} ions. K_{sp} for $Mg(OH)_2$ $= 1.0 \times 10^{-11}$.

(ii) How does solubility product and ionic product helps in predicting the nature of solution?

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. No, K remains constant.

2. As the reaction is exothermic hence on adding heat the reaction would move in the backward direction i.e. more 'a' and 'b' will be formed.

3. HAc is stronger since it has higher dissociation constant i.e. it would release more H^+ ion in solution than HCN.

4. $K_{sp} = [M^{2+}]\,[S^{-2}] = 1.3 \times 10^{-18}\ \text{mole}^2 / \ell^2$

$[0.10][S^{-2}] = 1.3 \times 10^{-18}$

$[S^{-2}] = 1.3 \times 10^{-17}$ M

5. At equilibrium, reaction does not stop rather it still continues, therefore, the equilibrium is dynamic in nature. It appears to stop because rate of forward reaction is equal to that of backward reaction.

6. Melting point or freezing point.

7. Solubility of gases in liquids decreases with increase in temperature.

8. AB is more stable. Higher the value of K more will be the stability of product formed.

9. Chilled cold drink will dissolve more CO_2 because solubility of gases in liquid increases with decrease in temperature.

10. Since decrease in volume takes place, high pressure is favourable for gas to dissolve. Since absorption of heat takes place, high temperature will be suitable to dissolve maximum amount of gas.

11. Strong electrolytes can dissociate into ions completely in aqueous solution whereas weak electrolytes do not dissociate into ions completely and there exist an equilibrium between ions and unionised molecules, called Ionic Equilibrium.

12. On dilution, i.e., at a very low concentration, weak electrolyte has high degree of ionisation.

13. The degree of dissociation increases with increase in temperature.

14. Cations are grouped on the basis of their solubility product (K_{sp}).

15. K_{sp} increases with increase in temperature because solubility increases.

16. Lewis concept includes some of compounds like BF_3, BCl_3, $AlCl_3$ as acids which Bronsted-Lowry concept does not.

17. No, because $Fe(OH)_3$ will dissolve in strongly acidic medium.

18. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{\,2-}(aq)$

$\Rightarrow\ K_{sp} = [Ag^+]^2\,[CrO_4^{\,2-}]$

19. Acid 'A' with $pK_a = 1.5$ is strongest acid, lower the value of

pK_a stronger will be the acid.

20. (i) Buffer solution is used in medicines.

(ii) Blood buffers maintain the pH of blood.

21. $\underset{\text{Base}}{NH_3} + H_2O \longrightarrow NH_4^+ + OH^-$

NH_3 is Arrhenius base because it gives OH^- in aqueous solution.

22. $\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$

$\underset{\text{Base}_1}{NH_3} + \underset{\text{Acid}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{OH^-}$

23. $AlCl_3$ is strongest Lewis acid because its octet is not complete.

24. Carbonated beverages and soda water in sealed bottle.

25. Formation of co–ordinate bond takes place.

26. Bronsted acids can donate H^+ easily but they may not be able to donate electrons e.g., HCl, H_2SO_4, HNO_3. Therefore, all Bronsted acids are not Lewis acids.

27. CH^-_3 is strongest conjugate base.

28. It increases with increase in temperature because dissociation of water is endothermic process.

29. $K_p = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$ [Fe and Fe_3O_4 are solids]

30. $CH_4(g) + 2H_2S(g) \rightarrow 4H_2(g) + CS_2(g)$

31. Addition of inert gas at constant pressure will shift the equilibrium towards larger number of gases moles (right hand side) forward direction.

32. The pK's of the conjugate acid and base are related to each other by the equation:

$pK_a + pK_b = pK_w = 14$ (at 298 K)

33. $NaNO_3$ will not be hydrolysed as it is a salt derived from strong acid and strong base. It undergoes hydration, no change in pH is observed.

$NaNO_3\,(s) + H_2O(l) \rightarrow Na^+(aq) + NO^-_3\,(aq)$

34. The choice of an indicator depends on the abrupt change in the pH during neutralisation process near the equivalence point.

35. Carbonic acid/bicarbonate present as a buffer in blood which maintains the pH of blood in the range of 7.38 to 7.42

Short Answer Questions

1. $K = \frac{[c][d]}{[a]^2} = 1.0 \times 10^{-3}$

$1.0 \times 10^{-3} = \frac{(1.2\times10^{-3})(3.8\times10^{-6})}{[a]^2}$

$[a]^2 = \frac{(1.2\times10^{-3})(3.8\times10^{-6})}{1.0\times10^{-3}}$

$= 4.56 \times 10^{-6}\ \text{mol}^2/l^2$

$\therefore\ [a] = 2.13 \times 10^{-3}$ M

2. At equilibrium, $[d] = 0.2 - 0.1 = 0.1$M

$[e] = 1.2 - 2(0.1) = 1.0$M

$[f] = 0.1$ M

$K = \frac{[f]}{[d][e]^2} = \frac{(0.1)}{(0.1)(1.0)^2} = 1 l^2/\text{mole}^2$

3. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Let x = molar concentration of acetic acid solution. Then $[H^+] = [CH_3COO^-] = 0.020x$ and $[CH_3COOH] = x - 0.020x \approx x$, since assumption is taken as dissociation constant of the acid is very small.

$K_a = \frac{[CH_3COOH^-][H^+]}{[CH_3COOH]}$

$= \frac{(0.020x)(0.020x)}{x} = 1.8 \times 10^{-5}$

On solving x = 0.045 M

4. (i) Group IV precipitate as sulphides like group II, but they do not precipitate in group II since the solubility products of group IV is higher than solubility products of group II sulphides.

(ii) It is done so as to reduce concentration of $[S^{2-}]$ by common ion effect so that only group 2 radicals get precipitated whereas higher group radicals do not.

5. $AgCl \rightleftharpoons Ag^+ + Cl^-$,

If x is the solubility of the salt, then from the stoichiometry of the compound

$K_{sp} = 1.8\times10^{-10} = [Ag^+][Cl^-] = x^2$

Then x = 1.34×10^{-5} M

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = 1.2\times10^{-11} = [Mg^{2+}][OH^-]^2$

$= (x)\,(2x)^2 = 4x^3$

On solving, x = 1.4×10^{-4} M hence $Mg(OH)_2$ has greater molarity.

6. (a) Since the forward reaction is endothermic, while the backward reaction is exothermic, increase in temperature would favour the forward reaction while decrease in temperature would favour the backward reaction.

(b) Increase in pressure favours the reaction towards less number of moles of gaseous species hence it would go in the backward direction while decrease in pressure will favour reaction to proceed in the forward direction.

7. Before mixing pH = 5 $\therefore\ [H_3O^+] = 10^{-5}$ M

pH = 3 $\therefore\ [H_3O^+] = 10^{-3}$M

After mixing the total volume becomes double, hence the new concentration of $[H_3O^+]$ becomes

$= (10^{-5} + 10^{-3})/2 = 5\times 10^{-4}$

$pH = -\log[H_3O^+] = -\log(5 \times 10^{-4})$

$= -(\log 5 - 4) = 4 - \log 5 = 4 - 0.699 = 3.301$

8. According to Henderson's equation

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.745$

Putting the values in above equation, we get

$$4 = 4.745 + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$\log[\text{salt}]/0.1 = 4 - 4.745 = -0.745$

$[\text{salt}]/0.1 = \text{antilog} -0.745 = 0.1798$

$[\text{salt}] = 0.1798 \times 0.1$

$= 0.01798 = 1.798 \times 10^{-2}$ mol/lit

9. We need consider only the first step in the stepwise reaction of carbonate ion with water. The equilibrium and the equilibrium law are $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

$$K_{b_1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

Initial concentration of CO_3^{2-} is 0. 50 M. Let the concentration of CO_3^{2-} ion decreases by x and the concentration of HCO_3 and OH^- increase by x.

This gives

	Initial Molar Concentrations	Change	Equilibrium Molar Concentrations
HCO_3^-	0. 0	x	x
OH^-	0. 0	x	x
CO_3^{2-}	0. 50	–x	0. 50 – x

As x is small in comparison to the initial concentration of CO_3^{2-}

$\therefore\ 0.50 - x \approx 0.50$

Substituting these equilibrium concentration values in K_{b_1} gives $(x)(x)/0.50 = 1.8 \times 10^{-4}$

Solving for x gives $x = 9.5 \times 10^{-3}$

We have $x = 9.5 \times 10^{-3} M = [OH^-]$

Now $pOH = -\log[OH^-]$

$= -\log[9.8 \times 10^{-3}]$

$= 3 \log 10 - \log 9.8$

$= 3 - 0.9912 = 2.008$

$\therefore\ pH = 14 - 2.008 = 11.992$

10. Sugar does not ionise in water but NaCl ionises completely in water and produces Na^+ and Cl^- ions. Conductance increases with increase in concentration of salt due to release of more ions.

11. Order of extent of ionisation at equilibrium is as follows:
Dimethylamine > Ammonia > Pyridine > Urea
Since dimethylamine will ionise to the maximum extent it is the strongest base out of the four given bases.

12. (i) pH = 5

$[H^+] = 10^{-5}$ mol L^{-1}

On 100 times dilution

$[H^+] = 10^{-7}$ mol L^{-1}

On calculating the pH using the equation pH = – log $[H^+]$, value or pH comes out to be 7. It is not possible. This indicates that solution is very dilute. Hence,

Total hydrogen ion concentration = $[H^+]$

$$= \begin{bmatrix}\text{Contribution of} \\ H_3O^+\text{ion} \\ \text{Concentration of} \\ \text{acid}\end{bmatrix} + \begin{bmatrix}\text{Contribution of} \\ H_3O^+\text{ ion} \\ \text{concentration} \\ \text{of water}\end{bmatrix} = 10^{-7} + 10^{-7}.$$

$pH = 2 \times 10^{-7} = 7 - \log 2 = 7 - 0.3010 = 6.6990$

13. $\Delta_r H^\ominus$

$\Delta_f H^\ominus[CaO(s)] + \Delta_f H^\ominus\ [CO_2(g)] - \Delta_f H^\ominus\ [CaCO_3(s)]$

$\therefore\quad \Delta_r H^\ominus = 178.3\ \text{kJ mol}^{-1}$

The reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature.

14. (i) Homogeneous equilibrium
(ii) Homogeneous equilibrium
(iii) Heterogeneous equilibrium
(iv) Homogeneous equilibrium

15. $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{+2}(aq) + 2Ag(s)$

As $K = 2.0 \times 10^{15}$ (given), the reaction is favourable in the forward direction in which Cu has displaced Ag^+ from its solution.

Therefore, Cu is more reactive than Ag.

In $Cu(s) + Zn^{+2}(aq) \rightleftharpoons Cu^{+2}$ aq + Zn(s), as $K = 2.0 \times 10^{-19}$ is very low, Cu cannot reduce Zn^{+2} to Zn but Zn will displace Cu^{+2} from its solution. Therefore Zn is more reactive than Cu. Hence, the increasing reactivity order of three metals is

Ag < Cu < Zn

16. $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g);$

$\Delta n = 0$

	$H_2O(g)$	$CO(g)$	$H_2(g)$	$CO_2(g)$
Initial moles	1.0	1.0	0	0
Moles at equilibrium	1 – 0.4 = 0.6	1 – 0.4 = 0.6	0.4	0.4

As $\Delta n = 0$

$$K_c = K_p = K_n = \frac{n_{H_2}\, n_{CO_2}}{n_{H_2O}\, n_{CO}}$$

where K_n = equilibrium constant in terms of number of moles.

$$K = \frac{0.4 \times 0.4}{0.6 \times 0.6} = \frac{4}{9} = 0.444$$

17. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

$K_p = 1.6 \times 10^5$

For the reaction

$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

$$K_p = \frac{1}{1.6 \times 10^5} = 6.25 \times 10^{-6}$$

	$2HBr(g)$	$H_2(g)$	$Br_2(g)$
Initial pressure	10.0	0	0
at equilibrium	10.0 – 2x	x	x

$$\therefore\quad K_p' = \frac{p_{H_2}\, p_{Br_2}}{p_{HBr}^2}$$

$$6.25 \times 10^{-6} = \frac{x^2}{(10.0 - 2x)^2}$$

or $\dfrac{x}{10.0 - 2x} = 2.5 \times 10^{-3}$

and $x \approx 2.5 \times 10^{-2}$

$p_{H_2} = p_{Br_2} = 2.5 \times 10^{-2}$ bar

$p_{HBr} = 10.0 - 5.0 \times 10^{-2}$

≈ 10.0 bar

18. $Q_c = \dfrac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$

(i) $Q_c = \dfrac{(0.90)(1.78)^4}{(1.07)(1.20)^2} = 5.86$

As $Q_c > K_c$ the reaction will proceed in the reverse direction (Reactant side)

(ii) $Q_c = \dfrac{(1.25)(1.75)^4}{(1.45)(1.29)^2}, Q_c = 4.86$

As $Q_c > K_c$, the reaction will proceed in the direction of reactants.

19. Refer to ans. to Q. No. 7.3

20. (i) A catalyst does affect rate constant. It increases the rate constant.

(ii) A catalyst increases the rate constant of forward reaction and backward reaction by the same factor. Therefore, it does not affect equilibrium constant.

21. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

(i) When the volume is reduced to half, concentration becomes doubled

$$\therefore \quad Q_c = \frac{(2[CH_3OH])}{[2[CO]][2[H_2]]^2} = \frac{K_c}{4}$$

As $Q_c < K_c$, the reaction will shift towards right.

(ii) when partial pressure of hydrogen is suddenly doubled, then Q_c becomes $\dfrac{K_c}{4}$ and more CH_3OH will be formed.

(iii) Adding inert gas has no effect at all. The equilibrium does not shift.

22.

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

23. $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

Initial Conc.	C	0	0
Conc. at equilibrium	C(1–α)	Cα	Cα

We know that

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1(0.0134)^2}{1-0.0134}$$

$K_a = 1.82 \times 10^{-5}$

24. (i) HNO_3 is a strong acid and is present in solution completely as ions.

Every mole of HNO_3 contributes one mole of H^+ ion.

$\therefore \quad [HNO_3] = [H^+]$

The H^+ concentration is 0.15 M.

The OH^- concentration is obtained from K_w equation.

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

$\therefore \quad [OH^-] = \dfrac{1.0}{0.15} \times 10^{-14}$

$= 6.7 \times 10^{-14}$ M

(ii) $Ca(OH)_2(aq) \xrightarrow{H_2O} Ca^{+2}(aq) + 2OH^-(aq)$

1 mol $Ca(OH)_2$ (aq) furnishes 2 mol OH^-

$\therefore$ 0.010 M $Ca(OH)_2$ will furnish 2×0.010 M OH^-

$[OH^-] = 0.020$ M

$[H^+] = \dfrac{1.0 \times 10^{-14}}{0.020} = 5.0 \times 10^{-13}$ M

25. $K_a \bullet K_b = 10^{-14}$

HF, the conjugate base is F^-

$\therefore \quad K_b = \dfrac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$

For HCOOH, the conjugate base in $HCOO^-$ and its

$K_b = \dfrac{10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$

and for the conjugate base of HCN,

$K_b = \dfrac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$

26. Molar mass of $Sr(OH)_2$ = 121.62 g mol^{-1}

Concentration of $Sr(OH)_2 = \dfrac{19.23 \text{ g/L}}{121.62 \text{ g mol}^{-1}} = 0.158$ mol/L

$Sr(OH)_{2(aq)} \longrightarrow Sr^{2+}_{(aq)} + 2OH^-_{(aq)}$

$[Sr^{2+}] = [Sr(OH)_2] = 0.158$ M

and $[OH^-] = 2\,[(Sr(OH)_2]$

$= 2 \times 0.158 = 0.316$ M

$\therefore \quad [H^+] = \dfrac{1.0 \times 10^{-14}}{0.316}$ since $[OH^-][H^+] = 1.0 \times 10^{-14}$

$= 3.16 \times 10^{-14}$ M

and $pH = -\log 3.16 \times 10^{-14}$

$pH = 14 - \log 3.16$

$pH = 13.50$

27. The ionization of aniline in water is represented by the equation

$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH^+_3(aq) + OH^-(aq)$

$[C_6H_5NH^+_3] = [OH^-] = C\alpha$

when $\alpha = \sqrt{\dfrac{K_b}{C}} = \sqrt{\dfrac{4.27 \times 10^{-10}}{0.001}}$

$\alpha = 6.53 \times 10^{-4}$

Now, $[OH^-] = C\alpha$

$= 0.001 \times 6.53 \times 10^{-4}$

$[OH^-] = 6.53 \times 10^{-7}$ M

and $[H^+] = \dfrac{10^{-14}}{6.53 \times 10^{-7}} = 1.53 \times 10^{-8}$ M

and $pH = -\log(1.53 \times 10^{-8})$

$pH = 7.81$

For the ionization constant of the conjugate acid of aniline

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

$$K_a = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]} = \frac{K_w}{K_b}$$

K_a of the conjugate acid

$$= \frac{1.0 \times 10^{-14}}{4.27 \times 10^{-10}}$$

$K_a = 2.34 \times 10^{-5}$

28. Number of moles of sodium acetate added

$$= \frac{2.461 g}{82.03 g\,mol^{-1}}$$

$= 3.00 \times 10^{-2}\,mol = 0.0300\,mol$

$$CH_3COO^-(aq) + H_3O^+(aq) \rightleftharpoons CH_3COOH(aq) + H_2O$$

Number of moles of H_3O^+ added

$= (0.1000\,L)(0.120\,M) = 0.0120\,mol.$

There is excess weak base.

According to equation, 0.0120 mol of H_3O^+ react with 0.0120 mol of CH_3COO^- to form 0.0120 mol CH_3COOH.

The number of moles of acetate ion in excess is

$= 0.0300 - 0.012 = 0.0180\,mol$

The solution after mixing the two reagents contains 0.0120 mol of CH_3COOH and 0.0180 mol of CH_3COO^- in a total volume of 0.1500 L.

$$[CH_3COOH] = \frac{0.0120\,mol}{0.1500\,L} = 0.0800\,M$$

$$[CH_3COO^-] = \frac{0.0180\,mol}{0.1500\,L} = 0.1200\,M$$

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$

$pK_a = -\log 1.8 \times 10^{-5} = 5 - \log 1.8 = 4.74$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 4.74 + \log\left(\frac{1.20}{0.0800}\right)$$

$pH = 5.92$

29. At the instant of mixing, the total volume = 100 cm^3 = 0.1 L and concentration of silver ion is

$$[Ag^+] = \frac{0.001\,mol/L \times 0.025L}{0.1L}$$

$= 2.5 \times 10^{-4}\,M$

$$\text{and } [CO_3^{2-}] = \frac{0.01\,mol/L \times 0.075L}{0.1L}$$

$= 7.5 \times 10^{-4}\,M$

We are considering the reaction

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

and $Q_{sp} = [Ag^+]^2[CO_3^{2-}]$

$= (2.5 \times 10^{-4})^2(7.5 \times 10^{-4})$

$Q_{sp} = 4.69 \times 10^{-11}$

As $Q_{sp} > K_{sp}$ the solution is saturated and Ag_2CO_2 will precipitate.

30. We know that with the rise in temperature, vapour pressure of a liquid increases and at the boiling point, vapour pressure of a liquid becomes equal to the atmospheric pressure. A liquid with lower vapour pressure will boil at a higher temperature and vice-versa.

∴ Acetone has the lowest boiling point and water has the highest boiling point.

At 293 K, water evaporates least in the sealed container before equilibrium is reached.

31. All Arrhenius acids are Bronsted acids also since former furnishes H^+ ions in aq. solution while the later furnishes a proton, which is the same, however, Arrhenius bases must possess an OH^- ion whereas it is not a necessary condition for a Bronsted base.

32. Bronsted and Lewis bases are the same as the former accepts a proton, while the latter possesses a lone pair of electrons which readily accepts a proton.

However, Lewis acids are different from Bronsted acids, as former is an electron deficient species while the latter furnishes a proton.

33. $A \rightleftharpoons E \quad K = \frac{[E]}{[A]}$

$$K_1 = \frac{[B]}{[A]} \quad K_2 = \frac{[C]}{[B]} \quad K_3 = \frac{[D]}{[C]} \quad K_4 = \frac{[E]}{[D]}$$

$$K = K_1 \times K_2 \times K_3 \times K_4 = \frac{[E]}{[A]}$$

$= 1 \times 2 \times 3 \times 4 = 24$

Long Answer Questions

1. (1) $pH = pK_a + \log \frac{[salt]}{[acid]}$

$$4.91 = 4.76 + \log \frac{[salt]}{[acid]}$$

or $\log \frac{[salt]}{[acid]} = 0.15$

or $\frac{[salt]}{[acid]} = \text{antilog } 0.15 = 1.41$

$$\frac{\text{moles of salt / litre}}{\text{moles of acid / litre}} = 1.41$$

$$= \frac{(0.2/1000) \times 50}{(0.1/1000) \times V} = 1.41$$

or $V = 10/1.41 = 70.92\,ml$

(ii)	PCl_5	⇌	PCl_3	+	Cl_2
Initial moles	1		0		0
At equilibrium	1–0.5		0.5		0.5

(as it is 50% dissociated, x = 0.5)

	= 0.5	0.5	0.5
Total number of moles	= 1.5		

If 'P' is the total pressure, then $p(PCl_5) = \frac{0.5 \times P}{1.5}$,

$$p(PCl_3) = \frac{0.5 \times P}{1.5}, \text{ and } p(Cl_2) = \frac{0.5 \times P}{1.5}$$

Now,

$$\therefore K_p = \frac{p(PCl_3) \times p(Cl_2)}{p(PCl_5)} = \frac{(P/3)(P/3)}{(P/3)} = \frac{P}{3}$$

or $3K_p = P$

2. (i) The 0.10 M solution of HCl contains 0.10 mol/L of H^+, because HCl is a strong acid. This is the concentration of H^+ before the CH_3COOH is added. Then we add 0. 10 M CH_3COOH into it. The initial concentrations of H^+ and CH_3COOH

$[H^+]_{initial} = 0.10$ M

$[CH_3COOH]_{initial} = 0.10$ M

Now we have to consider the ionization of the acetic acid.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Since there is no CH_3COO^- ion present initially, some of it must form by the dissociation of the CH_3COOH. Let the concentration of CH_3COOH decreases by x and the concentration of H^+ and CH_3COO^- increases by x, and then add the initial concentrations and the changes to get the equilibrium quantities.

	Initial Molar Concentrations	Change	Equilibrium Molar Concentrations
H^+	0. 10	+x	$0.10 + x \approx 0.10$
CH_3COO^-	0	+x	x
CH_3COOH	0. 10	–x	$0.10 - x \approx 0.10$

When a solution contains both a strong acid and a weak acid, it is the concentration of the strong acid that determines the pH of the solution.

We expect x to be small, so we've assumed $0.10 \pm x \approx 0.10$.

Substituting into the K_a expression

$$1.8 \times 10^{-5} = K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{(0.10)(x)}{(0.10)}$$

$$x = 1.8 \times 10^{-5}$$

We see that x is very small as compared to 0. 10, so in the solution $[H^+] = 0.10$ M. This gives pH of 1. 00

(ii) We begin with the chemical equation and the equilibrium law,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

	$H_2O + CH_3COOH \rightleftharpoons$	H_3O^+	$+ CH_3COO^-$
Initial molarity	0.50	0	0
At equilibrium	$(0.50 - x)$	x	x

Substituting these values into the equilibrium expression gives us $(x)(x)/(0.50 - x) = 1.8 \times 10^{-5}$

As x is very small thus x will be negligible compared to 0. 50; thus

$0.50 - x \approx 0.50$

Our equation then becomes

$x^2/0.50 = 1.8 \times 10^{-5}$ or $x = 3.0 \times 10^{-3}$

Equilibrium Concentrations (M)

H^+	3.0×10^{-3}
CH_3COO^-	3.0×10^{-3}
CH_3COOH	0. 50

3. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$

$K_{a_1} = [H^+][HCO_3^{-1}]/[H_2CO_3] = 4.3 \times 10^{-7}$

And $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$K_{a_2} = [H^+][CO_3^{2-}]/[HCO_3^-] = 5.6 \times 10^{-11}$

As K_{a_1} is much larger than K_{a_2}, we can safely assume that nearly all the hydrogen ion in the solution is derived from the first step of the dissociation. In addition, only very little amount of the HCO_3^- ion formed in the first step will undergo further dissociation. On the basis of this we can calculate the equilibrium concentrations of H^+ and HCO_3^- by using the expression for K_{a_1} alone.

$K_{a_1} = [H^+][HCO_3^-]/[H_2CO_3]$

If we consider x be the number of moles per litre of H_2CO_3 that dissociate, we obtain, from the stoichiometry of the first step, x mol/L of H^+ and x mol/L of HCO_3^-. At equilibrium, there will be (0. 10 – x) mol/L of H_2CO_3 remaining.

	Initial Molar Concentrations	Change	Equilibrium Molar Concentrations
H^+	0. 0	+x	x
HCO_3^-	0. 0	+x	x
H_2CO_3	0. 10	–x	$0.10 - x \approx 0.10$

As x is very small, we may assume that x will be negligible in comparison to 0. 10 and thus equilibrium concentration of $[H_2CO_3] = 0.10 - x = 0.10$ M

substituting these equilibrium concentration values into the expression for K_{a_1} we have

$(x)(x)/0.10 = 4.3 \times 10^{-7}$

$x^2 = 4.3 \times 10^{-8}$ or $x = 2.07 \times 10^{-4}$

therefore, the equilibrium concentrations from first dissociation are

$[H^+] = 2.07 \times 10^{-4}$M; $[HCO_3^-] = 2.07 \times 10^{-4}$M;

$[H_2CO_3] = 0.10$ M

By employing K_{a_2}, we can now calculate the equilibrium concentration of CO_3^{2-}

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Consider y be the number of moles per litre of HCO_3^- that dissociates. Thus, the total hydrogen ion concentration from both the first and second dissociations will be $(2.07 \times 10^{-4} + y)$, and y mol/L of CO_3^{2-}. At equilibrium, there will be $(2.07 \times 10^{-4} - y)$ mol / L of HCO_3^-

	Initial Concentrations	Change	Equilibrium Concentrations
H^+	2.07×10^{-4}	$+y$	$2.07 \times 10^{-4} + y$
CO_3^{2-}	0.0	$+y$	y
HCO_3^-	2.07×10^{-4}	$-y$	$2.07 \times 10^{-4} - y$

Make the assumption that y will be negligible as compared to 2.07×10^{-4}. Our equilibrium concentrations then become

$[H^+] = 2.07 \times 10^{-4} + y \approx 2.07 \times 10^{-4}$ M

$[CO_3^{2-}] = y$

$[HCO_3^-] = 2.07 \times 10^{-4} - y \approx 2.07 \times 10^{-4}$ M

Note that the value of y is very much smaller than the value of x obtained for the first step in the dissociation.

By substituting these equilibrium concentration values in Ka_2, we obtain

$$Ka_2 = \frac{(2.1 \times 10^{-4})(y)}{(2.1 \times 10^{-4})} = 5.6 \times 10^{-11}$$

$y = 5.6 \times 10^{-11}$

Therefore equilibrium concentrations of all species,

$[H^+] = 2.07 \times 10^{-4}$ M ; $[HCO_3^-] = 2.07 \times 10^{-4}$ M; $[CO_3^{2-}] = 5.6 \times 10^{-11}$ M ; $[H_2CO_3] = 0.10$M

4.

	$2N_2(g)$	+ $O_2(g) \rightleftharpoons$	$2N_2O(g)$
Initial moles :	0.482	0.933	0
moles at equilibrium:	$(0.482 - 2x)$	$(0.933 - x)$	$2x$
Conc. at equilibrium :	$\left(\frac{0.482-2x}{10}\right)$	$\left(\frac{0.933-x}{10}\right)$	$\frac{2x}{10}$

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]} = \frac{\left(\frac{2x}{10}\right)^2}{\left(\frac{0.482-2x}{10}\right)^2\left(\frac{0.933-x}{10}\right)}$$

$= 2.0 \times 10^{-37}$

$10x^2 + 1.016 \times 10^{-37} x - 0.1082 \times 10^{-37} = 0$

This is a quadratic equation, therefore

$$x = \frac{-1.016 \times 10^{-37} + \sqrt{1.03 \times 10^{-74} + 4.328 \times 10^{-37}}}{20}$$

$x = 3.3 \times 10^{-20}$

$$[N_2O]_{eq} = \frac{2x}{10} = \frac{2}{10} \times 3.3 \times 10^{-20} = 6.6 \times 10^{-21} \text{ M}$$

$$[N_2]_{eq} = \frac{0.482 - 2 \times 3.3 \times 10^{-20}}{10} \approx \frac{0.482}{10} = 0.0482 \text{ M}$$

$$\text{and } [O_2]_{eq} = \frac{0.933 - x}{10} \approx \frac{0.933}{10} = 0.0933 \text{ M}$$

5. $$\text{pH} = (14 - pK_b) + \log\frac{[\text{base}]}{[\text{salt}]}$$

$$\text{pH} = (14 - 4.75) + \log\frac{[\text{base}]}{[\text{salt}]}$$

For a buffer solution of pH 8.65, suppose V ml = volume of NH_4OH added, then

$$8.65 = 9.25 + \log\left(\frac{\frac{0.3\,V}{30+V}}{\frac{0.2 \times 30}{30+V}}\right)$$

$$-0.6 = \log\left(\frac{0.3\,V}{6}\right)$$

$$\frac{0.1V}{2} = \text{antilog}\,(-0.6) = 0.25$$

$\therefore$ V = 5 mL

For a buffer solution of pH 10, we have

$$10 = 9.25 + \log\left(\frac{\frac{0.3\,V}{30+V}}{\frac{0.2 \times 30}{30+V}}\right)$$

$$0.75 = \log\left(\frac{0.1V}{2}\right) \quad \text{and} \quad V = 12.94 \text{ mL}$$

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. As equilibrium constant has increased with temperature, the reaction is endothermic (in the forward direction).
2. Concentration of 10^{-8} mol dm^{-3} indicates that the solution is very dilute. Hence, the contribution of H_3O^+ concentration from water is significant and should also be included for the calculation of pH.

Short Answer Questions

1. The ionic product of water will *increase* with increase in temperature.

   On increasing temperature the degree of ionisation of water increases (i.e. more ions are formed) and so there occurs an increase in ionic product of water.
2. The value of Q (reaction quotient) for the given reaction is

$$Q = \frac{p_{NO}^2 \times p_{Br_2}^2}{p_{NOBr}^2}$$

$$= \frac{(0.40)^2 \times (0.20)}{(0.50)^2} = 0.13$$

   Since the value of K_p (equilibrium constant) given is $K = 0.0225$ which is smaller than that of Q (i.e. 0.13). Thus

   $K_p < Q$

   So the reaction should proceed *spontaneously* in the *reverse direction.*
3. Let *x* mole of $NH_4HS(s)$ is added to flask containing 0.5 moles of $NH_3(g)$.

$NH_4HS(s) \rightleftharpoons$	$NH_3(g)$ +	$H_2S(s)$	
x mole	0	*y*	Initial conc.
	$\frac{\alpha}{2}$		Conc. at equilib.

$$K_p = P_{NH_3} \times P_{H_2S}$$

$$0.11 = (y + 0.5)(y)$$

or $y^2 + 0.5y - 0.11 = 0$

$$y = 0.1653 \text{ atm.}$$

$\therefore$ $P_{NH_3} = 0.5 + 0.1653 = \mathbf{0.6653}$ atm and

$P_{H_2S} = \mathbf{0.1653\ atm.}$

4. Suppose solubility of AB = a mol L^{-1}. Then $AB \rightleftharpoons A^+ + B^-$, $K_{sp} = [A^+][B^-] = a \times a = a^2$

$\therefore$ $a = \sqrt{K_{sp}}$

Suppose solubility of salt $XY_2 = b$ mol L^{-1}. Then

$XY_2 \rightleftharpoons X^{2+} + 2Y^-$, $K_{sp} = [X^{2+}][Y^-]^2 = b(2b)^2$ i.e.,

$4b^3 = K_{sp}$ or $b = (K_{sp/4})^{1/3}$

Obviously $b > a$ (as K_{sp} have values with negative powers of 10). Hence, salt XY_2 is more soluble.

5. The K_P value for the given reaction is

$$K_P = P_{NH_3} \times P_{H_2S} \qquad [\because P_{NH_4HS} = 1]$$

Since equal number of moles of NH_3 (g) and H_2S (g) formed by dissociation of NH_4HS so pressure exerted by each [i.e. NH_3 (g) and H_2S (g)] must also be equal

$\therefore$ $P_{NH_3} = P_{H_2S}$

Total pressure = $P_{NH_3} + P_{H_2S}$

$$\therefore \quad P_{NH_3} = P_{H_2S} = \frac{\text{Total Pressure}}{2}$$

$$= \frac{1.12}{2} \text{ atmosphere}$$

$$= 0.56 \text{ atmosphere}$$

Hence, $K_P = 0.56 \times 0.56 = \mathbf{0.3136.}$

6.

	$BaSO_4(s)$	$\rightleftharpoons Ba^{2+}(aq)$	$+ SO_4^{2-}(aq)$
At t = 0	1	0	0
At equilibrium in water	1–S	S	S
At equilibrium in the presence of sulphuric acid	1–S	S	(S+0.01)

K_{sp} for $BaSO_4$ in water = $[Ba^{2+}][SO_4^{-2}] = [S][S] = S^2$

But $S = 8 \times 10^{-4}$ mol dm^{-3}

$\therefore$ $K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$ ...(1)

The expression for K_{sp} in the presence of sulphuric acid will be as follows :

$K_{sp} = (S)(S + 0.01)$ ...(2)

Since value of K_{sp} will not change in the presence of sulphuric acid, therefore from (1) and (2)

$(S)(S + 0.01) = 64 \times 10^{-8}$

$\Rightarrow$ $S^2 + 0.01\,S = 64 \times 10^{-8}$

$\Rightarrow$ $S^2 + 0.01\,S - 64 \times 10^{-8} = 0$

$$\Rightarrow \quad S = \frac{-0.01 \pm \sqrt{(0.01)^2 + \left(4 \times 64 \times 10^{-8}\right)}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + \left(256 \times 10^{-8}\right)}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + \left(1 + 256 \times 10^{-2}\right)}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1 + 0.256}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1.256}}{2}$$

$$= \frac{-10^{-2} + \left(1.12 \times 10^{-2}\right)}{2}$$

$$= \frac{-(-1 + 1.12) \times 10^{-2}}{2} = \frac{0.12}{2} \times 10^{-2}$$

$= 6 \times 10^{-4}$ mol dm^{-3}

7. pH of Solution A = 6

Therefore, concentration of $[H^+]$ ion in solution A = 10^{-6} mol L^{-1}

pH of Solution B = 4

Therefore, Concentration of $[H^+]$ ion concentration of solution B = 10^{-4} mol L^{-1}

On mixing one litre of each solution, total volume

= 1 L + 1 L = 2L

Amount of H^+ ions in 1L of solution A

= Concentration × volume V

= 10^{-6} mol × 1 L

Amount of H^+ ions in 1L of solution B = 10^{-4} mol × 1L

$\therefore$ Total amount of H^+ ions in the solution formed by mixing solution A and B is (10^{-6} mol + 10^{-4} mol)

This amount is present in 2L solution.

$$\therefore \text{ Total } [H^+] = \frac{10^{-4}(1 + 0.01)}{2} = \frac{1.01 \times 10^{-4}}{2} \text{ mol } L^{-1}$$

$$= \frac{1.01 \times 10^{-4}}{2} \text{ mol } L^{-1}$$

$$= 0.5 \times 10^{-4} \text{ mol } L^{-1}$$

$$= 5 \times 10^{-5} \text{ mol } L^{-1}$$

$$pH = -\log\left[H^+\right] = -\log\left(5 \times 10^{-5}\right)$$

$$= -\left[\log 5 + (-5 \log 10)\right]$$

$$= -\log 5 + 5$$

$$= 5 - \log 5$$

$$= 5 - 0.6990$$

$$= 4.3010 = 4.3$$

8. K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$

Let S be the solubility of $PbCl_2$.

	$PbCl_2(s)$	$\rightleftharpoons Pb^{2+}(aq)$	$+ 2Cl^-(aq)$
Concentration of species at t = 0	1	0	0
Concentration of various species at equilibrium	1–S	S	2S

$$K_{sp} = \left[Pb^{2+}\right]\left[Cl^{-1}\right]^2 = (S)(2S)^2 = 4S^3$$

$$K_{sp} = 4S^3$$

$$S^3 = \frac{K_{sp}}{4} = \frac{3.2\times10^{-8}}{4} \text{mol L}^{-1} = 8\times10^{-9} \text{mol L}^{-1}$$

$$S = \sqrt[3]{8\times10^{-9}} = 2\times10^{-3} \text{mol L}^{-1} \therefore S = 2\times10^{-3} \text{mol L}^{-1}$$

Molar mass of $PbCl_2 = 278$

∴ Solubility of $PbCl_2$ in g L^{-1}

$= 2 \times 10^{-3} \times 278$ g L^{-1}

$= 556 \times 10^{-3}$ g L^{-1}

$= 0.556$ g L^{-1}

To get saturated solution, 0.556 g of $PbCl_2$ is dissolved in 1 L water.

0.1 g $PbCl_2$ is dissolved in $\frac{0.1}{0.556}$ L = 0.1798 L water.

To make a saturated solution, dissolution of 0.1 g $PbCl_2$ in 0.1798 L ≈ 0.2 L of water will be required.

Long Answer Questions

1. Tooth enemel consists of an insoluble substance known as hydroxyaptite, $Ca_5(PO_4)_3OH$. The dissolving of this substance from the teeth is called *demineralization*, and its formation is called *remineralization.* In the mouth there is an equilibrium.

$$Ca_5(PO_4)_3OH(s) \underset{\text{(Re mineralization)}}{\overset{\text{(de mineralization)}}{\rightleftharpoons}}$$

$$5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

This equilibrium is established even with healthy teeth. However when sugar is absorbed on teeth and ferments, H^+ is produced that upsets the equilibrium by combining with OH^- to form water and with PO_4^{3-} to form HPO_4^{2-}. It thus removes OH^- and PO_4^{3-} and cause more of $Ca_5(PO_4)_3$ OH to dissolve, resulting in tooth decay.

Fluoride helps to prevent tooth decay by replacing OH^- in hydroxyaptite. the resulting $Ca_5(PO_4)_3$ F is very resistant to acid attack.

2.

Reaction	H_2	$+ \; I_2$	$\rightleftharpoons$ 2HI
Initial amounts (mol)	1	2	3
Change (mol)	$-x$	$-x$	$+2x$
Equilibrium amounts (mol)	$(1-x)$	$(2-x)$	$(3+2x)$
Equilibrium concentration (mol/L)	$\frac{(1-x)}{1}$	$\frac{(2-x)}{1}$	$\frac{(3+2x)}{1}$

$$\therefore \quad K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3+2x)^2}{(1-x)(2-x)} = 45.9$$

or $$45.9 = \frac{9+4x^2+12x}{2-3x+x^2}$$

or $45.9(2-3x+x^2) = 9+4x^2+12x$

or $41.9x^2 - 149.7x + 82.8 = 0$

Solving for x, we have

$$x = \frac{-(-149.7) \pm \sqrt{(-149.7)^2 - 4\times41.9\times82.8}}{2\times41.9}$$

$$= \frac{149.7 \pm \sqrt{22,410.09 - 13,877.28}}{83.8}$$

$= 0.684$ or 2.88

Hence, $x = 2.88$ is not permissible, because $2.88 > 1$.

Hence, $x = 0.684$

Thus;

$$[H_2] = \left(\frac{1-x}{1}\right)\frac{mol}{L} = \frac{(1-0.684)}{L}\frac{mol}{L} = 0.316\frac{mol}{L}$$

$$[I_2] = \left(\frac{2-x}{1}\right)\frac{mol}{L} = (2-0.684)\frac{mol}{L} = 1.316\frac{mol}{L}$$

$[HI] = (3+2x)$ mol/L $= (3 + 2 \times 0.684)$ mol/L $= 4.38$ mol/L.

3. $\Delta G = \Delta G^\ominus + RT \ln Q$

$\Delta G^\ominus$ = Change in free energy as the reaction proceeds

ΔG = Standard free energy change

Q = Reaction quotient

R = Gas constant

T = Absolute temperature

Since $\Delta G^\ominus = -RT \ln K$

$$\therefore \ \Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

If Q < K , ΔG will be negative. Reaction proceeds in the forward direction.

If Q = K, ΔG = 0, no net reaction.

[Hint : Next relate Q with concentration of CO, H_2, CH_4 and H_2O in view of reduced volume (increased pressure). Show that Q < K and hence the reaction proceeds in forward direction.]

CHAPTER TEST

1. If one of the products (usually gases) are allowed to escape i.e. reaction is carried out in an open system, reversible reactions become irreversible.

2. If ionic product > solubility product, then precipitation takes place.

3. Ice begins to melt.

4.

	2HI $\rightleftharpoons$	H_2	$+ \; I_2$
Initial	2 mole	0	0
At equilibrium	$2-2x$	x	x

Now x = 22% = 0.22

$2-2(0.22)$	0.22	0.22
$2-0.44$	0.22	0.22
1.56	0.22	0.22

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.22\times0.22}{(1.56)^2} = 0.0198$$

5. Na_2CO_3 is a salt of weak acid and strong base thus on adding in water anion undergoes hydrolysis to form a weak carbonic acid H_2CO_3 while a strong base NaOH is formed by hydrolysis of cation which makes the solution alkaline.

In $CuSO_4$ it is a salt of strong acid and weak base thus on addition of water cation hydrolysis occurs due to which a weak base $Cu(OH)_2$ gets formed while anion hydrolysis results into formation of strong acid (H_2SO_4) which makes the solution acidic.

6. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Initial amount of $PCl_5 = 2$ moles (given)

%age dissociation at equilibrium = 40% = 0.40

PCl_5 dissociated at equilibrium $= 2 \times 0.4 = 0.8$

Amounts of PCl_5, PCl_3 and Cl_2 at equilibrium will be

$PCl_5 = 2 - 0.8 = 1.2$ mole ; $PCl_3 = 0.8$ mole;

$Cl_2 = 0.8$ mole

Molar concentrations in 2 L vessel

$[PCl_5] = 1.2/2 = 0.6 \text{ mol L}^{-1}$

$[PCl_3] = 0.8/2 = 0.4 \text{ mol L}^{-1}$

$[Cl_2] = 0.8/2 = 0.4 \text{ mol L}^{-1}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ mol L}^{-1}$$

Now for this reaction

$K_p = K_c(RT)^{\Delta n}$

since $\Delta n = 2 - 1 = 1$

$= 0.267 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times (327 + 273$

$= 0.267 \times 0.0821 \times 600 = 13.152$ atm

7. (i) $[Mg^{2+}] = 0.10 \text{ M} = 10^{-1}\text{M}$; $K_{sp} = 1.0 \times 10^{-11}$

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$[OH^-]^2 = K_{sp} / [Mg^{2+}] = 10^{-11}/10^{-1} = 10^{-10}$ hence $[OH^-] = 10^{-5}$M

$K_w = [H_3O^+][OH^-]$

and the value of $K_w = 10^{-14}$

$[H_3O^+] = K_w / [OH^-] = 10^{-14} / 10^{-5} = 10^{-9}$

$pH = -\log [H_3O^+] = -\log [10^{-9}] = 9$

(ii) If ionic product < solubility product, the solution is unsaturated, if ionic product is equal to solubility product , the solution is saturated and if ionic product > solubility product then the solution is super–saturated.

8

Chapter

Redox Reactions

INTRODUCTION

Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as oxidation-reduction or redox reactions. A number of phenomena, both physical as well as biological, industrial, metallurgical and agricultural areas are concerned with redox reactions.

These reactions have wide applications in areas like burning of fuels, electrochemical processes etc. Recently, environmental issues like hydrogen economy and development of ozone hole also involves redox reaction.

CLASSICAL CONCEPT OF OXIDATION AND REDUCTION REACTIONS

According to classical concept, **oxidation** is that process which involve addition of oxygen or electronegative element or removal of hydrogen or electropositive element. For example

(a) $2Mg + O_2 \longrightarrow 2MgO$ (Addition of oxygen)
(b) $H_2S + Cl_2 \longrightarrow 2HCl + S$ (Removal of hydrogen)
(c) $SnCl_2 + Cl_2 \longrightarrow SnCl_4$ (Addition of electronegative element)
(d) $2KI + Cl_2 \longrightarrow 2KCl + I_2$ (Removal of electropositive element)

An **oxidizing agent** is that substance which provides oxygen or any other electronegative element or removes hydrogen or any other electropositive element in a chemical reaction.

According to classical concept, **reduction** is that process which involve addition of hydrogen or electropositive element or removal of oxygen or electronegative element. For example,

(a) $Br_2 + H_2S \longrightarrow 2HBr + S$ (Addition of hydrogen)
(b) $CuO + C \longrightarrow Cu + CO$ (Removal of oxygen)
(c) $2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$ (Removal of electronegative element)
(d) $CuCl_2 + Cu \longrightarrow Cu_2Cl_2$ (Addition of electropositive element)

A **reducing agent** is that substance which provides hydrogen or any other electropositive element or removes oxygen or any other electronegative element in a chemical reaction.

REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER

Oxidation is defined as a process which involve loss of electrons by an atoms or an ion. The loss of electrons may result in increase in positive charge or decrease in negative charge. For example,

(a) $Mg \longrightarrow Mg^{2+} + 2e^-$
(b) $S^{2-} \longrightarrow S + 2e^-$
(c) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
(d) $[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^-$

Reduction is defined as a process which involve gain of electrons by an atom or an ion. The gain of electrons may result in decrease in positive charge or increase in negative charge. For example,

(a) $Hg^{2+} + e^- \longrightarrow Hg^+$
(b) $Cl_2 + 2e^- \longrightarrow 2Cl^-$
(c) $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$
(d) $[Fe(CN)_6]^{3-} + 3e^- \longrightarrow [Fe(CN)_6]^{6-}$

According to electronic concept, oxidising agent is a substance which accepts electrons whereas reducing agent is a substance which involve loss of electrons during a redox reaction.

$$\text{Reducing agent} \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} \text{Oxidising agent} + \text{Electrons.}$$

Competitive Electron Transfer Reactions

When a metallic rod of Zn is placed in a solutions of $Cu(NO_3)_2$ folllowing changes are observed:

(a) Zinc rod starts dissolving with reddish brown deposit.

(b) Blue colour of $Cu(NO_3)_2$ starts fading and ultimately become colourless (Zn^{2+} ions are formed in solution, their presence can be detected by passing H_2S through solution).

(c) Reaction is exothermic and solution become hot.

(d) Solution remains electrically neutral.

- Reactions in solution
  $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
- Electron transfer reaction to Cu and $AgNO_3$ solution
  $Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
- Electron transfer reaction to Co and $NiSO_4$
  $Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$

This competition for release of electrons incidently reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order : Zn > Cu > Ag. We would love to make our list more vast and design a **metal activity series or electrochemical series**.

OXIDATION NUMBER

The oxidation number is defined as the charge which an atom appears to possess when all other atoms are removed from it as ions. The oxidation number of an atom can be zero, positive, negative or a fraction. For the same atom oxidation number varies from compound to compound and thus it differs from valency. The term interchangeably used with oxidation number is oxidation state.

(i) If electrons are gained by an atom in the formation of compound, oxidation number is given negative sign.

(ii) If electrons are lost by an atom in the formation of compound, oxidation number is given positive sign.

(iii) It represents the real charge in case of ionic compounds and represents the imaginary charge in case of covalent compounds.

Valency

Valency is the capacity of an element to combine with other elements. It is purely a number and has no plus or minus sign associated with it. For example, oxidation no. of Fe in Fe_3O_4 is 8/3 while its valency is both 2 and 3, Fe_3O_4 being a mixture of $FeO + Fe_2O_3$.

Rules for Assigning Oxidation Number

(a) Oxidation number of an atom in its elementary state is always zero. For example, in N_2 , Cl_2. H_2 , O_2 , P_4 , S_8 , Zn , etc., the oxidation number of each atom is zero.

(b) Oxidation number of hydrogen is + 1 in all its compounds except in metal hydrides e.g. MgH_2 , CaH_2 etc. where it is –1.

(c) Oxidation number of oxygen is –2 in most of its compounds except peroxides (like H_2O_2 , Na_2O_2 , BaO_2 etc.) where it is – 1, superoxides like KO_2 RbO_2, etc., in which oxidation number of oxygen is – 1/2 and in oxygen fluoride (OF_2) it is + 2, and dioxygen difluoride (O_2F_2) where it is +1.

(d) Fluorine is the most electronegative element and is assigned an oxidation number of – 1 in all its compounds (e.g., OF_2 , NF_3 , IF_7, etc.). For other halogens the oxidation number is –1 except when they are bonded to more electronegative element. For example ClO_2 , IF_5 where chlorine has oxidation number + 4 and iodine has + 5 respectively. In oxoacids and oxanions, Cl, Br and I have positive oxidation numbers.

(e) In sulphides, the oxidation number of sulphur is – 2.

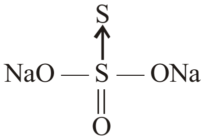
(f) The oxidation number of an ion is the same as its charge. For example, the oxidation number of Li^+ , $Al^{3+,}$ SO_4^{2-} , PO_4^{3-} and $[Fe(CN)_6]^4$ are +1, +3, –2, –3 and –4 respectively

(g) Oxidation number of alkali metals (e.g., Li, Na, K, etc.) is always + 1and those of alkaline earth metals (Be, Mg, Ca, etc.,) is always + 2.

(h) Sum of the oxidation numbers of all atoms in the neutral molecule is always zero [e.g., in CO_2 , Sum of oxidation numbers of carbon and two oxygen atoms is equal to zero], while for an ion the sum of oxidation number is equal to its charge e.g., in $[Fe(CN)_6]^{3-}$ the sum of oxidation numbers of Fe and six CN^- must be equal to – 3.

(i) The oxidation number of metals in carbonyl compounds is always zero i.e. oxidation number of Ni in $Ni(CO)_4$ and Fe in $Fe(CO)_5$ is zero.

(j) In compounds formed by union of two elements, more electronegative atom have negative oxidation state whereas less electronegative element possess positive oxidation number. For example, N shows oxidation number –3 in NH_3 and +3 in NF_3. Sometimes same atoms in a compound show different O.S. For example : $Na_2S_2O_3$, the oxidation state of the two S-atoms is –2 and +6.



$$NaO-\overset{\overset{S}{\uparrow}}{\underset{\underset{O}{\|}}{S}}-ONa$$

The acceptor S-atom has an oxidation number of –2. The oxidation number of the other S-atom can be calculated as :

$2(+1)+3(-2)+x+1(-2)=0$

(for Na) (for O) (for coordinates)

or $+2-6+x-2=0$

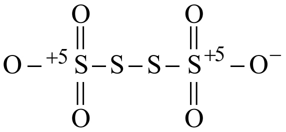
$\Rightarrow$ $x=+6$

Fractional Oxidation States

Some elements shows fractional oxidation state. This is not feasible practically as electrons can not be shared in fractions. In actual practise this fractional oxidation state is the average oxidation state of element under consideration and differemt atoms of same element in these molecules possess different oxidation states.

For example : oxidation state of oxygen in superoxides of alkali metals (KO_2, SO_2, RbO_2) is –1/2

In $S_4O_6^{2-}$ ion S has fractional oxidation state.



$$O-\overset{+5}{}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+5}{}-O^-$$

O.S. of middle S atoms is zero each and O.S. of end S atoms is +5 each. Hence, average oxidation state = 10/4 = 2.5

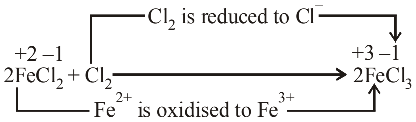
In Fe_3O_4, Fe shows its oxidation state as 8/3 as it is a mixed oxide and can be written as Fe^{II} $Fe_2^{III}O_4$. Similarly oxidation states of boron in B_4O_{10} and B_5H_9 is –2.5 and –1.8 respectively.

Note: The highest oxidatioin number of a representative element is the group number for the first two groups and the group number minus 10 for the other groups.

This concept of oxidation number can be also used to define oxidatioin and reduction.

Oxidation and Reduction in Terms of Oxidation Numbers

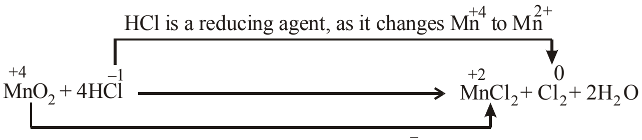
A chemical change involving an increase in the oxidation number is called oxidation whereas a chemical change involving a decrease in the oxidation number is called reduction



$$2\overset{+2\,-1}{FeCl_2}+Cl_2\longrightarrow 2\overset{+3\,-1}{FeCl_3}$$

Oxidizing and Reducing Agents in Terms of Oxidation Number

The oxidizing agent is that substance whose oxidation number decreases and as a consequence it increases the oxidation number of other substance. On the other hand, a reducing agent is that substance whose oxidation number increases. Thus reducing agent is that substance which cause decrease in oxidation number of other substance in a chemical reaction. For example :



$$\overset{+4}{Mn}O_2+4H\overset{-1}{Cl}\longrightarrow \overset{+2}{Mn}Cl_2+\overset{0}{Cl_2}+2H_2O$$

Summary Describing Oxidation and Reduction

Term	Change in oxidation number	Change in electrons
Oxidation	Increase	Loss of electrons
Reduction	Decrease	Gain of electrons
Oxidising agent	Decrease	Accepts electrons
Reducing agent	Increase	Donates electrons
Substance oxidised	Increase	Loses electrons
Substance reduced	Decrease	Gain electrons

Types of Oxidation-Reduction (Redox) Reactions

(i) Combination reactions: Denoted as, $A + B \rightarrow C$

Here either A or B or both must be in elemental form for a redox reaction. For example,

$$C(s)+O_2(g)\xrightarrow{\Delta}C^{+4}O_2^{-2}(g)$$

(ii) Decomposition reactions: These are opposite of combination reactions. For example,

$$2Na^{+1}H^{-1}(s)\xrightarrow{\Delta}2Na(s)+H_2^0(g)$$

Note: All decomposition reactions are not redox reactions

(iii) Displacement reactions: Denoted as, $C + AB \rightarrow BC + A$

These are of two types

(a) **Metal displacement :** A least reactive metal in reaction is displaced by more reactive metal.

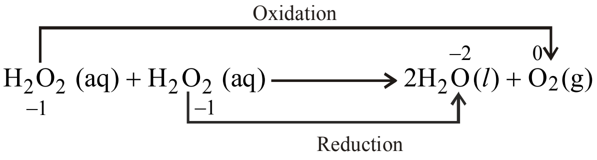
$$V_2^{+5}O_5^{-2}(s)+5Ca^0(s)\xrightarrow{\Delta}2V^0(s)+5Ca^{+2}O^{-2}(s)$$
$$Cr_2^{+3}O_3^{-2}(s)+2Al^0(s)\xrightarrow{\Delta}Al_2^{+3}O_3^{-2}(s)+2Cr^0(s)$$

(b) **Non-metal displacement :** This generally includes hydrogen displacement and rarely displacement of oxygen

$$Ca^0(s)+2H_2^{+1}O^{-2}(l)\rightarrow Ca^{+2}\left(\overset{-2\ +1}{OH}\right)_2+\overset{0}{H_2}(g)$$
$$Zn^0(s)+2H^{+1}Cl^{-1}(aq)\rightarrow Zn^{+2}Cl_2^{-1}(aq)+H_2(g)$$
$$2\overset{+1-1}{KX}(aq)+\overset{0}{X_2}(g)\rightarrow 2\overset{+1-1}{KX1}(aq)+X_2(g|l|s)$$

F_2 can replace, chloride, bromide and iodide whereas Cl_2 can replace bromide and iodide. Br_2 can replace iodide ionly. As Br_2 and I_2 are coloured and soluble in CCl_4 these reactions forms the basis for their tests known as 'Layer Test'.

(iv) Disproportionation: There are some substances which function as both oxidising as well as reducing agents e.g., H_2O_2, SO_2, H_2SO_3, HNO_2, O_3, etc. This can be explained by the following example,



$$\underset{-1}{H_2O_2}(aq)+\underset{-1}{H_2O_2}(aq)\longrightarrow 2H_2\overset{-2}{O}(l)+\overset{0}{O_2}(g)$$

Thus H_2O_2 is acting both as oxidising as well as reducing agent. Such molecules undergo disproportionation.

BALANCING OF REDOX EQUATIONS

Following two methods are applied for the balancing of redox reactions

Oxidation Number Method

This method is based on the fact that the number of electrons gained during reduction must be equal to the number of electrons lost during oxidation. Following steps are to be followed while balancing redox equations by this method:

(a) Write the skeletal redox equation representing the chemical change.
(b) With the help of oxidation number of elements, find out which atom is undergoing oxidation and reduction.
(c) Write separate equation for the atoms undergoing oxidation and reduction.
(d) Add the respective electrons on the right for oxidation and on the left for reduction equation.
(e) Multiply the oxidation and reduction equations by suitable integers so that total electrons lost in one equation is equal to the total electrons gained by other equation.
(f) Transfer the coefficients of the oxidising and reducing agents and their products to all the concerned molecules or ions.
(g) Now balance hydrogen and oxygen.
(h) If the reaction is taking place in acidic medium, add H^+ ions to the side deficient in hydrogen atom.
(i) If the reaction is taking place in alkaline medium, add water to the side deficient in hydrogen and simultaneously add equal number of OH^- ion to the other side of the equation.

Ion electron method (half reaction method): Balancing of redox equation by this method involves the following steps

(a) Find out the element whose oxidation numbers have changed.
(b) Divide the complete equation into two half reactions, one representing oxidation and the other reduction.
(c) Balance the atoms in each half reactions separately according to the following steps.
  (i) Balance the atoms other than H and O.
  (ii) Add electrons to whichever side is necessary to equate the charges.
  (iii) If the reaction is taking place in acidic or neutral medium, oxygen atoms are balanced by adding molecules of water to the side deficient of oxygen atom while hydrogen atoms are added to the side deficient in hydrogen atoms.
  (iv) If the reaction is in alkaline medium, every excess of oxygen, atom is balanced by adding one H_2O to the same side and $2OH^-$ to the other side. If hydrogen is still unbalanced add one OH^- for every excess of H^+ on the same side and one H_2O on the other side.
(d) Multiply the two half reactions by suitable integers to cancel out the number of electrons gained and lost in two half reactions.
(e) Add the two balance half reactions and cancel any term common to both sides.

OXIDATION-REDUCTION TITRATIONS

These are also called redox titrations. The chemical reactions proceed with transfer of electrons i.e, simultaneous loss and gain of electrons among the reacting ions in solution. These titrations are named after the reagent used. For ex:

Permanganate Titrations

In these titrations, potassium permanganate is used as oxidising agent in acidic medium. Acidic medium is maintained by addition of dilute sulphuric acid. As $KMnO_4$ is coloured, it acts as self indicator.

$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\,(O)$.

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

Before the end point, the solution remains colourless but after the equivalence point, one extra drop of $KMnO_4$ solution imparts pink colour. It is used to estimate oxalates, oxalic acid, H_2O_2, ferrous salts etc.

Dichromate Titrations

In these titrations, potassium dichromate is used as an oxidising agent in acidic medium. Acidic medium is maintained by addition of dilute sulphuric acid.

It acts as an oxidising agent as follows:

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$

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

It is mainly used for the estimation of ferrous salts and iodides. During these titrations indicators are used.

Iodometric Titrations

The reactions in which reduction of free iodine to iodite takes place are called iodimetric titrations i.e, $I_2 + 2e^- \longrightarrow 2I^-$.

A solution of free iodine is prepared by dissolving it in KI solution. This solution is standardised before use. This standard solution is then employed for estimation of sulphite, thiosulphate, arsenite etc.

In iodometric titrations iodide is oxidised to iodine with an oxidising agent in acidic or neutral media.

i.e., $2I^- + 2e^- \longrightarrow I_2$

The liberated iodine is then titrated with thiosulphate, oxyhalogens, dichromate, cupric ion etc.

During these titrations, starch is used as an indicator. Starch solution gives blue or violet colour with iodine. At the end point, the blue or violet colour disappears when the free iodine is converted to iodide.

REDOX REACTIONS AND ELECTRODE PROCESSES

A device in which the redox reaction is carried indirectly and decrease in energy appears as the electrical energy is called electrochemical cell. An electrochemical cell has two electrodes. An electrode at which oxidation occurs is known as anode and an electrode at which reduction occurs is known as cathode. Both the electrodes are placed in respective electrolytes, connected through a salt bridge at each electrode redox half reaction occurs electrons flow in the direction of anode to cathode and the flow of electricity in opposite of this i.e., from cathode to anode. A redox couple is usually denoted as M^{n+}/M (oxidised state / reduced state).

Daniel Cell

The beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig.). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by metallic wire with a provision for an ammeter and a switch. As the switch is in the on position, we make the following observations are made:

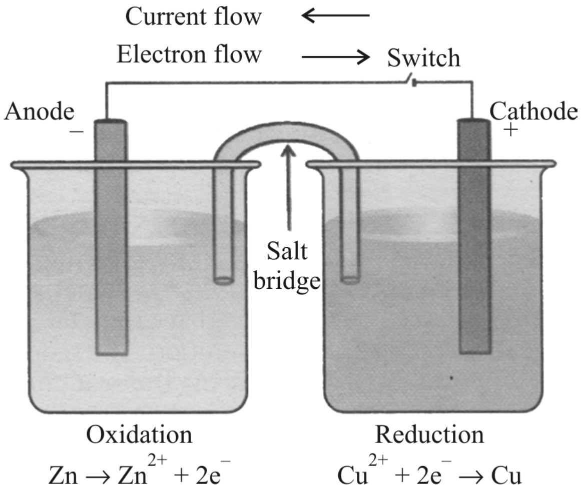


Fig. The set-up for Daniell cell.

1. The electrons move from Zn to Cu^{2+} through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.
2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. The flow of current is possible only if there is a potential difference between the copper and zinc rods known as **electrodes** here.

Electrode Potential

Electrode potential may be defined as the tendency of an electrode to either lose or gain electrons when it is in contact with the solution of its own ions.

The electrode potential of the half cell may be termed as oxidation potential when oxidation takes place at the electrode with respect to standard hydrogen electrode or reduction potential when reduction takes place at the electrode considering standard hydrogen electrode as reference electrode.

Redox couple consists of oxidised and reduced form of the same substance taking part in an oxidation or reduction half reaction. For example, $Zn^{2+}(aq)/Zn$, $Cl_2(g)/Cl^-(aq)$, etc.

Standard Electrode Potential

The electrode potential developed in the half cell when an electrode is suspended in a solution of one molar concentration of its ions at 298 K is called as standard electrode potential. It is represented by notation E° . Standard conditions for gas electrode (inert electrode) is 1 atmospheric pressure and a temperature of 298 K.

Electrochemical Series

The arrangement of metal ions in order of increasing value of standard reduction potentials is known as electrochemical series.

Elements	Electrode reactions	E°_{red} (volts)
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
H_2	$H_2O(\ell) + 2e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	-0.41

Cd	$Cd^{2+}(aq)+2e^{-}\longrightarrow Cd(s)$	-0.40
Pb	$PbSO_4(s)+2e^{-}\longrightarrow Pb(s)+SO_4^{2-}(aq)$	-0.31
Co	$Co^{2+}(aq)+2e^{-}\longrightarrow Co(s)$	-0.28
Ni	$Ni^{2+}(aq)+2e^{-}\longrightarrow Ni(s)$	-0.25
Sn	$Sn^{2+}(aq)+2e^{-}\longrightarrow Sn(s)$	-0.14
Pb	$Pb^{2+}(aq)+2e^{-}\longrightarrow Pb(s)$	-0.13
	$2H^{+}+2e^{-}\rightarrow H_2(g)$	0. 00
Cu	$Cu^{2+}(aq)+2e^{-}\longrightarrow Cu(s)$	$+0.34$
I_2	$I_2(s)+2e^{-}\longrightarrow 2I^{-}(s)$	$+0.54$
Fe	$Fe^{3+}(aq)+e^{-}\longrightarrow Fe^{2+}(aq)$	$+0.77$
Hg	$Hg_2{}^{2+}(aq)+2e^{-}\longrightarrow 2Hg(\ell)$	$+0.79$
Ag	$Ag^{+}(aq)+e^{-}\longrightarrow Ag(s)$	$+0.80$
Hg	$Hg^{2+}(aq)+2e^{-}\longrightarrow Hg(\ell)$	$+0.85$
Br_2	$Br_2(aq)+2e^{-}\longrightarrow 2Br^{-}(aq)$	$+1.08$
O_2	$1/2\,O_2(g)+2H_3O^{+}(aq)+2e^{-}\longrightarrow 3H_2O$	$+1.08$
Cr	$Cr_2O_7{}^{-}+14H^{+}+6e^{-}\longrightarrow 2Cr^{3+}+7H_2O$	$+1.33$
Cl_2	$Cl_2(g)+2e^{-}\longrightarrow 2Cl^{-}(aq)$	$+1.36$
Au	$Au^{3+}(aq)+3e^{-}\longrightarrow Au(s)$	$+1.42$
Mn	$MnO_4{}^{-}(aq)+8H_3O^{+}(aq)+5e^{-}\longrightarrow Mn^{2+}(aq)+12H_2O(\ell)$	$+1.51$
F_2	$F_2(g)+2e^{-}\longrightarrow 2F^{-}(g)$	$+2.87$

CONCEPT MAP

REDOX REACTIONS

Classical concept of oxidation and reduction
Oxidation involves addition of oxygen/ electronegative element or removal of hydrogen /electropositive element.
Reduction involves addition of hydrogen/ electropositive elements or removal of oxygen/ electronegative element.

Redox reaction in terms of electron transfer
Oxidation (loss of electrons) Reduction (gain of electrons) oxidising agent accepts electrons. Whereas reducing agent lose electrons.
Metals compete for the release of electrons. Deep study of electron transfer reactions of metals leads to construction of electrochemical series.

Oxidation number
Charge possessed by an atom when all the other atoms are removed from it as ions. It can be zero positive/ negative or a fraction. Oxidation (increase in oxidation number)
Reduction (decrease in oxidation number).
Oxidizing agent (increases the oxidation number of other substances)
Reducing agent (decreases the oxidation number of other substances).

Types of redox reactions

(a) Combination
$3\ Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

(b) Decomposition
$2\ KClO_3(s) \xrightarrow{\Delta} K2Cl(s) + 3O_2(g)$

(c) Displacement

(i) Metal displacement :-
$CuSO_4(aq) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq)$

(ii) Non-Metal displacement :-
$2Fe(s) + 3H_2O(l) \xrightarrow{\Delta} Fe_2O_3(s) + 3H_2(g)$

(d) Disproportionation:-
$2\ H_2O_2(aq) \longrightarrow 2\ H_2O(l) + O_2(g)$

Balancing of redox reactions
Oxidation number (number of e^-s gained in reduction = number of e^-s lost in oxidation).
Ion electron method (two half equations are balanced separately and then added).

Redox reactions and electrode processes
Electrode potential is the tendency of an electrode to either lose or gain electrons when it is in contact with solution of its own ions.
Electrochemical series : Arrangement of metal ions in order of increasing value of standard reduction potentials.

Textbook Exercises

8.1 Assign oxidation number to the underlined elements in each of the following species :

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$
(c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$
(e) $Ca\,\underline{O}_2$ (f) $Na\underline{B}H_4$
(g) $H_2\underline{S}_2O_7$ (h) $KAl\,(\underline{S}O_4)_2.12H_2O$

Ans. (a) Let the oxidation number of P be x. Writing the oxidation number of each atom above its symbol, we have,

$$\overset{+1}{Na}\,\overset{+1}{H_2}\,\overset{x}{P}\overset{-2}{O_4}$$

Sum of oxidation numbers of various atom in NaH_2PO_4 $= 1\,(+1) + 2\,(+1) + 1\,(x) + 4\,(-2) = x - 5$ But the sum of oxidation number of various atoms in NaH_2PO_4 (neutral) is zero

$\therefore$ $x - 5 = 0$ or $x = +5$ Thus, the oxidation number of P in $NaH_2PO_4 = +5$.

(b) $\overset{+1}{Na}\overset{+1}{H}\,\overset{x}{S}\overset{-2}{O_4}$

$1(+1) + 1(+1) + x + 4(-2) = 0$

or $x = +6$

Thus, the oxidation number of S in $NaHSO_4 = +6$.

(c) $\overset{+1}{H_4}\,\overset{x}{P_2}\,\overset{-2}{O_7}$

$4(+1) + 2(x) + 7(-2) = 0$

or $x = +5$

Thus, the oxidation number of P in $H_4P_2O_7 = +5$.

(d) $\overset{+1}{K_2}\overset{x}{Mn}\overset{-1}{O_4}$

$2(+1) + 1(x) + 4(-2) = 0$

or $x = +6$

Thus, the oxidation number of Mn in $K_2MnO_4 = +6$.

(e) Let the oxidation number of oxygen be x.

Thus, $\overset{+2}{Ca}\,\overset{x}{O_2}$

$\therefore$ $2 + 2x = 0,\ x = -1$

Thus, oxidation number of oxygen in $CaO_2 = -1$.

(f) In $NaBH_4$, H is present as hydride ion. Therefore, its oxidation number is – 1. Thus,

$\overset{+1}{Na}\,\overset{x}{B}\,\overset{-1}{H_4}$

$1 + 1(x) + 4\,(-1) = 0$ or $x = +3$

Thus, the oxidation number of B in $NaBH_4 = +3$.

(g) $\overset{+1}{H_2}\,\overset{x}{S_2}\,\overset{-2}{O_7}$

$2(+1) + 2(x) + 7(-2) = 0$

or $x = +6$

Thus, the oxidation number of S in $H_2S_2O_7 = +6$.

(h) $\overset{+1}{K}\,\overset{+3}{Al}\left(\overset{x-2}{SO_4}\right)_2 12\left(\overset{+1}{H_2}O\right)^{-2}$

or $+1 + 3 + 2x - 16 = 2x - 12$

or $x = +6$

Alternatively, since H_2O is a neutral molecule, therefore, sum of oxidation numbers of all the atoms in H_2O may be taken as zero. As such water molecules may be ignored while computing the oxidation number of S.

$\therefore$ $+1 + 3 + 2x - 16 = 0$ or $x = +6$

Thus, the oxidation number of S in $KAl\,(SO_4)_2.\ 12H_2O = +6$.

8.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$
(c) $\underline{Fe}_3O_4$ (d) $\underline{C}H_3\underline{C}H_2OH$
(e) $\underline{C}H_3\underline{C}OOH$

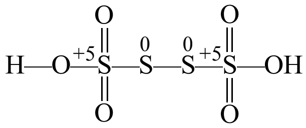
Ans. (a) In KI_3, since the oxidation number of K is + 1, therefore, the average oxidation number of iodine $= -1/3$. But the oxidation number cannot be fractional. Therefore, we must consider its structure, $K^+\,[I - I \longleftarrow I]^-$. Here, a coordinate bond is formed between I_2 molecule and I^- ion. The oxidation number of two iodine atoms forming the I_2 molecule is zero while that of iodine forming the coordinate bond is – 1.

(b) By conventional method, $H_2S_4O_6$

$2\,(+1) + 4x + 6\,(-2) = 0$ or $x = +2.5$ (wrong)

But it is wrong because all the four S atoms cannot be in the same oxidation state.

By chemical bonding method. the structure of $H_2S_4O_6$ is shown below :



The O.N. of each of the S–atoms linked with each other in the middle is zero while that of each of remaining two S–atoms is + 5.

(c) By conventional method, Fe_3O_4

$3x + 4\,(-2) = 0$ or $x = 8/3$

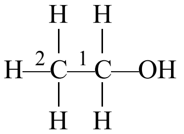
By stoichiometry $Fe_3O_4 = \overset{+2}{Fe}\,\overset{-2}{O}\,.\,\overset{+3}{Fe_2}\,\overset{-2}{O_3}$

Fe has O. N. of + 2 and + 3

(d) By conventional method. CH_3CH_2OH

$= C_2\,H_6O$ or $2x + 6\,(+1) + 1(-2) = 0$ or $x = -2$

By chemical bonding C_2 is attached to three H–atoms (less electronegative than carbon and one CH_2OH group (more electronegative than carbon), therefore, O. N. of



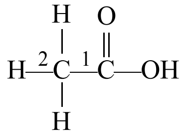
$C_2 = 3(+1) + x + 2\,(+1) - 2 + 1(-1) = 0$ or $x = -2$ C_1 is, however, attached to one OH (O. N. –1) and one CH_3 (O. N. = +1) group, therefore,

O. N.of C_1= + 1 + 2(+ 1) + x + 1 (–1) = 0 or x = – 2

(e) By conventional method

$$CH_3COOH = \overset{x}{C_2}\,\overset{+1}{H_4}\,\overset{-2}{O_2}$$

$2x + 4(+1) + 2(–2) = 0$
or $2x + 4 – 4$ or $x = 0$



By chemical bonding method

C_2 is attached to three H–atoms (less electronegative than carbon)

And one–COOH group (more electro-negative than carbon), therefore,

O.N. of $C_2 = 3(+1) + x + 1(+1) = 0$ or $x = +4$

C_1 is however, attached to one oxygen atom by a double bond, one OH (O.N. = – 1) and one CH_3 (O.N. = +1) group, therefore O.N. of C_1 = +1 + x + 1(–2) + 1(–1) = 0 or x = +2

8.3 Justify that the following reactions are redox reactions.

(a) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$

(c) $4\,BCl_3(g) + 3\,LiAlH_4(s) \longrightarrow 2\,B_2H_6(g) + 3\,LiCl(s) + 3\,AlCl_3(s)$

(d) $2\,K(s) + F_2(g) \longrightarrow 2\,K^+F^-(s)$

(e) $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$

Ans. (a) $\overset{+2\;-2}{CuO}(s) + H_2(g) \longrightarrow Cu(s) + \overset{+1}{H_2}\,\overset{-2}{O}(g)$

Here, O is removed from CuO, therefore, it is reduced to Cu while O is added to H_2 to form H_2O, therefore, it is oxidized. Further, O. N. of Cu decreases from + 2 in CuO to 0 in Cu but that of H increases from 0 in H_2 to + 1 in H_2O. Therefore, CuO is reduced to Cu but H_2 is oxidized to H_2O. Thus, this is a redox reaction.

(b) $\overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\,\overset{+2}{C}\,\overset{-2}{O}(g) \longrightarrow 2Fe(s) + 3\,\overset{+4}{C}\overset{-2}{O_2}(g)$

Here O.N. of Fe decreases from +3 is Fe_2O_3 to 0 in Fe while that of C increases from + 2 in CO to + 4 in CO_2. Further, oxygen is removed from Fe_2O_3 and added to CO, therefore. Fe_2O_3 is reduced while CO is oxidized. Thus, this is a redox reaction.

(c) $4\,\overset{+3}{B}\,\overset{-1}{Cl_3}(g) + 2\,\overset{+1}{Li}\,\overset{+3}{Al}\,\overset{-1}{H_4}(s) \longrightarrow$

$2\,\overset{-3}{B_2}\,\overset{+1}{H_6}(g) + 3\,\overset{+1}{Li}\,\overset{-1}{Cl}(s) + 3\,\overset{+3}{Al}\overset{-1}{Cl_3}(s)$

Here, O. N. of B decreases from + 3 in BCl_3 to –3 in B_2H_6 while that of H increases from –1 in $LiAlH_4$ to + 1 in B_2H_6. Therefore, BCl_3 is reduced while $LiAlH_4$ is oxidized. Further, H is added to BCl_3 but is removed from $LiAlH_4$, therefore, BCl_3 is reduced while $LiAlH_4$ is oxidized. Thus, it is a redox reaction.

(d) $2\,K(s) + F_2(g) \longrightarrow 2\,K^+F^-(s)$

Here, each K atom has lost one electron to form K^+ while F_2 has gained two electrons to form two F^{-1} ions. Therefore, K is oxidized while F_2 is reduced. Thus, it is a redox reaction.

(e) $4\,\overset{-3}{N}\,\overset{+1}{H_3}(g) + 5\overset{0}{O_2}(g) \longrightarrow 4\overset{+2}{N}\overset{-2}{O}(g) + 6\overset{+1}{H_2}\,\overset{-2}{O}(g)$

Here, O. N. of N increases from –3 in NH_3 to +2 in NO while that O decreases from 0 in O_2 to –2 in NO or H_2O. Therefore, NH_3 is oxidized while O_2 is reduced. Further H has been removed from NH_3 but added to O_2. Therefore, NH_3 has been oxidized while O_2 is reduced. Thus, this is a redox reaction.

8.4 Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \longrightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

Ans. Here, F_2 is reduced to HF and oxidized to HOF, therefore, it is a redox reaction. HOF is an highly unstable molecule and hence decomposes to form O_2 and HF

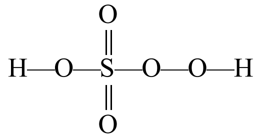
$$2\overset{+1}{H}\,\overset{-2}{O}\,\overset{+1}{F} \longrightarrow 2\overset{+1}{H}\,\overset{-1}{F} + \overset{0}{O_2}$$

In this reaction, F of HOF is reduced while O of HOF is oxidized. Therefore, it is a redox reaction but not a disproportionation reaction.

8.5 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these three compounds. Count for the fallacy.

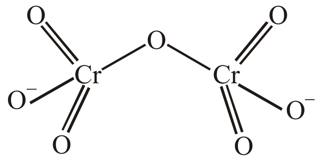
Ans. (i) By conventional method, the O. N. of S in H_2SO_5 is $2(+1) + x + 5(–2) = 0$ or $x = + 8$

This is impossible because the maximum O.N. of S cannot be more than six since it has only six electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of S by chemical bonding method.



2x (+1) + x + 2(–1) + 3x(–2) = 0 or x = + 6
(for H) (for S) for (O – O) (for other O atoms)

(ii) Oxidation number of chromium in $Cr_2O_7^{2-}$:



Structure of dichromate.

Let the Oxidation number of chromium = x

$\therefore\; 2x + 7(–2) = –2 \;\Rightarrow\; 2x – 14 = –2$

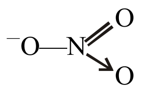
$\Rightarrow\; 2x = –2 + 14 \;\Rightarrow\; 2x = + 12$

$\Rightarrow\; x = + 6$

Thus the oxidation number of chromium = + 6

(iii) O. N. of N in NO_3^-

According to conventional method, O. N. of N in NO_3^- = x + 3 (– 2) = – 1 or x = + 5



According to chemical bonding method,

x + 1 (–1) + 1 (–2) + 1 (–2) = 0 or x + 5
(for O^-) (for = O) for O

Thus, there is no fallacy about the O. N. of N in NO_3^- whether one calculates by conventional method or by chemical bonding method.

8.6 Write formulas for the following compounds :

(a) Mercury (II) chloride

(b) Nickel (II) sulphate

(c) Tin (IV) oxide

(d) Thallium (I) sulphate

(e) Iron (III) sulphate

(f) Chromium (III) oxide

Ans. (a) $Hg(II)Cl_2$ (b) $Ni(II)SO_4$

(c) $Sn(IV)O_2$ (d) $Tl(I)SO_4$

(e) $Fe_2(III)(SO_4)_3$ (f) $Cr_2(III)O_3$

8.7 Suggest a list of the substances where carbon can exhibit oxidation states from – 4 to +4 and nitrogen from –3 to + 5.

Ans.

Compounds of Carbon	**O. N. of Carbon**
CH_4	– 4
CH_3CH_3	– 3
CH_3Cl	– 2
$CH \equiv CH$	– 1
CH_2Cl_2	0
$CHCl_3$	+2
CCl_4	+4

Compounds of Nitrogen	**O. N. of Carbon**
NH_3	– 3
NH_2NH_2	– 2
$NH{=}NH$	– 1
$N \equiv N$	0
N_2O	+1
NO	+2
N_2O_3	+3
N_2O_4	+4
N_2O_5	+5

8.8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

Ans. (i) In SO_2,O.N. of S is +4. In principle, S can have a minimum O.N. of –2 and maximum of +6. Therefore, S in SO_2 can either decrease or increase its O.N. and hence can act both as an oxidizing as well as a reducing agent.

(ii) In H_2O_2, the O.N. of O is -1. In principle, O can have a minimum O.N. of-2 and maximum of zero (+2 is possible only with OF_2). Therefore, O in H_2O_2 can either decrease its O. N. from -1 to -2 or can increase its O.N.from -1 to zero. Therefore, H_2O_2 acts both as an oxidizing as well as a reducing agent.

(iii) In O_3, the O.N. of O is zero. It can only decrease its O. N. from zero to -1 or -2, but cannot increase to + 2. Therefore, O_3 acts only as an oxidant.

(iv) In HNO_3, O, N. of N is + 5 which is maximum. Therefore, it can only decrease its O. N. and hence it acts as an oxidant only.

8.9 Consider the reactions :

(a) $6\,CO_2\,(g) + 6\,H_2O\,(\ell) \longrightarrow C_6H_{12}O_6\,(aq) + 6\,O_2\,(g)$

(b) $O_3\,(g) + H_2O_2\,(\ell) \longrightarrow H_2O\,(\ell) + 2\,O_2\,(g)$

Why it is more appropriate to write these reactions as :

(a) $6\,CO_2\,(g) + 12\,H_2O\,(\ell) \longrightarrow C_6H_{12}O_6\,(aq) + 6\,H_2O\,(\ell) + 6\,O_2\,(g)$

(b) $O_3(g) + H_2O_2(\ell) \longrightarrow H_2O(\ell) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

Ans. (a) Although the mechanism of photosynthesis is very complex but broadly speaking it may be visualized to occur in two steps. In the first step, H_2O decomposes to give H_2 and O_2 in presence of chlorophyll and the H_2 thus produced reduces CO_2 to $C_6H_{12}O_6$ in the second step. During the second step, some H_2O molecules are also produced as shown below:

$$12\,H_2O\,(\ell) \longrightarrow 12\,H_2\,(g) + 6\,O_2\,(g) \quad \text{...(i)}$$

$$6\,CO_2\,(g) + 12\,H_2\,(g) \longrightarrow C_6H_{12}O_6\,(s) + 6\,H_2O\,(\ell) \quad \text{...(ii)}$$

$$6CO_2\,(g) + 12\,H_2O\,(\ell) \longrightarrow C_6H_{12}O_6\,(s) + 6\,H_2O\,(\ell) + 6\,O_2\,(g) \quad \text{...(iii)}$$

Therefore, it is more appropriate to write the equation for photosynthesis as (iii) because it emphasizes that 12 H_2O are used per molecule of carbohydrate formed and 6 H_2O are produced during the process.

(b) The purpose of writing O_2 two times suggests that O_2 is being obtained from each of the two reactants.

$$O_3\,(g) \longrightarrow O_2\,g) + O\,(g)$$

$$H_2O_2\,(\ell) + O\,(g) \longrightarrow H_2O\,(\ell) + O_2\,(g)$$

$$O_3\,(g) + H_2O_2\,(\ell) \longrightarrow H_2O\,(\ell) + O_2\,(g) + O_2(g)$$

The path of reactions (a) and (b) can be determined by using H_2O^{18} in reaction (a) or by using $H_2O_2^{18}$ or O_3^{18} in reaction (b).

8.10 The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

Ans. In AgF_2, oxidation state of Ag is +2 which is very very unstable. Therefore, it quickly accepts an electron to form the more stable +1 oxidation state.

$$Ag^{2+} + e^- \longrightarrow Ag^+.$$

Therefore, AgF_2, if formed, will act as a strong oxidising agent.

8.11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

Ans. (i) C is a reducing agent while O_2 is an oxidizing agent. If excess of carbon is burnt in a limited supply of O_2, CO is formed in which the oxidation state of C is + 2. If, however, excess of O_2 is used, the initially formed CO gets oxidized to CO_2 in which oxidation state of C is + 4.

$$\underset{\text{(Excess)}}{2C(s)} + O_2(g) \longrightarrow 2\,\overset{+2}{C}\,\overset{-2}{O}(g);$$

$$C(s) + \underset{\text{(Excess)}}{O_2\,(g)} \longrightarrow \overset{+4-4}{CO_2}(g)$$

(ii) P_4 is a reducing agent while Cl_2 is an oxidizing agent. When excess of P_4 is used, PCl_3 is formed in which the oxidation state of P is + 3. If, however, excess of Cl_2 is used, the initially formed PCl_3 reacts further to form PCl_5 in which the oxidation state of P is + 5

$$\underset{\text{(Excess)}}{P_4} + 6Cl_2(g) \longrightarrow 4\overset{+3}{P}Cl_3\,;$$

$$P_4(s) + \underset{\text{(Excess)}}{10Cl_2} \longrightarrow 4\overset{+5}{P}Cl_5$$

(iii) Na is a reducing agent while O_2 is an oxidizing agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is –2. If, however, excess of O_2 is used, Na_2O_2 is formed in which the oxidation state of O is –1 which is higher than –2.

$$\underset{\text{(Excess)}}{Na(s)} + O_2(g) \longrightarrow Na_2\overset{-2}{O}(s);$$

$$2Na(s) + \underset{\text{(Excess)}}{2O_2(g)} \longrightarrow Na_2\overset{-1}{O_2}(s)$$

8.12 How do you count for the following observations?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

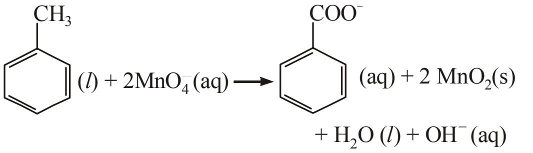
(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ?

Ans. (a) In the manufacture of benzoic acid from toluene, alcoholic medium is preferred over acidic or alkaline medium due to following reasons:

(1) In alcoholic medium, neither acid nor base is added externally which reduces the cost of manufacturing process.

(2) Alcohol has non-polar alkyl groups as well as polar –OH group. Thus, if alcohol is used as a solvent, it will help in the formation of a homogeneous mixture between toluene (non-polar) and $KMnO_4$ (ionic).

The balanced reaction is :



(b) When conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

$$2\,NaCl + 2\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + 2\,HCl$$

$$2\,HCl + H_2SO_4 \longrightarrow Cl_2 + SO_2 + 2\,H_2O$$

Since HCl is a very weak reducing agent, it can not reduce H_2SO_4 to SO_2 and hence HCl is not oxidized to Cl_2

However, when the mixture contains bromide ion, the initially produced HBr being a stronger reducing agent reduces H_2SO_4 to SO_2 and is itself oxidized to produce red vapour of Br_2.

$$2\,NaBr + 2\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + 2\,HBr$$

$$2\,HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2\,H_2O$$

8.13 Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions :

(a) $2\,AgBr\,(s) + C_6H_6O_2\,(aq) \longrightarrow 2\,Ag\,(s) + 2\,HBr\,(aq) + C_6H_4O_2\,(aq)$

(b) $HCHO(\ell) + 2\,[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \longrightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2\,H_2O\,(\ell)$

(c) $HCHO(\ell) + 2\,Cu^{2+}(aq) + 5\,OH^-(aq) \longrightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(\ell)$

(d) $N_2H_4(\ell) + 2H_2O_2\,(\ell) \longrightarrow N_2\,(g) + 4\,H_2O\,(\ell)$

(e) $Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(\ell)$

Ans.

	Substance oxidised	**Substance reduced**	**Oxidising agent**	**Reducing agent**
(a)	$C_6H_6O_2$ (aq)	AgBr (s)	AgBr(s)	$C_6H_6O_2$ (aq)
(b)	HCHO (aq)	$[Ag(NH_3)_2]^+$	$[Ag(NH_3)_2]^+$	HCHO (aq)
(c)	HCHO (aq)	Cu^{2+} (aq)	Cu^{2+} (aq)	HCHO (aq)
(d)	$N_2H_4(\ell)$	$H_2O_2\,(\ell)$	$H_2O_2\,(\ell)$	$N_2H_4(\ell)$
(e)	Pb (s)	PbO_2 (s)	PbO_2 (s)	Pb (s)

8.14 Consider the reactions:

$$2S_2O_3^{2-}(aq) + I_2(s) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

$$S_2O_3^{-2}(aq) + 2Br_2(\ell) + 5H_2O(\ell) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10\,H^+(aq)$$

Why does the same reductant, thiosulphate react differently with iodine and bromine?

Ans. The average O. N. of S in $S_2O_3^{2-}$ is + 2 while in $S_4O_6^{2-}$ it is + 2.5. The O.N. of S in SO_4^{2-} is + 6. Since Br_2 is a stronger oxidising agent that I_2, it oxidises S of $S_2O_3^{2-}$ to a higher oxidation state of + 6 and hence forms SO_4^{2-} ion. I_2, however, being a weaker oxidising agent oxidises S of $S_2O_3^{2-}$ ion to a lower oxidation state of + 2. 5 in $S_4O_6^{2-}$ ion. It is because of this reason that thiosulphate reacts differently with Br_2 and I_2.

8.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

Ans. The oxidizing power of halogens decreases in the order: $F_2 > Cl_2 > Br_2 > I_2$. This is evident from the observation that F_2 oxidizes Cl^- to Cl_2, Br^- to Br_2, I^- to I_2 Cl_2 oxidizes Br^- to Br_2

and I^- to I_2 but not F^- to F_2. Br_2, however, oxidizes I^- to I_2 but not F^- to F_2, and Cl^- to Cl_2.

$F_2(g) + 2Cl^-(aq) \longrightarrow 2F^-(aq) + Cl_2(g)$;
$F_2(g) + 2Br^-(aq) \longrightarrow 2F^-(aq) + Br_2(\ell)$
$F_2(g) + 2I^-(aq) \longrightarrow 2F^-(aq) + I_2(s)$;
$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(\ell)$
$Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$
and $Br_2(\ell) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$

Thus F_2 is the best oxidant

Among hydrohalic acids, the reducing power decreases in the order: HI > HBr > HCl > HF. Thus, HI and HBr reduce H_2SO_4 to SO_2 while HCl and HF do not.

$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$
$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

Further I^- reduces Cu^{2+} to Cu^+ but Br^- does not.

$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$
$Cu^{2+}(aq) + 2Br^- \longrightarrow$ No reaction.

Further among HCl and HF, HCl is a stronger reducing agent than HF because HCl reduces MnO_2 to Mn^{2+} but HF does not.

$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O$
$MnO_2(s) + 4HF(\ell) \longrightarrow$ No reaction.

8.16 Why does the following reaction occur ?

$XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \longrightarrow XeO_3(g) + F_2(g) + 3H_2O(\ell)$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction.

Ans. $$\overset{+8}{Xe}O_6^{-4}(aq) + 2\overset{-1}{F^-}(aq) + 6H^+(aq) \longrightarrow \overset{+6}{Xe}O_3(s) + F_2(g) + 3H_2O(\ell)$$

Here, O. N. of Xe decreases from +8 in XeO_6^{4-} to + 6 in XeO_3 while that of F increases from –1 in F^- to 0 in F_2. Therefore, XeO_6^{4-} is reduced while F^- is oxidized. This reaction occurs because $Na_4XeO_6^{4-}$ (or XeO_6^{4-}) is a stronger oxidizing agent than F_2.

8.17 Consider the reactions:

(a) $H_3PO_2(aq) + 4AgNO_3(aq) + 2H_2O(\ell) \longrightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$

(b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2H_2O(\ell) \longrightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$

(c) $C_6H_5CHO(\ell) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \longrightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O(\ell)$

(d) $C_6H_5CHO(\ell) + 2Cu^{2+}(aq) + 5OH^-(aq) \longrightarrow$ No change observed.

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions?

Ans. Reactions (a) and (b) indicate that H_3PO_2 (hypophosphorus acid) is a reducing agent and thus reduces both $AgNO_3$ and $CuSO_4$ to Ag and Cu respectively. Conversely, both $AgNO_3$ and $CuSO_4$ act as oxidizing agent and thus oxidize H_3PO_2 to H_3PO_4 (phosphorus acid) Reaction (c) suggests that $[Ag(NH_3)_2]^+$ oxidizes C_6H_5CHO (benzaldehyde) to $C_6H_5COO^-$ (benzoate ion) but reaction (d) indicates that Cu^{2+} ions cannot oxidize C_6H_5CHO to $C_6H_5COO^-$. Therefore, from the above reactions, we conclude that Ag^+ ion is a stronger oxidizing agent than Cu^{2+} ion.

8.18 Balance the following redox reactions by ion –electron method:

(a) $MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$ (in basic medium)

(b) $MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ (in acidic solution)

(c) $H_2O_2(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + H_2O(\ell)$ (in acidic solution)

(d) $Cr_2O_7^{2-}(aq) + SO_2(g) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution)

Ans. (a) Oxidation half equation:

$2I^- \longrightarrow I_2 + 2e^-$

Reduction half equation:

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

Now to cancel out the electrons multiply oxidation half by 3 and reduction half equation by 2 and add it. We get

$6I^- \longrightarrow 3I_2 + 6e^-$
$2MnO_4^- + 4H_2O + 6e^- \longrightarrow 2MnO_2 + 8OH^-$
$2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$

(b) Oxidation half equation:

$SO_2(g) + 2H_2O(l) \longrightarrow HSO_4^-(aq) + 3H^+(aq) + 2e^-$ ... (i)

Reduction half equation:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(\ell)$ .. (ii)

Multiply Eq. (i) by 5 and Eq. (ii) by 2 and add, we have,

$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(\ell) + H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5HSO_4^-(aq)$

(c) Oxidation half equation:

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$ ...(i)

Reduction half equation:

$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(\ell)$ ... (ii)

Multiply Eq. (i) by 2 and add it to Eq. (ii), we have,

$H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(\ell)$

(d) Oxidation half equation:

$SO_2(g) + 2H_2O(\ell) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ ... (i)

Reduction half equation:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(\ell)$ ... (ii)

Multiply Eq. (i) by 3 and add it to Eq. (ii), we have,

$Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^-(aq) + H_2O(\ell)$

8.19 Balance the following equations in basic medium by ion electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

(a) $P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + HPO_2^-(aq)$

(b) $N_2H_4(\ell) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(g)$

(c) $Cl_2O_7(g) + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g) + H^+$

Ans. (a) O. N. decreases by 3 per P atom

$$\overset{0}{P_4}(s) + OH^-(aq) \longrightarrow \overset{-3}{P}H_3(g) + H_2\overset{+1}{P}O_2^-$$

O. N. increases by 1 per P atom.

P_4 acts like both as an oxidizing as well as reducing agent.

Oxidation number method :

Total decrease in O. N. of P_4 in $PH_3 = 3\times 4 = 12$

Total increase in O. N. of P_4 in $H_2PO_2^- = 1\times4 = 4$

Therefore, to balance increase/decreases in O. N. multiply PH_3 by 1 and $H_2PO_2^-$ by 3, we have,

$P_4\,(s) + OH^-\,(aq) \longrightarrow PH_3\,(g) + 3H_2PO_2^-\,(aq)$

To balance O atoms, multiply OH^- by 6, we have,

$P_4\,(s) + 6\,OH^-(aq) \longrightarrow PH_3\,(g) + 3H_2PO_2^-(aq)$

To balance H atoms, add $3H_2O$ to deficient side and $3OH^-$ to the other side, now we have

$$P_4(s) + 6OH^-\,(aq) + 3H_2O\,(\ell) \longrightarrow PH_3(g) + 3H_2PO_2^-\,(aq) + 3OH^-(aq)$$

To cancel out species present in both sides, we have

$P_4(s) + 3OH^-\,(aq) + 3H_2O(\ell) \longrightarrow PH_3(g) + 3H_2PO_2^-\,(aq)$

This represents the correct balanced equation.

Ion electron method :

Oxidation half equation :

$$\overset{0}{P_4} \longrightarrow H_2\overset{+1}{P}O_2^-$$

Balance P atoms, $P_4 \longrightarrow 4\,H_2PO_2^-$

Balance H atom O atoms by adding OH^-

$P_4 + 8OH^- \longrightarrow 4H_2PO_2^-$

Now balance charge

$P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e^-$ ...... (i)

Thus, Eq. (i) represents the correct balanced oxidation half equation.

Reduction half equation :

$$\overset{0}{P_4} \longrightarrow \overset{-3}{P}H_3$$

Balance P atoms, $P_4 \longrightarrow 4PH_3$

Balance H atoms by adding OH^- and H_2O,

$P_4 + 12H_2O + 12\,e^- \longrightarrow 4PH_3 + 12\,OH^-$ .... (ii)

Thus, Eq. (ii) represents the correct balanced reduction half equation.

To cancel out electrons gained and lost, multiply Eq. (i) by 3 and add with Eq. (ii) by cancelling common terms, we have,

$P_4(s) + 3OH^-\,(aq) + 3H_2O(\ell) \longrightarrow PH_3(g) + 3H_2PO_2^-\,(aq)$

O.N. increases by 4 per N atom

(b) $\overset{-2}{N_2}H_4(l) + \overset{+5}{Cl}O_3^-(aq) \longrightarrow \overset{+2}{N}O(g) + \overset{-1}{Cl^-}(g)$

O.N. decreases by 6 per Cl atom

Thus, N_2H_4 is acting as a reducing agent while ClO_3^- is acting as an oxidising agent.

Oxidation number method :

Total increase in O. N. of N in NO $= 4 \times 2 = 8$

Total increase in O. N. of Cl in $ClO_3^- = 6 \times 1 = 6$

Therefore, to balance increase/decrease in O.N. multiply NO by 6 and ClO_3^- by 4 we have

$N_2H_4 + 4\,ClO_3^- \longrightarrow 6NO + Cl^-$

Balance N and Cl atoms,

$3N_2H_4 + 4ClO_3^- \longrightarrow 6\,NO + 4Cl^-$

To balance H atoms, add $6H_2O$ to deficient side

$$3N_2H_4(s) + 4ClO_3^-\,(aq) \longrightarrow 6\,NO(g) + 4Cl^-(aq) + 6H_2O(\ell)$$

This represents the correct balanced equation.

Ion electron method : Oxidation half equation:

$$\overset{-2}{N_2}H_4(\ell) \longrightarrow \overset{+2}{N}O(g)$$

Balance N atoms, $N_2H_4\,(\ell) \longrightarrow 2\,NO\,(g)$

Balance H atom by adding OH^- and H_2O

$N_2H_4 + 4OH^- \longrightarrow 2NO + 4H_2O$

Balance O atoms again by adding H_2O and OH^-

$$N_2H_4\,(\ell) + 4\,OH^-(aq) + 4OH^- \longrightarrow 2\,NO\,(g) + 4\,H_2O\,(\ell) + 2H_2O$$

Now balance charge

$N_2H_4\,(l) + 8OH^-\,(aq) \longrightarrow 2NO + 6H_2O + 8e^-$ (i)

Thus, Eq. (i) represents the correct balanced oxidation half equation.

Reduction half equation $\overset{+5}{Cl}O_3^-\,(aq) \longrightarrow Cl^-\,(aq)$

Balance O. N. by adding electrons,

$ClO_3^-\,(aq) + 6\,e^- \longrightarrow Cl^-\,(aq)$

Balance charge by adding OH^- ions,

$ClO_3^-\,(aq) + 6\,e^- \longrightarrow Cl^-\,(aq) + 6\,OH^-\,(aq)$

Balance O atoms by adding $3\,H_2O$,

$$ClO_3^-\,(aq) + 3\,H_2O\,(\ell) + 6\,e^- \longrightarrow Cl^-\,(aq) + 6\,OH^-\,(aq) \ldots \text{(ii)}$$

Thus, Eq. (ii) represents the correct balanced reduction half equation.

To cancel out electrons gained and lost, multiply Eq. (i) by 3 and Eq. (ii) by 4 and add, we have,

$$3\,N_2H_4\,(\ell) + 4\,ClO_3^-\,(aq) \longrightarrow 6\,NO\,(g) + 4\,Cl^-\,(aq) + 6\,H_2O\,(\ell)$$

This represents the correct balanced equation

(c) O. N. decreases by 4 per Cl atom

$$\overset{+7}{Cl_2}O_7(g) + H_2\overset{-1}{O_2}(aq) \longrightarrow \overset{+3}{Cl}O_2^-\,(g) + \overset{0}{O_2}(g) + H^+$$

O. N. increases by 1 per O atom. Thus, Cl_2O_7 (g) acts an oxidizing agent while H_2O_2 (aq) as the reducing agent.

Oxidation number method : Total decrease in O. N. of $Cl_2O_7 = 4 \times 2 = 8$

Total increase in O. N. of $H_2O_2 = 2 \times 1 = 2$

∴ To balance increase/decrease in O. N. multiply H_2O_2 and O_2 by 4, we have,

$Cl_2O_7\,(g) + 4\,H_2O_2(aq) \longrightarrow ClO_2^-(aq) + 4\,O_2\,(g)$

To balance Cl atoms, multiply ClO^-_2 by 2, we have,

$Cl_2O_7(g) + 4\,H_2O_2(aq) \longrightarrow 2\,ClO_2^-(aq) + 4\,O_2(g)$

To balance O atoms, add 3 H_2O to R. H. S., we have,

$Cl_2O_7(g) + 4\,H_2O_2(aq) \longrightarrow$
$2\,ClO_2^-(aq) + 4\,O_2(g) + 3\,H_2O(\ell)$

To balance H atoms, add 2 H_2O to R. H. S. and 2 OH^- to L. H. S., we have,

$Cl_2O_7(g) + 4\,H_2O_2(g) + 2\,OH^-(aq) \longrightarrow$
$2\,ClO_2^-(aq) + 4O_2(g) + 5\,H_2O$

This represents the balanced redox equation.

Ion electron method : Oxidation half equation:

$H_2O_2(aq) \longrightarrow O_2(g)$

Balance O. N. by adding electrons,

$H_2O_2(aq) \longrightarrow O_2(g) + 2e^-$

Balance charge by adding OH^- ions,

$H_2O_2(aq) + 2\,OH^-(aq) \longrightarrow O_2(g) + 2\,e^-$

Balance O atoms by adding H_2O,

$H_2O_2(aq) + 2\,OH^-(aq) \longrightarrow O_2(g) + 2\,H_2O(\ell) + 2\,e^-$ ... (i)

Reduction half equation: $Cl_2O_7(g) \longrightarrow ClO_2^-(aq)$

Balance Cl atoms; $Cl_2O_7(g) \longrightarrow 2\,ClO_2^-(aq)$

Balance O. N. by adding electrons,

$Cl_2O_7(g) + 8\,e^- \longrightarrow 2\,ClO_2^-(aq)$

Add OH^- ions to balance charge:

$Cl_2O_7(g) + 8\,e^- \longrightarrow 2\,ClO_2^-(aq) + 6\,OH^-$

Balance O atoms by adding 3 H_2O to L. H. S., we have,

$Cl_2O_7(g) + 3\,H_2O(\ell) + 8\,e^- \longrightarrow$
$2\,ClO_2^-(aq) + 6\,OH^-(aq)$ ... (ii)

To cancel out electrons, multiply Eq. (i) by 4 and add it to Eq. (ii), we have,

$4\,H_2O_2(aq) + 8\,OH^-(aq) + Cl_2O_7(g) + 3H_2O(\ell) \longrightarrow$
$2\,ClO_2^- + (aq) + 6\,OH^-(aq) + 4\,O_2(g) + 8\,H_2O(\ell)$

or $Cl_2O_7(g) + 4\,H_2O_2(aq) + 2\,OH^-(aq) \longrightarrow 2ClO_2^-(aq) + 4\,O_2(g) + 5\,H_2O(\ell)$

8.20 What sorts of information can you draw from the following reactions :

$(CN)_2(g) + 2\,OH^-(aq) \longrightarrow$
$CN^-(aq) + CNO^-(aq) + H_2O(\ell)$

Ans. (i) It is a disproportionation reaction.

(ii) Cyanogen $(CN)_2$ gets simultaneously reduced to CN^- ion as well as oxidized to cyanate ion.

(iii) O. N. of N in $(CN)_2$ is – 3 while that in CN^- is –2 and in CNO^- is –5

(iv) The reaction occurs in basic medium.

8.21 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2 and H^+ ion. Write a balanced ionic equation for the reaction.

Ans. The skeletal equation is: $Mn^{3+}(aq) \longrightarrow$
$Mn^{2+}(aq) + MnO_2(s) + H^+(aq)$

Oxidation half equation:

$\overset{+3}{Mn^{3+}}(aq) \longrightarrow \overset{+4}{Mn}O_2(s)$

Balance O. N. by adding electrons,

$Mn^{3+}(aq) \longrightarrow MnO_2(s) + e^-$

Balance charge by adding H^+ ions,

$Mn^{3+}(aq) \longrightarrow MnO_2(s) + 4\,H^+(aq) + e^-$

Balance O atoms by adding H_2O:

$Mn^{3+}(aq) + 2\,H_2O(\ell) \longrightarrow$
$MnO_2(s) + 4\,H^+(aq) + e^-$ ... (i)

Reduction half equation : $\overset{+3}{Mn^{3+}} \longrightarrow \overset{+2}{Mn^{2+}}$

Balance O. N. by adding electron :

$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq)$ ... (ii)

Adding Eq. (i) and Eq. (ii), the balanced equation for the disproportionation reaction is

$2\,Mn^{3+}(aq) + 2\,H_2O(\ell) \longrightarrow$
$MnO_2(s) + Mn^{2+}(aq) + 4H^+(aq)$

8.22 Consider the elements : Cs, Ne, I and F only

(a) Identify the element that exhibits only – ve oxidation state.

(b) Identify the element that exhibits only + ve oxidation state

(c) Identify the element that exhibits both + ve and – ve oxidation states

(d) Identify the element which neither exhibits – ve nor + ve oxidation state.

Ans. (a) Fluorine being most electronegative element shows only a –ve oxidation state of –1.

(b) Cs, Alkali metals because of the presence of a single electron in the valence shell, exhibit an oxidation state of + 1.

(c) I, Because of the presence of seven electrons in the valence shell, I shows an oxidation state of –1 and because of the presence of d–orbitals it also exhibits +ve oxidation states of +1, +3, +5 and +7.

(d) Ne, It is an inert gas and hence it neither exhibits –ve nor +ve oxidation states.

8.23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess chlorine is removed by treating with sulphur dioxide. Present a balanced equation for the reaction for this redox change taking place in water.

Ans. The skeletal equation is:

$Cl_2(aq) + SO_2(aq) + H_2O(\ell) \longrightarrow 2\,Cl^-(aq) + SO_4^{2-}(aq)$

Reduction half equation: $Cl_2(aq) \longrightarrow Cl^-(aq)$

Balance Cl atoms, $\overset{0}{Cl_2}(aq) \longrightarrow 2Cl^-(aq)$

Balance O. N. by adding electrons:

$Cl_2(aq) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$ ...(i)

Oxidation half equation:

$\overset{+4}{S}O_2(aq) \longrightarrow \overset{+6}{S}O_4^{2-}(aq) + 2e^-$

Balance O. N. by adding electrons:

$SO_2(aq) \longrightarrow SO_4^{2-}(aq) + 2\,e^-$

Balance charge by adding H^+ ions:

$SO_2(aq) \longrightarrow SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$

Balance O atoms by adding 2 H_2O,

$SO_2(aq) + 2\,H_2O(\ell) \longrightarrow$
$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$ ...(ii)

Adding Eq. (i) and Eq. (ii), we have,

$Cl_2(aq) + SO_2(aq) + 2\,H_2O(\ell) \longrightarrow$
$2\,Cl^-(aq) + SO_4^{2-}(aq) + 4\,H^+(aq)$

This represents the balanced redox reaction.

8.24 Refer to the periodic table given in your book and now answer the following questions.

(a) Select the possible non-metals that can show disproportionation reaction.

(b) Select three metals that can show disproportionation reaction.

Ans. (a) The non–metals are: P_4, Cl_2 and S_8.

(i) $P_4\,(s) + 3\,OH^-\,(aq) + 3\,H_2O\,(\ell) \longrightarrow PH_3\,(g) + 3\,H_2PO_2^-\,(aq)$

(ii) $Cl_2\,(aq) + 2\,OH^-\,(aq) \longrightarrow Cl^-\,(aq) + ClO^-\,(aq) + H_2O\,(\ell)$

(iii) $S_8\,(s) + 12\,OH^- \longrightarrow 4\,S^{2-}\,(aq) + 2\,S_2O_3^{2-}\,(aq) + 6\,H_2O\,(\ell)$

(b) The metals are: Cu^+, Ga^+, In^+ etc.

$2\,Cu^+\,(aq) \longrightarrow Cu^{2+}\,(aq) + Cu\,(s)$

$3\,Ga^+\,(aq) \longrightarrow Ga^{3+}\,(aq) + 2\,Ga\,(s)$

$3\,In^+\,(aq) \longrightarrow In^{3+}\,(aq) + 2\,In\,(s)$

8.25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.0 g of ammonia and 20.0 g of oxygen?

Ans. The balanced equation for the reaction is:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

4×17 5×32 4×30

$= 68g$ $=160g$ $= 120g$

Here, 160 g of O_2 will react with $NH_3 = 68$ g

20g of O_2 will react with $NH_3 = (68/160) \times 20 = 8{\cdot}5$ g

Thus, O_2 is the limiting reagent, therefore, the calculations must be based upon the amount of O_2 taken and not on the amount of NH_3 taken.

From the equation,

160 g of O_2 produce NO = 120 g

20 g of O_2 will produce NO = $(120/160) \times 20 = 15$ g

8.26 Using the standard electrode potentials given in table 8.1 (NCERT), predict if the reaction between the following is feasible:

(a) Fe^{3+}(aq) and I^-(aq) **(b) Ag^+(aq) and Cu(s)**

(c) Fe^{3+}(aq) and Cu(s) **(d) Ag(s) and Fe^{3+}(aq)**

(e) Br_2(aq) and Fe^{2+}(aq)

Ans. A reaction is feasible if E.M.F. of the cell is + ve.

(a) $E^o_{Fe^{3+}/Fe^{2+}} = +0.77V$; $E^o_{I_2/2I^-} = +0.54V$. Since we have to determine a reaction between Fe^{3+} and I^-, the reaction should be $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ at cathode

$2I^- \longrightarrow I_2 + 2e^-$ at anode .

We know that EMF = $E^o_{cathode} - E^o_{anode} = 0.77 - 0.54 = 0.23$ V as it is positive the reaction is feasible and the following reaction would occur.

$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

(b) $E^o_{Ag^+/Ag} = +0.80V$;

$E^o_{Cu^{2+}/Cu} = +\,0.34V$. Since we have to determine a reaction between Ag^+ and Cu, the reaction should be

$Ag^+ + e^- \longrightarrow Ag$ at cathode

$Cu \longrightarrow Cu^{2+} + 2e^-$ at anode.

We know that EMF = $E^o_{cathode} - E^o_{anode} = 0.80 - 0.34 = 0.46$ V as it is positive the reaction is feasible and the following reaction would occur.

$2Ag^+ + Cu \longrightarrow 2Ag + Cu^{2+}$

(c) $E^o_{Fe^{3+}/Fe^{2+}} = +0.77V$; $E^o_{Cu^{2+}/Cu} = +\,0.34V$. Since, we have to determine a reaction between Fe^{3+} and Cu, the reaction should be $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ at cathode

$Cu \longrightarrow Cu^{2+} + 2e^-$ at anode .

We know that EMF = $E^o_{cathode} - E^o_{anode} = 0.77 - 0.34 = 0.43$ V as it is positive the reaction is feasible and the following reaction would occur.

$2Fe^{3+} + Cu \longrightarrow 2Fe^{2+} + Cu^{2+}$

(d) $E^o_{Fe^{3+}/Fe^{2+}} = +\,0.77V$; $E^o_{Ag^+/Ag} = +\,0.80V$. Since we have to determine a reaction between Fe^{3+} and Ag, the reaction should be $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ at cathode

$Ag \longrightarrow Ag^+ + e^-$ at anode .

We know that EMF = $E^o_{cathode} - E^o_{anode} = 0.77 - 0.80 = -\,0.03$ V as it is negative the reaction is not feasible .

(e) $E^o_{Fe^{3+}/Fe^{2+}} = +\,0.77V$; $E^o_{Br_2/2Br^-} = +\,1.09V$. Since, we have to determine a reaction between Fe^{2+} and Br_2, the reaction should be $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ at anode

$Br_2 + 2e^- \longrightarrow 2Br^-$ at cathode .

We know that EMF = $E^o_{cathode} - E^o_{anode} = 1.09 - 0.77 = 0.32$ V as it is positive the reaction is feasible and the following reaction would occur.

$2Fe^{2+} + Br_2 \longrightarrow 2Fe^{3+} + 2Br^-$

8.27 Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes

(iii) A dilute solution of H_2SO_4 with platinum electrodes

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes

Ans. (i) Electrolysis of aqueous solution of $AgNO_3$ with silver electrodes.

At cathode : $Ag^+ + e^- \longrightarrow Ag$

At anode : $Ag \longrightarrow Ag^+ + e^-$

(ii) Electrolysis of aqueous solution of $AgNO_3$ using platinum electrodes.

At cathode : $Ag^+ + e^- \longrightarrow Ag$ since reduction potential of Ag is higher than water.

At anode : $OH^- \longrightarrow OH + e^-$,

$4OH \longrightarrow 2H_2O + O_2$ since reduction potential of water is less than nitrate ion. Thus oxygen gas will be liberated.

(iii) Electrolysis of dil.H_2SO_4 with platinum electrode.

$H_2SO_4 \longrightarrow 2H^+(aq) + SO_4^{-2}(aq)$

$H_2O \longrightarrow H^+ + OH^-$

At cathode : $2H^+ + 2e^- \longrightarrow H_2$ hydrogen gas will be liberated.

At anode: $OH^- \longrightarrow OH + e^-$,

$4OH \longrightarrow 2H_2O + O_2$

since reduction potential of water is less than sulphate ion. Thus oxygen gas will be liberated.

(iv) Electrolysis of $CuCl_2$ (aq) with platinum electrode.

$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$

$H_2O \longrightarrow H^+ + OH^-$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$, copper will be liberated as copper has higher reduction potential than water.

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$, chlorine will be discharged due to over–voltage.

8.28 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg, and Zn .

Ans. This is based upon the relative positions of these metals in the activity series. The metal placed lower in the series can displace the metals occupying a higher position present as its salt. Based upon this, the correct order is: Mg, Al, Zn, Fe, Cu, Ag.

8.29 Given the standard electrode potentials, $K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79V$, $Mg^{2+}/Mg = -2.37V$. $Cr^{3+}/Cr = -0.74V$

Arrange these metals in their increasing order of their reducing power.

Ans. Lower the reduction potential, more easily the metal is oxidized and hence greater is the reducing power. Thus increasing order of reducing power will be Ag < Hg < Cr < Mg < K.

8.30 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

(i) which of the electrode is negatively charged,

(ii) the carriers of current in the cell, and

(iii) individual reaction at each electrode.

Ans. $Zn|Zn^{2+}||Ag^+|Ag$; i.e. Zinc acts as anode and Ag acts as cathode.

(i) Zinc is negatively charged.

(ii) Electrons flow from Zn electrode to silver electrodes while current flows from silver electrodes toward zinc through wires fitted externally..

(iii) At cathode : $Ag^+ + e^- \longrightarrow Ag$

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$.

Practice Questions

Very Short Answer Questions [1 Mark]

1. Identify the oxidizing agent and the reducing agent in the following reaction

$H_2S + HNO_3 \longrightarrow NO + S + H_2O$

2. In a binary compound of two non–metals, the positive oxidation state is assigned to which metal?
3. What is the oxidation number of C in C_6H_6 ?
4. What does negative electrode potential signify ?
5. At what concentration of Cu^{2+}(aq), will its electrode potential become equal to its standard electrode potential?
6. Why is anode called oxidation electrode whereas cathode is called reduction electrode?
7. Zn rod is immersed in $CuSO_4$ solution. What will you observe after an hour? Explain your observation in terms of redox reaction.
8. Why can $CuSO_4$ solution not be stored in an iron vessel?
9. Fe decomposes steam while Cu does not, why?
10. What is meant by inert electrolyte used in salt bridge?
11. What is oxidation state of Cr in CrO_5 and why?
12. What is meant by oxidation potential of an electrode?
13. What is relationship between standard oxidation potential and standard reduction potential?
14. Find the oxidation number of Cl in HCl, HClO, ClO^-_4, and Ca(OCl)Cl.
15. Find the oxidation number of sulphur in $S_2O_7^{2-}$.
16. Arrange the following in order of increasing oxidation number of iodine. I_2, HI, ICl.
17. Does the redox reaction in a cell go to completion?
18. What happens when a silver plate is dipped in copper sulphate solution?
19. What is electronation?
20. Is the valency of an element, same as its oxidation number?
21. In the reaction given below which species is called a spectator ion and why?

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) + SO_4^{2-}(aq)$$

22. What is a redox couple?
23. What is a disproportionation reaction? Give one example.
24. What is the function of platinum electrode?

Short Answer Questions [2 & 3 Marks]

1. Explain the difference between the electromotive force and the potential difference.
2. Zinc liberates hydrogen from dil.HCl while copper fails to do so. Why?
3. How does the electron and current flow in the Daniel cell?
4. Show that oxidation and reduction go side by side by taking a suitable example.

5. Complete and balance the following skeleton equation for a reaction in acidic solution.

   $H_2O_2 + MnO_4^- + H^+ \longrightarrow Mn^{2+} + H_2O + O_2$

6. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

7. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain why?

8. Identify the oxidant and reductant in the following reactions:

   (i) $10H^+(aq) + 4Zn(s) + NO_3^-(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$

   (ii) $I_2(g) + H_2S(g) \rightarrow 2HI(g) + S(s)$

9. Balance the following equation using oxidation number method

   $HNO_3(aq) + Cu_2O(s) \rightarrow Cu(NO_3)_2(aq) + NO(g) + H_2O(l) + 2OH^-$

10. Starting with the correct half-reaction, write the correct overall net ionic reaction in the following changes.

    (i) Chromite ion (CrO_3^-) is oxidised by H_2O_2 in strongly basic solution.

    (ii) Iodate ion (IO_3^-) oxidises the iodide I^- to I_2 in acidic solution.

    (iii) Permanganate ion $MnO^-{}_4$ oxidises the oxalate ion ($C_2O^2{}_4{}^-$) to CO_2 in acidic solution.

11. Explain with example, the oxidation and reduction in terms of change in oxidation number.

12. Balance the following equation in acidic medium by both oxidation number and ion electron method and identify the oxidants and the reductants:

    $H_2S(aq) + Cl_2(g) \rightarrow S(s) + Cl^-(aq)$

13. Is it possible to store:

    (i) copper sulphate solution in a zinc vessel?

    (ii) copper sulphate solution in a nickel vessel?

    (iii) copper sulphate solution in a silver vessel?

    (iv) copper sulphate solution in a gold vessel?

    (Take help from electrochemical series)

14. Arrange A, B, C, D, E and H is order of increasing electrode potential in the electrochemical series:

    $A + H_2SO_4 \rightarrow ASO_4 + H_2$

    $ACl_2 + C \rightarrow CCl_2 + A$

    $ECl_2 + C \rightarrow$ No reaction

    $2BCl + D \rightarrow DCl_2 + 2B$

    $H_2SO_4 + D \rightarrow$ No reaction

15. Can we find the reduction potential of a single electrode in an electrochemical cell?

16. With the help of the electro-chemical series, check the feasibility of the redox reaction:

    $Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2Ag(s)$

17. Arrange the metals Mg, Na, Ag, Cu, Fe, Zn in the increasing order of reactivity. Which one will be the strongest reducing agent and which one will be the weakest one?

18. What is meant by electrochemical series? What are characteristics of electrochemical series?

Long Answer Questions [5 Marks]

1. **(i)** Balance the following reaction by ion-electron method

   $K^+ MnO_4^- + H^+ Cl^- \longrightarrow K^+Cl^- + Mn^{2+}(Cl^{-1})_2 + H_2O + Cl_2$

   (ii) Balance the following reaction by oxidation number method

   $As_2S_5 + H^+ NO_3^-(conc.) \longrightarrow H_3AsO_4 + 5H_2SO_4 + H_2O + NO_2$

2. **(i)** Balance the following equations using half-reaction method in the acidic medium.

   (a) $Zn + NO_3^- \longrightarrow Zn^{2+} + NH_4^+$

   (b) $MnO_4^- + H_2C_2O_4 \longrightarrow Mn^{2+} + CO_2$

   (c) $Cr_2O_7^{2-} + Cl^- \longrightarrow Cr^{3+} + Cl_2$

   (ii) Balance the following redox reaction in basic medium using the half-reaction method:

   (a) $Mn^{2+} + ClO_3^- \rightarrow MnO_2 + ClO_2$

   (b) $Cl_2 \rightarrow Cl^- + ClO_3^-$

3. Calculate the oxidation number of the underlined atom in the following species:

   (i) $\underline{Zn}(OH)_4^{2-}$ (ii) $\underline{C}_6H_{12}O_6$

   (iii) $[\underline{Fe}(CN)_6]^{3-}$ (iv) $\underline{N}H_4^{+1}$

   (v) $K\underline{Br}O_4$

4. **(i)** What are the highest oxidation numbers of N, S and Cl ?

   (ii) Is $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ a redox reaction?

   (iii) Calculate oxidation number of :

   (a) Cr in CrO_5 (b) S in H_2SO_5 (c) Fe in Fe_3O_4.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Out of zinc and copper vessel, which one will be more suitable to store 1M HCl solution? **[HOTS]**
2. A solution of silver nitrate solution was stirred with iron rod. Will it cause any change in concentration of silver and nitrate ions? **[HOTS]**
3. What is the oxidation number of C in $C_{12}H_{22}O_{11}$. **[HOTS]**
4. Select which of the following is not an example of disproportionation reaction.
   (a) $5P_2H_4 \rightarrow 6PH_3 + P_4H_2$
   (b) $3CuO + NH_3 \rightarrow 2N_2 + 3H_2O + 3Cu$
   (c) $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$
   (d) $Cus + 2CuO \rightarrow 3Cu + SO_2$ **[HOTS]**
5. Can we store copper sulphate solution in a silver vessel? Explain your answer
   (Given : $E^{\circ}_{Cu^{2+}/Cu} = 0.34V$; $E^{\circ}_{Ag^{+}/Ag} = 0.80V$.) **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. The standard electrode potential corresponding to the reaction
   $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$ is + 1.42 V.
   Predict if gold can be dissolved in 1 M HCl solution and on passing H_2 gas through gold solution, metallic gold will be precipitated or not? **[HOTS]**
2. Determine the oxidation number of elements marked with asterisk. **[HOTS]**
   (a) $[Cu(\overset{*}{N}H_3)_4](OH)_2$ (b) $\overset{*}{O}_2\,PtF_6$
   (c) $Rb_4Na[H\overset{*}{V}_{10}O_{28}]$
3. Nitric acid acts only as an oxidising agent while nitrous acid acts both as an oxidising as well as a reducing agent. Why? **[HOTS]**
4. Which of the following are oxidizing agents and which are reducing agents? Justify your answer with half equations.
   Br_2, Fe^{3+}, NO_3^{-}, I^{-}, Na **[HOTS]**
5. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain why? **[Examplar]**
6. Calculate the oxidation number of each sulphur atom in the following compounds: **[Examplar]**
   (a) $Na_2S_2O_3$ (b) $Na_2S_4O_6$
   (c) Na_2SO_3 (d) Na_2SO_4

Long Answer Questions [5 Marks]

1. Name one compound each in which Oxidation Number of
   (a) oxygen is + 2 (b) oxygen is – 1
   (c) hydrogen is –1 (d) nitrogen is +1
   (e) Cl is +4 (f) oxygen is –2 **[HOTS]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. What is the oxidation number of C in CH_2O?
2. Can Fe^{3+} oxidize Br^{-} to Br_2 at 1M concentration?
   $E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77V$ and $E^{\circ}(Br_2/2Br^{-}) = +1.09V$
3. Balance the following reaction: $MnO_4^{-} + H_2O_2 \longrightarrow MnO_2 + O_2$ (alkaline medium)
4. The electrode potentials of four metallic elements A, B, C and D are respectively + 0.79 V, – 0.74V, + 1.08 V and –0.31V. Arrange these in order of decreasing electropositive character. Why?
5. Arrange the following molecules in decreasing order of oxidation state (+ve to –ve) of nitrogen:
   NO_2, NH_3, HN_3, NO_2^{-}, N_2H_4.
6. (a) Write the functions of salt bridge.
   (b) Give the construction of S.H.E.
7. Given $K^{+} + e^{-} \longrightarrow K$, $E^{\circ} = -2.93V$
   $Zn^{2+} + 2e^{-} \longrightarrow Zn$, $E^{\circ} = -0.76V$
   $Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$, $E^{\circ} = 1.36V$
   (a) Which is the best oxidizing agent?
   (b) Which is the best reducing agent?
   (c) Can KCl solution be stored in a zinc vessel?
   (d) Can $ZnCl_2$ solution be stored in a potassium vessel?
   (e) Can Zn react with Cl_2?

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. $\overset{(-2)}{H_2S} + \overset{(+5)}{HNO_3} \longrightarrow \overset{(+2)}{NO} + \overset{0}{S} + H_2O$

In the reaction HNO_3 is an oxidizing agent since it itself gets reduced from +5 to +2. While H_2S is an reducing agent since it itself gets oxidized from –2 to 0.

2. Less electronegative metal amongst the two.
3. It is –1.
4. It signifies that electrode has larger tendency to loose electrons than hydrogen electrode.
5. At 1 M concentration.
6. At anode, loss of electrons takes place, i.e., oxidation takes place whereas at cathode, gain of electrons takes place, i.e., reduction takes place therefore cathode is called reduction electrode and anode is called oxidation electrode.
7. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

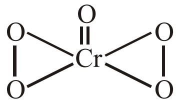
The blue colour will get discharged and reddish brown copper metal will get deposited.

8. It is because $E^\circ_{Fe^{2+}/Fe} = -0.44$ V which is lower than that of Cu

$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Fe^{2+}/Fe} = +0.34\text{ V} - (-0.44\text{ V}) = 0.78$ V.

Since, $E^\circ_{cell} = +$ ve, $\Delta G = -$ ve, i.e., reaction will take place. We cannot store $CuSO_4$ in an iron container.

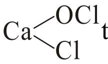
9. Fe is more reactive than hydrogen, it has lower reduction potential than hydrogen whereas Cu has higher reduction potential than H_2.
10. Inert electrolyte is an electrolyte which does not react with any of the solution present in two half cells.
11. Cr has + 6 oxidation state because it has 6 valence electrons, therefore, can form 6 covalent bonds



12. Oxidation potential measures the tendency of an element or anion to lose electrons.
13. Both are equal in magnitude but opposite in sign.
14. Cl in HCl is $+1 + x = 0 \Rightarrow x = -1$

Cl in HClO is $+1 + x - 2 = 0 \Rightarrow x = +1$

Cl in ClO_4^- is $x - 8 = -1 \Rightarrow x = +7$

In  $Ca{<}^{OCl}_{Cl}$ there are two chlorine atoms, one of chlorine is in form of Cl^- whose oxidation state is –1, other one is in form ClO^- (hypochlorite ion) in which oxidation state is + 1 $(x - 2 = -1 \Rightarrow x = +1)$.

The average oxidation state of two Chlorine atoms in $CaOCl_2$ is 0 $(-1 + 1 = 0)$ or $+2 - 2 + 2x = 0$

$\Rightarrow x = 0$

15. $+6, 2x - 14 = -2 \Rightarrow 2x = 12$

$\Rightarrow x = +6.$

16. I_2 has oxidation number zero, in HI. iodine has oxidation number–1.

In ICl, iodine has oxidation number + 1.

HI, I_2, ICl is order of increasing oxidation number.

17. No, it is not completed.
18. No change will be noticed.
19. The process in which gain of electrons takes place is called electronation.
20. No. they are not always same.
21. SO_4^{2-} ion is the spectator ion as it does not participate in the reaction.
22. Refer theory.
23. Refer theory.
24. Platinum electrode is used for non–metals like hydrogen, chlorine, etc. It being a noble metal and have a large surface area, all the cell reactions can take place on its surface. It acts as a sink for electron transfer in the cells.

Short Answer Questions

1.

S.No.	E.M.F.	Potential Difference
1	It is the potential difference between the two electrodes when no current is flowing through the circuit i.e., in the open circuit.	It is difference between the electrode potentials of two electrodes when current is flowing through the circuit.
2	It is the maximum voltage obtainable from the cell.	It is always less than the emf of cell.
3	The work calculated from e.m.f. is the maximum work obtainable from the cell.	The work calculated from the potential difference is less than maximum work obtainable from the cell.
4	It is responsible for the flow of steady current through the circuit.	It is not responsible for the flow of steady current through the circuit.

2. We know zinc has a negative reduction potential $Zn^{2+}/Zn = -0.76V$ and it lies below hydrogen in the electrochemical series. Therefore, the electron accepting tendency of zinc is less than that of hydrogen thus zinc can loose electrons to H^+ ions of the acid, as a result hydrogen gas is liberated. Since copper has positive reduction potential value (+0.34V) and it lies above hydrogen in the electrochemical series, therefore, it cannot lose electrons to H^+ and thus hydrogen is not liberated.

3. In Daniel cell Zn / Zn^{2+} acts as anode while Cu^{2+} / Cu acts as cathode, the electrons flow from Zn electrode to Cu electrode while current flows from Cu to Zn electrodes. We know that flow of current is possible only if there is a potential difference between the copper and zinc electrodes.

4. Refer theory.
In the above example Zn is oxidized while Cu is reduced.

5. MnO_4^- contains manganese in its highest oxidation state. Hence, if reaction occurs at all, MnO_4^- must be reduced. Since the solution is acidic in nature, the reduction product will be Mn^{2+}. The H_2O_2 therefore act as a reducing agent in this reaction, and its only possible oxidation product is O_2. The usual procedure for balancing may be followed from this point, as follows.

$$2 \times [MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O]$$
$$5 \times [H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-]$$
$$2MnO_4^- + 16H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2 + 10H^+$$

After cancelling, $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

The above equation is an ionic equation. If we have to write an equation in terms of neutral substances, we are free to decide which salt of MnO_4^- and which acid to be used. we use $KMnO_4$ and H_2SO_4, we obtain

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow 2MnSO_4 + 8H_2O + K_2SO_4 + 5O_2$$

6. In MnO_4^-, Mn is in the highest oxidation state i.e. +7. Therefore, it does not undergo disproportionation. MnO_4^{2-} undergoes disproportionation as follows:

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

7. PbO is a basic oxide and simple acid base reaction takes place between PbO and HNO_3. On the other hand in PbO_2, lead is in + 4 oxidation state and cannot be oxidised further. Therefore no reaction takes place. Thus, PbO_2 is passive, only PbO reacts with HNO_3.

$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$ (Acid base reaction)

8. (i) O.N. of Zn is changing from zero to +2 (increase in O.N.), therefore Zn is a reductant. O.N. of N is changing from +5 in NO_3^- to –3 in NH^+_4. Therefore, NO^-_3 is oxidant.

(ii) I_2 is an oxidant as it is changing its O.N. from zero in I_2 to –1 in HI.
H_2S is a reductant as S is changing its O.N. from –2 in H_2S to zero in sulphur.

9. $HNO_3(aq) + Cu_2O(s) \rightarrow Cu\,(NO_3)\,(aq) + NO(g) + H_2O(l)$

(i) The oxidation number of N changes from + 5 in HNO_3 to + 2 in NO.

(ii) The oxidation number of Cu changes from +1 in Cu_2O to + 2 in $Cu\,(NO_3)$

(iii) Electron balance diagrams can be written as follows

$N^{+5} + 3e^- \rightarrow N^{+2}$ ...(1)

$Cu^{+1} \rightarrow Cu^{+2} + e^-$ ...(2)

(iv) In order that the number of electrons lost shall be equal the number gained, multiply equation (1) by 2 and (2) by 6

$2N^{+5} + 6e^- \rightarrow 2N^{+2}$

$6Cu^{+1} \rightarrow 6Cu^{+2} + 6e^-$

Hence, the coefficients of HNO_3 and of NO are 2 and those of Cu_2O is 3 and $Cu\,(NO_3)_2$ is 6. Part of the skeleton equation can now be written as

$2HNO_3 + 3Cu_2O \rightarrow 2NO + 6Cu\,(NO_3)_2$

The two atoms of H form one H_2O on the right.

$2HNO_3 + 3Cu_2O \rightarrow 2NO + 6\,Cu(NO_3) + H_2O$

Although the N atoms that change oxidation number have been balanced, other N atoms are present as NO^-_3 ions in $6Cu\,(NO_3)_2$, For this reason, we add $12HNO_3$ to the $2HNO_3$ already on the left side and then balance H_2O molecule. The complete balanced equation is

$$14HNO_3(aq) + 3Cu_2O(s) \rightarrow 6Cu\,(NO_3)_2\,(aq) + 2NO(s) + 7H_2O(l)$$

10. (i) Oxidation half-reaction:

$$\overset{+5}{CrO_3^-} + 2OH^- \longrightarrow \overset{+6}{CrO_4^{-2}} + H_2O + e^-$$

Reduction half-reaction:

$$\overset{-1}{H_2O_2} + 2e^- \longrightarrow 2OH^-$$

Over all cell reaction

$$2CrO_3^- + H_2O_2 \longrightarrow 2CrO_4^{-2} + H_2O$$

(ii) Oxidation half-reaction

$\{2I^- \rightarrow I_2 + 2e^-\} \times 5$

Reduction half-reaction.

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

Overall cell reaction:

$$2IO_3^- + 10I^- + 12H^+ \longrightarrow 6I_2 + 6H_2O$$

or $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

(iii) Oxidation half-reaction:

$$\left\{\overset{+3}{C_2O_4^{-2}} \longrightarrow \overset{+4}{2CO_2} + 2e^-\right\} \times 5$$

Reduction half-reaction:

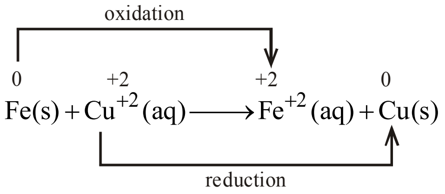
$$\left\{MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O\right\} \times 2$$

Overall cell reaction:

$$5C_2O_4^{-2} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

11. Oxidation is the part of an oxidation reduction reaction in which there is an increase in the oxidation number of an atom. Reduction is a reaction in which there is a decrease in the oxidation number of an atom.

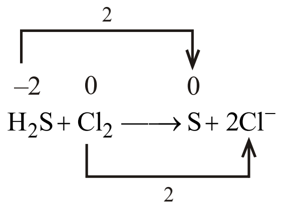
Example:



$$\overset{0}{Fe}(s) + \overset{+2}{Cu^{+2}}(aq) \longrightarrow \overset{+2}{Fe^{+2}}(aq) + \overset{0}{Cu}(s)$$

12. $H_2S\,(aq) + Cl_2(g) \to S(s) + Cl^-\,(aq)$

Oxidation number method



$$\overset{-2}{H_2S} + \overset{0}{Cl_2} \longrightarrow \overset{0}{S} + 2Cl^-$$

Net reaction is $H_2S + Cl_2 \to S + 2Cl^- + 2H^+$

Ion-electron method

Oxidation half-reaction:

$H_2S \to S + 2H^+ + 2e^-$

Reduction half-reaction:

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

Net reaction :

$$H_2S + Cl_2 \to S + 2Cl^- + 2H^+$$

Oxidant : Cl_2 ; Reductant : H_2S

13. (i) No, zinc will displace copper from $CuSO_4$ solution because

$$E^o_{Zn^{2+}/Zn} < E^o_{Cu^{2+}/Cu}$$

(ii) No, copper sulphate solution can not be stored in nickel vessel.

(iii) Yes, copper sulphate solution can be stored in silver vessel as

$E^o_{Cu^{2+}/Cu} < E^o_{Ag^+/Ag}$. Silver will not displace copper from $CuSO_4$ solution.

(iv) Yes, gold vessel can easily store $CuSO_4$ solution.

14. $E < C < A < H < D < B$.

15. It is not possible to calculate the reduction potential of a single electrode in an electrochemical cell. Because, a single electrode constitutes a half cell, which can't work independently.

16. It is not possible to calculate the reduction potential of a single electrode in an electrochemical cell. Because, a single electrode constitutes a half cell, which can't work independently.

17. Refer theory

18. Refer theory

Long Answer Questions

1. **(i)** $MnO_4^- + Cl^- \longrightarrow Mn^{2+} + Cl_2$

The half–reactions are : $\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn^{2+}}$,

$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

$8H^+ + MnO_4^{-1} \longrightarrow Mn^{2+} + 4H_2O$

Balance total charge with adding electron on higher charge side . As the higher charge is +7 and it decreases to +2 thus add $5e^-$ to +7 side of reaction so that the total charge for this half reaction is balanced.

$5e^- + 8H^+ + MnO_4^{-1} \longrightarrow Mn^{2+} + 4H_2O$ ...(i)

$2Cl^- \longrightarrow Cl_2$

$2Cl^- \longrightarrow Cl_2 + 2e^-$ ...(ii)

Now combine equation (i) and (ii). The electrons should get cancelled out thus multiply eqn (i) by 2 and eqn (ii) by 5

$10e^- + 16H^+ + 2MnO_4^{-1} \longrightarrow 2Mn^{2+} + 8H_2O$

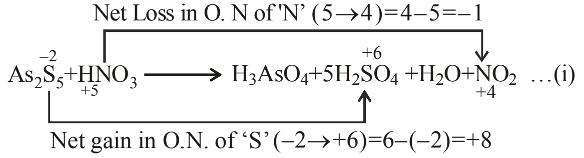
$10Cl^{-1} \longrightarrow 5Cl_2 + 10e^-$

Combining the half–reactions:

$10Cl^- + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$

or $16HCl + 2KMnO_4 \longrightarrow 2MnCl_2 + 8H_2O + 5Cl_2 + 2KCl$

(ii)



$$As_2\overset{-2}{S_5} + H\underset{+5}{N}O_3 \longrightarrow H_3AsO_4 + 5H_2\overset{+6}{S}O_4 + H_2O + \underset{+4}{N}O_2 \quad ...(i)$$

Here O.N. of 'N' decreases from + 5 to +4 while that of 'S' increases in from – 2 to +6. Since there are five 'S' atoms in reactants as well as in products and one 'N' atom in reactants as well as products in eqn(i), now balance increase / decrease in O.N. The total increase in O.N. of S is + 8 i.e. by a factor 40 since there are 5 'S' atoms and decrease in O.N. of N is –1. Multiply As_2S_5 by 1 and HNO_3^- by 40 we get

Balance the elements which change oxidation state:

$$As_2S_5 + 40HNO_3 \longrightarrow H_3AsO_4 + 5H_2SO_4 + H_2O + 40NO_2$$

Balance atoms other than "O" and "H".

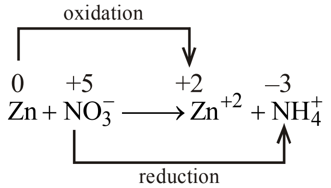
$$As_2S_5 + 40\,HNO_3 \longrightarrow 2H_3AsO_4 + 5H_2SO_4 + H_2O + 40NO_2$$

Balance the 'O' and 'H' atoms. Since there are 120 'O' atoms on the reactant side and 109 'O' atoms on the product side add $11H_2O$ on the product side to balance the equation. There are 40 'H' atoms on reactant side and 18 'H' atoms on the product side initially but after adding 11 H_2O the 'H' atoms get balanced.

$$As_2S_5 + 40HNO_3 \longrightarrow 2H_3AsO_4 + 5H_2SO_4 + 12H_2O + 40NO_2$$

2. **(i)**

(a)



$$\overset{0}{Zn} + \overset{+5}{NO_3^-} \longrightarrow \overset{+2}{Zn^{+2}} + \overset{-3}{NH_4^+}$$

Oxidation half-reaction:

$[Zn \to Zn^{+2} + 2e^-] \times 4$

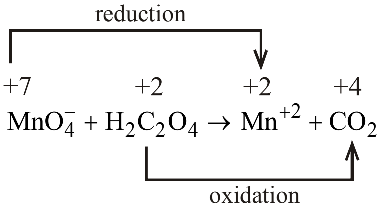
Reduction half-reaction:

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

Net balanced redox reaction:

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

(b)



$$\overset{+7}{MnO_4^-} + \overset{+2}{H_2C_2O_4} \rightarrow \overset{+2}{Mn^{+2}} + \overset{+4}{CO_2}$$

Oxidation half-reaction:

$$[H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-] \times 5$$

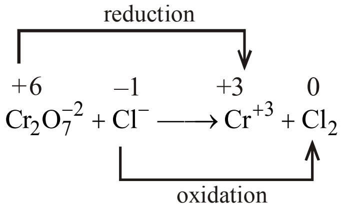
Reduction half-reaction:

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

Net balanced redox reaction:

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

(c)



$$\overset{+6}{Cr_2O_7^{-2}} + \overset{-1}{Cl^-} \longrightarrow \overset{+3}{Cr^{+3}} + \overset{0}{Cl_2}$$

Oxidation half-reaction:

$$\{2Cl^- \rightarrow Cl_2 + 2e^-\} \times 3$$

Reduction half-reaction:

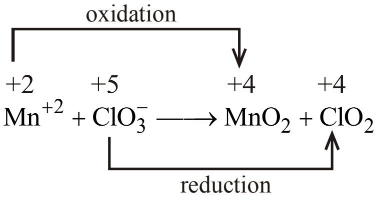
$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

Net balanced redox reaction :

$$Cr_2O_7^{-2} + 6Cl^- + 14H^+ \rightarrow 2Cr^{+3} + Cl_2 + 7H_2O$$

(ii)

(a)



$$\overset{+2}{Mn^{+2}} + \overset{+5}{ClO_3^-} \longrightarrow \overset{+4}{MnO_2} + \overset{+4}{ClO_2}$$

Oxidation half-reaction:

$$Mn^{+2} + 4OH^- \rightarrow MnO_2 + 2e^- + 2H_2O$$

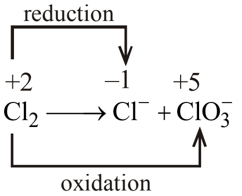
Reduction half-reaction:

$$\{ClO_3^- + H_2O + e^- \rightarrow ClO_2 + 2OH^-\} \times 2$$

Net balanced redox reaction:

$$2ClO_3^- + Mn^{+2} \rightarrow 2ClO_2 + MnO_2$$

(b)



$$\overset{+2}{Cl_2} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$$

Oxidation half-reaction:

$$Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10e^- + 6H_2O$$

Reduction half-reaction:

$$\{Cl_2 + 2e^- \rightarrow 2Cl^-\} \times 5$$

Net balanced redox reaction:

$$6Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10Cl^- + 6H_2O$$

OR

$$3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- 3H_2O$$

3. (i) $Zn(OH)^{-2}{}_4 = x_{Zn} + 4x_{OH} = -2$

$= x_{Zn} + 4(-1) = -2$

$\therefore \quad x_{Zn} = +2$

(ii) $C_6H_{12}O_6 = 6x_C + 12(1) + 6(-2) = 0$

$\therefore \quad x_C = 0$

(iii) $[Fe(CN)_6]^{-3} = x_{Fe} + 6(-1) = -3$

$x_{Fe} = +3$

(iv) $NH^+{}_4 = x_N + 4(1) = +1$

$\therefore \quad x_N = -3$

(v) $K_{BrO4} = +1 + x_{Br} + 4(-2) = 0 \quad \therefore \quad x_{Br} = +7$

4. (i) The highest oxidation numbers for N, S and Cl are +5, +6 and +7 respectively.

(ii) The reaction

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-}$$

$+2H^+$ cannot be regarded as a redox reaction because the O. No. of 'Cr' in $Cr_2O_7^{2-}$ and CrO_4^{2-} is same (+6).

(a) Refer ans. 11 (Very Short Answer)

(b) Refer Textbook Ans 8.5

(c) Refer Textbook Ans. 8.2 (c)

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. Copper vessel.
[In electrochemical series copper lies above hydrogen].

2. Concentration of silver ions will change.

3. Zero.

4. In Equations (b) and (d) the reactants are not undergoing simultaneous oxidation and reduction. Hence (b) and (d) are not the examples of disproportionation reactions.

5. Yes, copper sulphate solution can be stored in a silver vessel.
From the given E° values we find that copper is more reactive than silver. Thus silver can not displace copper from copper sulphate solution and so the following reaction will not occur.

$$Cu^{2+}(aq) + Ag(s) \longrightarrow \text{No reaction} \cdot$$

Short Answer Questions

1. As $E^o_{Au^{3+}/Au}$ is greater than $E^o_{H^+/H_2}$

Gold can not be oxidised by hydrogen ion to give hydrogen. Hence, gold does not dissolve in 1 M HCl solution. On the contrary, if hydrogen gas is passed through the salt solution of the gold it will reduce Au^{3+} ion and metallic gold will be precipitated.

$3H_2(g) + 2Au^{3+}(aq) \rightarrow 6H^+(aq) + 2\,Au(s)$

2. (a) NH_3 is a neutral ligand. Therefore oxidation state of nitrogen is same as in ammonia, i.e.,

$x + 3 = 0$ or $x = -3$

(b) In this compound, platinum has maximum oxidation state of +4. Therefore oxidation state of O_2 is determined by taking x.

$2x + 4 - 6 = 0$ or $x = +1$

(c) Let oxidation state of vanadium is x, then

$+4 + 1 + 1 + 10x - (28 \times 2) = 0$

or $10x = 50$ or $x = +5$

3. (i) HNO_3 : Oxidation number of N is $HNO_3 = +5$

Maximum oxidation number of N = + 5

Minimum oxidation number of N = –3

Since the oxidation number of N in HNO_3 is maximum (+5), therefore, it can only decrease by accepting electrons. Hence HNO_3 acts only as an oxidising agent.

(ii) HNO_2 : Oxidation number of N in $HNO_2 = +3$

Maximum oxidation number of N = +5

Minimum oxidation number of N = –3

Thus, the oxidation number of N can either increase by losing electrons or can decrease by accepting electrons. Therefore, HNO_2 acts both as an oxidising as well as a reducing agent.

4. Oxidants : Br_2, Fe^{3+}, NO_3^-

$Fe^{3+} + e \longrightarrow Fe^{2+}$

$N^{5+} + 2e \longrightarrow N^{3+}$

$Br_2 + 2e \longrightarrow 2Br^-$

reductants : I^-, Na

$Na \longrightarrow Na^+ + e$

$2I^- \longrightarrow I_2 + 2e$

5. PbO is a basic oxide and simple acid base reaction takes place between PbO and HNO_3. On the other hand in PbO_2 lead is in +4 oxidation state and cannot be oxidised further. Therefore no reaction takes place. Thus, PbO_2 is passive, only PbO reacts with HNO_3.

$2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$ (Acid base reaction)

6. (a) +2 (b) +5, 0, 0, +5 (c) +4 (d) +6

Long Answer Questions

1.
(a) F_2O (b) H_2O_2
(c) NaH (d) N_2O
(e) ClO_2 (f) H_2O

CHAPTER TEST

1. Zero.

2. No since the $E^o_{cell} = 0.77 - 1.09 = -0.32V$ (negative) the reaction is not feasible.

3. $2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 2OH^- + 3O_2 + 2H_2O$

4. B > D > A > C. For elements lower the value of reduction potential (electrode potential) more will be metallic or electropositive character. Hence B is most metallic or electropositive as it has the minimum value of electrode potential (– 0.74V).

5. $\underset{+4}{NO_2} > \underset{+3}{NO_2^-} > \underset{+2}{N_2H_4} > \underset{1/3}{HN_3} > \underset{-3}{NH_3}$

6. (a) (i) It allows the movement of ions from one solution to the other without mixing of two solutions. Thus the electrons flow in the outer circuit while the inner circuit is completed by flow of ions.

(ii) It helps to maintain the electrical neutrality of the solutions in the two half cells due to the flow of ions.

(b) It consists of platinum electrode dipped into a molar(1M) solution of H^+ ions and the hydrogen gas is continuously passed through it at 298K and 1 atm pressure. This electrode may serve as anode or cathode depending upon the nature of another electrode to which it is connected.

7. (a) Cl_2

(b) K

(c) Yes, KCl can be stored since its emf is negative.

(d) No, since emf is positive.

(e) Yes, Zn can react with Cl_2.

9

Chapter

Hydrogen

INTRODUCTION

Hydrogen is the first and the lightest element in the periodic table. In elemental form it exists as diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other elements.

Global concern regarding energy can be overcome or managed by the use of hydrogen as fuel.

POSITION OF HYDROGEN IN THE PERIODIC TABLE

Outer shell electronic configuration is $1s^1$ which indicates its resemblance with that of alkali metals(ns^1) and halogens (ns^2 np^5) because all of these are short by one electron from noble gas configuration. Hydrogen therefore has resemblance with alkali metals which lose one electron to form unipositive ion as well as with halogens which gain one electron to form uninegative ion.

However it differs from them as well. Hydrogen like alkali metals forms halides, oxides and sulphides but it does not posses metallic character. Like halogens, hydrogen forms diatomic molecules and covalent compounds but hydrogen is less reactive as compared to halogens. It is unique in behaviour and is best placed separately in the periodic table.

DIHYDROGEN

Occurence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course in the combined form it constitutes 15.4% of the earth's crust and the oceans.

Isotopes of Hydrogen

There are three isotopes of hydrogen, which differ from each other in their number of neutrons, such as protium $\left({}_1^1H\right)$, deuterium $\left({}_1^2H\right)$, tritium $\left({}_1^3H\right)$, containing 0, 1 and 2 neutrons respectively. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD molecule. The tritium concentration is about one atom per 10^{18} atoms of protium. Among these, tritium is radioactive. These isotopes possess same chemical properties due to same number of electrons, but they differ in their physical properties due to their different atomic masses. Deuterium is used as moderator in nuclear reactors and in artificial transmutation of elements. Tritium is used as tracer element in the study of bio-chemical reactions and also in preparation of hydrogen bomb.

Physical constants of H_2, D_2 and T_2.

Property	Hydrogen (H_2)	Deuterium (D_2)	Tritium (T_2)
Molecular mass (amu)	2.016	4.028	6.03
Melting point (K)	13.8	18.7	20.63
Boiling point (K)	20.4	23.9	25.00
Bond energy (kJ mol^{-1})	435.9	443.4	446.9
Heat of fusion (kJ mol^{-1})	0.117	0.197	0.25
Heat of vaporisation (kJ mol^{-1})	0.904	1.226	1.393

Methods of Preparation

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

(i) Lab preparation of H_2

(a) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn\,(s) + 2H^+\,(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

(b) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn(s) + 2NaOH\,(aq) \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2\,(aq)} + H_2(g)$$

(ii) Commercial preparation of dihydrogen

(a) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(\ell) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(b) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(c) It is obtained as a by-product in the manufacture of sodium hydroxide and chlorine in the electrolysis of brine solution. During electrolysis, the reactions that take place are:

At anode : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

At cathode : $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$$2Na^+(aq) + 2Cl^- + 2H_2O(\ell) \longrightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(d) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n\pm2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (3n+1)H_2$$

e.g., $CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270K} CO(g) + 3H_2(g)$

The mixture of CO and H_2 is called water gas. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas' . Now a days ‘syngas’ is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing syngas from coal is called coal gasification.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{670K} CO_2(g) + H_2(g)$$

This is called water-gas shift reaction. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently ~77% of the industrial dihydrogen is produced from petrochemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

Properties of Dihydrogen

(i) Physical properties

Colourless, odourless, tasteless combustible gas.

It is lighter than air and insoluble in water. Some other physical properties of dihydrogen are mentioned in table above.

(ii) Chemical properties

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H – H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. It is because of this fact that the dissociation of dihydrogen into its atoms is only ~ 0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H – H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by

- loss of an electron to give H^+
- gain of an electron to form H^-, and
- sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

(i) Reaction with halogens : It reacts with halogens, X_2 to give hydrogen halides, HX,

$H_2(g) + X_2(g) \rightarrow 2HX(g)$ (X = F, Cl, Br, I)

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

(ii) Reaction with dioxygen : It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(\ell)\ \Delta H = -285.9\ \text{kJ mol}^{-1}.$$

(iii) Reaction with dinitrogen: With dinitrogen, it forms ammonia.

$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{673K,\ 200\ atm} 2NH_3(g)$

$\Delta H = -92.6\ kJ\ mol^{-1}$.

This is the method for the manufacture of ammonia by the Haber's process.

(iv) Reaction with metals: With many metals, it combines at high temperature to yield the corresponding hydrides

$H_2(g) + 2M(g) \longrightarrow 2MH(s)$; (M = alkali metal)

(v) Reaction with metal ions and metal oxides :

It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$$

$$yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(\ell)$$

(vi) Reactions with organic compounds : It reacts with many organic compounds in the presence of catalysts, to give useful hydrogenated products of commercial importance.

Example :

- Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)
- Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

Uses of Dihydrogen

(i) It is used in the manufacture of ammonia, methyl alcohol (from CO), gasoline (synthetic petrol), HCl, etc.
(ii) It is used in the manufacture of vegetable ghee (hydrogenation of oils of fats).
(iii) Oxy-hydrogen flame (oxy-hydrogen torch) and atomic hydrogen flame (atomic hydrogen torch) are used for cutting and welding steel and other hard metals.
(iv) It is used for providing reducing atmosphere is furnaces.
(v) Due to its low density, hydrogen is used in filling baloons and gas bags for air ships. However, it is now replaced by helium.
(vi) Several fuel gases (e.g. coal gas, water gas, oil gas) contain hydrogen as an important constitutent.
(vii) It is used in fuel cells for generating electrical energy.

HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If E is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6). The hydrides are classified into three categories

Ionic Hydrides

These are formed by metals which have low electronegativity values and are electropositive (s-block elements) with respect to hydrogen, i.e., alkali and alkaline earth metals (except Be and Mg). For example

(i) $2\ Na + H_2 \longrightarrow 2NaH$, (ii) $Ca + H_2 \longrightarrow CaH_2$.

Interstitial Hydrides

They are also called metallic or non-stoichiometric hydrides. These are formed by Be, Mg (both are s-block elements), d-block and f-block elements. These are interstitial compounds as the hydrogen atoms occupy interstitial places in the metal lattices. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. These are non-stoichiometric compounds and give out hydrogen easily on strong heating and are thus used as strong reducing agents. This suggests that hydrogen is present in the atomic state.

Note: Hydride gap - Metals of group 7,8 & 9 do not form hydrides. Even from group 6, only chromium forms CrH.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media.

Covalent Hydrides

Dihydrogen forms molecular compounds with most of the p-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of nonmetals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative number of electrons and bonds in their Lewis structure into :

(i) electron-deficient (ii) electron-precise (iii) electron-rich hydrides

(i) **Electron-deficient :** An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

(ii) **Electron-precise :** Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

(iii) **Electron-rich hydrides :** Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH_3 has 1-lone pair, H_2O - 2 and HF -3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

Thus the boiling point of NH_3, H_2O and HF will be higher than hydrides of other group members.

WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. Water, because of its high dielectric constant has the ability to dissolve most of the inorganic (ionic) compounds and thus is regarded as universal solvent. Water has amphoteric character.

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \longrightarrow \underset{\text{acid}}{NH_3^+} + \underset{\text{base}}{OH^-}$$

Physical Properties

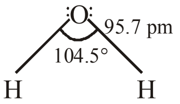
Water is a colourless liquid and possesses a high dielectric constant. It has strong intermolecular H-bonding due to which it has high enthalpy of vaporization, high enthalpy of fusion and high polarity (good solvent). Water is a good solvent for ionic compounds but a poor solvent for covalent compounds. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Water molecule is a bent molecule with a bond angle of 104.5°. The resultant dipole moment of water is 1.840 D. Due to the high electronegativity of oxygen, several H_2O molecules associate through hydrogen bonding.

On the other hand, solubility of some organic compounds (Covalent) like alcohol, carboxylic acids, carbohydrates, urea, etc. in water is because of their capability of forming hydrogen bonds with water.

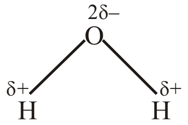
Note : Insolubility of some ionic compounds like AgCl, $BaSO_4$, CaF_2, AlF_3 in water is due to their exceptionally high attractive forces in the lattice. On the other hand, solubility of some organic compounds (covalent) like alcohols, carboxylic acids and carbohydrates in water is because of their capability of forming hydrogen bonding with water.

Structure of Water

In H_2O each oxygen forms four sp^3-hybridized orbital. Two of these form sp^3-s, O–H bonds while other two contain a lone pair of electrons each. In the gas phase, water is a bent molecule with a bond angle of 104.5° and O–H bond length of 95.7 pm. It is a highly polar molecule.



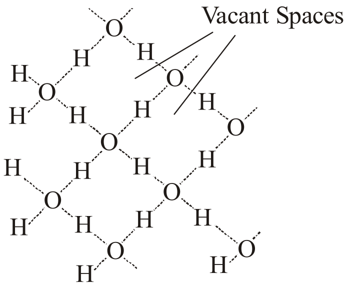
Bent structure



Dipolar structure

Structure of Ice

Ice has a highly ordered 3D H-bonded structure in which each O-atom is tetrahedrally surrounded by four other H-atoms at a distance of 276 pm. This gives ice an open cage like structure. Density of ice is less than that of water. Thus, ice floats on water.



Chemical Properties

(i) It acts as both acid & base i.e., amphoteric in nature. It also undergoes auto protolysis

$$\underset{\text{Bronsted base}}{H_2O} + H_2S \rightleftharpoons H_3O^+ + HS^-$$

$$\underset{\substack{\text{Bronsted}\\\text{acid}}}{H_2O} + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

The auto-protolysis (self-ionization) of water takes place as follows :

$$\underset{\substack{\text{acid-1}\\\text{(acid)}}}{H_2O(\ell)} + \underset{\substack{\text{base-2}\\\text{(base)}}}{H_2O(\ell)} \rightleftharpoons \underset{\substack{\text{acid-2}\\\text{(conjugate}\\\text{acid)}}}{H_3O^+(aq)} + \underset{\substack{\text{base-1}\\\text{(conjugate}\\\text{base)}}}{OH^-(aq)}$$

(ii) **Redox reactions involving water:**

$$2H_2O(\ell) + 2Na(s) \longrightarrow 2NaOH(aq) + H_2(g)$$

$$6CO_2(g) + 12H_2O(\ell) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(\ell) + 6O_2(g)$$

$$2F_2(g) + 2H_2O(\ell) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(iii) **Hydrolysis of compounds:-** Due to high dielectric constant of water it has very strong hydrating tendency. e.g.

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

$$P_4O_{10}(s) + 6H_2O(\ell) \longrightarrow 4H_3PO_4(aq)$$

$$SiCl_4(\ell) + 2H_2O(\ell) \longrightarrow SiO_2(s) + 4HCl(aq)$$

(iv) **Forms hydrates with metal salts :** From aqueous solutions many salts can be crystallised as hydrated salts.The association of water is of three types.

(i) Coordinate bonded water e.g. $[Ni(H_2O)_6]^{2+}(NO_3^-)_2$

(ii) Hydrogen bonded water e.g. $[Cu(H_2O)_4]SO_4.H_2O$

(iii) Interstitial water e.g. $BaCl_2.2H_2O$

HARD & SOFT WATER

Water containing bicarbonates, sulphates and chlorides of calcium and magnesium is called hard water. The water is called hard as it is hard to get lather when soap is added to such a sample of water. Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$2\ C_{17}H_{35}COONa\ (aq) + M^{2+}\ (aq) \longrightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+(aq)\ (M = Ca, Mg)$

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scum. This reduces the efficiency of the boiler. On the other hand, soft water easily gives lather with soap. Hardness of water is of two types :

Temporary Hardness:

Temporary hardness is due to the presence of magnesium and calcium hydrogen carbonates. It can be removed by :

(i) Boiling : During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$. Hence $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii) Clark's method : In this method, calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

Permanent Hardness :

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) Treatment with washing soda (sodium carbonate) :

Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + 2NaCl\ (M = Mg, Ca)$$

$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + Na_2SO_4$$

(ii) Calgon's method : When sodium hexametaphosphate ($Na_6P_6O_{18}$) commercially called 'calgon', is added to hard water, the following reactions take place :

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

$$(M = Mg, Ca)$$

The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method : This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reaction takes place.

$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^+(aq)$ $(M = Mg, Ca)$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$MZ_2(s) + 2NaCl\,(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$

(iv) Synthetic resins method : Now a days hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with – SO_3H group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft. Here R is resin anion.

$2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$

In this cation exchange process, H^+ exchanges for Na^+, Ca^{2+}, Mg^{2+} and other cations present in water. This process results in proton release and thus makes the water acidic, In the anion exchange process:

$$RNH_2(s) + H_2O(\ell) \rightleftharpoons RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH(s) + X^-(aq) \rightleftharpoons RNH_3^+.X^-(s) + OH^-(aq)$$

OH^- exchanges for anions like Cl^-, HCO_3^-, SO_4^{2-} etc. present in water. OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\,(\ell)$$

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

HEAVY WATER (D_2O)

It is discovered by Urey. Ordinary water contains a fraction (about 1 part in 6000 parts) of heavy water. On a large scale, it is produced by repeated electrolysis of ordinary water containing alkali.

It is made up of two deuterium atoms and one oxygen atom. Its molecular weight is 20. Physical properties of D_2O is different from that H_2O due to greater nuclear mass of deuterium. It has a greater degree of association. The chemical properties of D_2O are almost similar to that of H_2O. However the reaction velocity, in general is slightly less in case of D_2O reactions. Such differences in the rates of reactions due to the difference in the mass number of isotopes are known as isotopic effect.

D_2O is used as a moderator (for slowing down speed of neutrons) in nuclear reactors and as a tracer compound. It is also used in the preparation of deuterium. Moreover other deuterium containing compounds of use can also be prepared by D_2O.

$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$

$SO_3 + D_2O \rightarrow D_2SO_4$

$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$

Six different varieties of heavy water are possible in terms of three different isotopes of oxygen.

(a) $H—O^{16}—D$ (b) $D—O^{16}—D$ (c) $H—O^{17}—D$

(d) $D—O^{17}—D$ (e) $H—O^{18}—D$ (f) $D—O^{18}—D$

Comparision between the properties of water & heavy water.

Property	H_2O	D_2O
Denisty at 293 K	0.9982	1.1056
Freezing point	273.2 K	276.8 K
Boiling point	373.2 K	374.4 K
Temperature of max. denisty	277 K	284.6 K
Ionisation constant	1.008×10^{-14}	1.95×10^{-15}

HYDROGEN PEROXIDE

Hydrogen peroxide is an important chemical discovered by the French Chemist J.L Thenard in 1818. It is also called oxygenated water.

Methods of Preparation

(i) By the action of H_2SO_4 on hydrated barium peroxide .

$BaO_2.8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8\,H_2O$

Note : anhydrous barium peroxide does not react readily with sulphuric acid because a coating of insoluble barium sulphate is formed on its surface which stops further action of the acid. Hence hydrated barium peroxide, $BaO_2.\,8H_2O$, must be used.

H_2O_2 prepared by this method contains Ba^{2+} ions which catalyse the decomposition of H_2O_2. Thus H_2O_2 prepared cannot be stored for long period. Moreover H_2SO_4 also catalyse the decomposition of H_2O_2 therefore weaker acids like H_2CO_3 and H_3PO_4 are preferred over H_2SO_4.

$$BaO_2 + H_2CO_3 \longrightarrow BaCO_3 \downarrow + H_2O_2$$

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 3H_2O_2$$

Advantage of above method is that the heavy metal impurities present in BaO_2 which catalyse the decomposition of H_2O_2 gets removed as insoluble phosphates.

(ii) **From Na_2O_2 (Merck's method) :** Na_2O_2 is gradually added to ice-cold solution of 20% H_2SO_4.

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

(iii) **Manufacture of hydrogen peroxide**. The electrolysis of 50% sulphuric acid give perdisulphuric acid ($H_2S_2O_8$) which on distillation yields 30% solution of hydrogen peroxide.

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$$

At cathode (Cu coil) : $2H^+ + 2e^- \longrightarrow 2H \rightarrow H_2 \uparrow$

At anode (Pt): $2HSO_4^- \longrightarrow 2HSO_4 + 2e^-$

$$2HSO_4 \longrightarrow \underset{\text{Perdisulphuric acid}}{H_2S_2O_8}$$

Peroxodisulphuric acid is then distilled with water under reduced pressure.

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

(iv) **By the auto-oxidation of 2-ethylanthraquinol**. This is the most modern method. In this process, air is passed through 10% solution of 2-ethylanthraquionol in a mixture of benzene and cyclohexane.

$$\begin{tikzcd}\text{2-Ethyl anthraquinol} \arrow[r, "\text{air}"] & \text{2-Ethyl anthraquinone} + H_2O_2 \arrow[l, bend left, "H_2/\text{pd}"]\end{tikzcd}$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure.

Physical Properties

(i) It is thick syrupy pale blue liquid.
(ii) The dipole moment is slightly more than water.
(iii) It is more viscous than water.
(iv) It is completely miscible with water, alcohol and ether.
(v) It is diamagnetic in nature.
(vfi) Pure H_2O_2 is a weak dibasic acid. It is stored in coloured, plastic bottles away from sunlight otherwise it disintegrates.

Strength of H_2O_2 Solution

Concentration of H_2O_2 is expressed in terms of volume strength e. g. 10 volume, 15 volume, etc., or as percentage of H_2O_2 in solution (W/V).

e.g., 10 volume of H_2O_2 solution means 1 ml of this solution on decomposition evolves 10 ml O_2 at N. T. P.

30% solution of H_2O_2 means 30 g of H_2O_2 is present in 100 ml of its solution. It means that one millilitre of 30% H_2O_2 solution will give 100 ml of oxygen at STP.

Chemical Properties

H_2O_2 can act both as oxidising as well as reducing agent, as the oxidation number of O (–1) in H_2O_2can be changed to (–2) in OH^- state or (0) in O_2 state. However H_2O_2 is a powerful oxidizing agent but a poor reducing agent. Oxidation by H_2O_2 is slow in acidic medium but rapid in basic medium.

(i) **Oxidizing action :** H_2O_2 can act as a strong oxidizing agent in both acidic as well as basic medium.

(a) **In acidic medium:** The basic reaction is H_2O_2 is used as a bleaching agent due to its ability to oxidise the coloured matter,

$$H_2O_2 \longrightarrow H_2O + [O],\ H_2O_2 \longrightarrow H_2O + O$$

For example, (i) $2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$

(ii) $H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$

(iii) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

(b) **In basic medium:** The basic reaction is $H_2O_2 + 2OH^- + 2e^- \longrightarrow 2H_2O + 2O^-$

For example, (i) $Mn^{2+} + H_2O_2 + 2OH \longrightarrow Mn^{4+} + 2H_2O$

(ii) $2HCHO + H_2O_2 \xrightarrow{\text{pyrogallol}} 2HCOOH + H_2$

(ii) Reducing action: It acts as a reducing agent towards oxidising agents in acidic as well in alkaline medium.

(a) In acidic solution : $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

For example, (i) $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(ii) $HOCl + H_2O_2 \longrightarrow Cl^- + O_2 + H_3O^+$

(b) Alkaline medium:- $H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$

(i) $Cl_2 + H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 2H_2O + O_2$

(ii) $2Fe^{3+} + H_2O_2 + 2OH^- \longrightarrow 2Fe^{2+} + 2H_2O + O_2$

Note : Reducing action in acidic solution in somewhat slow than that in alkaline solution.

(iii) Bleaching action: H_2O_2 is used as bleaching agent due to its ability to oxidise the coloured matter

$H_2O_2 \rightarrow H_2O + [O]$

Colouring matter + [O] → Oxidised coloured matter.

(iv) Storage : Pure H_2O_2 is unstable and decompose as $2H_2O_2 \rightarrow 2H_2O + O_2$ on exposure to light. In presence of metals or traces of alkali this decomposition gets catalysed. Thus it is stored in wax lined bottles or plastic vessels in dark. Urea can be added as a stabiliser. It is kept-away from dust as it can induce explosive decomposition of the compound.

Uses of H_2O_2

It is used

(a) For bleaching delicate articles like wool, hair, leather, ivory, etc.
(b) In production of epoxide, propylene oxide, etc.
(c) As an antiseptic for washing wounds, teeth, ears under the name of perhydrol.
(d) As a propellent for torpendose.
(e) As an oxidant for rocket.
(f) H_2O_2 is used to remove excess chlorine from textiles so this property is called *antichlor*.
(g) H_2O_2 is now used to check environmental pollution, i.e., treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic condition to sewage wastes,etc.

DIHYDROGEN AS A FUEL

On a mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloys like $NaNi_5$, $Ti\text{-}TiH_2$, $Mg\text{–}MgH_2$ etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

HYDROGEN ECONOMY

The hydrogen economy refers to a hypothetical future system of delivering energy through the use of hydrogen (H_2). The term was coined by John Bockris at 1970. The proposal to use hydrogen as a fuel in industry. Power plants and possibly also in homes and motor vehicles is called hydrogen economy. The basic principle of hydrogen economy is production, storage and transportation in the form of liquid or gaseous dihydrogen.

CONCEPT MAP

HYDROGEN

Position in Periodic table : Outer shell electronic configuration resembles both alkali metals and halogens, still unique and hence H is placed separately

Hydrides : Binary compounds formed by combination of metals and non-metals with H_2.

(a) **Ionic Hydrides:** Stoichiometric compounds of H_2 with s-block elements

(b) **Covalent Hydrides:** Dihydrogen forms molecular compounds with most of the p-block elements.

(c) **Metallic Hydrides:** Non-stoichiometric compounds of H_2 with Be, Mg and d-and f-block elements. Metals of group 7, 8 and 9 do not form hydride.

Hydrogen Peroxide (H_2O_2)

Preparation : By the action of H_2SO_4, H_2CO_3 or H_3PO_4 on $BaO_2.8H_2O$

Manufacture: Electrolysis of 50% H_2SO_4

Properties: Syrupy pale blue liquid, viscous, diamagnetic and miscible with water, alcohol and ether. H_2O_2 acts as both oxidising as well as reducing agent.

Storage : Kept in wax lined bottles.

Uses : For bleaching, as antiseptic, as oxidant for rocket, used to control environmental pollution etc.

Dihydrogen

Occurence : Most abundant element in the universe (70% of the total mass of the universe)

Isotopes : Protium (^1_1H), deuterium (^2_1H) and tritium (^3_1H)

Preparation : Reaction of Zn with dil. acid or aqueous alkali.

Electrolysis of acidified water, by product in manufacture of NaOH and Cl_2.

Reaction of steam on hydrocarbons or coke at high temperatures in presence of catalyst.

Properties : It is a colourless, odourless, combustible gas, insoluble water. It undergoes reaction with X_2, O_2, N_2, metals, organic compounds etc.

Uses

It is used in,

(a) Synthesis of NH_3

(b) Manufacture of vanaspati fat

(c) Manufacture of organic compounds

(d) Cutting and welding properties

Water : Major part of all living organism.

Properties : Colourless, tasteless liquid with intermolecular H – bonding. This leads to high freezing point, high boiling point, high heat of vaporization, high heat of fusion etc.

It has amphoteric nature, undergoes hydrolysis reaction and form hydrates.

Hard water. It contains bicarbonates, chlorides and sulphate of calcium and magnesium.

Temporary water hardness is due to bicarbonates of Ca and Mg.

Permanent water hardness is due to chloride and sulphates of Ca and Mg.

Heavy Water (D_2O)

Preparation : On a large scale, it is produced by repeated electrolysis of ordinary water having alkali. Physical properties of D_2O are different from H_2O whereas chemical properties of D_2O are similar to H_2O.

Uses : As a moderator in nuclear reactor and as a tracer compound.

Hydrogen Economy

It is one of the alternative to meet the energy needs as dihydrogen releases large quantities of heat in combustion without causing any major pollution.

Textbook Exercises

9.1 Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

Ans. Hydrogen is the first element in the periodic table but its position is ambiguous because of following reason:

(i) Since it has 1 valence electron in its s-subshell, it is placed in group-1 along with alkali metals.

(ii) It also shows properties of halogens of group-17 by picking up electron showing electronegative character like them.

(iii) In some yet another properties, hydrogen differs both from alkali metals and halogens.

9.2 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

Ans. Protium ${}_1H^1$, Deuterium ${}_1H^2$ or D, Tritium ${}_1H^3$ or T. The mass ratios of protium: deuterium: tritium = 1: 2: 3

9.3 Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions ?

Ans. Hydrogen atom has only one electron and thus has one electron less than the stable inert gas configuration of helium. Therefore, to achieve stable inert gas configuration of helium, it shares its single electron with electron of other hydrogen atom to form a stable diatomic molecule.

9.4 How can the production of dihydrogen, obtained from 'coal gasification', be increased?

Ans. The process of producing syngas or synthesis gas from coal is called 'coal gasification'.

$$\underset{\text{Coal}}{C(s)}+\underset{\text{Steam}}{H_2O(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} \underbrace{CO(g)+H_2(g)}_{\text{Syngas}}$$

The production of hydrogen can be increased by reacting carbon monoxide of syngas with steam in presence of iron chromate as catalyst at 673 K.

$$CO(g)+H_2O(g) \xrightarrow[FeCrO_4]{673K} CO_2(g)+H_2(g)$$

The CO_2 thus produced is removed by scrubbing with a solution of sodium arsenite.

9.5 Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process ?

Ans. Dihydrogen of high purity is usually obtained by electrolysis of water in presence of small amount of acid or base. During electrolysis, dihydrogen is collected at cathode while dioxygen is collected at anode.

At cathode: $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2$

At anode: $OH^- \longrightarrow OH + e^-$

$4OH \longrightarrow 2H_2O + O_2$

The role of the electrolyte is to make water conducting since pure water is bad conductor of electricity and is weakly ionized.

9.6 Complete the following reactions:

(i) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(ii) $CO(g) + H_2(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(iii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(iv) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}}$

Ans. (i) $H_2(g)+M_mO_o(s) \xrightarrow{\Delta} mM(s)+o\,H_2O(\ell)$

(ii) $CO(g)+2H_2(g) \xrightarrow[\text{Catalyst}]{\Delta} \underset{\text{methanol}}{CH_3OH(\ell)}$

(iii) $C_3H_8(g)+3H_2O(g) \xrightarrow[1270K]{Ni} 3CO(g)+7H_2(g)$

(iv) $Zn(s)+2NaOH(aq) \xrightarrow{\text{heat}} \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)}+H_2(g)$

9.7 Discuss the consequences of high enthalpy of H—H bond in terms of chemical reactivity of dihydrogen.

Ans. Due to high enthalpy of H-H bond, hydrogen is quite unreactive at room temperature. However, at high temperatures or in presence of catalysts, it combines with many metals and non-metals to form hydrides.

9.8 What do you understand by

(i) electron-deficient,

(ii) electron-precise, and

(iii) electron-rich compounds of hydrogen ?

Provide justification with suitable examples.

Ans. Refer theory

9.9 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions.

Ans. Electron deficient hydrides do not have sufficient electrons to form normal covalent bonds. Therefore, to make up this deficiency they generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AlH_3)n$, etc. Further to make up this deficiency of electrons, they react with many metals, non-metals and their compounds. Hence, electron-deficient hydrides are very reactive as shown below:

$$B_2H_6(g)+3O_2(g) \longrightarrow B_2O_3(s)+3\,H_2O(g)$$

$$2NaH(s)+B_2H_6(g) \xrightarrow{\text{Diethyl ether}} \underset{\text{Sod. borohydride}}{2Na^+[BH_4]^-(s)}$$

Being electron deficient compounds, they act as **Lewis acids** and thus form complex with Lewis bases.

For example.

$$\underset{\text{Diborane}}{B_2H_6} + \underset{\text{Trimethylamine}}{2\ddot{N}Me_3} \longrightarrow \underset{\text{Complex}}{[2H_3B \longleftarrow NMe_3]}$$

$$B_2H_6 + \underset{\text{Carbon monoxide}}{2CO} \longrightarrow \underset{\text{Complex}}{[2H_3B \longleftarrow CO]}$$

9.10 Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as Lewis acid or base ? Justify your answer.

Ans. Carbon hydride of the type (C_nH_{2n+2}) are electron-precise hydrides. In other words, they have exact numbers of electrons required to form covalent bonds. Therefore, they do not have any tendency to either gain or lose electrons and hence they neither act as Lewis acids or Lewis bases.

9.11 What do you understand by the term" non-stoichiometric hydrides" ? Do you expect this type of the hydrides to be formed by alkali metals ? Justify your answer.

Ans. Hydrides which are deficient in hydrogen and in which the ratio of the metal to hydrogen is fractional are called non-stoichiometric hydrides. Furthermore, this fractional ratio is not fixed but varies with the temperature and the pressure. These type of hydrides are formed by d-and f-block elements. In these hydrides, the hydrogen atoms occupy holes in the metal lattice. Usually some holes always remain unoccupied and hence these metals form non-stoichiometric hydrides. Since alkali metals are highly reducing, they transfer their lone electron to the H atom, thereby forming H^- ions. In other words, alkali metal hydrides are ionic in which H^- ions occupy holes in the lattice. Since a hydride ion is formed by complete transfer of an electron, therefore, the ratio of metal to hydrogen is always fixed and hence alkali metals form only stoichiometric hydrides. In other words, alkali metals do not form non-stoichiometric hydrides.

9.12 How do you expect the metallic hydrides to be useful for hydrogen storage ? Explain

Ans. In metallic hydrides, hydrogen is absorbed as H-atoms. Due to the inclusion of H atoms, the metal lattice expands and thus becomes less stable. Therefore, when the metallic hydride is heated, it decomposes to form hydrogen and very finely divided metal.

The hydrogen thus evolved can be used as a fuel. Thus, transition metals or their alloys can be used to store and transport hydrogen to be used as a fuel. This is called hydrogen economy.

9.13 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

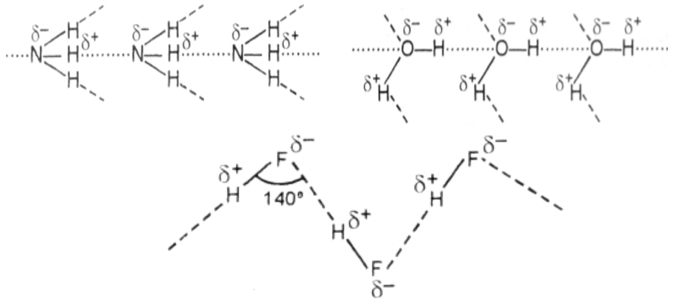
Ans. Atomic hydrogen is produced when molecular hydrogen is passed through an electric arc struck between tungsten electrodes (3773 – 4273 K).

$$H_2 \xrightarrow[3773-4273\text{K}]{\text{Electric arc,}} 2H;\ \Delta H = 435.9 \text{ kJ mol}^{-1}$$

The lifetime of atomic hydrogen is 0. 3 sec. and hence it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes in form of atomic hydrogen torch.

9.14 Among NH_3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why ?

Ans. Due to greater electronegativity of N, O and F over H. all these molecules undergo intermolecular H-bonding.



However, since electronegativity of F is highest, therefore, magnitude of the +ve charge on hydrogen and –ve charge on F is the highest and hence electrostatic attraction or the H-bonding is strongest in H-F.

9.15 Saline hydrides are known to react with water violently producing fire: Can CO_2, a well known fire extinguisher, be used in this case ? Explain.

Ans. Saline hydrides (such as NaH, CaH_2, etc.), react with water violently to form the corresponding metal hydroxides with the evolution of dihydrogen.

$$NaH\,(s) + H_2O\,(\ell) \longrightarrow NaOH\,(aq) + H_2\,(g)$$

$$CaH_2(s) + 2\,H_2O\,(\ell) \longrightarrow Ca(OH)_2(aq) + 2\,H_2(g)$$

The reactions are so much exothermic that the evolved H_2 catches fire. The fire so produced cannot be extinguished by CO_2 because it gets reduced by the hot metal hydride to form sodium formate.

$$NaH + CO_2 \longrightarrow HCOONa.$$

However, sand is useful since it is a highly stable solid.

9.16 Arrange the following:

(i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(ii) LiH, NaH and CsH in order of increasing ionic character.

(iii) H–H, D–D and F–F in order of increasing bond dissociation enthalpy.

(iv) NaH, MgH_2 and H_2O in order of increasing reducing property.

Ans. (i) BeH_2 is a covalent hydride, therefore, it does not conduct electricity at all. CaH_2 conduct electricity in the fused state while TiH_2 conduct electricity at room temperature. Thus, the order of increasing electrical conductance is: $BeH_2 < CaH_2 < TiH_2$.

(ii) Electronegativity decreases down the group from Li to Cs, therefore, the ionic character of their hydrides also increases in the same order, i. e., LiH < NaH < CsH.

(iii) Due to smaller size of D as compared to H, D-D bond has the highest bond dissociation enthalpy followed by H-H. However, due to repulsions between lone pairs of F and the bond pair, F-F bond dissociation enthalpy is the minimum. Thus the bond dissociation enthalpy increases in the order:

F –F < H–H<D–D.

(iv) Ionic hydrides are powerful reducing agents. Both MgH_2 and H_2O are covalent hydrides but the bond dissociation energy of H_2O is much higher than that of MgH_2. Therefore, the reducing character increases in the order: $H_2O < MgH_2 < NaH$

9.17 Compare the structures of H_2O and H_2O_2.

Ans. In water, O is, sp^3-hybridized. Due to stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the HOH bond angle decreases from 109. 5° to 104. 5°. Thus, water is a bent molecule. H_2O_2 has a non-planar structure. The two oxygen atoms are linked to each other by a single covalent bond (i.e., peroxide bond) and each oxygen is further linked to a hydrogen atom by a single covalent bond. The two O-H bonds are, however, in different planes. The dihedral angle between the two planes being 111. 5° in the gas phase. Thus, the structure of H_2O_2 is like that of an open book.

9.18 What do you understand by the term 'auto-protolysis' of water? What is its significance?

Ans. Refer theory

9.19 Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction which species are oxidised/ reduced ?

Ans. $$\underset{\text{(Oxidant)}}{2\,F_2\,(g)} + \underset{\text{(Reductant)}}{2H_2O\,(\ell)} \longrightarrow O_2\,(g) + 4\,H^+\,(aq)^+\,4\,F^-\,(aq)$$

or $$\underset{\text{(Oxidant)}}{3F_2(g)} + \underset{\text{(Reductant)}}{3H_2O(\ell)} \longrightarrow O_3(g) + 6H^+(aq) + 6\,F^-(aq)$$

In these reactions, water acts as a reducing agent and hence itself gets oxidised to either O_2 or O_3. On the other hand, F_2 acts as an oxidising agent and hence itself gets to reduced F^-ion.

9.20 Complete the following chemical reactions:

(i) $PbS\,(s) + H_2O_2\,(aq) \longrightarrow$

(ii) $MnO_4^-\,(aq) + H_2O_2\,(aq) \longrightarrow$

(iii) $CaO\,(s) + H_2O\,(g) \longrightarrow$

(iv) $AlCl_3\,(g) + H_2O\,(\ell) \longrightarrow$

(v) $Ca_3N_2(s) + H_2O\,(\ell) \longrightarrow$

Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions.

Ans. (i) $PbS(s) + 4\,H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(\ell)$

(ii) $2MnO_4^-\,(aq) + 5H_2O_2(\ell) + 6H^+(aq) \longrightarrow$
$2Mn^{2+}\,(aq) + 8\,H_2O\,(\ell) + 5\,O_2\,(g)$

(iii) $CaO(s) + H_2O(g) \longrightarrow Ca(OH)_2(aq)$

(iv) $AlCl_3\,(s) + 3\,H_2O\,(\ell) \longrightarrow Al(OH)_3\,(s) + 3\,HCl\,(aq)$

(v) $Ca_3N_2\,(s) + 6\,H_2O\,(\ell) \longrightarrow 3\,Ca(OH)_2\,(aq) + 2\,NH_3\,(g)$

(a) Hydrolysis reactions : (iii), (iv), and (v). (b) Redox reactions : (i) and (ii).

9.21 Describe the structure of the common form of ice.

Ans. Refer theory

9.22 What causes the temporary and permanent hardness of water?

Ans. Refer theory

9.23 Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

Ans. Synthetic ion exchange resins are of two types : Cation exchange resins and anion exchange resins. **Cation exchange resins** are either carboxylic acids or sulphonic acids having the general formula, R-COOH or R $-SO_2OH$ where R represents the giant hydrocarbon framework. These resins exchange their H^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water.

$$\underset{\substack{\text{(Cation exchange}\\ \text{resin)}}}{2R-COO^-H^+} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{CaCl_2} \longrightarrow \underset{\text{(Exhausted resin)}}{(RCOO)_2Ca + 2H^+ + 2Cl^-}$$

$$\underset{\substack{\text{(Cation exchange}\\ \text{resin)}}}{2R-SO_2O^-H^+} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{MgSO_4} \longrightarrow \underset{\text{(Exhausted resin)}}{(RSO_2O)_2Mg + 2H^+ + SO_4^{2-}}$$

Anion exchange resins, on the other hand, are substituted ammonium hydroxides having the general formula, R $-NH_3^+$ OH where R denotes the giant hydrocarbon framework. These resins exchange their OH^-ions with Cl^- and SO_4^{2-} ions present in hard water.

$$\underset{\substack{\text{Anion exchange}\\ \text{resin)}}}{R-NH_3{}^+OH^-} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{Cl^{-1}} \longrightarrow \underset{\text{(Exhausted resin)}}{R-\overset{+}{N}H_3\,Cl^- + OH^-}$$

$$\underset{\substack{\text{(Anion exchange}\\ \text{resin)}}}{2R-NH_3{}^+OH^-} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{SO_4^{2-}} \longrightarrow \underset{\text{(Exhausted resin)}}{(R-\overset{+}{N}H_3)_2SO_4 + 2\,OH^-}$$

Similarly, the H^+ ions produced from cation exchange resins and OH^- ions produced from anion exchange resins combine to form H_2O.

The hard water is first passed through cation exchange resin and then through anion exchange resin. The resulting water is freed from both cations and anions and hence is called demineralised water or deionised water and is as good as distilled water.

9.24 Write chemical reactions to show the amphoteric nature of water?

Ans. Refer theory

9.25 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

Ans. Refer theory

9.26 What is meant by 'demineralised water' and how can it be obtained?

Ans. Water which is free from all cations and anions is called demineralised water. It is obtained by passing hard water first through cation exchange resin and then through anion exchange resin. (For details refer to Ans. to Q. 23.)

9.27 Is demineralised or distilled water useful for drinking purposes? If not, how can it be made useful?

Ans. Demineralised or distilled water is not useful for drinking purposes since it does not contain even useful minerals. Therefore, to make it useful for drinking purposes, useful minerals in proper amounts should be added.

9.28 Describe the usefulness of water in biosphere and biological systems.

Ans. Water is essential for all forms of life. It constitutes about 65-70% of the body weight of animals and plants. In comparison to other liquids, water has a high specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in biosphere. The high heat of vaporization and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of minerals and other nutrients for plant and animal metabolism. Water is also required for photosynthesis in plants which releases O_2 into the atmosphere.

9.29 What properties of water make it useful as a solvent? What types of compound can it (i) dissolve (ii) hydrolyse?

Ans. Water has a high dielectric constant (79.39) and high dipole moment (1.84 D). Because of these properties, water dissolves most of the inorganic (ionic) compounds and many covalent compounds. That is why water is called an universal solvent whereas ionic compounds dissolve in water due to ion-dipole interaction or solvation of ions, covalent compounds such as alcohols, amines, urea, glucose, sugar, etc. dissolve in water due to H-bonding.

Water can hydrolyze many oxides (metallic or non-metallic), hydrides, carbides, nitrides, phosphides and other salts. In these reaction, H^+ and OH^-ions of water interact with anions and cations respectively leading to the formation of an acid or a base or both as shown below:

$$CaO\,(s) + H_2O\,(\ell) \longrightarrow Ca(OH)_2\,(aq)$$
$$SO_2\,(g) + H_2O\,(\ell) \longrightarrow H_2SO_3(aq)$$
$$CaH_2\,(s) + 2\,H_2O\,(\ell) \longrightarrow Ca\,(OH)_2\,(aq) + 2\,H_2\,(g)$$
$$CaC_2\,(s) + 2\,H_2O(s) \longrightarrow Ca(OH)_2\,(aq) + \underset{\text{Acetylene}}{HC \equiv CH\,(g)}$$

9.30 Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

Ans. Heavy water is injurious to human beings, plants and animals since it slows down the rates of reactions occurring in them. Thus, heavy water does not support life so well as does ordinary water.

9.31 What is the difference between the terms 'hydrolysis' and 'hydration'?

Ans. Interaction of H^+ and OH^- ions of H_2O with the anion and the cation of a salt respectively to give the original acid and the original base is called hydrolysis. For example,

$$\underset{\text{Salt}}{Na_2CO_3} + 2H_2O \longrightarrow \underset{\text{Base}}{2NaOH} + \underset{\text{Acid}}{H_2CO_3}$$

Hydration, on the other hand, means addition of H_2O to ions or molecules to form hydrated ions or hydrated salts. For example,

$$\underset{\text{Colourless}}{CuSO_4} + 5\,H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4\,.5H_2O}$$

9.32 How can saline hydrides remove traces of water from organic compounds?

Ans. Saline hydrides (i.e., NaH, CaH_2, etc.) react with water forming their corresponding metal hydroxides with the liberation of H_2 gas. Thus, traces of water present in organic solvents can be easily removed by distilling them over saline hydrides when H_2 escapes into the atmosphere, metal hydroxide is left in the flask while dry organic solvent distils over.

Alternatively, organic compounds containing traces of water can be dried by placing them in a desiccator containing saline hydrides at the bottom for a few hours or preferably overnight.

9.33 What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen ? Compare their behaviour towards water.

Ans. (i) Element with Z = 15 is a non-metal (i.e. P) and hence forms covalent hydride (i.e. PH_3).

(ii) Element with Z = 19 is an alkali metal (i.e. K) and hence forms saline or ionic hydride (Le. $K^+ H^-$).

(iii) Element with atomic number Z = 23 is a transition metal (i.e. V) of group 3 and hence forms a metallic or interstitial hydride (i.e. $VH_{1.6}$)

(iv) Element with Z = 44 is a transition metal (i.e. Ru) of group 8 and hence does not form any hydride.

Behaviour towards water : only ionic hydrides react with water evolving H_2 gas. Thus,

$$2\,KH\,(s) + 2\,H_2O\,(s) \rightarrow 2\,KOH\,(aq) + 2\,H_2\,(g)$$

9.34 Do you expect different products in solution when aluminium (III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water ? Write equations wherever necessary.

Ans. KCl is the salt of a strong acid and a strong base. It does not undergo hydrolysis in normal water. It just dissociates to give K^+ (aq) and Cl^-(aq) ion.

$$KCl(s) \xrightarrow{\text{Water}} K^+(aq) + Cl^-(aq)$$

Since the aqueous solution of KCl is neutral, therefore, in acidified water or in alkaline water, the ions do not react further and stay as such.

$AlCl_3$, on the other hand, is a salt of a weak base $Al(OH)_3$ and a strong acid (HCl). Therefore, in normal water, it undergoes hydrolysis to form, weak base $Al(OH)_3$ and a strong acid H^+ and Cl^- ions.

$$AlCl_3\,(s) + 3\,H_2O\,(\ell) \longrightarrow Al(OH)_3(s) + 3H^+\,(aq) + 3\,Cl^-\,(aq)$$

In acidic water, the H^+ ions react with $Al(OH)_3$ to form Al^{3+} (aq) ions and H_2O. Thus, in acidic water, $AlCl_3$ exists as Al^{3+}(aq) and Cl^-(aq) ions.

$$AlCl_3\,(s) \xrightarrow{\text{Acidified water}} Al^{3+}\,(aq) + 3Cl^-\,(aq)$$

In alkaline water, $Al(OH)_3$ reacts to form soluble tetrahydroxoaluminate complex or meta-aluminate ion, i.e.,

$$Al(OH)_3\,(s) + OH^-\,(aq) \longrightarrow \underset{\text{Tetrahydroxoaluminate}}{[Al(OH)_4]^-\,(aq)}$$

or $\underset{\text{meta-aluminate ion}}{AlO_2^-\,(aq)^+} \;+\; 2\,H_2O\,(\ell)$

The complete equation may be written as:

$$AlCl_3(s) \xrightarrow[\text{water}]{\text{Alkaline}} Al[(OH)_4]^- + 3Cl^-\,(aq)$$
$$\downarrow$$
$$AlO_2^-\,(aq) + 2\,H_2O(\ell) + 3Cl^-\,(aq)$$

9.35 How does H_2O_2 behave as a bleaching agent ?

Ans. The bleaching action of H_2O_2 is due to the nascent oxygen which it liberates on decomposition.

$$H_2O_2 \longrightarrow H_2O + O$$

The nascent oxygen combines with colouring matter which, in turn, gets oxidized. Thus, the bleaching action of H_2O_2 is due to the oxidation of colouring matter by nascent oxygen. It is used for the bleaching of delicate materials like ivory, feather, silk, wool, etc.

9.36 What do you understand by the terms ?

(i) hydrogen economy

(ii) hydrogenation

(iii) 'syngas'

(iv) water-gas shift reaction

(v) fuel-cell

Ans. (i) **Hydrogen economy:** The proposal to use hydrogen as a fuel in industry, power plants and also in homes and motor vehicles is called hydrogen economy. The basic principle of hydrogen economy is the production, transportation and storage of energy in the form of liquid or gaseous dihydrogen.

(ii) **Hydrogenation** means addition of hydrogen across double and triple bonds to form saturated compounds. The vegetables oils such as soyabean oil, cotton seed oil, groundnut oil, etc. are called polyunsaturated oils since they contain many C = C bonds. When these oils are exposed to air for prolonged periods, the double bonds present in them undergo oxidation, i.e., develop unpleasant taste. To avoid this, double bonds are hydrogenated. For this purpose, dihydrogen is bubbled through edible oils in presence of finely divided nickel at 473 K when the oils are converted with solid fats.

$$\text{Vegatable oil} + H_2 \xrightarrow{\text{Ni, 473K}} \text{Vegetable Ghee}$$

This process is called hydrogenation or hardening of oils and is used in the manufacture of vegetable ghee like Dalda, Gagan, Rath, etc. from vegetable oils. It may, however, be noted that hydrogenation reduces the number of double bonds but does not completely eliminate them.

(iii) **Refer theory**

(iv) **Refer theory**

(v) **Fuel cell.** Fuel cell is a device which converts the energy produced during the combustion of a fuel directly into electrical energy. Dihydrogen is used in hydrogen–oxygen fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels. It does not produce any pollution, releases more amount of energy per unit mass of fuel as compared to gasoline and other fuels.

Practice Questions

Very Short Answer Questions [1 Mark]

1. Why is 2-ethylanthraquinone preferred in the commercial production of H_2O_2?
2. Which would have higher electrical conductivity H_2O or D_2O?
3. Give an example to show that ionic hydrides forms complexes.
4. Anhydrous BaO_2 is not used for preparing H_2O_2. Why?
5. Why H_2 gas is not found in earth's atmosphere?
6. Give the order of reactivity of dihydrogen with the halogens.
7. What is the reason for hardness of water ?
8. Which gas is evolved when Mg_3N_2 (magnesium nitride) is treated with H_2O? Give chemical reaction.
9. How is heavy water produced from ordinary water?
10. Why does hard water react with soap?
11. Which compounds cause temporary hardness of water?
12. How would you prepare a sample of ND_3?
13. Which isotope of hydrogen does not have neutron?
14. What is the trade name of sodium hexa-metaphosphate?
15. What is cause of bleaching action of H_2O_2?
16. Which types of hydrides are generally non-stoichiometric in nature?
17. How does heavy water react with Al_4C_3?
18. Why is hydrogen molecule highly polar?
19. What is the action of water on hydrolith?
20. What is the trade name of H_2O_2 used as antiseptic?
21. Arrange H_2, D_2 and T_2 in the decreasing order of their boiling points.
22. What is the molecular mass of the compound formed by burning tritium in air?
23. Name the phenomenon of adsorption of hydrogen on metal surface.
24. Which gas is used for filling airships and balloons?
25. Give one example of zeolite used in softening of hard water.
26. Ionic hydrides are generally used to remove traces of water from organic compounds, why?
27. What is the importance of deuterium in organic reactions?
28. What is the use of hydrogen in the manufacture of vanaspati ghee?
29. Which type of elements form interstitial (metallic) hydrides?
30. Explain why dihedral angle (111.5°) of H_2O_2 reduces to 90.2° in the solid state?

Short Answer Questions [2 & 3 Marks]

1. How is decomposition of H_2O_2 accelerated?
2. How would you prepare dihydrogen gas from (i) acid (ii) alkali.
3. Discuss three characteristics in which hydrogen resembles alkali metals.
4. What are the advantages of using hydrogen as a fuel?
5. Can phosphorous with outer electronic configuration $3s^2$ $3p^3$ form PH_5?
6. Why ice is less dense than water ?
7. Calculate the normality of 20 volumes hydrogen peroxide solution?
8. Statues coated with white lead on long exposure to atmosphere turn black and original colour can be restored on treatment with H_2O_2. Why?
9. Give different types of hydrides along with examples.
10. How will you show that H_2O_2 will act like oxidizing agent in acidic as well as basic medium?
11. Why hard water is not used in industrial boilers for producing steam?
12. Describe the permutit process for softening of hard water.
13. Describe the principle of sequestration of softening of hard water.
14. What is understood by 'water gas shift reaction'? Discuss its uses for the preparation of hydrogen.
15. Calculate the mass of hydrogen peroxide present in 2 litres of a 2 M solution. Also calculate the volume of oxygen at N.T.P. liberated upon the complete decomposition of 100 ml of the above solution.
16. Why do lakes freeze from top towards bottom?
17. What happens when–
    (i) Water reacts with cyanamide of calcium
    (ii) Peroxosulphuric acid is hydrolysed.
    (iii) Moist silver oxide reacts with H_2O_2
18. Describe the industrial application of H_2 dependent on
    (i) the heat liberated when its atoms are made to combine on the surface of a metal
    (ii) its effect on unsaturated organic system is presence of catalyst
    (iii) its ability to combine with N_2 under specific conditions
19. The process $\frac{1}{2}H_2(g)+e^- \rightarrow H^-(g)$ is endo-thermic with $\Delta H = +151$ kJ/mol, yet salt like hydrides are known. How do you account for this?
20. Give two points of differences between hydrogen and alkali metals.
21. How hydrogen differs from halogens?
22. A mixture of hydrazine and H_2O_2 with Cu (II) catalyst is used as a rocket propellant. Why?
23. Give two tests for hydrogen peroxide.

Long Answer Questions [5 Marks]

1. (i) What are the ways in which water molecules are bound to an anhydrous salt to form hydrate?
    (ii) Why water is an excellent solvent?

2. Distinguish between (i) hard water and soft water (ii) temporary and permanent hardness.

3. Give the half reactions and the complete redox reactions for the following:
  - (i) oxidation of ferrous to ferric ion by H_2O_2 in acidic medium
  - (ii) oxidation of iodide to iodine by H_2O_2 in acidic medium
  - (iii) H_2O_2 oxidises basic manganese (II) sulphate
  - (iv) H_2O_2 reduces ferricyanide ion in alkaline medium to ferrocyanide
  - (v) H_2O_2 reduces permaganate ion in acidic medium.

4. Complete the following reactions :
  - (i) $P_4O_{10} + H_2O \rightarrow$
  - (ii) $AlCl_3 + H_2O \rightarrow$
  - (iii) $SiCl_4 + H_2O \rightarrow$
  - (vi) $Ca_3P_2 + H_2O \rightarrow$
  - (vii) $NaH + H_2O \rightarrow$

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Why does elemental hydrogen react with other substances slowly at room temperature? **[HOTS]**

2. Can sea animals live in distilled water? **[HOTS]**

3. Why ionic hydrides are kept away from moisture? **[HOTS]**

4. Conc. H_2SO_4 cannot be used for drying H_2, why? **[HOTS]**

5. Is it possible to concentrate a dilute solution of H_2O_2 by strong heating? Explain. **[HOTS]**

6. Why are m.p. and b.p. of heavy water more than those of ordinary water? **[HOTS]**

7. A small amount of phosphoric acid or glycerol or acetanilide is added in H_2O_2 during its storage. Explain. **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. Why should a bottle of H_2O_2 be cooled before opening it? **[HOTS]**

2. Why are ionic hydrides generally used for removal of traces of water from organic compounds? **[HOTS]**

3. Why is H_2O_2 stored in coloured wax lined bottles in presence of a stabilizer? **[HOTS]**

4. Although D_2O resembles H_2O chemically yet it is a toxic substance. Explain. **[HOTS]**

5. Calculate the strength of 5 volume H_2O_2 solution. **[Exemplar]**

6. Dihydrogen reacts with dioxygen (O_2) to form water. Write the name and formula of the product when the isotope of hydrogen which has one proton and one neutron in its nucleus is treated with oxygen. Will the reactivity of both the isotopes be the same towards oxygen? Justify your answer. **[Exemplar]**

Long Answer Questions [5 Marks]

1. How does dihydrogen react with
  - (i) O_2 (ii) C
  - (iii) N_2 (iv) F_2
  - (v) Cl_2? **[HOTS]**

2. How will you concentrate H_2O_2? Show differences between structures of H_2O_2 and H_2O by drawing spatial structures. Mention three important uses of H_2O_2. **[Exemplar]**

CHAPTER TEST

Time : *30 min.* **Max. Marks :** *15*

Directions :
- *(i) Attempt all questions*
- *(ii) Questions 1 to 3 carry 1 mark each.*
- *(iii) Questions 4 and 5 carry 2 marks each.*
- *(iv) Question 6 carry 3 marks*
- *(v) Question 7 carry 5 marks*

1. Give a reaction in which dihydrogen acts as an oxidizing agent?

2. Why water has higher boiling point than H_2S?

3. Arrange NaH, MgH_2 and H_2O in order of increasing reducing property.

4. (i) What do you mean by 10 volume H_2O_2 solution?
  (ii) Give an example of a reaction where H_2O_2 acts as an oxidizing agent under acidic media.

5. What is water gas ? How is it prepared?

6. Find the volume strength of 1.6 N H_2O_2 solution.

7. (a) Why H_3PO_4 is preferred over dil. H_2SO_4 to prepare H_2O_2 from hydrated BaO_2 ?
  (b) How does H_2O_2 react with
    (i) Bleaching powder
    (ii) Ag_2O

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. It gets regenerated during the reaction by hydrogenation of 2–ethylanthrahydroquinone.

2. Water due its greater degree of dissociation

$\left(pK_{H_2O} = 13.997\ pK_{D_2O} = 14.869\right)$.

3. $8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$.

4. Anhydrous BaO_2 is not used because the $BaSO_4$ formed during the reaction forms a protective layer around unreacted BaO_2 and the reaction stops after some time.

5. Earth does not possess enough gravitational pull to retain light H_2 molecule, therefore it is not found in our atmosphere.

6. The decreasing order is $F_2 > Cl_2 > Br_2 > I_2$. The reaction with fluorine occurs even in the dark whereas with iodine it requires a catalyst.

7. Hardness of water is due to the presence of bicarbonates , chlorides and sulphates of calcium and magnesium in water.

8. NH_3 gas is evolved.

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$.

9. It is obtained by repeated electrolysis of ordinary water.

10. Hard water containing Ca^{2+} and Mg^{2+} ions react with soap to form insoluble substance, i.e., calcium or magnesium salt of fatty acid.

11. $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$.

12. $Mg_3N_2 + \underset{\text{Heavy water}}{6D_2O} \rightarrow 3Mg(OD)_2 + \underset{\text{Deutero ammonia}}{2ND_3}$

13. ^1_1H does not have neutron. It is called protium or ordinary hydrogen.

14. Calgon.

15. Refer theory

16. Interstitial hydrides are generally non-stoichiometric in nature.

17. $Al_4C_3 + 12D_2O \rightarrow 4Al(OD)_3 + 3CD_4$

18. It is due to small size of hydrogen atom and high electronegativity.

19. $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$

20. H_2O_2 commercially is called perhydrol.

21. $T_2 > D_2 > H_2$.

22. The compound T_2O is formed having molecular mass 22 a.m.u.

23. Occulusion.

24. Since hydrogen is inflammable. A mixture of 85% He and 15% H_2 is used in filling of airships and balloons.

25. Hydrated sodium aluminium silicate,

$Na_2Al_2Si_2O_8 . xH_2O$

26. Ionic hydrides give H^- ions which react with H_2O to give H_2 gas.

$Na^+ H^-\ H_2O \rightarrow NaOH + H_2$

∴ Ionic hydrides are used to remove traces of water from organic compounds.

27. Heavy hydrogen, deuterium (D) is used as a tracer to study the mechanism of organic reactions.

28. H_2 is used as reducing agent to convert vegetable oil into vegetable ghee.

29. d- and f-block elements.

30. The dihedral angle (111.5°) reduces to 90.2° in hydrogen peroxide crystal due to hydrogen bonding. The H_2O_2 has a non-planar structure.

Short Answer Questions

1. It can be accelerated by:

(a) Sunlight (b) Rough surfaces

(c) Carbon or metals (d) MnO_2

2. (i) From acid :

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

(ii) From alkali :

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

3. (i) Liberation at cathode:- When an aqueous solution of HCl is electrolysed, hydrogen is liberated at cathode in the same way as alkali metals are liberated during electrolysis of their salt in molten form

$2HCl\,(aq) \longrightarrow H_2 + Cl_2$

cathode

$2NaCl \longrightarrow 2Na + Cl_2$

(ii) Reducing agent:- Like alkali metals, hydrogen also acts as a strong reducing agent.

$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$

$B_2O_3 + 6K \longrightarrow 2B + 3K_2O$

(iii) Electropositive nature:- Like alkali metals, hydrogen can also loose one electron to form unipositive ion.

$[H \longrightarrow H^+ + e^-]$

4. (i) High heat of combustion.

$2H_2(g) + O_2(g) \xrightarrow[\text{Catalyst}]{} 2H_2O(l)$

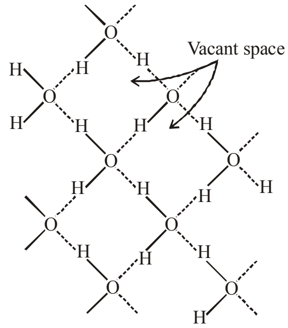
$\Delta H = -285.9\ kJ\ mol^{-1}$

(ii) No emission of polluting gases CO_2 , SO_2 , NO_2, etc

(iii) Fuel cells with hydrogen having efficiency 70-85% have been made and operated successfully.

5. Although P shows oxidation states of +3 and +5, it cannot form PH_5 . It is because due to high bond dissociation energy of hydrogen along with slightly negative electron gain enthalpy dihydrogen acts as a weak oxidizing agent and can only oxidize P to +3 oxidation state and not up to +5 oxidation state.

6. In ice, water molecules are tetrahedrally linked (each oxygen is tetrahedrally surrounded by four hydrogen atoms) in which two hydrogen atoms form covalent bonds with oxygen atoms while other two hydrogen atoms form hydrogen bonds. This results in formation of a cage like structure. It has lot of vacant spaces in the crystal structure and, therefore gives rise to large volume for a given mass of water. Thus, density of ice is lesser than that of water. When the ice melts, some of the hydrogen bonds are broken and the water molecules go in between the vacant spaces in the structure. As a result, the structure of liquid water is less open than structure of ice. Therefore, the density of water is more than that of ice.



7. H_2O_2 decomposes as :

$$\underset{2\times 34 = 68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{\substack{22{,}400\text{ ml}\\ \text{at N.T.P.}}}{O_2}$$

According to the above equation, 1 mole of oxygen (or 22.4 L of oxygen) at N.T.P. is liberated from 2 mol (or 68 g) of H_2O_2.

22.4 L of oxygen at N.T.P. is produced from $H_2O_2 = 68$ g

1 L of oxygen at N.T.P. is produced from

$$H_2O_2 = \frac{68}{22.4}\text{ g}$$

20 L of oxygen at N.T.P. are produced from

$$H_2O_2 = \frac{68}{22.4} \times 20\text{ g} = 60.7\text{ g}$$

$\therefore$ 1 L of H_2O_2 solution of 20 volume $= 60.7$ g H_2O_2

Strength of 20 volume $H_2O_2 = 60.7$ g/litre.

Now equivalent weight of $H_2O_2 = \frac{34}{2} = 17$

Normality = Strength / Eq. weight

$$= \frac{60.7}{17} = 3.57\text{ N}$$

8. On long exposure to atmosphere, white lead is converted into black PbS due to action of H_2S present in the atmosphere. As a result statues turn black

$$PbO + H_2S \longrightarrow PbS + H_2O$$

To restore the colour of lead paintings, it is dipped in aqueous solution of H_2O_2 then the lead sulphide is oxidised to lead sulphate which is white in colour.

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

9. **There are three types of hydrides :**

(i) Ionic hydrides —— NaH

(ii) Metallic or interstitial hydrides —— LaH_2

(iii) Molecular or covalent hydrides —— H_2O

10. In H_2O_2, the oxidation state of O is – 1. H_2O_2 can be reduced to H_2O or OH^- in which the oxidation number of O is –2. As this is a gain of electron, H_2O is an oxidizing agent. H_2O_2 can act as oxidizing agent in acidic as well as in basic medium.

Acidic :

$$H_2O_2(aq) + 2H^+ (aq) + 2e^- \rightarrow 2H_2O(l)$$

Basic :

$$H_2O_2\ (aq) + OH^-(aq) + 2e^- \rightarrow 3OH^-\ (aq)$$

11. Hard water cannot be used in industrial boilers as it contains the bicarbonates of calcium and magnesium. These bicarbonates decomposes on heating giving insoluble carbonates which settle at the bottom of the tanks as precipitate.

12. Refer theory

13. The Ca^{+2} and Mg^{+2} ions in hard water rendered ineffective by the addition of sodium hexametaphosphate (Calgon). The hexametaphosphate of Ca^{+2} or Mg^{+2} so formed remain dissolved in water but they do not cause hindrance in the formation of good lather. This is because Ca^{+2} and Mg^{+2} ions are not free to react with soap but these have been tied up in a stable complex. This is known as sequestration of Ca^{+2} and Mg^{+2} ions.

$$2Ca^{+2} + \underset{\text{Calgon}}{Na_2\ [Na_4\ (PO_3)_6]} \rightarrow \underset{\text{stable soluble complex}}{Na_2\ [Ca_2\ PO_3)_6]} + 4Na^+$$

14. Refer theory

15. Molecular mass of H_2O_2

$$= 2 \times 1 + 2 \times 16$$
$$= 2 + 32 = 34$$

We know that

$$\text{Molarity} = \frac{\text{Strength (g / l)}}{\text{Molecular mass}}$$

$$2 = \frac{\text{Strength}}{34}$$

$\therefore$ Strength of $H_2O_2 = 2 \times 34 = 68$ g/l

Hence 1 L of 2M H_2O_2 contains $H_2O_2 = 68$ g

$\therefore$ 2 L of 2M H_2O_2 contains H_2O_2

$$= 68 \times 2$$
$$= 136\text{ g}$$

1 L or 1000 ml of 2M H_2O_2 contains H_2O_2

$$= 68\text{g}$$

$\therefore$ 100 ml of 2M H_2O_2 contains H_2O_2

$$= \frac{68}{1000} \times 100$$
$$= 6.8\text{ g}$$

We know that

$$\begin{array}{lcl} 2H_2O_2 & \rightarrow & 2H_2O + O_2 \\ 2(34) & & 1\text{ mole} \\ = 68\text{ g} & & = 22400\text{ ml} \\ & & \text{at NTP} \end{array}$$

68 g of H_2O_2 gives O_2 at NTP

$$= 22400\text{ ml}$$

6.8 g of H_2O_2 gives O_2 at NTP

$$= \frac{22400}{68} \times 6.8 = 2240\text{ ml} = 2.24\text{ L}$$

16. Ice is having less density than water and hence floats on it. But water's density is maximum at 4°C. In cold upper layer of water freezes and protects the lower lying water from getting freezed as its density is heavier than solidified ice. This phenomenon helps in the existence of aquatic life in cold conditions.

17. (i) $\underset{\text{(Cal. cyanamide)}}{Ca(CN)_2} + 4H_2O \rightarrow CaCO_3 + NH_4OH.$

(ii) $\underset{\text{(Peroxosulphuric acid)}}{H_2S_2O_8} + 2H_2O \rightarrow \underset{\text{(Sulpuric acid)}}{2H_2SO_4} + \underset{\text{(Hydrogen peroxide)}}{H_2O_2}$

(iii) $H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$

18. (i) Atomic hydrogen torch is used industrially to melt refractory materials like tungsten, tantalum, etc.

(ii) It is used to hydrogenate the unsaturated vegetable oil to vanaspati ghee (saturated) in presence of Raney Ni.

$$\text{Oil} + H_2 \xrightarrow[450K/5atm]{Ni} \text{saturated vanaspati ghee}$$

(iii) It combines with H_2 in presence of Fe (as catalyst) and Mo (as promoter) at about 400°C, 200 atm and to form ammonia (NH_3).

The process is called Haber's process

$$N_2(g) + 3H_2(g) \xrightarrow[Fe/Mo]{400°C/200atm} 2NH_3(g)$$

19. Formation of H^- is endothermic yet alkali and alkaline earth metals form salt like hydrides. This is due to the reason that high lattice energy released more than compensates the energy needed for the formation of H^- ions from H_2 gas.

20. (i) The ionisation energy of hydrogen (1312 kJ mol^{-1}) is very high as compared to those of alkali metals, e.g. Li (520 kJ mol^{-1}), Na (495 kJ mol^{-1}), etc.

(ii) At room temperature hydrogen is a gas while alkali metals are solids.

21. (i) Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which form halide ion (X^-) very easily.

(ii) Hydrogen molecule has no unshared pairs of electrons while halogen molecule has six unshared pairs of electrons i.e.

$$H—H, \quad :\underset{..}{\ddot{Cl}}—\underset{..}{\ddot{Cl}}:$$

22. The reaction between hydrazine and hydrogen peroxide in the presence of copper (II) is highly exothermic and is accompanied by a large increase in the volume of the product and hence this mixture is used as a rocket propellant.

$$NH_2-NH_2(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2(g) + 4H_2O(g) + \text{Heat}$$

23. (i) It decolourises the pink colour of acidified permanganate solution.

(ii) It liberates iodine from acidified KI solution which turns starch paper blue.

Long Answer Questions

1. (i) Water molecules may be bounded to an anhydrous salts in the following three ways:

(a) Water molecules are coordinated to the central metal ion in complex ions such as $[Ni(H_2O)_6]^+Cl^-$.

(b) Water molecules may occupy, voids in the crystal lattice as interstitial water. e.g. $BaCl_2 . 2H_2O$.

(c) Water molecules may be bonded by hydrogen bonds in certain oxygen containing anions.e.g. in $CuSO_4.5H_2O$, four water molecules are coordinated to a central Cu^{2+} ion while the fifth water molecule is hydrogen bonded to sulphate SO_4^{2-} group.

(ii) Water is highly polar solvent with high dielectric constant. It interacts with polar or ionic substances effectively with the liberation of considerable amount of energy that is responsible for breaking of crystal lattice and explain the solubility. The dissolution of covalent compounds like alcohols, urea glucose, etc. is due to tendency of these molecules to form hydrogen bond with water.

2. Refer theory

3. (i) $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ [reduction]

$2Fe^{+2}(aq) \rightarrow 2Fe^{+3}(aq) + 2e^-$ [oxidation]

$2Fe^{+2}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{+3}(aq) + 2H_2O(l)$

(ii) $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ [reduction]

$2I^-(aq) \rightarrow I_2(s) + 2e^-$ [oxidation]

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(s) + 2H_2O(l)$

(iii) $H_2O_2(aq) + 2e^- \rightarrow 2OH^-(aq)$ [reduction]

$Mn^{+2}(aq) \rightarrow Mn^{+4}(aq) + 2e^-$ [oxidation]

$Mn^{+2}(aq) + H_2O_2(aq) \rightarrow Mn^{+4}(aq) + 2OH^-(aq)$

(iv) $H_2O_2 + 2OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 2e^-$ [oxidation]

$\underset{\text{Ferricyanide ion}}{2[Fe(CN)_6]^{-3}(aq)} + 2e^- \rightarrow \underset{\text{ferrocyanide ion}}{2[Fe(CN)_6]^{-2}}$ [reduction]

$$H_2O_2(aq) + 2[Fe(CN)_6]^{-3}(aq) + 2OH^- \rightarrow$$
$$2H_2O(l) + O_2(g) + 2[Fe(CN)_6]^{-2}$$

(v) $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq)^+ 2e^-] \times 5$

[oxidation]

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow$$
$$2\,Mn^{+2}(aq) + 8H_2O(l)$$

[reduction]

$$2MnO^-{}_4(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow$$
$$2Mn^{+2}(aq) + 8H_2O(l) + 5O_2(g)$$

4. (i) $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

(ii) $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]Cl_3$

(iii) $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

(iv) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + PH_3$

(v) $NaH + H_2O \rightarrow NaOH + H_2$

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. It is because it has high bond dissociation energy (436 kJ mol^{-1}).

2. No. they cannot, as it does not contain any oxygen.

3. Traces of water decomposes ionic hydrides as:

$$NaH + H_2O \rightarrow NaOH + H_2 \uparrow$$

4. Conc. H_2SO_4 on absorbing water from moist hydrogen produces so much heat that hydrogen catches fire.

5. **No,** because on strong heating H_2O_2 decomposes into H_2 and O_2.

6. It is due to *higher molecular mass* of heavy water than ordinary water.

There is a greater degree of association in heavy water than in ordinary water.

7. All the three additives act as negative catalyst for the decomposition of H_2O_2 and thus decomposition of H_2O_2 is checked off.

Short Answer Questions

1. H_2O_2 being unstable liquid, decomposes into water and oxygen either on standing or on heating. Bottle of H_2O_2 is therefore cooled before opening to lower the vapour pressure of contents in it otherwise bumping of liquid may take place.

2. Ionic hydrides release H^- (hydride ion) which acts as a strong *Bronsted base* (H_2O is a weak Bronsted acid). They combine with water to liberate H_2 gas.

$$Na^+H^- + H_2O \longrightarrow NaOH + H_2(g)$$

As a result, these hydrides are generally used for removal of traces of water from organic compounds.

3. H_2O_2 is fairly stable and decomposes only slowly on its own, but decomposition is rapid in the presence of traces of heavy metal ions such as Cu^{+2}

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

For this reason, we always store hydrogen peroxide in coloured wax-lined bottles containing stabilizer such as glycerol, acetanilide or phosphoric acid.

4. D_2O is a toxic substance though it resembles H_2O chemically because D^+ ion is having a slower rate of reaction involved in enzymatic catalysis as compared to H^+ ions.

5. 5 volume H_2O_2 solution means that hydrogen peroxide contained in 1 volume of this solution will decompose to give 5 volumes of oxygen at STP i.e. if 1L of this solution is taken, then 5 L of oxygen can be produced from this at STP. Chemical equation for the decomposition of H_2O_2 is

$$2H_2O_2(l) \longrightarrow O_2(g) + 2H_2O(l).$$

It shows that 68 g H_2O_2 gives 22.7 L of O_2 at STP, so 5 L oxygen will be obtained from :

$$\frac{68g \times 5L}{22.7L} = \frac{3400}{227} g\ H_2O_2 = 14.9\ g \approx 15g\ H_2O_2$$

i.e., 15 g H_2O_2 dissolved in 1 L solution will give 5 L oxygen or 1.5 g H_2O_2 / 100 mL solution will give 500 mL oxygen. Thus 15g/L or 1.5% solution is known as 5V solution of H_2O_2.

6. [***Hint:*** Heavy water; Bond dissociation energy of dihydrogen is less than dideuterium]

Long Answer Questions

1. (i) With oxygen (O_2) :

$$2H_2(g) + O_2(g) \xrightarrow{\text{Heat}} 2H_2O(g)$$

(ii) With carbon

$$2C(s) + H_2(g) \xrightarrow[\text{Electric arc}]{\text{3300K}} C_2H_2(g)$$

(iii) With nitrogen:

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Fe/Mo}]{\text{673K}} 2NH_3(g)$$

(iv) With F_2 :

$$H_2(g) + F_2(g) \xrightarrow{\text{Dark}} 2HF(l)$$

(v) With Cl_2 :

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} 2HCl(g)$$

2. Refer Theory

CHAPTER TEST

1. $2Na + H_2 \longrightarrow 2NaH$
2. Water forms intermolecular hydrogen bonding while H_2S is unable to form.
3. $H_2O < MgH_2 < NaH$
4. (i) 1L of given solution of H_2O_2 gives 10 L of O_2 at NTP.

   (ii) $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$
5. An equimolar composition mixture of CO and H_2 is called water gas.

   Preparation: $C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$
6. Strength = Normality × equivalent weight.

   $= 1.6 \times 34/2 = 1.6 \times 17$

   $2H_2O_2 \longrightarrow 2H_2O + O_2$

   2×34 g 22400 ml at NTP

   68 g of H_2O_2 gives = 22400 ml of O_2 at NTP

   hence, 1.6×17 g would give

   $= \frac{22400 \times 1.6 \times 17}{68} = 8960$ ml of O_2 at NTP

   But 1.6×17 g of H_2O_2 are present in 1000 ml of solution

   Hence, 1000 ml of this H_2O_2 gives = 8960 ml of O_2 at NTP

   Therefore 1 ml would give = 8960 /1000 = 8.96 ml of O_2 at NTP (as per definition)

   Thus volume strength of 1.6N H_2O_2 solution = 8.96 volume.
7. (a) The hydrogen peroxide solution prepared by this method contains some heavy Ba^{2+} ions. These catalyse the decomposition of hydrogen peroxide and, thus, the solution cannot be stored for a long time. To prevent this, sulphuric acid is replaced by phosphoric acid. In this method, barium phosphate gets completely precipitated and the solution does not contain any free Ba^{2+} ions to catalyse the decomposition of hydrogen peroxide.

   $$3BaO_2.8H_2O + 2H_3PO_4 \longrightarrow \underset{ppt}{Ba_3(PO_4)_2} + 24H_2O + 3H_2O_2$$

   (b) (i) $CaOCl_2 + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$

   (ii) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

10

Chapter

The s-Block Elements

INTRODUCTION

Elements of group 1 (or I A) and 2 (or II A) are known as s-block element because elements of these groups contain 1 or 2 electrons in the outermost s-orbital. Elements in group 1 are Li, Na, K, Rb, Cs and Fr (radioactive). These elements are collectively known as alkali metals. They are called so as hydroxides of these metals are strongly alkaline in nature. Elements in group 2 are Be, Mg, Ca, Sr, Ba, Ra (radioactive). These elements we collectively known as alkaline earth metals as their oxides and hydroxides are alkaline in nature and found in the earth's crust. Among alkali metals Na and K are more abundant then Li, Rb and Cs. In alkaline earth metals Ca and Mg ranks fifth and sixth in abundance. They are highly electropositive metals and form ionic compounds. Ions like Na^+, K^+, Ca^{2+} and Mg^{2+} has vital role in biological function.

Both alkali and alkaline earth metals are highly reactive and hence do not occur in the free state but are widely distributed in nature in the combined state. Whereas alkali metals mostly occur as halides, oxides, silicates, borates and nitrates; alkaline earth metals mainly occur as silicates, carbonates, sulphates and phosphates.

All metals of group –1 and 2 are extracted by electrolysis, since they are most reducing elements, they cannot be reduced by any other elements.

GROUP 1 ELEMENTS : ALKALI METALS

Physical Properties

(i) **General electronic configuration:** General configuration of alkali metals is ns^1. They are highly electropositive metals, thus not found in free state in nature.

(ii) All elements are silver-white, soft and lighter metal. These are highly malleable and ductile. When freshly cut, they have a bright lustre which quickly tarnishes on exposure to air.

(iii) **Atomic and ionic radii :** Atoms of the alkali metals are largest in their corresponding periods. Atomic as well as ionic size increases from Li to Cs due to the addition of an extra shell on moving down the group.

(iv) **Density :** The density of alkali metals are quite low as compared to other metals. Atomic weight increases from Li to Cs in the group and volume also increases, but increase in atomic weight is more as compared to volume. Therefore, density increases from Li to Cs.

Exception : Density of Na is more than that of K.

Density : $Li < K < Na < Rb < Cs$

(v) **Melting and boiling points :** The melting and boiling points are very low because of weak bonding in the crystal lattice of the metals due to presence of only one electron in their valence shell. Melting and boiling points decrease on moving down the group from Li (m.p. 459 K) to Cs (m.p. 301.5 K)

(vi) **Ionisation energy :** Their ionisation energies are low and decreases on moving down from Li to Cs. Thus, Cs is the most electropositive element in the periodic table.

(vii) **Electropositive character**: Alkali metals are strongly electropositive (or metallic in nature), the electropositive character increases in going down from Li to Cs.

(viii) **Oxidation state:** The alkali metal atom shown only + 1 oxidation state as there is large difference between first and second ionisation potentials.

(ix) **Electronegativity :** The electronegativity (i.e. tendency to attract electrons) values of alkali metals are very low. The electronegativity decreases from Li to Cs.

(x) **Conductivity:** The alkali metals are good conductors of heat and electricity.

(xi) **Flame colouration :** The alkali metals and their salts, when introduced into the flame, give characteristic colour to flame.

Li	Na	K	Rb	Cs
crimson red	Golden yellow	Pale violet	Violet	Violet

Flame colouration is due to the heat from the flame which excites the outermost orbital electron to higher energy level by absorption of energy from the flame. When the excited electron comes back to the ground state, there is emission of radiation in the visible region.

When light falls on the surface of these metals, sometimes the energy provided is sufficient to make atom lose electron(s). This property of K and Cs are utilised when used on as electrodes in photoeletric cells.

(xii) Hydration of ions: The degree of hydration depends upon the size of the cation.

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \text{ (size of cation)}$$
$$Li^+ > Na^+ > K^+ > Rb^+ < Cs^+ \text{ (degree of hydration)}$$

Due to high degree of hydration of Li, its salts are mostly hydrated. Since the degree of hydration of M^+ ions decreases as we go down the group, the hydration energy of alkali metal ions decrease from Li^+ to Cs^+. Thus with the decrease of hydration down the group, size of ion also decreases and electric conductance increases.

(xiii) Tendency of forming complex compounds : These metals have weak tendency of forming complex compounds due to large size and low charge density.

Chemical Properties

Due to their low ionisation energies, and large atomic radius alkali metals are highly reactive. This reactivity increases down the group.

(i) Reaction with air: The alkali metals tarnish in air due to the formation of oxides and hydroxides at their surface and hence they are kept under kerosene or paraffin oil. These hydroxides can further react with CO_2 present in air to form carbonates.

$$4M + O_2 \rightarrow 2M_2O$$
$$M_2O + H_2O\,(\text{moisture}) \rightarrow 2MOH$$
$$2MOH + CO_2 \rightarrow M_2CO_3 + H_2O$$
$$M = K, Rb, Cs$$

Lithium cannot be stored in kerosene oil because it has very low density and floats on the surface of the oil. As an exception, it reacts with the N_2 present in the air to form nitride.

Li forms monoxide, Na forms peroxide and other metals form superoxides. Li being a small cation has a strong positive field around it and can combine with oxide ion (O^{2-}) which has a strong negative field around it. Na^+ being larger has weaker positive field and can stabilise peroxide ion (O_2^{2-}). The even larger cations like K^+, Rb^+, Cs^+ have still weaker positive field and can stabilise only very weak negative field anions like superoxide (O_2^-).

(ii) Reaction with water :

$$2M + 2H_2O \longrightarrow 2MOH + H_2 \text{ (M is an alkali metal)}$$

Due to its small size and high IE, Li reacts less vigorously with water as compared to other alkali metals which react explosively with water. They also react with proton donors such as alcohol, gaseous ammonia and alkynes

(iii) Reaction with hydrogen : Alkali metals react with hydrogen forming ionic hydrides, $M^+ H^-$ with high melting points.

$$2M + H_2 \xrightarrow{673\,K} 2MH$$

Temperature of above reaction is higher around 1073K for Li.

(iv) Reaction with halogens : The alkali metal combine readily with halogens forming halides, M^+X^-.

Except lithium halides which are covalent, other alkali metal halides are ionic in nature. Li^+ ion due to its small size has high capability to distort electron cloud of anion. Moreover anion with large size can be easily distorted, thus LiI is the most covalent in nature.

(v) Solubility in liquid ammonia : All alkali metals are soluble in liquid ammonia. Dilute alkali metal- ammonia solutions are blue in colour. Blue colour of the solutions is due to presence of ammoniated electrons which absorb energy in the visible region of light and thus imparts blue colour to the solution.

$$M \longrightarrow M^+ + e^-$$
$$M^+ + xNH_3 \longrightarrow [M(NH_3)_x]^+$$
$$e^- + yNH_3 \longrightarrow [e(NH_3)_y]^-$$
$$M + (x+y)\,NH_3 \longrightarrow \underset{\text{Ammoniated metal cation}}{[M(NH_3)_x]^+} + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^-}$$

The blue solution has high electrical conductivity. The solution is paramagnetic and also a strong reducing agent. On standing, the solution slowly liberates hydrogen resulting in the formation of amide.

With increasing concentration of metal in ammonia the blue colour starts changing to bronze colour after which further amount of metal can be dissolved and the solution becomes diamagnetic in nature

$$M^+(am) + e^- + NH_3(\ell) \longrightarrow MNH_2\,(am) + \frac{1}{2}H_2(g)$$

(vi) The reducing character of alkali metals follows the order. Li > Cs > Rb > K > Na

The greater reducing power of Li though it has the highest ionisation energy is because of the large heat of hydration which in turn is due to its small size.

General Characteristics of The Compounds of Alkali Metals

(i) Oxides: Alkali metals when burnt in air form oxides. Under ordinary conditions, lithium forms the monoxide (Li_2O), sodium forms the peroxide (Na_2O_2) and the other alkali metals form mainly superoxides (MO_2) along with a small amount of peroxides. This increase in the stability of peroxide or superoxide with the size of metal ion is due to the fact that large anions are stabilised with large cations.

Basic nature, ionic character and reactivity of these oxides increases from Li to Cs.

- (a) Basic nature of these oxides increases from Li to Cs, due to increase in the size of cation. As we move down in a group the ionization energy decreases. Therefore, the tendency of donating electrons increases from Li to Cs.
- (b) Size of cation increases from Li to Cs. Therefore, according to Fajan's rule, ionic character of these oxides increases from Li to Cs, due to which melting and boiling points increase.
- (c) Solubility in water increases from Li to Cs oxides, due to increase in ionic character of these metal oxides.
- (d) Due to increase in atomic size from Li to Cs, reactivity of these metal oxides increases.

(ii) Hydroxides: Alkali metal hydroxides, MOH, are prepared by dissolving the corresponding oxide in water.

- (a) These are white crystalline solids, highly soluble in water and alcohol.
- (b) They dissolve freely in water with the evolution of much heat. The basic character of the alkali metal hydroxides decreases from CsOH to LiOH. CsOH > RbOH > KOH > NaOH > LiOH
- (c) They melt without decomposition and are good conductors of electricity in the fused state.
- (d) These are stable to heat and do not lose water even at red heat. Ionic character, melting point, boiling point, reactivity, thermal stability and solubility in water increase from Li to Cs.
- (e) The aqueous solution of KOH is called potash lye.

(iii) Halides: Alkali metal halides are easily prepared by the direct combination of the elements, M and halogen. They can also be prepared by the reaction of appropriate oxide, hydroxide or carbonate with aqueous HX. They are normally represented by the formula M^+X^- but Cs and Rb, being of large size, also form polyhalides, i.e., CsI_3. As evident from their following properties, alkali metal halides are ideal ionic compounds.

- (a) All alkali metal halides except LiF and CsI are freely soluble in water.
- (b) They have high melting and boiling points. The melting points of alkali metal chlorides decreases (expect LiCl) from NaCl to CsCl.
- (c) They are good conductors of electricity in the fused state.
- (d) They have ionic crystal structure. However, lithium halides have partly covalent character due to polarising power of Li^+ ions.

(iv) Salts of oxoacids : Oxoacids are those in which the acidic proton is on a hydroxyl group. Examples are H_2CO_3, H_3PO_4, H_2SO_4, HNO_3, HNO_2, etc.

- (a) They are generally soluble in water and stable towards heat.
- (b) All alkali metals form carbonates of the type M_2CO_3.
- (c) Their carbonates are highly stable to heat. K_2CO_3 is known as pearl ash.
- (d) Li_2CO_3 is least stable out of all these carbonates, because it is covalent and decomposes to Li_2O and CO_2 at low temperature. Order of their stability is as follows : $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- (e) These metals form $MHCO_3$ type bicarbonates and thermal stability of these bicarbonates increases from Li to Cs.

Anomalous Behaviour of Lithium

Lithium shows anomalous behaviour and departs from the general group trend.

The anomalous behaviour of Li is due to:

- (a) its exceptionally small size
- (b) high polarising power

(i) Difference between lithium and other alkali metals

- (a) Li forms mono-oxide while others can form peroxides as well as super oxides.
- (b) It combines with nitrogen to form nitrides while other alkali metals do not.

$$6Li + N_2 \longrightarrow 2Li_3N.$$

- (c) LiOH is a weak base and on heating it decomposes to form Li_2O while other alkali metals are strong bases and they do not decompose easily. LiOH is used to remove carbon dioxide from exhaled air in submarines and space vehicles.
- (d) The carbonate of lithium decomposes on heating while other alkali metal carbonates do not.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

- (e) Lithium nitrate on heating decomposes to form Li_2O, NO_2 and O_2 while other alkali metal nitrates gives alkali metal nitrite and oxygen.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

- (f) Lithium halides are covalent and are soluble in organic solvent. LiCl is deliquescent and crystallizes as hydrate, $LiCl.2H_2O$. whereas other alkali metal chlorides do not form hydrates.

(ii) Similarities between lithium and magnesium

(a) Both LiOH and $Mg(OH)_2$ are weak bases.

(b) Both form ionic nitrides with nitrogen e.g., $6Li + N_2 \longrightarrow 2Li_3N$; $3Mg + N_2 \longrightarrow Mg_3N_2$

(c) The hydroxides and carbonates of both Li and Mg decompose on heating.

(d) Both Li and Mg do not form solid bicarbonates.

(e) Li and Mg do not combine with excess oxygen to form peroxides and super oxides.

(f) Halides of both are covalent and their chlorides are deliquescent. $MgCl_2.6H_2O$

(g) Lithium form complexes because it is comparatively smaller in size and has high tendency to accept electrons. Similarly, Mg is the central atom for chlorophyll , the green pigment found in plant leaves.

SOME IMPORTANT COMPOUNDS OF SODIUM

Sodium Chloride, NaCl

Preparation :

Sea water is the major source of sodium chloride. It contains about 2.7–2.9% of NaCl. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Crude sodium chloride contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. To obtain pure sodium chloride, the crude salt (obtained by solar evaporation) is dissolved in minimum amount of the water and filtered to remove insoluble impurities. Hydrogen chloride gas is passed through the filtrate where crystals of pure NaCl separate out due to common ion effect, leaving behind calcium chloride and magnesium chloride in solution.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

Properties :

(a) It is a white crystalline solid.

(b) Pure sodium chloride is non-hygroscopic but the usual impurities of $CaCl_2.\ 2H_2O$ and $MgCl_2.2H_2O$ make it hygroscopic.

(c) It is soluble in water and its solubility is 36 g per 100 g of water at 273 K which does not increase much with the rise in temperature.

Uses :

(a) It is used as a table salt, an essential constituent of our food.

(b) It is used in the manufacture of Na_2O_2, Na_2CO_3, NaOH, HCl, Cl_2 etc.

(c) It is used in soap industry for salting out of soap

(d) It is used as freezing mixture in ice factories as well as in laboratory.

(e) It is used in food preservation, tanning and textile industry.

Sodium Hydroxide, NaOH

Preparation:

It is prepared by electrolysis of NaCl in Castner-Kellner cell. Brine solution is electrolysed using Hg cathode and C anode.

At cathode: $Na^+ + e^- \xrightarrow{Hg} Na - \text{amalgam}$

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

$2Na - \text{amalgam} + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$

Properties:

(a) It is a white, translucent solid which melts at 591 K.

(b) It dissolves in water to give an alkaline solution.

(c) Crystals of NaOH are deliquescent.

(d) It reacts with CO_2 in the atmosphere to form Na_2CO_3.

Uses: It is used

(a) in manufacture of soap, paper, artificial silk and chemicals.

(b) in petroleum refining

(c) in purification of bauxite

(d) for preparation of fats and oils

(e) as a laboratory reagent.

Sodium Carbonate, Na_2CO_3

It exists in various forms, namely anhydrous sodium carbonate Na_2CO_3 (soda-ash); monohydrate, $Na_2CO_3.\ H_2O$ (crystal carbonate); heptahydrate, $NaCO_3.\ 7H_2O$ and decahydrate, $Na_2CO_3.10\ H_2O$ (washing soda or sal soda)

Manufacture (solvay or ammonia soda process)

The process is based on the principle that when carbon dioxide is passed through a brine solution (about 30% sodium chloride solution), saturated with ammonia, sodium bicarbonate (being sparingly soluble) crystallizes out.

$$NH_3 + CO_2 + H_2O \longrightarrow \underset{\text{Amm. bicarbonate}}{NH_4HCO_3}$$

$$\underset{\text{Amm. bicarbonate}}{NH_4HCO_3} + NaCl \longrightarrow \underset{\text{Sod. bicarbonate}}{NaHCO_3 \downarrow} + NH_4Cl$$

The precipitated sodium bicarbonate is filtered, dried and heated to give sodium carbonate.

$$\underset{\text{Sod. bicarbonate}}{2NaHCO_3} \xrightarrow{\text{heat}} \underset{\text{Sod. carbonate}}{Na_2CO_3} + CO_2 + H_2O$$

Note : (a) K_2CO_3 cannot be prepared by this method because $KHCO_3$ is too soluble to be precipitated by addition of NH_4HCO_3 to saturated solution of KCl

(b) NH_3 in this process is recovered when solution containing NH_4Cl is treated with $Ca(OH)_2$.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + H_2O$$

Properties :

(a) Sodium carbonate crystallizes from water as decahydrate. It is white solid which effloresces on exposure to dry air forming the monohydrate.

$$Na_2CO_3.10H_2O \xrightarrow[\text{air}]{\text{dry}} Na_2CO_3.H_2O + 9H_2O$$

Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3 \cdot H_2O \xrightarrow{> 373\text{ K}} Na_2CO_3 + H_2O$$

(b) It is soluble in water with considerable evolution of heat.

$$\underset{\text{Sod. carbonate}}{Na_2CO_3} + 2H_2O \rightleftharpoons \underset{\text{weak acid}}{H_2CO_3} + \underset{\text{strong alkali}}{2NaOH}$$

Uses: Sodium carbonate is used:

(a) in laundries and in softening of hard water as washing soda,
(b) in the manufacture of glass, caustic soda, soap powders, etc,
(c) as laboratory reagent ($Na_2CO_3 + K_2CO_3$ mixture is known as fusion mixture), and
(d) in textile and petroleum refining.

Sodium Bicarbonate or Baking Soda, $NaHCO_3$

Preparation: Commercially, it is obtained by Solvay process, described for Na_2CO_3. However, in the laboratory it is prepared by saturating a cold solution of Na_2CO_3 with CO_2.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Properties :

(a) Sodium bicarbonate is a white crystalline substance, sparingly soluble in water. The aqueous solution is alkaline in nature.

$$NaHCO_3 + H_2O \rightleftharpoons H_2CO_3 + NaOH$$

(b) It is called baking soda because it decomposes on heating to generate bubbles of CO_2 gas. Because of this property it is added to cake and pastries thereby making them light and fluffy.

Uses : Sodium bicarbonate is used :

(a) in the preparation of baking powder,
(b) in the preparation of effervescent drinks and fruit salts,
(c) in medicines to remove acidity of the stomach (i.e. as antacid), and
(d) in fire extinguishers.

BIOLOGICAL IMPORTANCE OF Na AND K

Importance of Na^+

Na^+ ions are found on the outside of cells and participate in transmission of nerve signals, in regulating flow of water across cell membranes and in transport of sugars and amino acids into cell.

Importance of K^+

K^+ ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP and with sodium, are responsible for the transmission of nerve signals.

GROUP 2 ELEMENTS : ALKALINE EARTH METALS

Physical Properties

(i) Electronic Configuration : General electronic configuration of alkaline earth metals is [noble gas] ns^2. Their compounds are ionic in nature.

(ii) Physical appearance : They possess silvery white lustre when freshly cut, but tarnish soon after their exposure to air. They are malleable and ductile but less than the alkali metals.

(iii) Atomic volume, atomic and ionic radii. Because of the addition of an extra shell of electrons to each element form Be to Ba, the atomic volume/radii increases from Be to Ba. Their radii are smaller than alkali metals due to increased nuclear charge.

(iv) Density. They are denser than the alkali metals. Atomic weight increase from Be to Ba in a group and volume also increases, but increase in atomic weight is more as compared to volume. Therefore, density increases from Be to Ba.

Exception : Density of Mg is more as compared to Ca (Ca < Mg).
Density : Ca < Mg < Be < Sr < Ba

(v) Melting and boiling points : They have high melting points than those of alkali metals.
Hardness decreases from Be to Ba, due to which melting and boiling points decrease.
Be > Ca > Sr > Ba > Mg

(vi) Ionisation energy : They have low IE due to large size and their IE decreases down the group. The first IE of group 2 elements are higher than those of group 1 elements due to their smaller size than group 1 elements. Second IE's of group 2 elements are smaller than those of group 1 elements. This is because removal of second e^- from group 2 elements results in stable noble gas configuration. On other hand, second e^- in group 1 has to be removed from noble gas core which needs large amount of energy.

(vii) Oxidation state : Due to the presence of two *s*-electrons in the outermost orbital, the alkaline earth metals are bivalent. These metals exhibit + 2 oxidation state, difference of their second and first ionisation potentials is 11eV. Therefore, the +2 oxidation state of these metals is more stable.

(viii) Electropositive character : Due to their large size and comparatively low ionisation energies the alkaline earth metals are strongly electropositive elements. However, these are not as strongly electropositive as the alkali metals. Their standard electrode potentials (oxidation potentials) are lower than those of alkali metals and increase in the group with increase in atomic size from Be to Ba.

Be < Mg < Ca < Sr < Ba

(ix) Electronegativity : They have low electronegativity which decreases on moving down the group. The relatively high value of Be is due to the small size.

(x) Heat and electrical conductivity : Due to the presence of two loosely held valence electrons, the alkaline earth metals are good conductor of heat and electricity.

(xi) Flame colouration : Chlorides of alkaline earth metals, except that of Be and Mg, produce characteristic colour to flame due to easy excitation of electrons to higher energy levels.
Size of Be and Mg is very small and their electrons are strongly bonded to the nucleus. These electrons cannot be excited to higher energy level by the flame of the burner. Thus, Be and Mg do not impart any colour to the flame.

Element	Be	Mg	Ca	Sr	Ba
Flame	–	–	Brick green	Blood red	Apple red

(xii) Hydration Energy : Hydration energy of the metal ions (M^{+2}) is higher than that of the elements of group 1, because the size of these cations is small and charge is high. Hydration energy decreases on going down in the group, due to increase in the size of cations.

Be > Mg > Ca > Sr > Ba

(xiii) Reducing nature: The alkaline earth metals are strong reducing agents. However, their reducing power is less than those of corresponding alkali metals. The reducing nature of Be is due to large hydration energy associated with small size of Be^{2+} ion and relatively large value of the atomisation enthalpy of the metal.

Chemical Properties

Due to smaller size and greater charge and hence high ionisation energy, these are much less reactive than the corresponding alkali metals. Their reactivity increases from Be to Ba.

(i) Action of air. When burnt in air they form ionic oxides of the type MO, except Ba and Ra which give peroxides. Thus the tendency of the metal to form higher oxides like peroxide increases on moving down the group. Blocks of Be and Mg are inert to O_2 and H_2O due to formation of protective exide film. On the other hand in powdered state, Ca, Sr and Ba are readily attacked by air to form the oxide and nitride.

(ii) Action of water. Group 2 elements are less reactive with water as compared to alkali metals.

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2 \text{ (where M = Mg, Ca, Sr, or Ba)}$$

The reaction with water becomes vigorous on moving down the group. Be does not react even with boiling water and Ba react vigorously even with cold water.

(iii) **Action of hydrogen**. All these elements, expect beryllium, combine with hydrogen to form hydrides, MH_2. BeH_2 is prepared by:

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Thermal stability of these hydrides is as follows.

$$BeH_2 < MgH_2 > CaH_2 > SrH_2 > BaH_2$$

BeH_2 and MgH_2 get polymerized. Thermal stability of BeH_2 is high due to low electropositive character of Be, which decreases from BeH_2 to BaH_2.

All the hydrides react with water to evolve hydrogen and behave as strong reducing agents.

$$MH_2 + 2H_2O \longrightarrow M(OH)_2 + 2H_2$$

(iv) **Action of halogens**. All these elements combine with halogens at elevated temperatures forming halides, MX_2.

$$M + X_2 \longrightarrow MX_2\ (X = F, Cl, Br, I)$$

BeF_2 is prepared by thermal decomposition of $(NH_4)_2BeF_4$. To prepare $BeCl_2$, BeO is heated at 600 – 800 K with C and Cl_2.

(v) **Action with acids**.

$$M + 2HCl \longrightarrow MCl_2 + H_2$$

$BeCl_2$ is soluble in organic solvent since it is covalent in nature. Similarly $MgBr_2$ and MgI_2 are also soluble in organic solvent for the same reason. The reactivity of alkaline earth metals increases on moving down the group.

(vi) **Complex formation, Tendency of forming Complex Compounds :** These metals have weak tendency of forming complex compounds due to large size and low charge density . But these metals have higher tendency of forming complex compounds as compared to alkali metals, due to their relatively smaller size. This tendency decreases from Be to Ba. Beryllium, due to its small size, forms a number of stable complexes, e.g.,

$$[BeF_2]^{-}, [BeF_4]^{2-}, [Be(H_2O)_4]^{+2} \text{ etc.}$$

(vii) **Solubility in liquid ammonia**. Like alkali metals, alkaline earth metals dissolve in liquid ammonia giving coloured solutions. when the metal-ammonia solution are evaporated hexammoniates $M(NH_3)_6$ are formed. The ammoniates are good conductors of electricity and decompose at high temperatures. Solutions of Ca, Sr, Ba in liquid ammonia are paramagnetic in nature.

$$M + (x + y)\,NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e\,(NH_3)_y]^{-}$$

General Characteristics of Compounds of the Alkaline Earth Metals

(i) Oxides and Hydroxides : The alkaline earth metal oxides, MO are prepared either by heating the metal in oxygen or better by calcination (heating at high temperature) of carbonates. For example,

Reducting Properties. Due to their large size and low ionisation energy, they are strong reducing agents.

$$2Ca + O_2 \xrightarrow{\text{heat}} 2CaO$$

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

These are extremely stable, white crystalline solids. BeO is covalent while other halides are ionic in nature. Basic nature (BeO < MgO < CaO < SrO < BaO), ionic character, melting point, boiling point, thermal stability, reactivity and solubility in water of these oxides increases from Be to Ba, BeO shows amphoteric nature and therefore, react with acids as well as bases. MgO is a weak base, while CaO, SrO and BaO are strongly basic. All metal oxides except BeO react with water to form soluble hydroxides which are strong bases.

$$MO + H_2O \rightarrow M(OH)_2 + \text{Heat}$$

The oxides of beryllium are amphoteric. Whereas the hydroxides of the other metals are basic in character and their basicity increases on moving down the group. Ionic character, melting point, boiling point, reactivity, thermal stability and solubility in water increases from Be to Ba. Increasing order of basic character of these hydroxides is as follows :

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

$Be(OH)_2$ reacts with acids as well as bases, due to its amphoteric nature. Other hydroxides react with acids only.

$$Be(OH)_2 + 2OH^{-} \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{--}}$$

$$Be(OH)_2 + 2HCl + 2H_2O \longrightarrow [Be(OH)_4]Cl_2$$

(ii) Halides : The alkaline earth metal halides are obtained

(a) by heating the metal with halogens at high temperature or

(b) by treating metal carbonates with dilute halogen acids.

Beryllium halides are covalent compounds while the chlorides, fluorides, bromides and iodides of other alkaline earth metals are ionic solids. Alkaline earth metal halides possess the following characteristics :

(a) The melting and boiling points are high

(b) They conduct electricity in the molten state.

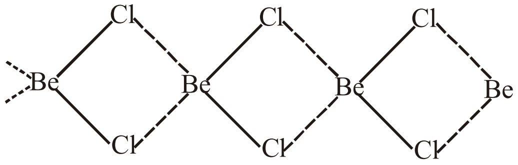
(c) They are hygroscopic and readily form hydrates, e.g. $MgCl_2 . 6H_2O$. However tendency to form halide hydrates gradually decreases down the group. These hydrates can be dehydrated by heating.

(d) The halides (except fluorides) of the alkaline earth metals are soluble in water and their solubility decreases with increasing atomic number of the metal.

Solubility order

$$BeCl_2 > MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2 CaF_2 < CaCl_2 < CaBr_2 < CaI_2$$

Structure of beryllium chloride : Beryllium chloride exhibits different structures in the vapour and in the solid states. In the solid state, it exists as a polymeric solid, $(BeCl_2)_n$, through halogen bonding in the chain form.



Salts of Oxoacids

(i) Carbonates : The carbonates are invariably insoluble and, therefore, occur as solid rock minerals in nature. Limestone is the most important mineral containing, calcium carbonate.

Two important characteristics of alkaline earth metal carbonates are following:

(a) **Solubility in water.** Alkaline earth metal carbonates are insoluble in water and their solubility in water decreases on moving down the group.

(b) **Decomposition.** All the carbonates decompose on heating to give CO_2 and the oxide.

$$MCO_3 \rightleftharpoons MO + CO_2$$

The stability of carbonates increases with the rise in atomic number, i.e., on moving down the group. Thus the stability order of group 2 carbonates is

$$\underset{1360°C}{BaCO_3} > \underset{1290°C}{SrCO_3} > \underset{900°C}{CaCO_3} > \underset{540°C}{MgCO_3} > \underset{<100°C}{BeCO_3}$$

$BeCO_3$ is least stable out of all these carbonates because it is covalent and decomposes to BeO and CO_2 at low temperature.

(ii) Sulphates. These can be prepared by dissolving the metal oxide in H_2SO_4.

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

The solubility of sulphates decreases regularly on moving down the group. This decrease in solubility of sulphates on moving down the group is due to decrease in the hydration enthalpies of alkali metal ions on moving down the group with increase in ionic size. Therefore on moving down the group the reduced value of hydration enthalpy is not able to overcome the lattice enthalpy factor.

Solubility of Sulphates :

$$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

Increasing order of thermal stability

$$BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$$

(iii) Nitrates : These metals also form $M(NO_3)_2$ and all nitrates give oxides on decomposition.

(iv) Bicarbonates : These metals form $M(HCO_3)_2$ type bicarbonates. The thermal stability of bicarbonates increases from Be to Ba.

Anomalous Behavior of Beryllium

Beryllium the first member of group 2 differs from the other members of its group. This is primarily due to

(i) its small size (ii) relatively high electronegativity (iii) availability of only four orbitals in the valence shell.

(i) Differences between beryllium and other alkaline earth metals :

(a) Beryllium is harder than other members of its group and has higher melting and boiling point.

(b) Beryllium does not react with water even at high temperature, while other metals do.

(c) Beryllium forms covalent compounds because of high charge density and hence greater polarizing power whereas other members form ionic compounds.

(d) BeO and $Be(OH)_2$ are amphoteric whereas other oxides and hydroxides of alkaline earth metals are basic.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O ;$$

$$BeO + 2NaOH \longrightarrow \underset{}{Na_2BeO_2} \text{ (Sod. Beryllate) } + H_2O$$

(e) Beryllium carbides(covalent) reacts with water to form methane while other carbides which are ionic, on hydrolysis give acetylene.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2;$$

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

(f) Beryllium forms fluoro complex anion (BeF_4^{2-}) whereas other members of the group do not form fluoro complex anion.

(ii) Similarities between Beryllium with aluminium are:

(a) Both metals have tendency to form covalent compounds.

(b) Both $BeCl_2$ and $AlCl_3$ act as strong Lewis acids.

(c) Both $BeCl_2$ and $AlCl_3$ have chloro-bridge structures in vapour phase.

(d) Both metals dissolve in strong alkalies to form soluble complexes: beryllate $[Be(OH)_4]^{2-}$ and aluminate $[Al(OH)_4]^-$

(e) The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide solution as well as in hydrochloric acid.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O\,;$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

(f) Carbides of both metals react with water liberating methane gas.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(g) Because of similar polarizing power both beryllium and aluminium forms complexes, $[BeF_4]^{2-}$ $[AlF_6]^3$.

SOME IMPORTANT COMPOUNDS OF CALCIUM

Calcium Oxide (Quick Lime), CaO

Preparation :

$$CaCO_3 \xrightleftharpoons[\text{limestone}]{\text{1070-1270K}} CaO + CO_2\,.$$

Note : Carbon dioxide has to be removed as soon as it is formed to prevent a reversible reaction.

Properties:

(a) It is a white amorphous solid.

(b) When exposed to air, it absorbs moisture and carbon dioxide forming $CaCO_3$

(c) It reacts readily with water releasing large amount of heat . This process is called slaking of lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + \text{heat.}$$

(d) It is basic oxide and thus reacts with acids and acidic oxides forming salts.

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

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Uses :

Calcium oxide is used

(a) in the manufacture of bleaching powder, slaked lime and lime colours,

(b) in the manufacture of calcium carbide, cement, glass, mortar (slaked lime + sand + water), etc.,

(c) in the conversion of Na_2CO_3 into caustic soda,

(d) in the purification of sugar,

(e) in the purification of coal gas and softening of water,

(f) as basic lining in furnaces, and

(g) for producing ammonia gas in the laboratory.

Calcium Hydroxide (Slaked Lime), $Ca(OH)_2$

Preparation:-

(a) $CaO + H_2O \longrightarrow Ca(OH)_2$

(b) $CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$

Properties:-

(a) It is white amorphous powder sparingly soluble in water, the solubility decreases further with rise in temperature. An aqueous solution is known as lime water.

(b) **Decomposition :**

$$Ca(OH)_2 \longrightarrow CaO + H_2O$$

(c) **Action of chlorine :** $\underset{\text{Milk of lime}}{2Ca(OH)_2} + 2Cl_2 \xrightarrow{\text{cold}} CaCl_2 + \underset{\substack{\text{Cal. hypochlorite}\\ \text{(Bleaching power)}}}{Ca(OCl)_2} + 2H_2O$

(d) **Reaction with carbon dioxide :**

When CO_2 is passed through lime water it turns milky due to the formation of $CaCO_3$.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_3} + H_2O$$

On passing excess of CO_2, the ppt dissolves to form $Ca(HCO_3)$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

$Ca(HCO_3)_2$ is soluble hence milkiness disappears.

Uses :

Calcium hydroxide is used: (a) in the manufacture of bleaching powder and caustic soda, (b) for white washing buildings and for softening of water, and (c) in the preparation of soda-lime (mixture of cal. hydroxide and caustic soda) which is a good adsorbent for a number of gases. Soda-lime is also used in decarboxylation of sodium salts of fatty acids.

Plaster of Paris ($CaSO_4 . \frac{1}{2} H_2O$):

It is hemihydrate of $CaSO_4$

Preparation :

$$\underset{\text{Gypsum}}{2(CaSO_4.2H_2O)} \xrightarrow{393K} \underset{\text{Plaster of paris}}{2CaSO_4.\frac{1}{2}H_2O} + 3H_2O$$

Properties :

Plaster of Paris is a white powder which when mixed with water takes up the water of crystallisation again, thus converted back into the dihydrate and sets to a hard mass with slight expansion (1%). Setting takes about 10–15 minutes and may be catalysed by the action of common salt or delayed by the use of alum or borax.

$$\underset{\text{Plaster of Paris}}{CaSO_4.\frac{1}{2}H_2O} \xrightarrow[\text{setting}]{H_2O} \underset{\text{Orthorhombic}}{CaSO_4.2H_2O} \xrightarrow{\text{hardening}} \underset{\text{Monoclinic (gypsum)}}{CaSO_4.2H_2O}$$

Plaster of Paris or gypsum when heated to about 393 K is converted into anhydrous calcium sulphate. The anhydrous form (anhydrite) is known as dead burnt plaster because it does not set like Plaster of Paris when moistened with water.

Uses :

Plaster of Paris is used (a) in making moulds for casting. (b) for preparing black board chalks. (c) in surgical bandages for plastering broken or fractured bones of the body. (d) for making statues, models and other decorative materials.

Portland Cement

It was first discovered in England. It is essentially a mixture of lime stone and clay. It was called Portland cement because in presence of water it sets to a hard stone-like mass resembling with the famous Portland rock. The approximate composition of Portland cement is

Calcium oxide (CaO)	62%
Silica (SiO_2)	22%
Alumina (Al_2O_3)	7.5%
Magnesia (MgO)	2.5%
Ferric oxide (Fe_2O_3)	2.5%

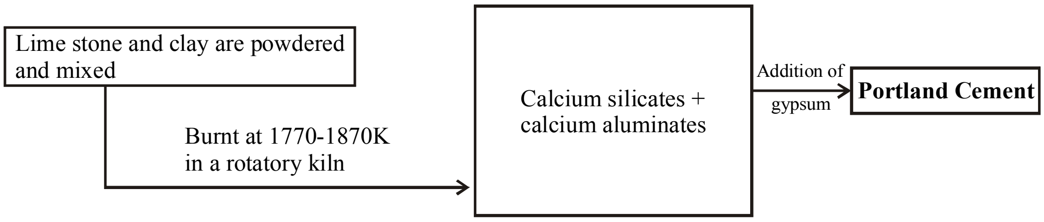
The above compounds are provided by the two raw materials, namely lime stone (which provides CaO) and clay (which provides SiO_2, Al_2O_3 and Fe_2O_3). In cement, almost entire amount of lime is present in the combined state as calcium silicate ($2CaO. SiO_2$ and $3CaO. SiO_2$) and calcium aluminates ($3CaO. Al_2O_3$ and $4 CaO. Al_2O_3$).

(a) Cement containing excess amount of lime cracks during setting; while cement containing less amount of lime is weak in strength.

(b) Cement with excess of silica is slow-setting and that having an excess of alumina is quick-setting.

(c) Cement containing no iron is white but hard to burn.

Cement is manufactured by two processes, viz. wet and dry. A small amount (2–3%) of gypsum is added to slow down the setting of the cement so that it gets sufficiently hardened. Setting of cement is an exothermic process and involves hydration of calcium aluminates and calcium silicates.



BIOLOGICAL IMPORTANCE OF Ca AND Mg

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium.

About 99% of body calcium is present in bones and teeth. It also plays important roles in neuromuscular functions, interneuronal transmission, cell membrane integrity and blood coagulation.

CONCEPT MAP

The *s*-Block Elements

Alkali Metals

Physical properties:
In alkali metals, on moving from Li to Cs
- (a) atomic or ionic radii increases
- (b) density increases
- (c) m.p. and b.p. decrease
- (d) I.E. decreases
- (e) electropositive character increases
- (f) electronegativity decreases
- (g) hydration energy decreases

Characteristics of alkali metal compounds.
Li forms Li_2O, Na forms Na_2O_2 and others form MO_2
Ionic character, m.p., b.p. thermal stability and solubility increases from LiOH to CsOH decreasing order of hydrolysis
$LiCl > NaCl > KCl > RbCl > CsCl$
Stability of carbonates and bicarbonates increases from Li to Cs whereas solubilities also increase on descending the group.

Chemical properties:
Li forms monoxide, Na forms peroxide and other metals forms superoxides on reaction with air.
$2M + 2H_2O \longrightarrow 2MOH + H_2$
$2M + X_2 \longrightarrow 2MX$
$2M + H_2 \longrightarrow 2MH$
Alkali metals are strong reducing agents.
Alkali metals dissolve in NH_3 to give blue, conducting and paramagnetic solution.

Some Important Compounds of Sodium
NaCl: HCl is passed through the filtered solution of crude NaCl.
NaOH: Electrolysis of NaCl in Castner-Kellner cell by using a Hg cathode and Canode.
Na_2CO_3: CO_2 is passed through brine saturated with NH_3. $NaHCO_3$ formed is then heated to give Na_2CO_3
$NaHCO_3$: Saturating a cold solution of Na_2CO_3 with CO_2.

Alkaline Earth Metals

Physical properties
In alkaline earth metals, on moving from Be to Ba:
- (a) atomic or ionic radii increases
- (b) density increases
- (c) m.p. and b.p. decreases
- (d) I. E. decreases
- (e) electropositive character increases
- (f) electronegativity decreases
- (g) hydration energy decreases
- (h) reducing character increases.

Chemical properties
Be, Mg, Ca and Sr form MO type oxides whereas Ba and Ra forms peroxides.
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$
$M + X_2 \longrightarrow MX_2$
$M + H_2 \longrightarrow MH_2$
$M + 2HX \longrightarrow MX_2 + H_2$
Alkaline earth metals are also strong reducing agents although weaker than alkali metals.
Alkaline earth metals like alkali metals also get dissolved in NH_3 forming coloured solutions.

Some Important Compounds of Calcium
CaO: By heating limestone at 1070–1270K.
$Ca(OH)_2$: By adding water to quick lime.
$CaSO_4 . 1/2H_2O$: By heating gypsum at 393K
Portland cement: It is essentially a mix full of limestone and clay. Its approximates composition.
CaO 62%, SiO_2 22%, Al_2O_3 7.5%, MgO 2.5% and Fc_2O_3

Characteristics of alkali earth metal compounds
MO are prepared either by heating the metal in O_2 or by decomposing metal carbonate. Solubility, thermal stability and basic character of hydroxides increases on moving down the group, covalent character decreases from $BeCl_2$ to $BaCl_2$. The thermal stability of carbonates, bicarbonates and sulphates increases from Be to Ba

Textbook Exercises

10.1 What are the common physical and chemical features of alkali metals ?

Ans. Common physical properties

(a) Large atomic radii. The atomic radii of alkali metals are largest in their respective periods. It increases as we travel down the group from Li to Cs.

(b) The ionization enthalpies of the alkali metals are lowest as compared to the elements in the other groups.

(c) They all show +1 oxidation state.

(d) The elements of this group are typical metals and are soft.

(e) All of them form ionic bond in their compound though the ionic character increases down the group.

(f) All alkali metals impart a characteristic colour to the flame.

Common chemical properties.

(a) All alkali metals are highly reactive and have the reducing property.

(b) Alkali metal react with water to release hydrogen.

(c) All the alkali metals on exposure to atmosphere (air and moisture) get converted into oxides, hydroxides and finally to carbonates.

(d) Alkali metals react vigorously with halogens to form metal halides of the type MX.

(e) The metals and their oxides on reaction with water give a strong alkali.

(f) All alkali metals dissolve in liquid ammonia giving highly conducting deep blue solutions.

10.2 Discuss the general characteristics and gradation in properties of alkaline earth metals.

Ans. Trend in physical properties

(a) The atomic radii of alkaline earth metals are fairly large though smaller than the corresponding alkali metals and they increase down the group.

(b) The alkaline earth metals have fairly low ionization enthalpies though greater than those of the corresponding elements of group–I and they decrease down the group.

(c) They all exhibit the oxidation state of +2 in their solid state as well as in solution.

(d) They are less electropositive than alkali metals but are fairly electropositive and metallic.

(e) Like alkali metals, alkaline earth metals predominantly form ionic bonds in their compounds but are less ionic than alkali metals.

(f) The alkaline earth metals are less reducing than alkali metals. Their reducing character increases down the group.

Chemical properties :

(a) They are less reactive than alkali metals. Be does not react with water while Mg can only react with steam. But as we go down the group, their reactivity with the water increases. They react with water to give hydroxides and hydrogen gas.

(b) Their reactivity towards air is less than alkali metals. Be and Mg are kinetically inert to oxygen but down the group their reactivity increases. They form oxides and nitrides when reacted in air.

(c) All alkaline earth metals combine with halogens at elevated temperature forming their halides of the type MX_2.

(d) The metals and their oxides are quite basic since they form alkali when treated with water. However they are less alkaline than group–I metals. The basicities of their oxides increase down the group.

(e) Like alkali metals , alkaline earth metals dissolve in liquid ammonia.

10.3 Why are alkali metals not found in nature ?

Ans. Alkali metals are highly reactive and hence they do not occur in the free state.

10.4 Find out the oxidation state of sodium in Na_2O_2.

Ans. Let x be the oxidation state of Na in Na_2O_2. Since Na_2O_2 contains a peroxide linkage in which O has an oxidation state of – 1, therefore, Na_2O_2 or $2x + 2(-1) = 0$ or $x = +1$.

10.5 Explain why is sodium less reactive than potassium ?

Ans. The ionization enthalpy ($\Delta_i H$) of potassium (496 kJ mol^{-1}) is less than that of sodium (496 kJ mol^{-1}) or more precisely the standard electrode potential (E°) of potassium (–2.925V) is more negative than that of sodium (–2.714V) and hence potassium is more reactive than sodium.

10.6 Compare the alkali metals and alkaline earth metals with respect to (i) ionisation enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides.

Ans. (i) **Ionization enthalpy ($\Delta_i H$)**. Because of higher nuclear charge, the $\Delta_i H$ of alkaline earth metals are higher than those of the corresponding alkali metals.

(ii) **Basicity of oxides**. The oxides of alkali and alkaline earth metals dissolve in water to form their respective hydroxides. These hydroxides are strong bases. However, since the ionization enthalpy of alkali metals is lower or the electropositive character of alkali metals is higher than that of the corresponding alkaline earth metal, therefore the M– OH bond in alkali metals can more easily ionize ($MOH \longrightarrow M^+ + OH^-$), than in alkaline earth metals and hence alkali metal oxides are more basic than the corresponding alkaline earth metal oxides.

(iii) **Solubility of hydroxides**. Because of smaller size and higher ionic charge, the lattice enthalpies of alkaline earth metals are much higher than those of alkali metals and hence the solubility of alkali metal hydroxides is much higher than that of alkaline earth metal hydroxides. However, the solubility of the hydroxides of both alkali and alkaline earth metals increase down the group due to larger decrease in their lattices enthalpies as compared to their hydration enthalpies.

10.7 In what ways lithium shows similarities to magnesium in its chemical behaviour ?

Ans. Lithium resembles magnesium mainly due to same charge/radius ratio or polarizing power. The main points of similarity are:

(a) Both LiOH and $Mg(OH)_2$ are weak bases.

(b) Both form ionic nitrides when heated in atmosphere of nitrogen, Li_3N and Mg_3N_2.

(c) The hydroxides and carbonates of both of them decompose on heating.

$$2LiOH \longrightarrow Li_2O + H_2O$$
$$Mg(OH)_2 \longrightarrow MgO + H_2O$$
$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$

(d) Both Li and Mg do not form solid bicarbonates.

(e) Li and Mg do not form peroxides and super oxides.

(f) Both Li and Mg nitrates decompose on heating producing NO_2.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$
$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

(g) The hydroxides, carbonates and fluorides of lithium and magnesium are sparingly soluble in water.

(h) LiCl and $MgCl_2$ are highly soluble in ethanol.

10.8 Explain why Alkali and Alkaline earth metals not be obtained by chemical reduction methods ?

Ans. Alkali and alkaline earth metals are themselves strong reducing agents and reducing agents better than them are not available. Therefore, these metals cannot be obtained by reduction of their oxides or chlorides.

10.9 Why are potassium and caesium, rather than lithium used in photoelectric cells ?

Ans. Potassium and caesium have much lower ionization enthalpy than that of lithium. As a result, these metals on exposure to light, easily emit electrons but lithium does not. Therefore, K and Cs rather than Li are used in photoelectric cells.

10.10 When an alkali metal dissolves in liquid ammonia, the solution can acquire different colours. Explain the reasons for this type of colour change.

Ans. The dilute solutions of alkali metals in liquid ammonia exhibit dark blue colour because ammoniated electrons absorb energy corresponding the red region of the visible light.

$$M + (x+y)\,NH_3 \longrightarrow [M(NH_3)_x]^+ + \underset{\text{Ammoniated electrons}}{e^-(NH_3)_y}$$

However, if the concentration increases above 3M, the colour changes to copper–bronze and the solution acquires metallic lustre due to the formation of metal ion clusters.

10.11 Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why ?

Ans. Because of the small size, the ionization enthalpies of Be and Mg are much higher than those of other alkaline earth metals. Therefore, they need large amount of energy for excitation of their valence electrons to higher energy levels. Since such a large amount of energy is not available in Bunsen flame, therefore, these metals do not impart any colour to the flame.

10.12 Discuss the various reactions that occur in the Solvay process.

Ans. In Solvay ammonia process, CO_2 is passed through brine, (i.e., a concentrated solution of NaCl) saturated with ammonia where sodium bicarbonate being sparingly soluble gets precipitated.

$$NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3\downarrow + NH_4Cl \quad \text{...(i)}$$

Sodium bicarbonate on heating gives sodium carbonate.

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O \quad \text{...(ii)}$$

CO_2 needed for the reaction is prepared by heating calcium carbonate and the quick lime, CaO is dissolved in water to form slaked lime, $Ca(OH)_2$

$$CaCO_3 \longrightarrow CaO + CO_2,$$
$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad \text{...(iii)}$$

NH_3 needed for the purpose is prepared by heating NH_4Cl obtained in Eq(i) with $Ca(OH)_2$ obtained in Eq(iii)

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaCl_2 + 2\,H_2O$$

Therefore, the only by product of the reaction is calcium chloride, $CaCl_2$.

10.13 Potassium carbonate cannot be prepared by Solvay process. Why ?

Ans. Potassium carbonate cannot be prepared by Solvay process because potassium bicarbonate being more soluble than sodium bicarbonate does not get precipitated when CO_2 is passed through a concentrated solution of KCl saturated with ammonia.

$$KCl + CO_2 + NH_3 + H_2O \longrightarrow KHCO_3 + NH_4Cl$$

10.14 Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Ans. Li_2CO_3 is a salt of a weak acid (H_2CO_3) with a weak base (LiOH). Since the weak base cannot attract CO_2 strongly, therefore, Li_2CO_3 decomposes at lower temperature. On the other hand, NaOH is a much stronger base than LiOH and hence can attract CO_2 more strongly. Therefore, Na_2CO_3 is much more stable than Li_2CO_3 and hence decomposes at much higher temperature than Li_2CO_3

10.15 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals (a) Nitrates (b) Carbonates (c) Sulphates.

Ans. Solubility :

(a) **Alkali metals.** Nitrates, carbonates and sulphates of alkali metals are soluble in water. Their, solubility, however, increases as we move down the group since the lattice energies decrease more rapidly than the hydration energies.

(b) **Alkaline earth.** Nitrates of all alkaline earth metals are soluble in water. Their solubility, however, decreases as we move down the group because their hydration energies decrease more rapidly than the lattice energies. The size of CO_3^{2-} and SO_4^{2-} anions is much larger than the cations, therefore, within a particular group, lattice energies remain almost constant. Since the hydration energies decrease down the group, therefore, the solubility of alkaline earth carbonates' and sulphates decrease down the group. However, the hydration energy of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore, $BeSO_4$ and $MgSO_4$ are readily soluble in water while the solubility of other sulphates decreases down the group from $CaSO_4$ to $BaSO_4$.

Thermal stability :

(a) **Nitrates.** Nitrates of both alkali and alkaline earth metals decompose on heating. All alkaline earth metal nitrates decompose to form metal oxide, NO_2 and O_2.

$2M(NO_3)_2 \xrightarrow{\Delta} 2\,MO + 4\,NO_2 + O_2$ (M = Be, Mg, Ca, Sr or Ba). The nitrates of Na, K, Rb and Cs decompose to form metal nitrites and O_2.

$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2$ (M = Na, K, Rb, Cs)

However, due to diagonal relationship between Li and Mg, lithium nitrate decomposes like $Mg(NO_3)_2$ to form metal oxide, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

(b) **Carbonates**. Carbonates of alkaline earth metals decompose on heating to form metal oxide and CO_2

$MCO_3 \xrightarrow{\Delta} MO + CO_2$ (M = Be, Mg, Ca, Sr, Ba)

Further as the electropositive character of the metal increases down the group, the stability of these metal carbonates increases and hence the temperature of their decomposition increases as shown below:

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
< 373 K	813 K	1173 K	1563 K	1633 K

Due to diagonal relationship between Li and Mg, Li_2CO_3 decomposes in the same way as $MgCO_3$.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

All other alkali metal carbonates are stable and do not decompose even at high temperatures.

(c) **Sulphates**. Sulphates of alkaline earth metals decompose on heating giving the oxides and SO_3.

$$MSO_4 \longrightarrow MO + SO_3$$

The temperature of decomposition of these sulphates increases as the electropositive character of the metal or the basicity of the metal hydroxide increases down the group. For example,

Compound:	**Temp. of decomposition:**
$BeSO_4$	773 K
$MgSO_4$	1168K
$CaSO_4$	1422K
$SrSO_4$	1644K

Among alkali metals due to diagonal relationship, Li_2SO_4 decomposes like $MgSO_4$ to form the corresponding metal oxide and SO_3.

$$Li_2SO_4 \xrightarrow{\Delta} Li_2O + SO_3$$

$$MgSO_4 \xrightarrow{\Delta} MgO + SO_3$$

Other alkali metals are stable to heat and do not decompose easily.

10.16 Starting with sodium chloride how would you proceed to prepare
(i) sodium metal
(ii) sodium hydroxide
(iii) sodium peroxide and
(iv) sodium carbonate?

Ans. (i) Sodium metal is manufactured by electrolysis of a fused mixture of NaCl (40%) and $CaCl_2$ (60%) in Down's cell at 873 K using iron cathode and graphite anode. Na is liberated at the cathode while Cl_2 is evolved at the anode.

At cathode : $Na^+ (melt) + e^- \longrightarrow Na\ (l)$

At anode : $2\,Cl^- (melt) \longrightarrow Cl_2\,(g) + 2e^-$

(ii) Refer theory

(iii) Sodium peroxide is obtained by heating sodium in excess of air. The initially formed sodium oxide reacts with more O_2 to form Na_2O_2.

$4\,Na + O_2 \longrightarrow 2\,Na_2O$

$2\,Na_2O + O_2 \longrightarrow 2\,Na_2O_2$

(iv) Refer theory

10.17 What happens when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated ?

Ans. (i) $2\,Mg\,(s) + O_2\,(g) \xrightarrow{\Delta} 2\,MgO\,(s)$

(ii) $\underset{\text{Quick lime}}{CaO(s)} + \underset{\text{Silica}}{SiO_2(s)} \xrightarrow{\Delta} \underset{\text{Calcium silicate}}{CaSiO_3(s)}$

(iii) It reacts with Cl_2 to form calcium hypochlorite, $Ca(OCl)_2$–a constituent of bleaching powder

$$\underset{\text{Slaked lime}}{2Ca(OH)_2} + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{\text{Bleaching powder}} + 2H_2O$$

(iv) $2\,Ca(NO_3)_2(s) \longrightarrow 2\,CaO(s) + 4\,NO_2(g) + O_2\,(g)$

10.18 Describe two important uses of each of the following: (i) caustic soda (ii) sodium carbonate (iii) quicklime.

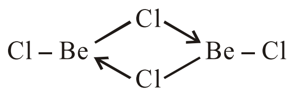
Ans. 1. Caustic soda :
   (i) It is used in the manufacture of soap, paper, artificial silk, etc. and in petroleum refining and purification of bauxite.
   (ii) It is used in the textile industries for mercerizing cotton fabrics.

2. Sodium carbonate :
   (i) It is used in water softening laundering and cleaning.
   (ii) It is used in the manufacture of glass, soap, borax, etc and in paper, paints and textile industries.

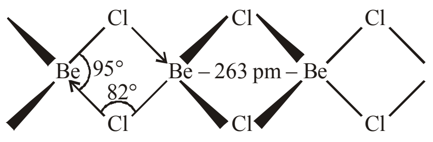
3. Quick lime :
   (i) It is used in the manufacture of sodium carbonate from caustic soda,
   (ii) It is employed in the purification of sugar and in the manufacture of dyestuffs.

10.19 Draw the structure of
(i) $BeCl_2$ (vapour) (ii) $BeCl_2$ (solid).

Ans. (i) In the vapour state, it exists as a chloro–bridged dimer.



(ii) In the solid state, $BeCl_2$ has polymeric structure with chloro bridges.



10.20 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

Ans. Due to larger size of Na and K as compared to that of Mg and Ca, the lattice energies of hydroxides and carbonates of sodium and potassium are much lower than those of the hydroxides and carbonates of magnesium and calcium. As a result, the hydroxides of Na and K are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water.

10.21 Describe the importance of the following:

(i) limestone (ii) cement

(iii) Plaster of Paris.

Ans. (i) **Limestone.** Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in toothpaste, a constituent of chewing gum and as a filler in cosmetics.

(ii) **Cement.** Refer theory

(iii) **Plaster of Paris.** Refer theory

10.22 Why are lithium salts commonly hydrated and those of the other alkali metal ions usually anhydrous?

Ans. Because of smallest size among alkali metals, Li^+ can polarize water molecules more easily than the other alkali metal ions and hence get attached to lithium salts as water of crystallization. For example, lithium chloride crystallizes as $LiCl.2\,H_2O$.

10.23 Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone?

Ans. Difference in lattice energy and hydration energy of LiCl is higher i.e. $-31\ kJmol^{-1}$ $[-876-(-845)]$ than that of LiF i.e. $-14\ kJ\ mol^{-1}$ $[-1019-(-1005)]$ and hence LiF is sparingly soluble in water while LiCl in soluble. In nut shell, we can say that LiF is almost insoluble in water because of much higher lattice energy ($-1005\ kJ\ mol^{-1}$) than that of LiCl ($-845\ kJ\ mol^{-1}$). Furthermore, Li^+ ion can polarize bigger Cl^- ion more easily than the smaller F^- ion. As a result, according to Fajan rules, LiCl has more covalent character than LiF and hence is soluble in organic solvents like acetone

10.24 Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

Ans. Refer theory

10.25 What happens when

(i) sodium metal is dropped in water ?

(ii) sodium metal is heated in free supply of air ?

(iii) sodium peroxide dissolves in water ?

Ans. (i) H_2 gas is evolved which catches fire due to the exothermicity of the reaction.

$$2Na(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2(g)$$

(ii) Na_2O_2 along with a small amount of Na_2O is formed.

$$2Na(s) + O_2 \longrightarrow \underset{(minor)}{Na_2O(s)}$$

$$Na_2O(s) + \tfrac{1}{2}O_2(s) \longrightarrow \underset{(major)}{Na_2O_2(s)}$$

(iii) H_2O_2 is formed.

$$Na_2O_2(s) + 2\,H_2O(\ell) \longrightarrow 2\,NaOH(aq) + H_2O_2\,(l)$$

10.26 Comment on each of the following observations:

(a) The mobilities of the alkali metal ions in aqueous solution are

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(b) Lithium is the only alkali metal to form a nitride directly.

(c) $E^\ominus$ for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

Ans. (a) Smaller the size of the ion, more highly it is hydrated and hence greater is the mass of the hydrated ion and hence smaller is its ionic mobility. Since the extent of hydration decreases in the order:

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

therefore, ionic mobility increases in the same order :

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(b) Because of the diagonal relationship of Li and Mg, lithium like magnesium forms a nitride while other alkali metals do not.

$$6Li(s) + N_2(g) \xrightarrow{\Delta} 2Li_3N(s)$$

(c) $E^\ominus$ of any M^{2+}/M electrode depends upon three factors:

(i) enthalpy of vaporization,

(ii) ionization enthalpy

(iii) enthalpy of hydration.

Since the combined effect of these factors is approximately the same for Ca, Sr and Ba, therefore, their electrode potentials are nearly constant.

10.27 State as to why

(a) A solution of Na_2CO_3 is alkaline?

(b) Alkali metals are prepared by electrolysis of their fused chlorides?

(c) Sodium is found to be more useful than potassium?

Ans. (a) Na_2CO_3 is a salt of a weak acid, carbonic acid (H_2CO_3) and a strong base, sodium hydroxide (NaOH) therefore, it undergoes hydrolysis to produce strong base NaOH and hence its aqueous solution is alkaline in nature.

$$Na_2CO_3(s) + H_2O(\ell) \rightarrow \underset{\text{Strong base}}{2NaOH(aq)} + \underset{\text{Weak acid}}{H_2CO_3(aq)}$$

(b) Since the discharge potential of alkali metals is much higher than that of hydrogen, therefore, when the aqueous solution of any alkali metal chloride is subjected to electrolysis. H_2 instead of the alkali metal is produced at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.

(c) Sodium ions are found primarily in the blood plasma and in the interstitial fluid which surrounds the cells while potassium ions are present within the cell fluids. Sodium ions help in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into the cells. Thus, sodium is found to be more useful than potassium.

10.28 Write balanced equations for the reactions between

(a) Na_2O_2 and water (b) KO_2 and water

(c) Na_2O and CO_2

Ans. (a) $Na_2O_2(s) + 2\,H_2O\,(\ell) \longrightarrow 2\,NaOH\,(aq) + H_2O_2\,(aq)$

(b) $2\,KO_2(s) + 2\,H_2O\,(\ell) \longrightarrow 2\,KOH\,(aq) + H_2O_2\,(aq) + O_2\,(g)$

(c) $Na_2O + CO_2 \longrightarrow Na_2CO_3$

10.29 How would you explain the following observations ?

(i) BeO is almost insoluble but $BeSO_4$ is soluble in water,

(ii) BaO is soluble but $BaSO_4$ is insoluble in water

(iii) LiI is more soluble than KI in ethanol.

Ans. (i) Because of smaller size, higher ionization enthalpy and higher electro negativity, BeO is essentially covalent and hence is insoluble in water. In contrast, $BeSO_4$ is ionic. Further because of small size of Be^{2+} ion, the hydration energy of $BeSO_4$ is much higher than its lattice energy and hence $BeSO_4$ is highly soluble in water.

(ii) Both BaO and $BaSO_4$ are ionic compounds. However, the size of O^{2-} ion is much smaller than that of the SO_4^{-2} ion. Since a bigger anion stabilizes a bigger cation more than a smaller anion stabilizes a bigger cation, therefore, the lattice energy of BaO is much smaller than that of $BaSO_4$ and hence BaO is soluble while $BaSO_4$ is insoluble in water.

(iii) Li^+ is much smaller than K^+ ion. Therefore, according to Fajan rule, Li^+ ion can polarize bigger I^- ion to a greater extent than K^+ ion. As a result, LiI is more covalent than KI and hence is more soluble in organic solvents like ethanol.

10.30 Which of the alkali metal is having least melting point ?

(a) Na (b) K

(c) Rb (d) Cs.

Ans. As the size of the metal increases, the strength of metallic bonding decreases and hence its melting point decreases. Since the size of Cs is the biggest, therefore, its melting point is the lowest. Thus, option (d) is correct.

10.31 Which one of the following alkali metals gives hydrated salts ?

(a) Li (b) Na

(c) K (d) Cs

Ans. Among alkali metal ions, Li^+ is the smallest. Therefore, it has the highest charge density and hence attracts the water molecules more strongly than any other alkali metal cation. Thus, option (a) is correct.

10.32 Which one of the alkaline earth metal carbonates is thermally the most stable ?

(a) $MgCO_3$ (b) $CaCO_3$

(c) $SrCO_3$ (d) $BaCO_3$

Ans. As the electropositive character of the metal increases or the basicities of their hydroxides increases down the group, their thermal stability increases. Thus, $BaCO_3$ is the most stable and hence option (d) is Correct.

Practice Questions

Very Short Answer Questions [1 Mark]

1. Why does a piece of burning magnesium ribbon continues to burn in sulphur dioxide ?

2. What is the function of adding gypsum to clinker cement ?

3. Why is anhydrous $CaSO_4$ used as drying agent? Why not plaster of paris ?

4. How the caves are formed in limestone regions ?

5. How is slaked lime prepared ?

6. Why group 2 elements (Mg and Ca) are harder and denser than group 1 elements?

7. Why are alkali metals used in photoelectric cells?

8. Why do alkali metals have low melting and boiling points?

9. Why do alkali metals have low density?

10. Why are alkali metals soft?

11. Why is second ionisation energy of alkali metals higher than alkaline earth metals?

12. Which out of K, Mg, Ca and Al form amphoteric oxide?

13. Complete the reaction : $LiI + KF \rightarrow$

14.. The second ionization enthalpy of Ca is higher than first and yet calcium forms $CaCl_2$ and not CaCl, why?

15. Name the metal which floats on water without apparent reaction.

16. Can we store sodium metal in air or water?

17. Give two uses of sodium carbonate.

18. Which is more basic, NaOH or $Mg(OH)_2$?

19. Which method is commonly used to extract sodium metal from its ores?

20. The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts, why?

21. Name the alkali metal which shows diagonal relationship with magnesium?

22. What happen when crystals of washing soda ($Na_2CO_3.10H_2O$) are exposed to air?

23. Why is the solution of alkali metals in liquid ammonia conducting in nature?

24. What is the oxidation state of K in KO_2?

25. Sodium peroxide forms a white compound when it comes into contact with moist air. Explain.

26. Account for the following :
Be has less negative value of the reduction potential (E°)

Short Answer Questions [2 & 3 Marks]

1. What happens when
(i) calcium is treated with nitrogen.
(ii) calcium is treated with dilute sulphuric acid.
(iii) calcium is heated in the atmosphere of SO_2.
(iv) calcium is treated with cold water .

2. How is quick lime prepared on a commercial scale ? How is it converted into slaked lime ?

3. What different changes occur when CO_2 is passed through lime water?

4. What happens when
(i) Plaster of paris is mixed with water.
(ii) Gypsum is heated at 473 K.

5. Mention the main constituents of portland cement.

6. Why
   (i) is Mg^+ ion unstable ?
   (ii) does beryllium form $BeCl_2$ although it has no unpaired electrons ?

7. Magnesium metal burns in air to give a white ash. When this ash is treated with water, the odour of ammonia can be detected ? Explain.

8. 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 components A and B.

9. How will you distinguish between
   (i) Slaked lime
   (ii) Milk of lime
   (iii) Limewater

10. Arrange the following in the order of property indicated :
   (i) $CaCl_2$, $MgCl_2$, $BeCl_2$, $SrCl_2$: Ionic character
   (ii) $Sr(OH)_2$, $Ba(OH)_2$, $Be(OH)_2$, $Mg(OH)_2$: Basic character
   (iii) $BeSO_4$, $SrSO_4$, $CaSO_4$, $BaSO_4$: Increasing solubility in water

11. Give reasons
   (i) Li & Mg show similar properties.
   (ii) Alkali metals show +1 oxidation state.
   (iii) Alkali metals have largest size in their period

12. Give reasons
   (i) $BeCl_2$ fumes in air.
   (ii) $BeCl_2$ differs from other halides of alkaline earth metals

13. Mention a few difficulties involved in the extraction of sodium from fused sodium chloride.

14. What is meant by 'diagonal relationship' in the periodic table? What is it due to?

15. Why is it that hydrated chlorides of Ca, Sr and Ba can be dehydrated by heating but those of Be and Mg suffer hydrolysis?

16. Alkali metals are paramagnetic but their salts are diamagnetic. Explain.

17. 'The chemistry of beryllium is not essentially ionic.' Justify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.

18. Beryllium exhibits some similarities with aluminium. Point out three such properties.

19. How $LiNO_3$ and $NaNO_3$ differ from each other on the action of water?

20. Why it is not advisable to dry alcohols with sodium metal, though it is used for drying ether?

21. Alkaline earth metal ions have a tendency to form complexes, whereas it is not so in case of alkali metals.

22. Why is MgO used as a refractory material ?

23. $BaSO_4$ is used during the X-ray of stomach, why?

24. What is the use of KO_2 in oxygen masks?

25. KOH is preferred to NaOH to absorb CO_2, why?

26. Explain why a pellet of sodium is covered with sodium carbonate layer when exposed to atmosphere?

27. Discuss thermal stability and the solubility of the oxosalts of alkaline earth metals.

28. Why is calcium preferred over sodium to remove last traces of moisture from alcohol?

Long Answer Questions [5 Marks]

1. What happens when
   (i) Magnesium is heated with water.
   (ii) Magnesium is treated with nitrogen.
   (iii) Magnesium is heated in an atmosphere of carbon dioxide.
   (iv) Magnesium is treated with dilute sulphuric acid
   (v) Magnesium is burnt in air.

2. Contrast the action of heat on the following and explain your answer.
   (i) Na_2CO_3 and $CaCO_3$
   (ii) $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$
   (iii) $Ca(NO_3)_2$ and $NaNO_3$.

3. Complete the following equations for the reaction between
   (i) $Ca + H_2O$ (ii) $Ca(OH)_2 + Cl_2$
   (iii) $BeO + NaOH$ (iv) $BeCl_2 + LiAlH_4$
   (v) $Ca_3N_2 + H_2O$

4. Give reasons
   (i) Alkali metals are good reducing agents.
   (ii) Alkali metals can be obtained only by electrolysis of their fused salts.
   (iii) Hydrogen is obtained on electrolysis of aqueous solution of salts of alkali metals.
   (iv) Alkali metals dissolve in liquid ammonia to give blue solutions.
   (v) The blue colour of metal–ammonia solution disappears on standing.

5. Give reasons
   (i) Unlike alkali metal compounds , compounds of Li are much less soluble in water.
   (ii) Although Li has highest I.E. in group –1 but it is the best reducing agent.
   (iii) Li differs from other members of its group.
   (iv) LiOH, $LiNO_3$, Li_2CO_3 decompose readily on heating, whereas the other alkali metal hydroxides & carbonates not decompose readily on heating.
   (v) Alkali & some alkaline earth metals impart colour to bunsen flame.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Consider the reaction

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

When the above reaction is carried out the water goes cloudy. Why? **[HOTS]**

2. Why is $BeCO_3$ stored in carbon dioxide atmosphere? **[HOTS]**

3. Why caesium can be used in photoelectric cell while lithium can not be ? **[HOTS]**

4. Halides of Be dissolve in organic solvents while those of Ba do not. Why is it so ? **[HOTS]**

5. Super oxides of alkali metals are coloured and paramagnetic in nature. Explain. **[HOTS]**

6. Why does beryllium form $BeCl_2$ although it has no unpaired electrons ? **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. Account for the following :
   (i) $Be(OH)_2$ is amphoteric while $Mg(OH)_2$ is basic.
   (ii) $Be(OH)_2$ is insoluble but $Ba(OH)_2$ is fairly soluble in water. **[HOTS]**
2. Why are BeO and BeF_2 covalent compounds though both O and F are highly electronegative elements? **[HOTS]**
3. Why solubility of alkaline earth metal compounds are comparatively less than the corresponding alkali metal compounds in water? **[HOTS]**
4. Lithium forms normal oxide, sodium forms peroxide and rest all alkali metals form superoxides. Explain. **[HOTS]**
5. Explain why halides of beryllium fume in moist air but other alkaline earth metal halides do not. **[HOTS]**
6. Unlike Na_2CO_3, K_2CO_3 cannot be prepared by Solvay ammonia soda process. Explain. **[HOTS]**
7. Lithium resembles magnesium in some of its properties. Mention two such properties and give reasons for this resemblance. **[Exemplar]**
8. Why are $BeSO_4$ and $MgSO_4$ readily soluble in water while $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble? **[Exemplar]**

Long Answer Questions [5 Marks]

1. Give reasons **[HOTS]**
   (i) Alkaline earth metal hydroxides are less basic than alkali metal hydroxides.
   (ii) Alkali & alkaline earth metal hydrides are ionic in nature
   (iii) Group 1 elements are called alkali metals
   (iv) Be resembles Al.
   (v) The fluorides of alkaline earth & alkali metal are relatively less soluble than chlorides
2. When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step. **[Exemplar]**
3. Lithium hydride can be used to prepare other useful hydrides. Beryllium hydride is one of them. Suggest a route for the preparation of beryllium hydride starting from lithium hydride. Write chemical equations involved in the process. **[Exemplar]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. Name the alkali metal which is radioactive.
2. Name the element which is invariably bivalent and whose oxide is soluble in excess of NaOH and its dipositive ion has a noble gas core.
3. Arrange the following in order of the increasing covalent character: MCl, MBr, MF, MI (where M = alkali metal)
4. Name one reagent or one operation to distinguish
   (i) $BeSO_4$ and $BaSO_4$
   (ii) $Be(OH)_2$ and $Ba(OH)_2$
5. (i) Sodium fire in the laboratory should not be extinguished by pouring water. Why?
   (ii) Why does table salt get wet in rainy season?
6. (i) Why is it that on being heated in excess supply of air, K, Rb and Cs form super oxides in preference to oxides?
   (ii) In which condition a cation is highly polarizing? In group –1 which cation has the highest polarizing power?
   (iii) Why does the solubility of alkaline earth metal carbonates and sulphates decrease down the group?
7. Give the principle and reactions involved in the manufacture of Na_2CO_3 by Solvay's process.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. This is because magnesium has high affinity to combine with oxygen of SO_2 to form MgO and S.

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

2. Gypsum is added to retard the rate of setting of cement. Gypsum reacts with tricalcium aluminate to form calcium sulphoaluminate.

$$3CaO.Al_2O_3 + 3CaSO_4 + nH_2O \longrightarrow 3CaO . Al_2O_3 .CaSO_4 . nH_2O$$

3. Anhydrous $CaSO_4$ can absorb water to form $CaSO_4 . 2H_2O$ and hence can be used as a drying agent. Plaster of paris is not used as a drying agent because it sets into a hard mass by absorbing water.
4. Caves in limestone regions get formed due to the dissolution of calcium carbonate in water containing carbon dioxide.
   $CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$
5. Refer theory
6. They have strong metallic bonds due to smaller size and have more number of valence electrons.
7. They have low ionisation energy and can lose electrons when light falls on them, that is why they are used in photoelectric cells.
8. It is due to weak metallic bonds which is due to bigger atomic size that is why they how low melting and boiling points.
9. Due to weak metallic bonds and large atomic size, their density is low.
10. They are soft metals due to less force of attraction between positively charged kernels and valence electrons cloud and due to large atomic size, i.e., weak metallic bond.
11. Refer theory
12. Al forms amphoteric oxide, i.e., acidic as well as basic in nature.
13. $LiI + KF \rightarrow LiF + KI$; larger cation stabilizes larger anion and smaller cation stabilizes smaller anion.
14. The hydration energy of Ca^{2+} overcomes the second ionisation energy of Ca, that is why Ca forms $CaCl_2$ and not CaCl. Ca^+ is not stable.
15. Beryllium
16. No, it reacts violently with water and catches fire.
17. Refer theory
18. NaOH.
19. Electrolytic reduction using *Down cell* is commonly used for the extraction of sodium metal.
20. This is because alkaline earth metals have smaller size and higher nuclear charges as compared to alkali metals.
21. Li.
22. Monohydrate ($Na_2CO_3 . H_2O$) is formed as a result of efflorescence.
23. Due to ammoniated electrons and cations.
24. K is +1.
25. Sodium peroxide when exposed to moist air turns white due to formation of NaOH and Na_2CO_3.
    $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$
    $2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$
26. The less negative value for Be arises from the large hydration energy associated with the small size of Be^{2+} and the relatively large value of the enthalpy of atomization of the metal.

Short Answer Questions

1. (i) Calcium nitride is formed.
   $3Ca(s) + N_2(g) \longrightarrow Ca_3N_2(s)$
   (ii) Dihydrogen gas is liberated.
   $Ca(s) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + H_2(g)$
   (iii) Calcium oxide is formed.
   $2Ca(s) + SO_2(g) \longrightarrow 2CaO(s) + S(s)$
   (iv) Dihydrogen gas is liberated.
   $Ca(s) + 2H_2O(\ell) \longrightarrow Ca(OH)_2(aq) + H_2(g)$
2. Quick lime is anhydrous calcium oxide (CaO) and is formed by heating lime stone ($CaCO_3$) in a specially designed kiln at 1070 – 1270 K

$$CaCO_3 \xrightleftharpoons{\text{Heat}} CaO + CO_2 ; \Delta H = +179.9 kJ$$

Formation of slaked lime. Slaked lime is formed when quick lime is added to water. The reaction is highly exothermic in nature and called slaking of lime.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 + Heat$$

3. On passing CO_2 through lime water, it turns milky due to the formation of insoluble calcium carbonate.
   $Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(\ell)$
   If carbon dioxide is passed in excess, a clear solution is again obtained. This is because the insoluble calcium carbonate changes into soluble calcium bicarbonate.
   $$CaCO_3(s) + H_2O(\ell) + CO_2(g) \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2(aq)}$$
   If the clear solution is heated, it again turns milky due to the decomposition of calcium bicarbonate into calcium carbonate.
   $$\underset{\text{Soluble}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Insoluble}}{CaCO_3(s)} + CO_2 + H_2O(\ell)$$
4. (i) Refer theory
   (ii) When gypsum is heated above 393K, no water of crystallisation is left and only $CaSO_4$ known as dead burnt plaster is formed.
   $$CaSO_4 . 2H_2O \xrightarrow{473K} \underset{\text{Dead burnt plaster}}{CaSO_4} + 2H_2O$$
5. Refer theory
6. (i) Because Mg^+ ion has the tendency to lose another electron to form Mg^{2+} ion which has stable noble gas configuration of the nearest inert gas (Neon).
   (ii) Beryllium (At.No.4) has electronic configuration $1s^2 2s^1 2p_x^1$ in the excited state. One s–orbital (2s) and one p–orbital (2p) can intermix to form two sp hybrid orbitals which can be used to form $BeCl_2$.
7. Magnesium burns in air to form MgO and Mg_3N_2.
   $2Mg + O_2 \longrightarrow 2MgO$
   $3Mg + N_2 \longrightarrow Mg_3N_2$
   Magnesium nitride on hydrolysis with H_2O gives NH_3.
   $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$
8. Calcium burns in N_2 to produce Ca_3N_2.
   $$3Ca + N_2 \rightarrow \underset{\text{White powder}}{Ca_3N_2}$$
   Calcium nitride (Ca_3N_2) on hydrolysis with water gives ammonia gas (A)
   $$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{(A)}{2NH_3}$$
   The alkaline solution of $Ca(OH)_2$ thus formed reacts with CO_2 present in the air to form calcium carbonate, $CaCO_3$ (B)
   $$Ca(OH)_2 + CO_2 \longrightarrow \underset{(B)}{CaCO_3} + H_2O$$
   Thus $A = NH_3$; $B = CaCO_3$.
9. (i) **Slaked lime:** White amorphous solid, formed when quick lime is added to water
   $$CaO + H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2}$$

(ii) **Milk of lime :** It is the suspension of slaked lime in water.

(iii) **Lime water :** When milk of lime is kept for some time solid particles suspended in water settled down and clear solution is obtained which is decanted is known as lime water.

10. (i) Increasing order of ionic character $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$

(ii) Increasing order of basic character $Be(OH)_2 < Mg(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(iii) Increasing order of solubility in water $BaSO_4 < SrSO_4 < CaSO_4 < BeSO_4$.

11. (i) This is due to diagonal relationship as they have same electronegativity, ionisation enthalpy and charge/radius ratio.

(ii) As alkali metal have ns^1 configuration , they loose one electron to achieve stable noble gas configuration.

(iii) Since across the period the incoming electrons enters in the same energy shell and due to increase in nuclear charge the valence electrons feels more attraction from nucleus as we move from left to right in a period. As alkali metals are the first group along the period they have largest radius in their respective periods.

12. (i) $BeCl_2$ gives HCl gas in moist air due to which fumes are observed.

$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$

(ii) Be have small size and high ionization enthalpy, thus its halides are mostly covalent . But as we go down the group the size increases and ionization enthalpy decreases thus other members of the groups form ionic halides. The halides of beryllium do not form hydrates while other do form.

13. It is slightly difficult to obtain sodium from fused sodium chloride due to the following:

(i) Sodium chloride melts at 1074 K and it is difficult to attain and maintain this temperature.

(ii) Sodium boils at about 1165 K and hence at the temperature of electrolysis, the metal liberated will vapourize.

(iii) Molten sodium forms a metallic fog (colloidal solution) with fused sodium chloride.

(iv) The products of electrolysis, sodium and chlorine, corrode the material of the cell at this high temperature.

14. The similarity in properties of the first element of each group with the elements to the lower right of the next period i.e. diagonally opposite element, is known as 'diagonal relationship. This is due to

(i) similarity in the size of the ions

e.g. $r_{Li^+} = 76$ pm, $r_{Mg^{2+}} = 72$ pm

(ii) similarity in polarizing power

$$\left[\frac{\text{ionic charge}}{(\text{ionic radius})^2}\right]$$

(iii) similarity in electropositive character.

15. $CaCl_2.6H_2O \xrightarrow{heat} CaCl_2 + 6H_2O$

$MgCl_2.6H_2O \xrightarrow{heat} MgO + 2HCl + 5H_2O$

$MgCl_2.\ 6H_2O$ or $BeCl_2.\ 4H_2O$ on heating suffer hydrolysis due to the small size of Mg^{2+} (or Be^{2+}).

16. Alkali metals contain unpaired electrons and hence are paramagnetic. But in the salts of alkali metals there are alkali metal cations which don't have unpaired electrons. Hence these are diamagnetic.

17. Due to exceptionally small size and high ionization enthalpy, the compounds of beryllium are largely covalent. For example: BeO is amphoteric while oxide of other elements of group-2 are basic in nature. BeO dissolves in alkali to form beryllate

$BeO + 2OH^- + H_2O \rightarrow [Be(OH)_4]^{2-}$

$BeCl_2$ is largely covalent and is soluble in organic solvents. BeF_2 is also highly covalent and due to high lattice enthalpy, the solubility is very less.

18. (i) Both Be and Al react with conc. sodium hydroxide to form beryllate ion $[Be(OH)_4]^{2-}$ or aluminate ion $[Al(OH)_6]^{2-}$.

(ii) Both BeO and Al_2O_3 are amphoteric in nature.

(iii) $BeCl_2$ and $AlCl_3$ both are covalent.

19. $NaNO_3$ is very readily soluble in water because it is ionic in nature while $LiNO_3$ is not readily soluble in water because it is covalent in nature.

20. Alcohols react with sodium metal liberating hydrogen gas, hence it can not be dried with sodium metal. Ether, on the other hand, does not react with sodium metal.

$$\underset{\text{(Alcohol)}}{2ROH} + 2Na \rightarrow 2RONa + H_2\uparrow$$

21. For the complex formation the central metal ion must have a strong charge density to attract the ligands towards itself. The alkaline earth metal cation (M^{2+}) can do so whereas alkali metal ions (M^+) with smaller charge density cannot do so.

22. Magnesium oxide is used as a **refractory material** that is a material which can withstand high temperature without melting or decomposition. It is due to the reason that the lattice energy of MgO is very high and thus it does not decompose at high temperature.

23. During the X-ray of the stomach or the alimentary canal, a suspension of $BaSO_4$ in water known as **barium meal** is administered to the patient because it is insoluble in water, Coats the inner surface or walls of the alimentary canal making them opaque for X-ray. The poisonous Ba^{2+} are not absorbed in blood due to the insoluble nature of $BaSO_4$.

24. Potassium superoxide (KO_2) finds its application in oxygen masks used for emergency breathing purposes particularly in mines etc. It is also used as a source of oxygen in space crafts and submarines also. The moisture of breathing decomposes potassium superoxide to release oxygen.

25. Alkali metal hydroxides absorb carbon dioxide gas but KOH is preferred to NaOH because K_2CO_3 formed on absorption of CO_2 being more soluble in water does not separate.

26. A pellet of sodium hydroxide when exposed to moisture developes a liquid layer around it because of its hygroscopic nature. This liquid layer gradually turns into a white powdery mass as aqueous sol. Sodium hydroxide absorbs moisture and forms sodium Carbonate.

27. Common oxosalts of alkaline earth metals are carbonates and sulphates. Thermal stability of carbonates, sulphates increases down the group because carbonates and sulphates are big anions which are more stabilized by bigger cations.

Solubility of the oxosalts also decreases down the group because hydration energy of the cations decrease down the group with increasing cationic size.

28. Both Na and K can react with water. But Na also reacts with alcohol whereas calcium does not or react slowly.

$$2C_2H_5OH + 2Na \rightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2\uparrow$$

Therefore, calcium is preferred over sodium to remove the last traces of moisture from alcohol.

Long Answer Questions

1. (i) Hydrogen gas is liberated.

$$Mg(s) + 2H_2O(\ell) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

(ii) Magnesium nitride is formed.

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

(iii) Magnesium oxide is formed.

$$2Mg(s) + CO_2(g) \longrightarrow 2MgO(s) + C(s)$$

(iv) Dihydrogen gas is liberated.

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$$

(v) A mixture of magnesium oxide and magnesium nitride is formed.

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$

2. (i) Na_2CO_3 and $CaCO_3$

No action of heat on Na_2CO_3 while $CaCO_3$ decomposes on heating.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

(ii) $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$.

$$MgCl_2 \cdot 6H_2O \xrightarrow{\text{Heat}} MgO + 2HCl + 5H_2O$$

$$CaCl_2 \cdot 6H_2O \xrightarrow{473K} CaCl_2 \cdot 2H_2O + 4H_2O$$

(iii) $Ca(NO_3)_2$ and $NaNO_3$

$$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

3. (i) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2(g)$

(ii) $Ca(OH)_2 + Cl_2 \rightarrow \underset{\text{Bleaching Powder}}{CaOCl_2} + H_2O$

(iii) $BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$

(iv) $2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$

(v) $Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2\,NH_3$

4. (i) Due to their large size, their ionization enthalpies are very small and hence can loose electrons very easily. Thus alkali metals are strong reducing agents.

(ii) Alkali metals are strong reducing agents and are also highly electropositive in nature, thus they cannot be displaced from aqueous solutions of their salts by other metals. Also they are more reducing than hydrogen thus they cannot be obtained from the electrolysis of their aqueous salts solution. Thus they are obtained only by electrolysis of their fused salts.

(iii) As alkali metals are more reducing than hydrogen thus they cannot be obtained from the electrolysis of their aqueous salts solution. Thus during electrolysis of aqueous solution of alkali metals hydrogen is liberated at cathode as it has high reduction potential than alkali metals.

(iv) These solutions contain ammoniated cations and ammoniated electrons as per the following reaction:

$$M + (x + y)\,NH_3 \rightarrow M^+(NH_3)_x + e^-(NH_3)_y$$

When ordinary light falls on these ammoniated electrons, they get excited to higher levels by absorbing energy corresponding to red region. As a result, transmitted light is blue which imparts blue colour to the solution.

(v) The blue colour disappears after sometimes as the reaction goes for completion to form metal amides with liberation of hydrogen.

5. (i) Because of covalent character in the compounds of lithium they are less soluble in water.

(ii) Due to small size of lithium it readily gets hydrated and this high hydration enthalpy compensates high Ionization enthalpy which makes lithium the most reducing element.

(iii) The anomalous behaviour of lithium is due to following reasons:

(a) very small size of lithium and its ion.

(b) High polarizing power of Li^+ resulting in increased covalent character of its compounds which is responsible for their solubility in organic solvent.

(c) Comparatively high ionization enthalpy and low electropositive character as compared to other members.

(iv) Lithium being the first element in it's group, has very small size due to which it has high polarizing power resulting in the generation of covalent character in its compounds. Thus its salt easily decompose on heating.

(v) The alkali metals have very low ionisation enthalpies. The energy from the flame of bunsen burner is sufficient to excite the electrons of alkali metals to higher energy levels. The excited state is quite unstable and therefore when these excited electrons come back to their original energy levels, they emit extra energy, which fall in the visible region of the electromagnetic spectrum and thus appear coloured.

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. The cloudiness is a precipitate of the partially soluble calcium hydroxide, $Ca(OH)_2$.

2. $BeCO_3$ is least stable alkaline earth metal carbonate. It is stored in carbon dioxide atmosphere so as to *slow down its decomposition.*

3. Caesium has the lowest while lithium has the highest ionisation enthalpy. Hence caesium can lose electron very easily while lithium can not.

4. Halides of Be are covalent because of high IE (ionisation enthalpy) of Be while those of Ba are ionic due to low IE of Ba.

5. Super oxide contains a three electron bond which makes it paramagnetic and coloured.

$$[:\ddot{O}\cdots\ddot{O}:]$$

6. Be (Z = 4) which has electronic configuration $1s^2\,2s^2$ shows electronic configuration of $1s^2\,2s^1\,2p_x^{\,1}$ in excited state and one *s*-orbital (2*s*) and one *p*-orbital (2*p*) can intermix to form two *sp* hybrid orbitals which can be used to form $BeCl_2$.

Short Answer Questions

1. (i) This is because I.E. of Mg < I.E. of Be. So bond M – OH can break more easily in $Mg(OH)_2$ than in $Be(OH)_2$.

(ii) This is because with the increase in size (from Be to Ba), the lattice enthalpy decreases significantly but hydration enthalpy remains almost constant.

2. The size of Be^{2+} is very small and so it has a high charge density and can thus easily polarise the O^{2-} and F^- ions in BeO and BeF_2. The oppositely charged ions mutually neutralize their charge to a large extent and therefore BeO and BeF_2 are covalent in nature.

3. Due to small size of bivalent ions of alkaline earth metals, the lattice enthalpy of alkaline earth metal compound is very high as compared to those of the metals of first group.

4. Lithium as well as the oxide ion, O^{2-} have small ionic radii and high charge densities. Hence these small ions pack together forming a very stable lattice of Li_2O. Similarly, formation of sodium peroxide, Na_2O_2 and superoxides of the larger alkali metals (e.g. potassium superoxide, KO_2) can be explained on the basis of the stable lattice formed by the packing of bigger cations and bigger anions.

In short, the increasing stability of peroxides and superoxides of alkali metals from Li to Cs is due to the stabilisation of larger anions by larger cations through lattice energy.

5. $BeCl_2$ being a salt of a weak base, $Be(OH)_2$ and a strong acid, HCl undergoes hydrolysis by water to form HCl which fumes in air. $BaCl_2$, on the other hand, being a salt of a strong base, $Ba(OH)_2$ and strong acid, HCl does not undergo hydrolysis by water to form HCl and hence does not fume in air.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

$$BaCl_2 + H_2O \not\longrightarrow Ba(OH)_2 + 2HCl$$

6. Unlike $NaHCO_3$, the intermediate $KHCO_3$ formed during reaction, is highly soluble in water and thus can not be taken out from solution to give K_2CO_3 later on.

7. Refer theory

8. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattie enthalpy factor and therefore their sulphates are soluble in water.

Long Answer Questions

1. Refer theory

2. Compound : A : CaO ; B : $Ca(OH)_2$; C : $CaCO_3$; D : $Ca(HCO_3)_2$
$Ca(HCO_3)_2$ is soluble in water. Hence, milkiness of solution disappears on passing excess carbon dioxide into the solution of compound B.

3. $8\,LiH + Al_2Cl_6 \rightarrow 2Li\,AlH_4 + 6LiCl$
$LiAl\,H_4 + 2BeCl_2 \rightarrow 2BeH_2 + LiCl + AlCl_3$

CHAPTER TEST

1. Francium

2. Be ; BeO dissolves in alkali to form beryllates.

3. As the size of the anion increases, covalent character increases and hence the order is MF < MCl < MBr < MI.

4. (i) $BeSO_4$ is soluble in water while $BaSO_4$ is not.

(ii) $Be(OH)_2$ dissolves in alkali but $Ba(OH)_2$ does not.

5. (i) Sodium reacts violently with water producing hydrogen gas which also catches fire. As a result the fire spreads.

(ii) Pure NaCl is not hygroscopic but table salt is impure NaCl containing $MgCl_2$, $CaCl_2$ etc which are all hygroscopic, as a result table salt get wet.

6. (i) Because of large size of K^+, Rb^+ and Cs^+ ions, the positive field is very weak and allows even peroxide ion, O_2^{2-} to combine with another oxygen atom to form superoxide ion, O_2^-.

$$\underset{\text{Oxide}}{O^{2-}} \xrightarrow{1/2\,O_2} \underset{\text{Peroxide}}{O_2^{2-}} \xrightarrow{O_2} \underset{\text{Superoxide}}{2O_2^-}$$

(ii) A cation is highly polarizing if its charge /size ratio is very high.
Li^+ ion has the highest polarizing power among the group–1 ions.

(iii) The size of CO_3^{-2} and SO_4^{-2} ions are much bigger than those of cations. Therefore, the lattice energies of carbonates and sulphates remain almost constant as we move down the group. Since the hydration enthalpies decrease as the size of the cations increases on moving down the group, the solubility of carbonates and sulphates of alkaline earth metals decreases on moving down the group.

7. Refer theory

11

Chapter

The p-Block Elements

INTRODUCTION

In atoms of these elements the last electron enters the outermost p-orbital. As the number of p-orbitals is three, therefore the maximum number of electrons which can be accomodated by p-orbital is six. Thus there are six groups of p-block elements, i.e., 13, 14, 15, 16, 17 and 18 each containing six elements.

The inner core of the electronic configuration may differ. This influences the physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. As a result, a lot of variation in properties of elements in a group of p-block observed.

Highest oxidation state shown by any p-block element is equal to the total number of valence electrons. In p-block elements oxidation state two units less than the group oxidation state becomes more pronounced as we move down the group due to inert pair effect (inability of valence s-electron to participate in bond formation).

GROUP 13 ELEMENTS: THE BORON FAMILY

Group 13 (or IIlA) of the long form of periodic table consists of five elements – boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Outer shell electronic configuration of group 13 elements is $ns^2\ np^1$

Physical Properties

Occurrence

Boron does not occur in the free state in the nature. It mainly occurs as borates, orthoboric acid (H_3BO_3) and borax ($Na_2B_4O_7.\ 10H_2O$). Aluminium does not occur in the free state in nature. After oxygen (45.5%) and silicon (27.7%), it is the third most abundant element (8.3% by mass) in the earth crust. Important minerals of aluminium are bauxite, $Al_2O_3.2H_2O$, cryolite, Na_3AlF_6. Gallium, indium and thallium are less abundant elements in nature.

(i) **Electronic configuration :** The elements of group 13 belong to p-block of the periodic table and these elements contain three electrons in the valence shell, therefore, their valence shell electronic configuration is ns^2np^1.

Elements	At. No.	Electronic Configuration	Valence shell Configuration
B	5	$[He]2s^2 2p^1$	$2s^2 2p^1$
Al	13	$[Ne]3s^2 3p^1$	$3s^2 3p^1$
Ga	31	$[Ar]3d^{10} 4s^2 4p^1$	$4s^2 4p^1$
In	49	$[Kr]4d^{10} 5s^2 5p^1$	$5s^2 5p^1$
Tl	81	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$	$6s^2 6p^1$

(ii) **Metallic character:-** Metallic character or electropositive nature increases from B to Tl. Boron is a semi-metal. Aluminium and other elements are metallic in nature.

(iii) **Atomic & ionic radius:-** The atomic radius, ionic radius and density increases from B to Tl. The atomic radius increases from boron to thallium. The abrupt increase in the atomic radius of Al is due to greater screening effect in Al (it has 8 electrons in the penultimate shell) than in B (it has 2 electrons in the penultimate shell). Further, there is not much increase at gallium and thallium due to the intervening *d* and *f* electrons which do not screen the nuclear charge effectively. The ionic radii (M^{3+}) increase from boron to thallium.

(iv) **Melting & boiling point:-** Melting points of group 13 elements do not show a regular trend. The melting point decreases from B to Ga and then increases. The boiling point decreases from B to Tl. Boron has a very high m.p because of its three dimensional (B_{12} - icosahedral) structure in which B atoms are held together by strong covalent bonds. Lower m.p of Ga is due to the fact that it consists of only Ga_2 molecules and Ga remains liquid upto 2273 K

(v) **Ionisation energy:-** The ionization energy decreases down the group due to increase in size. But ionization energy of Ga is higher than Al due to smaller atomic size of Ga resulting from less effective shielding of 3*d* electrons in Ga. Thus valence shell electrons experiences more effective nuclear charge in Ga than Al.

As a result first ionisation enthalpy of Ga is slightly higher than that of Al. Ionisation enthalpy value of Ga is higher than Al and that of Tl is higher then that of In. These are due to inability of *d*- and *f*- electrons; which have low screening effect, to compensate the increase in nuclear charge there by making first ionisation enthalpy of In lower than that of Ga.

IE of group 13 elements is less than the corresponding *s*–block element (alkaline earth metals). This is due to the fact that removal of electron from *p*–orbital is relatively easier than from *s*–orbital.

(vi) **Density :** Density increases from B to Tl due to increase in size of the atom. Aluminium has an extremely low density and hence used as an important structural material.

(vii) **Electronegativity:** Down the group, electronegativity first decreases from B to Al and then increases marginally. This is due to difference in atomic size of the elements.

Chemical Properties

(i) **Oxidation states and types of bonds: -**

All the elements of group 13 have three outer electrons. Apart from Tl they normally use these to form three bonds, giving an oxidation state of (+III). Bonds are covalent because of small size of the ions and their high charge of 3+, large value of the sum of the three IEs and higher electronegativity values. B always forms covalent compounds because of high IE which is again because of smaller size of boron.

Many simple compounds of the remaining elements, such as $AlCl_3$ and $GaCl_3$, are covalent when anhydrous. However, Al, Ga, In and Tl all form metal ions in solution. This change from covalent to ionic happens because the ions are hyrated, and the amount of hyydration energy evolved exceeds the ionisation energy.

In group 13, there is an increasing tendency to form covalent compounds. Compounds of Ga (I), In (I) and Tl (I) are known. Stability of lower oxidatiion state increases down the group. Tl (I) compounds are more stable than Tl (III) compounds. Monovalency is explained by the *s* electrons in the outer shell (which has s^2p^1 configuration) remaining paired, and not participating in bonding. This is called 'inert pair effect'. If the energy required to unpair them exceeds the energy evolved when they form bonds, the *s* electrons will remain paired.

(ii) **Action of air:-** All the metals of group 13 react with O_2 at high temperature to form trioxides of the formula, M_2O_3

$$4M + 3O_2 \longrightarrow 2M_2O_3$$

Boron is unreactive in the crystalline form. Aluminium does not react with dry air. However in moist air, its surface gets tarnished due to formation of a very thin oxide layer on the surface which protect the metal from further attack.

(iii) **Action of acids:-**

$$2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2,$$

Boron is not affected by non–oxidizing acids like HCl and dilute H_2SO_4 while other elements dissolve to form trivalent salts. Boron dissolves in HNO_3 forming H_3BO_3. Conc. HNO_3 reacts with all the group 13 elements, but HNO_3 makes Al passive due to the formation of protective film of oxide

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$
$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$
$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Thallium dissolves in acids forming univalent thallium ion; however hydrochloric acid makes it passive due to the formation of water insoluble thallium chloride.

(iv) **Action of alkalies:-**

Boron dissolves only in fused alkalies, aluminium and gallium dissolve in fused as well as in aqueous alkalies liberating hydrogen.

$2M + 2NaOH + 6H_2O \longrightarrow 2\,Na^+[M(OH)_4]^- + 3H_2$, Only B, Al and Ga react with alkali. In and Tl, however, do not react with alkalies.

Note : Al reacts with both acids and alkalies. Thus, Al shows amphoteric behaviour.

$2Al(s) + 6HCl\,(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$

Sodiumtetrahydroxoaluminate (III)

(v) **Action of halogen:-** $2M + 3X_2 \longrightarrow 2MX_3$, All the group 13 elements form trihalide except Tl. Tl form TlX.

Anomalous Behaviour of Boron

Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of *d*-electrons. The main point of differences between B and other elements of the group are:

(i) Boron is a typical non–metal whereas other members are metals. It is comparitively harder than other elements of the group.
(ii) Boron is a bad conductor of electricity whereas others are good conductors.
(iii) Boron alone exhibits allotropy.
(iv) Boron forms only covalent compounds whereas aluminium and other elements of group 13 also form some ionic compounds.

(v) Hydroxides and oxides of boron are acidic in nature whereas those of others are amphoteric and basic. The oxide and hydroxides of Al and Ga are amphoteric while those of In and Tl are basic.

(vi) The trihalides of boron (BX_3) exist as monomer. Becuse of small size of boron it cannot accomodate four large sized halogen atoms around it. On the other hand, aluminium halides exist as dimers (Al_2X_3).

(vii) Borates are more stable than aluminates.

(viii) Boron exhibits maximum covalency of four. e. g. BH_4^- ion while other members exhibit a maximum covalency of six. e. g. $[Al(OH)_6]^{3-}$

(ix) Boron does not decompose steam while other members do so.

(x) Concentrated nitric acid oxidizes boron to boric acid but no such action is noticed by other group members.

$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$

SOME IMPORTANT COMPOUNDS OF BORON

Boric Acid (H_3BO_3) or Orthoboric Acid

Preparation:

(i) From borax :-($Na_2B_4O_7$. $10H_2O$): – Boric acid can be prepared by adding a hot concentrated solution of borax to a calculated quantity of conc. H_2SO_4. The solution on cooling gives crystals of boric acid, which can be separated by filtration.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + \underset{\text{(Boric acid)}}{4H_3BO_3}$$

or

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$$

(ii) From boron compounds: H_3BO_3 can also be prepared by the hydrolysis of boron compounds such as halides, hydrides and nitrides.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$
$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

(iii) From colemanite: $Ca_2B_6O_{11}.5H_2O$. Boric acid is mainly prepared from the mineral *colemanite* (calcium borate). The mineral is powdered and mixed with boiling water. Sulphur dioxide is passed through the solution when boric acid and calcium sulphite are formed.

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O \longrightarrow 2CaSO_3 + 6H_3BO_3$$

The hot solution is cooled to give crystals of boric acid.

Properties:

(i) It is white crystalline solid with a soft soapy touch having density of 1.48 g cm^{-3}.

(ii) It is sparingly soluble in cold water but fairly soluble in hot water.

(iii) **Action of heat:**

$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow{373K} \underset{\text{metaboric acid}}{HBO_2} \xrightarrow{433K} \underset{\text{tetraboric acid}}{H_2B_4O_7} \xrightarrow[-H_2O]{\text{red hot}} \underset{\text{boron trioxide}}{B_2O_3}$$

(iv) Boric acid behaves as a weak monobasic acid.

(v) **Reaction with ethanol** : When burnt in presence of ethyl alcohol, it forms ethyl borate having green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$$

Structure:

Due to sp^2-hybridisation of boron, boric acid is a planar molecule and due to hydrogen bonding between different molecules, boric acid has layer structure as shown below

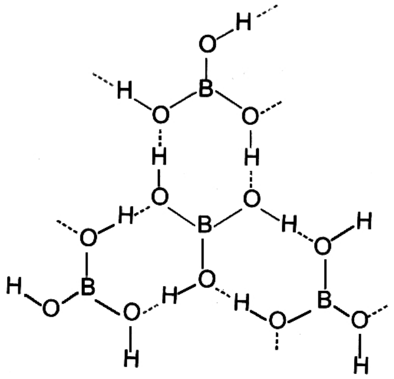


Fig. Structure of boric acid; the dotted lines represent hydrogen bonds

Uses:

(a) It is used as an antiseptic, as eye-wash (eye-lotion) and a food preservative.

(b) It is used in the preparation of glass, glazes and enamels.

(c) It is also used in leather industry.

BORAX ($NA_2B_4O_7$. $10H_2O$)

It is most important compound of boron. As the name represents, it is the sodium salt of tetraboric acid. The common Indian name of borax is Suhaga. It occurs naturally as *tincal* in certain dried up lakes of India, Tibet and California (U.S.A.). Tincal contains 55% of borax.

Preparation:

(i) **From colemanite**: It is obtained from colemanite by boiling it with Na_2CO_3 solution. The insoluble $CaCO_3$ is filtered off.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

CO_2 gas is passed through the mother liquor containing sodium metaborate to recover borax.

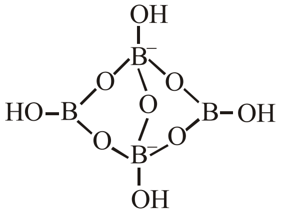
$$4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

(ii) From boric acid : Boric acid when boiled with soda-ash gives borax.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Structural Unit of Borax

It contain tetra nuclear units $[B_4O_5(OH)_4]^{2-}$ and hence the correct formula is $Na_2[B_4O_5(OH)_4]$. $8H_2O$. structure of tetranuclear unit $[B_4O_5(OH)_4]^-$



Properties:

(i) It is a white crystalline solid, less soluble in cold water but more soluble in hot water.

(ii) Its solution is basic in nature due to hydrolysis which results into formation of sodium hydroxide (*a strong base*) and boric acid (*a weak acid*).

$$\underset{\text{strong base}}{Na_2B_4O_7} + \underset{\text{weak acid}}{7H_2O} \rightleftharpoons 2NaOH + 4H_3BO_3$$

(iii) **Action of heat:** On heating, borax loses water and swells into a white mass which on further heating melts to forms a transparent glassy solid called **borax glass** and **borax bead**.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{} \underset{\text{anhydrous}}{Na_2B_4O_7} \xrightarrow{740°C} \uparrow 2NaBO_2 + \underset{\text{transparent bead}}{B_2O_3} \uparrow$$

Borax bead test:- Borax bead forms coloured glassy bead with coloured compounds of certain metals. It forms the basis of borax bead test. This test is used for qualitative analysis of various cations.

$$B_2O_3 + MnO \longrightarrow \underset{\text{Manganese metaborate (pink)}}{Mn(BO_2)_2}$$

$$B_2O_3 + NiO \longrightarrow \underset{\text{Nickel metaborate (brown)}}{Ni(BO_2)_2}$$

$$B_2O_3 + CuO \longrightarrow \underset{\text{Copper metaborate (blue)}}{Cu(BO_2)_2}$$

$$B_2O_3 + CoO \longrightarrow \underset{\text{Cobalt metaborate (blue)}}{Co(BO_2)_2}$$

(iv) On heating with ethyl alcohol and conc. H_2SO_4, it gives volatile vapours of triethylborate which burn with a green edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Triethylborate}}{B(OC_3H_5)_3} + 3H_2O$$

Uses :

(a) Borax is used in the manufacture of enamels, glazes, pyrex glass which in turn is used in the production of crystal glass, optical glass, soap and drying oils.

(b) It is also used as a cleansing and stiffening agent in laundry work and in candle industry.

(c) It is used for glazing paper, playing cards and also as an antiseptic.
(d) It is also used in water softening as it precipitates calcium ions yielding insoluble calcium borate.
(e) It is widely used as a flux since it dissolves many metal oxides to form borates of low melting points.
(f) It is frequently used for the borax bead test in qualitative analysis of several cations.
(g) It is also used in medicine.

DIBORANE (B_2H_6)

Boranes are the hydrides of boron (analogy with alkanes). It is important to note that boron does not form simple monomeric hydride, *i.e.* BH_3 although the analogous boron trihalides, BX_3 are well known and quite stable compounds. This is due to the fact that hydrogen atoms in BH_3 have no free electrons to form $p\pi$–$p\pi$ back-bonding and thus boron has incomplete octet. Actually, when BH_3 molecules come in contact with each other, they dimerise to form diborane, B_2H_6. Thus BH_3 can exist only as complex compounds like BH_3Z with donors (Z) like CO, $(CH_3)_3N$ and PF_3.

Preparation :

Boranes have great affinity for water and oxygen, hence they do not occur in nature (different from hydrocarbons which are found in nature). Moreover, boranes cannot be prepared directly from its elements as they have positive enthalpies and positive free energies of formation. Hence boranes are always prepared indirectly.

(i) Quantitatively, diborane is obtained by the reaction of sodium borohydride with boron trifluoride or by the reaction of lithium aluminium hydride with boron trichloride.

$$3NABH_4 + 4BF_3 \longrightarrow 3NABF_4 + 2B_2H_6$$
$$3LIALH_4 + 4BCl_3 \longrightarrow 3AlCl_3 + 3LiCl + 2B_2H_6$$

(ii) Laboratory method involves the oxidation of $NaBH_4$ with I_2

$$2NaBH_4 + I_2 \xrightarrow{\text{Polyether}} B_2H_6 + 2NaI + H_2$$

(iii) Industrally it is prepared by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Properties:

(i) Diborane is a colourless, highly toxic gas with a b.p. of 180K.

(ii) **Action of air:** It catches fire spontaneously upon exposure to air.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O;\ \Delta H_c = -1976\,kJ/mol^{-1}.$$

As it has high heat of combustion per unit mass, therefore used as a high energy fuel.

(iii) **Hydrolysis:** $B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 6H_2$

(iv) **With lithium hydride:** $2LiH + B_2H_6 \longrightarrow \underset{\text{Lithium Borohydride}}{2Li(BH_4)}$

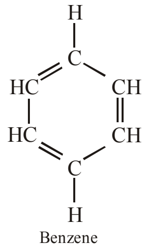
(v) **With Lewis bases:** Diborane undergoes clevage reactions with Lewis bases to give borane adducts, $BH_3.L$

$$B_2H_6 + 2NMe_3 \rightarrow 2BH_3 . NMe_3$$
$$B_2H_6 + 2CO \rightarrow 2BH_3 . CO$$

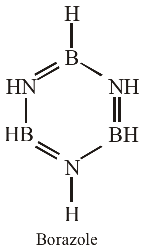
(vi) **Reaction with ammonia :**

$$2NH_3 + B_2H_6 \longrightarrow [BH_2(NH_3)_2]^+ BH_4^-$$
$$\underset{\text{Diammoniate of diborane}}{3[BH_2(NH_3)_2]^+ BH_4^-} \xrightarrow{450K} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

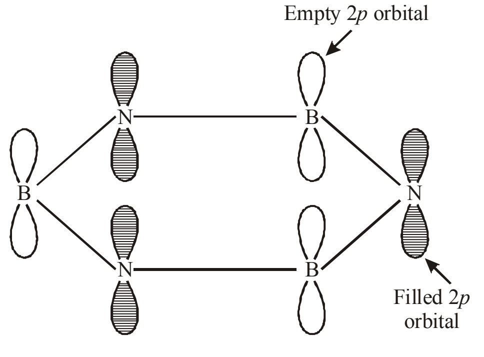
(It has similar structure with benzene thus also known as inorganic benzene).



Benzene



Borazole



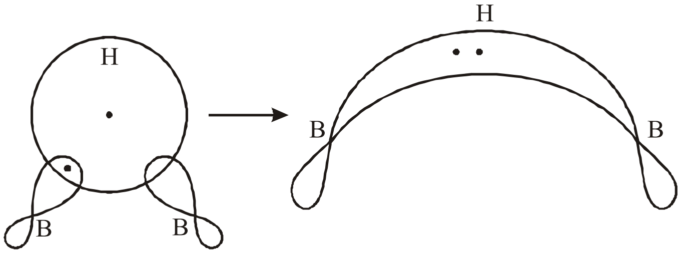
Borazole has been called as **inorganic benzene** because it is very close to benzene in structure and properties.

Borazole is isoelectronic with benzene. It is a planar molecule in which B and H atoms are sp^2 hybridized. The difference is that in borazole the π-bonding is dative and it arises from overlap of empty *p-orbitals of boron with filled p*-orbitals of nitrogen.

Borazole resembles benzene in some of its properties but there are many differences due to polarity of the N – B bond. Moreover, the six electrons in the π-orbitals are derived from three nitrogen atoms and not from each of the six atoms of the ring as in case of benzene.

Structure of Diborane

The complete structure of diborane can be explained on the basis of molecular orbital concept. According to molecular orbital theory, each of the two boron atoms is in sp^3 hybrid state. Of the four sp^3 hybrid orbitals, three have one electron each while the fourth is empty. Two of the four sp^3 orbitals of each of the boron atom overlap with 1 *s* orbitals of two terminal hydrogen atoms forming two normal B – H σ bonds. One of the remaining sp^3 hybrid orbital ((either filled or empty) of one of the boron atoms, the 1*s* orbital of the bridge hydrogen atom and one of the sp^3 hybrid orbitals (empty or filled respectively) of the second boron atom overlap to form a delocalised orbital covering the three nuclei. Thus a pair of electrons (one electron from B and other from H) acts as a bond between three atoms (centres) ; such bond is known as *three-centre two electron bonds* (3 *c* – 2 *e* bonds).



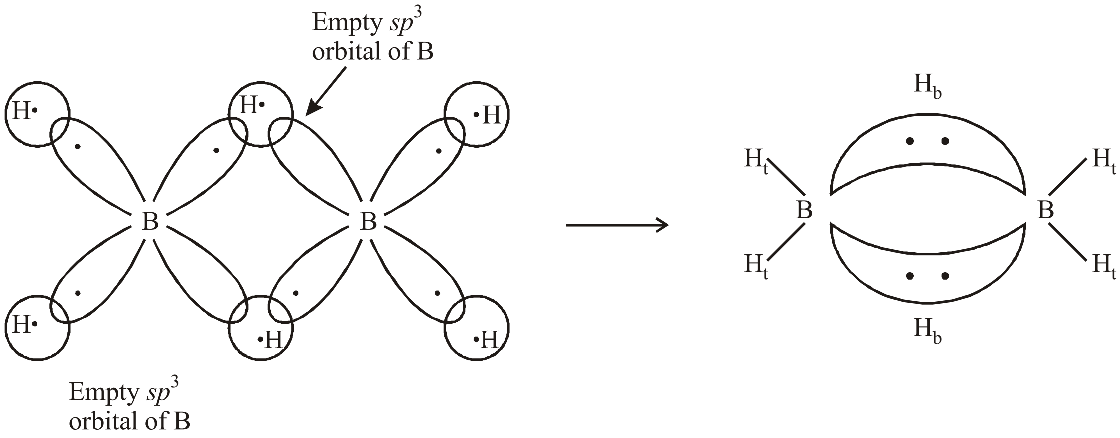
(a) (b)

Formation of three-centre-two electron bond, B – H – B

(a) overlapping of half-filled sp^3 hybrid orbital of one B atom, half-filled 1*s* orbital of H and empty sp^3 orbital of the second B atom

(b) Three centre-two electron molecular orbital covering all the three atoms; B, H and B.

Similar overlapping between a filled sp^3 orbital of another boron atom results in a delocalised orbital covering the three nuclei. Thus the formation of diborane molecule B_2H_6 can be depicted as in the following figure



Structure of diborane showing two three centre - two electron bonds.
H_t represents terminal H atom
H_b represents bridged H atom

Due to repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are bent away from each other in the middle giving the shape of banana ; and thus the three-centre-two electron bonds are also known as banana bonds.

Thus the diborane molecule has four two-centre-two electron bonds (2 *c* – 2 *e* bonds *i.e.* usual bonds) and two three-centre-two electron bonds (3*c* – 2*e*, B – H_b – B), the latter type of bonds is a common feature to higher boranes and all the electron-deficient compounds.

Uses of boranes

Among boranes, diborane is the only frequently used borane although other boranes may also find certain uses. The important uses of diborane are given here.

(a) It is used as a catalyst in polymerisation reactions.
(b) It is used as a reducing agent in organic reactions.
(c) It is used for welding torches.

(d) Diborane is also for preparing substances such as high energy fuels and propellents.
(e) Hydroboration is a useful method for preparing hydrocarbons, alcohols, ketones and acids.

Uses of B and Al

(i) Uses of boron

(a) As a semiconductor
(b) Boron steel or boron carbide rods are used to control the nuclear reactions.

$$_5B^{10} + _0n^1 \rightarrow _5B^{11}$$

(ii) Uses of Aluminium and Aluminium Compounds

Aluminium is a bright silvery white metal with high tensile strength.

(a) A mixture of aluminium powder and aluminium nitrate is known as ***Ammonal*** and is used in bombs.
(b) A mixture of Al powder in linseed oil is used as silver paint.
(c) The reduction of metal oxides by aluminium is called aluminothermy or thermite process or ***Goldschmidt aluminothermite process***.

GROUP 14 ELEMENT : THE CARBON FAMILY

Group 14 (or IV A) of long form of periodic table consists of five elements, carbon (C), silicon (Si),germanium (Ge), tin (Sn) and lead (Pb).Outer shell electronic configuration of the group is $ns^2\,np^2$

Carbon is the seventeenth most abundant element by weight in the earth's crust. Carbon is the important constituent of all organic matter while silicon is the main constituent of inorganic matter. Carbon is the only element of this group which occurs in free state, as in diamond, graphite and coal. In combined form it occurs in carbon dioxide, carbonates and hydrocarbons. Silicon, *the second commonest element of the earth's crust*, occurs as silica and silicates. Germanium is rare element. Tin and lead occur mainly as SnO_2 and galena (PbS) respectively.

Physical Properties

(i) Electronic Configuration: The valence shell electronic configuration of these elements is ns^2np^2.

Elements	At. No.	Electronic Configuration	Valence shell Configuration
Carbon	6	$[He]2s^2 2p^2$	$2s^2 2p^2$
Silicon	14	$[Ne]3s^2 3p^2$	$3s^2 3p^2$
Germanium	32	$[Ar]3d^{10} 4s^2 4p^2$	$4s^2 4p^2$
Tin	50	$[Kr]4d^{10} 5s^2 5p^2$	$5s^2 5p^2$
Lead	82	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

(ii) Metallic or electro-positive character- Carbon is a non–metal, carbon is a typical non-metal forming covalent bonds in the vast majority of its compounds using all its four valence electrons. Silicon is also a non-metal but in some physical properties it behaves as a semimetal, germanium is a metalloid, tin and lead are metals. The change from non–metallic to metallic character is due to less effective nuclear charge and increase in the number of available orbitals with increase in the size of the atom. Thus metallic or electropositive character increases down the group.
Note : They are less electropositive or metallic than the group 13 elements.

(iii) Atomic radii: The atomic radii increases from C to Pb. Increase in atomic radii is significant from C to Si, whereas from Si to Pb this increase is comparatively smaller. This is due to poor shielding effect of electrons present in *d*- and *f*-orbitals.

(iv) Ionisation energy- Ionisation enthalpy decreases on moving down the group from C to Sn. This decrease is sharp from C to Si while ionisation energy of Pb is greater in comparison to Sn.
Small decreases in ionisation energy from Si to Ge and Ge to Sn and slight increase in I.E. from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

(v) Melting and boiling point-On moving down the group, the melting and boiling point decreases due to decrease in interatomic forces of attraction. However, the melting point of Sn is lower than lead.
The melting and boiling points of carbon and silicon are very high. This is due to tendency of these elements to form giant molecules.

(vi) Electronegativity- Carbon is the most electronegative element of this group. The electronegativity decreases from C to Pb but not in a regular manner possibly due to filling of d- and f-orbitals.

Chemical Properties

(i) Oxidation states and trends in chemical reactivity

Elements of group 14 *exhibit oxidation states of* + 4 and + 2, in the + 4 oxidation state compounds are covalent while in the + 2 oxidation state compounds are ionic. The + 4 oxidation state is although shown by all elements, it is more important in C and

Si and becomes increasingly less important in Ge, Sn and Pb in which + 2 oxidation state (or ionic compounds formation) becomes increasingly important. This is also in accordance with the Fajan's rule which state that "*smaller the cation the greater is the amount of covalent character in its compounds*." Thus M^{4+} ion is smaller than M^{2+} ion, the compounds of M^{4+} ions are covalent in nature while those of M^{2+} ions are ionic. Thus the tendency for ionic compound formation increases from C to Pb.

(i) Action of air: They form two types of oxides : monoxide (MO) and dioxide (MO_2)

Oxides in higher oxidation state are more acidic than those in lower oxidation state. Down the group the acidic character decreases. CO_2, SiO_2, GeO_2 are acidic while SnO_2 and PbO_2 are amphoteric. CO is neutral, GeO is acidic, SnO and PbO are amphoteric. SiO only exists at high temperarture.

(i) Action of water: C, S, Ge and Pb are unaffected by H_2O. Tin decomposes steam to form dioxide and dihydrogen gas

$$Sn + 2H_2O \longrightarrow SnO_2 + 2H_2 \uparrow$$

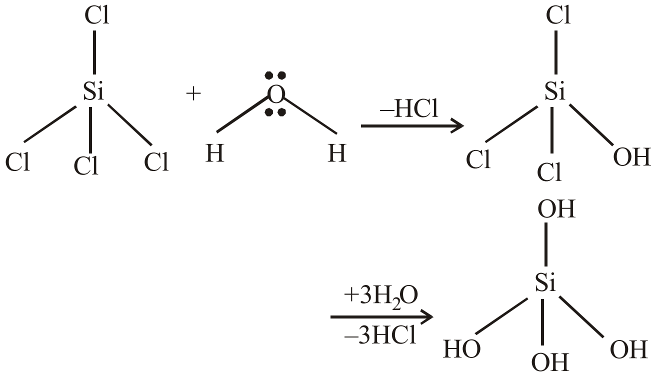
Note : Lead is unaffected by water probably due to oxide film formation on its surface.

(iii) Halides : They form halides of formula MX_2 and MX_4. Except carbon all other elements react directly with halogen under suitable conditions. Generally MX_4 halides are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. SnF_4 and PbF_4 are exceptions and they are ionic in nature. PbI_4 is not formed because Pb-I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Ge and Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group.

MX_4 halides undergo sp^3 hybridisation and the molecule is tetrahedral in shape.

Stability of dihalides increases down the group. Hence, GeX_4 is more stable than GeX_2 but PbX_2 is more stable than PbX_4.

Except CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can accomodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.



Silicic acid

Anomolous Behaviour of Carbon

Carbon behaves differently from rest of the members of the group due to its smaller size, higher electronegtivity, higher I.E. and unavailability of d-orbitals.

(i) due to non-anvailability of d-orbitals, it cannot extend its covalence beyond four.

(ii) carbon has a unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity (O, N, S). Heavier elements do not form $p\pi - p\pi$ bonds due to large size of their orbitals they form $d\pi$-$p\pi$ bonding.

(iii) C-shows the tendency of catenation i.e. carbon atoms link with one another through covalent bonds to form rings and chains. This is because the C–C bonds are very strong. Down the group, size increase, electronegativity decreases and thereby tendency to show catenation decreases.

(iv) The melting and boiling points of carbon are very high as compared to other members of the group.

(v) Carbon remains unaffected by alkalies while other members reacts with alkali as

$$Si + 2NaOH + \frac{1}{2}O_2 \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_2} + H_2$$

ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms: both crystalline and amorphous. Diamond, graphite and fullerenes are the allotropes of carbon.

Diamond

It has a rigid 3D network of C–atoms.

It has directional covalent bonds throughout the lattice.

It is very difficult to break extended covalent bonding and hence diamond is the hardest substance known. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

In diamond all the electrons are used in bond formation, there is no mobile electron in the system and hence the **diamond crystals are non-conductor of electricity.**

Graphite

It has a layered structure and the layers are held by van der Waals forces. The C atoms undergo sp^2 hybridisation, forming 3 σ–bonds. The fourth e^- forms a π- bond and is delocalised over the whole sheet. Electrons are mobile and this makes graphite a good conductor of electricity. It is soft and slippery and is thus used as a dry lubricant in machines running at high temperature.
Graphite is thermodynamically the most stable allotrope of carbon and thus, $\Delta_f H°$ for graphite is taken to be zero.
Graphite is used (i) in making electrodes and carbon arcs,(ii) as a lubricant, (iii) in crucible, (iv) in lead pencils, and (v) as a moderator in nuclear reactors.

Fullerenes

They are made by heating graphite in an electric arc in presence of inert gases such as He or Ar. They are pure form of carbon. Fullerenes are large cage like spheroidal molecules with general formula C_{2n} (where $n \geq 30$). Two important member are C_{60} and C_{70}. C_{60} fullerene looks like a soccer ball (so called bucky ball). C_{60} is called Buckminsterfullerene.

SOME IMPORTANT COMPOUNDS OF C AND Si

Oxides of Carbon

Carbon monoxide (CO)

(i) Preparation :

(a) $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$

(b) $HCOOH \xrightarrow[\text{conc.} H_2SO_4]{373\text{ K}} H_2O + CO$

(c) $C(s) + H_2O(g) \xrightarrow[1273\text{ K}]{473\text{ K}} \underset{\text{Water or synthesis gas}}{CO(g) + H_2(g)}$

(d) $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{K}} \underbrace{2CO(g) + 3N_2(g)}_{\text{Producer gas}}$

(e) $CO_2 + C \longrightarrow 2CO;\ CO_2 + Zn \longrightarrow ZnO + CO$

(f) $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(ii) Properties :

(a) It is colourless, odourless, water insoluble gas.
(b) It is a powerful reducing agent.
(c) It combines with haemoglobin (Hb) in the blood thus forming carboxyhaemoglobin which decreases oxygen carrying capacity of Hb.
(d) As a reducing agent

$Fe_2O_3 + 3CO \xrightarrow{600-900°C} 2Fe + 3CO_2$

$H_2O\ (\text{steam}) + CO \xrightarrow[\text{pressure, catalyst}]{\text{high temp.}} H_2 + CO_2$

(e) It behaves as an unsaturated compound and gives addition product with a number of substances.

$CO + 2H_2 \xrightarrow[ZnO+Cu]{150-400°C} \underset{\text{(methanol)}}{CH_3OH}$

$CO + Cl_2 \xrightarrow[\text{or camphor}]{\text{sunlight}} \underset{\text{Carbonyl chloride (phosgene)}}{COCl_2}$

$Ni + 4CO \underset{180°C}{\overset{50°C}{\rightleftharpoons}} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4}$

(iii) Uses :

(a) Carbon monoxide is used as a fuel in the form of *water gas* ($CO + H_2$) and *producer gas* ($CO + N_2$).
(b) It is used in making carbonyls which in turn are used in the extraction of iron and nickel.

$Ni + 4CO \longrightarrow Ni(CO)_4; Fe + 5CO \longrightarrow Fe(CO)_5$

(c) It is used in the manufacture of methanol, synthetic petrol and phosgene.
(d) It is used as a reducing agent in metallurgy of iron and in the manufacture of hydrogen.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$H_2O\ (\text{steam}) + CO \xrightarrow{\text{catalyst}} H_2 + CO_2$$

Carbon Dioxide (CO_2)

(i) Preparation :

(a) $C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$

(b) **Commercial method :**

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2 \uparrow$$

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + CO_2 + H_2O$$

(c) $CH_4(s) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$

(d) **Laboratory method :**

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + 2H_2O(l)$$

(ii) Properties :

(a) It is one of the gases responsible for greenhouse effect.
It is not poisonous as CO.

(b) It is obtained as a solid in form of dry ice by allowing liquefied CO_2 to expand rapidly.

(c) It exists as a resonance hybrid of two structures :

$$:\underset{..}{\ddot{O}} - C \equiv \overset{+}{O}: \leftrightarrow :\ddot{O} = C = \ddot{O}: \leftrightarrow :\overset{+}{O} \equiv C - \underset{..}{\ddot{O}}:^{-}$$

(d) It turns lime water milky

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

(e) **Action of NH_3 :**

$$2NH_3 + CO_2 \xrightarrow[200\text{atm}]{453-473K} [NH_2COONH_4] \\ \downarrow \\ \underset{\text{urea}}{NH_2CONH_2} + H_2O$$

(f) **Photosynthesis :**

$$6CO_2 + 6H_2O \xrightarrow[\text{light}]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$$

(iii) Uses :

(a) Dry ice is used as a refrigerant.

(b) Gaseous CO_2 is used in cold drinks, in fire extinguisher and to manufacture urea.

(c) It is used in manufacture of white lead and Na_2CO_3

Silicon Dioxide, SiO_2

(i) It is commonly known as silica.

(ii) It is a covalent, 3D network solid in which each Si atom is covalently bonded in a tetrahedral manner to four O-atoms.

(iii) In normal form, silica is non-reactive due to high Si–O bond enthalpy.

(iv) It is attacked by F_2, HF and NaOH.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

(v) Quartz (crystalline form of silica) is used as a piezoelectric material and has helped to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.

(vi) Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.

(vii) Kieselghur, an amorphous form of silica, is used in filteration plants.

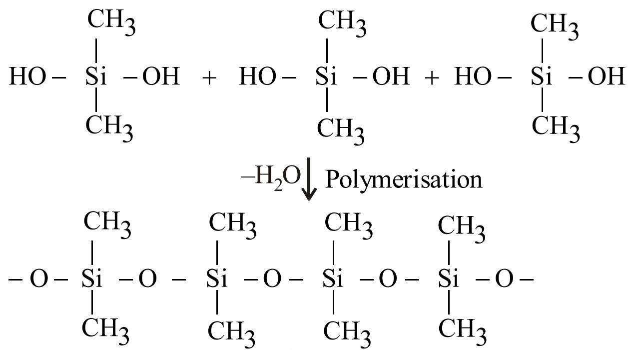
Silicones

They are a group of organosilicon polymers having $\text{-}(R_2SiO)\text{-}$ as a repeating unit. The starting materials for their preparation are alkyl or aryl substituted silicon chlorides $R_nSiCl_{(4-n)}$.

(i) Preparation :

(a) **Preparation of linear silicones :**

$$2CH_3Cl + Si \xrightarrow[570K]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$



$$\mathrm{HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH}$$

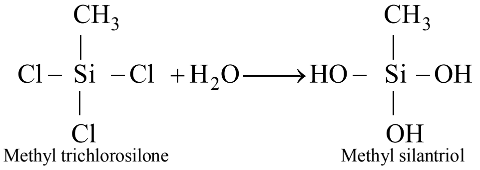
$$\Big\downarrow {}^{-H_2O}\ \text{Polymerisation}$$

$$\mathrm{-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-}$$

Linear silicon

(b) **Preparation of cyclic silicones:** Cyclic (ring) silicones are formed when water is eliminated from the terminal – OH groups of linear silicones.

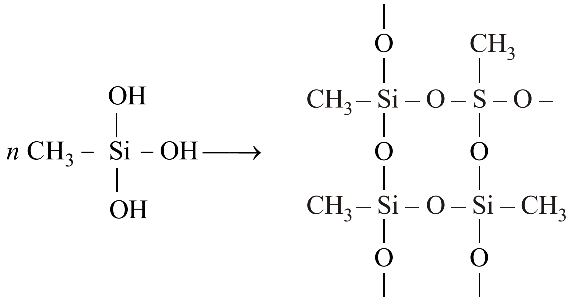
(c) **Preparation of cross linked silicones :** Hydrolysis of alkyl trichlorosilane, CH_3SiCl_3 gives the monomethylsillantriol which then undergoes polymerisation to a very complex *cross linked polymer*.



$$\mathrm{Cl-\underset{Cl}{\overset{CH_3}{Si}}-Cl + H_2O \longrightarrow HO-\underset{OH}{\overset{CH_3}{Si}}-OH}$$

Methyl trichlorosilone

Methyl silantriol



$$n\,\mathrm{CH_3-\underset{OH}{\overset{OH}{Si}}-OH} \longrightarrow \begin{array}{c} | \quad\quad\quad\quad \\ \mathrm{O \quad\quad\; CH_3} \\ |\quad\quad\quad\quad | \\ \mathrm{CH_3-Si-O-S-O-} \\ |\quad\quad\quad\quad | \\ \mathrm{O \quad\quad\quad O} \\ |\quad\quad\quad\quad | \\ \mathrm{CH_3-Si-O-Si-CH_3} \\ |\quad\quad\quad\quad | \\ \mathrm{O \quad\quad\quad O} \\ |\quad\quad\quad\quad | \end{array}$$

Cross-linked silicone

(ii) Properties :

(a) Being surrounded by non-polar alkyl groups, silicones are water repelling in nature.
(b) They have high thermal stability, high dielectric strength and resistance to oxidation.
(c) Silicone is non-toxic.
(d) Silicone products may be fluids, greases, resins or rubbers depending upon the size and type of polymer.

(iii) Uses :

They are used as sealant, greases, electrical insulators and for water proofing of fabrics.
They are also used as non-stick coating for pans, and are used in paints and varnish.

Silicates

(i) Its examples are felspar, zeolites, mica and asbestos.
(ii) Their basic structural unit is SiO_4^{4-}. Each Si atom is bonded to four O-atoms in tetrahedral fashion.
(iii) Silicates can be prepared by fusing an alkali metal carbonate with silica.

$$Na_2CO_3 \xrightarrow{1500°C} CO_2 + Na_2O \xrightarrow{SiO2} Na_2SiO_4, (Na_2SiO_3)_n \text{ and others.}$$

(iv) The various types of silicates are

(a)	Orthosilicates	(b)	Pyrosilicates
(c)	Cyclic or ring silicates	(d)	Chain silicates
(e)	Sheet silicates	(f)	Three dimensional silicates

(v) Two man-made silicates are glass and cement.

Zeolites

(i) They are formed when Al - atoms replace few Si-atoms in 3D network of SiO_2 such that the overall structure acquires a negative charge which is balanced by cations such as Na^+, K^+ or Ca^{2+}.
(ii) They act as molecular sieves by trapping small molecules in their interstices reversibly.
(iii) They are used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation.
(iv) Hydrated zeolites are used as ion exchangers in softening of hard water.

CONCEPT MAP

THE p-BLOCK ELEMENTS

Group 13 Elements

Chemical Properties

(a) Reaction with air : $4M + 3O_2 \rightarrow 2M_2O_3, 2M + N_2 \rightarrow 2MN$

(b) Reaction with acids : $2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$

(c) Reaction with alkalies : $2M + 2NaOH + 6H_2O \rightarrow 2\overset{+}{Na}[M(OH)_4]^- + 3H_2$

(d) Reaction with halogens : $2M + 3X_2 \rightarrow 2MX_3$

Physical Properties

On moving down in a group from B to Tl

(a) metallic or electropositive character increases

(b) atomic and ionic radius increases

(c) b.p. decreases, m.p decreases from B to Ga and then increases

(d) I.E decreases

(e) density increases

(f) electronegativity first decreases from B to Al and then increases marginally.

Anomalous Behaviour of Boron

Characteristics shown by boron and not by other elements of the group are followings:

(a) B is a non-metal and forms covalent compounds

(b) B is a bad-conductor of electricity

(c) Trihalides of B exist as monomer.

(d) hydroxides and oxides of B are acidic in nature

(e) B exhibits maximum covalency of four

Some Important Compounds of Boron

H_3BO_3 Preparation:

(a) Colemanite mineral powder is mixed with water and SO_2 is passed through the solution.

(b) By addition of HCl or H_2SO_4 to conc. solution of borox.

(c) By hydrolysis of boron compounds

$Na_2B_4O_7.10H_2O$ Preparation:

(a) Powdered colemanite is boiled with Na_2CO_3 solution.

(b) Boric acid when boiled with soda-ash gives borax

B_2H_6 Preparation:

(a) Quantitatively by reaction AlH_4 with BCl_3

(b) In laboratory by oxidation of $NaBH_4$ with I_2

(c) On industrial scale by reaction of BF_3 with NaH

Group 14 Elements

Physical Properties

On moving down in a group from C to Pb

(a) metallic or electropositive character increases

(b) atomic and ionic radius increases

(c) m.p and b.p decreases

(d) I.E decreases

(e) electronegativity decreases

Chemical Properties

(a) Reaction with air

$2M + O_2 \rightarrow 2MO$

$M + O_2 \rightarrow MO_2$

(b) Reaction with water

$Sn + H_2O \rightarrow SnO_2 + 2H_2$

(c) Reaction with halogens

Except carbon all other elements react directly with halogens.

Anomalous Behaviour of Carbon

Characteristics shown by carbon and not by other elements of the group are followings:

(a) exhibit covalence upto four only

(b) ability to form pπ-pπ multiple bonds.

(c) maximum tendency for catenation.

(d) Carbon remains unaffected by alkalies

Allotropes of Carbon

Diamond : It has a rigid 3D network

Graphite : It has layered structure in which layers are held by van der waal's forces.

Fullerenes : It is large cage like spheroidal molecule with general formula C_{2n}.

Some important compounds of C and Si:

Oxides of Carbon

CO : $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$

$HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{373\text{ K}} H_2O + CO$

$C(s) + H_2O(g) \xrightarrow{473-1273\text{K}} CO(g) + H_2(g)$

CO_2 : $C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$

$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O$

$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

SiO_2 : It is covalent, three dimensional network solid in which each Si atom is covalently bonded in tetrahedral manner.

Silicones : Group of organic silicon polymers having $-\!\!(R_2SiO)\!\!-$ as a representing unit.

Silicates : Their basic structural unit is SiO_4^{4-}. Each Si atom is bonded to four O-atoms in tetrahedral fashion.

Zeolites: Formed when aluminium atoms replace few silicon atoms in three-dimensional network of silicon.

Textbook Exercises

11.1 Discuss the pattern of variation in the oxidation states of (i) B to Tl (ii) C to Pb.

Ans. (i) B and Al have no *d*–or *f*–electrons. Therefore,they do not exhibit inert pair effect. Consequently, they show an oxidation state of +3 only due to the presence of two electrons in the *s*–and one electron in the *p*–orbital of the valence shell. In contrast, all other elements from Ga to Tl contain only *d*–or *d*–and *f*–electrons and hence show two oxidation states of +1 and +3 due to inert pair effect. Further, as the number of *d*– and *f*–electrons increases down the group, the inert pair effect becomes more and more pronounced. In other words, as we move down the group from Ga to Tl, the stability of+1 oxidation state increases (i.e., Ga < In < Tl) while that of +3 oxidation state decreases (i.e. Ga > In > Tl).

Thus, +1 oxidation state of Tl is more stable than its +3 oxidation state.

(ii) Carbon and silicon have no *d*–or *f*–electrons. Therefore, they do not exhibit inert pair effect. Consequently, they show an oxidation state of + 4 due to the presence of two electrons in the *s*–and two electrons in the *p*–orbital of the valence shell. In contrast, all other elements from Ge to Pb contain only *d*– or *d*– and *f*–electrons and hence show two oxidation states of +2 and +4 due to inert pair effect. Further, as the number of *d*– and *f*–electrons increases, the inert pair effect becomes more and more pronounced. In other words, as we move down the group from Ge to Pb, the stability of +2 oxidation state increases (i.e., Ge < Sn < Pb) while that of +4oxidation state decreases (i.e., Ge > Sn > Pb). Thus, +2 oxidation state of Pb is more stable than its +4 oxidation state.

11.2 How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

Ans. Due to the poor shielding of the *s*–electrons of the valence shell (6*s*) by the 3*d*, 4*d*, 5*d* and 4*f* electrons, inert pair effect is maximum in Tl. As a result, only $6p^1$ electron participates in bond formation and thus the most stable state of Tl is +1 and not +3.Therfore, TlCl is stable but $TlCl_3$ is unstable. In contrast, due to the absence of *d*– and *f*– electrons in B, all the three valence electrons (i.e., two 2*s*– and one 2*p*–) take part in bond formation and hence B shows an oxidation state of +3 and thus forms BCl_3. Thus, BCl_3 is more stable than $TlCl_3$.

11.3 Why does boron triflouride behave as a Lewis acid ?

Ans. The B atom in BF_3 has only 6 electrons in the valence shell and thus needs two more electrons to complete its octet. Therefore, it easily accepts a pair of electrons from nucleophiles such as F^-, $(C_2H_5)_2O$, RCH_2OH etc. and thus behaves as a Lewis acid.

11.4 Consider the compounds, BCl_3 and CCl_4. How will they behave with water? Justify.

Ans. The B atom in BCl_3 has only six electrons in the valence shell and hence is an electron–deficient molecule. It easily accepts a pair of electrons donated by water and hence BCl_3 undergoes hydrolysis to form boric acid (H_3BO_3) and HCl.

$$BCl_3 + 3\,H_2O \longrightarrow H_3BO_3 + 3\,HCl$$

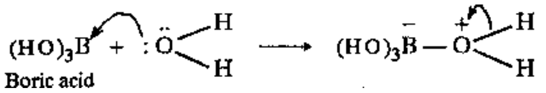
In contrast, C atom in CCl_4 has 8 electrons in the valence shell. Therefore, it is an electron–precise molecule and hence neither accepts nor donates a pair of electrons. In other words, it does not accept a pair of electrons from H_2O molecule and hence CCl_4 does not undergo hydrolysis in water.

11.5 Is boric acid a protic acid ? Explain.

Ans. It is a not a protic acid since it does not ionize in H_2O to give a proton :

$$H_3BO_3 + H_2O \rightleftharpoons H_2BO_3^- + H_3O^+$$

because of the small size of boron atom and presence of only six electrons in its valence shell, $B(OH)_3$ accepts a lone pair of electrons from the oxygen atom of the H_2O molecule to form a hydrated species.



The +ve charge on the O–atom, in turn, pulls the σ electrons of the O–H bond towards itself thereby facilitating the release of a proton. As a result, $B(OH)_3$ acts as a weak monobasic Lewis acid and thus reacts with NaOH solution to form sodium metaborate.

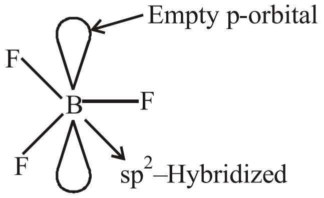
$$B(OH)_3 + NaOH \longrightarrow \underset{\text{Sod. metaborate}}{Na^+[B(OH)_4]^-}$$

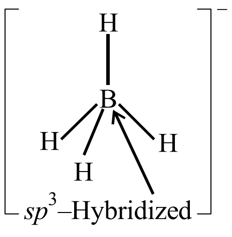
11.6 Explain what happens when boric acid is heated?

Ans. Refer theory

11.7 Describe the shapes of BF_3 and $[BH_4]^-$. Assign the hybridisation of boron in these species.

Ans. In BF_3, boron is sp^2–hybridized and, therefore, BF_3 is a planar molecule. On the other hand, in $[BH_4]^-$ boron is sp^3–hybridized and hence $[BH_4]^-$ is a tetrahedral species.





11.8 Write reactions to justify amphoteric nature of aluminium.

Ans. It dissolves both in acids and alkalis evolving dihydrogen.

$$2\,Al\,(s) + 3\,H_2SO_4\,(aq) \longrightarrow Al_2(SO_4)_3\,(aq) + 3\,H_2\,(g)$$

$$2\,Al\,(s) + 2\,NaOH\,(aq) + 6\,H_2O\,(\ell) \longrightarrow 2\,Na^+\,[Al(OH)_4]^-\,(aq) + 3\,H_2\,(g)$$

Sod. tetrahydroxoaluminate (III)

11.9 What are electron deficient compounds? Are BCl_3 and $SiCl_4$ electron deficient species? Explain.

Ans. Species in which the central atom either does not have eight electrons in the valence shell or those which have 8 electrons in the valence shell but can expand their covalency beyond 4 due to the presence of *d*–orbital, are called electron deficient molecules. For example,

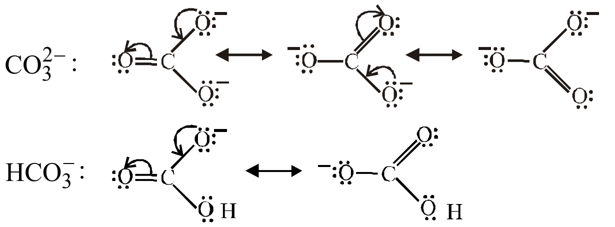
(i) In BCl_3, the central boron atom has only six electrons. Therefore, it is an electron deficient compound. As such, it accepts a pair of electrons from NH_3 to form an adduct

$$Cl_3B + :NH_3 \longrightarrow Cl_3B \leftarrow NH_3$$

(ii) In $SiCl_4$, the central Si atom has 8 electrons but it can expand its covalency beyond 4 due to the presence of vacant *d*–orbitals.

11.10 Write the resonance structures of CO_3^{2-} and HCO_3^-.

Ans. Resonance structures of CO_3^{-2} and HCO_3^- are :

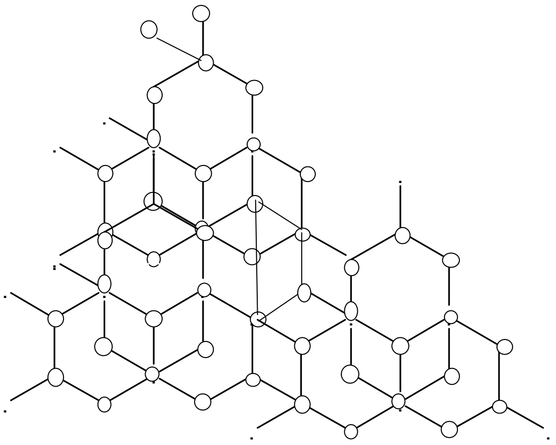


11.11 What is the state of hybridisation of carbon in (a) CO_3^{2-} (b) diamond (c) graphite ?

Ans. (a) sp^2 (b) sp^3 (c) sp^2

11.12 Explain the difference in properties of diamond and graphite on the basis of their structures.

Ans. In diamond, carbon is sp^3 hybridized. Each carbon is tetrahedrally linked to four neighboring carbon atoms through four strong C – C , sp^3 σ bonds, This network extends in three dimensions and is very rigid. Diamond is the purest form of carbon.



Since diamond exists as a 3D network solid, it is the hardest substance known with high density and melting point. It is a bad conductor of electricity as all the electrons are firmly held in C –C σ bonds. Because of its high refractive index, diamond can reflect and refract light. It is therefore transparent substance.

Graphite has carbon having sp^2 hybridization. Each carbon is thus linked to three other carbon atoms forming hexagonal rings. Thus graphite has a two dimensional sheet like structure. The various sheets are held together by weak vander Waal's forces of attraction. The bond lengths in graphite are smaller than diamond. Since any two successive layers are held together by weak forces of attraction, one layer can slip over another. This makes graphite a good lubricating agent. As only three electrons of each carbon are used in making hexagonal rings in graphite, fourth valence electron is free to move. This makes graphite a good conductor of heat and electricity. Unlike diamond, graphite is black and possesses a metallic lustre.

11.13 Rationalise the given statements and give chemical reactions :

(i) Lead (II) chloride reacts with Cl_2 to give $PbCl_4$.

(ii) Lead (IV) chloride is highly unstable towards heat.

(iii) Lead is known not to form an iodide, PbI_4.

Ans. (i) Due to inert pair effect, Pb is more stable in + 2 than in + 4 oxidation state. Therefore, lead (II) chloride is more stable than lead (IV) chloride and hence lead (II) chloride does not react with Cl_2 to form lead (IV) chloride.

(ii) Due to greater stability of +2 over +4 oxidation state because of inert pair effect, lead (IV) chloride on heating decomposes to give lead(II)chloride and Cl_2.

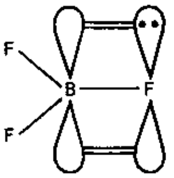
$$PbCl_4(\ell) \xrightarrow{\Delta} PbCl_2\,(s) + Cl_2\,(g)$$

(iii) I^- being a powerful reducing agent reduces Pb^{4+} to Pb^{2+} in solution. Thus, PbI_2 is formed.

$$Pb^{4+} + 2I^- \longrightarrow Pb^{2+} + I_2$$

11.14 Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ ?

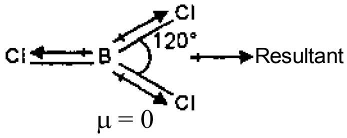
Ans. BF_3 is a planar molecule in which B is sp^2-hybridized. It has an empty 2*p*–orbital. F–atom has three lone pairs of electrons in the 2*p*–orbitals. Because of similar sizes, $p\pi$ – $p\pi$ back bonding occurs in which a lone pair is transferred from F to B as shown below :



As a result of this back bonding, B–F bond acquires some double bond character. In contrast, in $[BF_4]^-$ ion, B is sp^3– hybridized and hence does not have an empty *p*–orbital available to accept the electrons donated by the F atom. Consequently, in $[BF_4]^-$, B–F is a purely single bond. Since double bonds are shorter than single bonds. Therefore, the B–F bond length in BF_3 is shorter (130 pm) than B–F bond length (143 pm) in $[BF_4]^-$.

11.15 If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment?

Ans. Due to electro negativity difference between B (E.N. = 2.0) and Cl (E.N. = 3.0), the B–Cl bond is polar and hence has a finite dipole moment. The overall dipole moment of a molecule, however, depends upon its geometry. Now BCl_3 is a planar molecule in which the three B–Cl bonds are inclined at an angle of 120°. Therefore, the resultant of two B–Cl bonds is cancelled by equal and opposite dipole moment of the third B–Cl bond as shown below :



$\mu = 0$

As a result, overall dipole moment of BCl_3 is zero.

11.16 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

Ans. (i) Anhydrous HF is a covalent compound and is strongly H– bonded. Therefore,it does give F^- ions hence AlF_3 does not dissolve in HF. In contrast, NaF being an ionic compound contains F^- ions and hence combines with AlF_3 to form the soluble complex.

$$3NaF + AlF_3 \longrightarrow \underset{\substack{\text{Sod. hexafluoroaluminate (III)}\\ \text{(soluble complex)}}}{Na_3[AlF_6]}$$

(ii) Because of smaller size and higher electronegativity, B has much higher tendency to form complexes than Al, therefore, when BF_3 is added to the above solution, AlF_3 gets precipitated.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow \underset{\substack{\text{Sod. Tetra fluoro borate (III)}\\ \text{(soluble complex)}}}{3Na[BF_4] + AlF_3(S)}$$

11.17 Suggest a reason as to why CO is poisonous?

Ans. In the lungs, haemoglobin present in red blood cells combines with molecular oxygen loosely and reversibly to form oxyhaemoglobin.

$$\text{Haemoglobin} + O_2 \rightleftharpoons \text{Oxyhaemoglobin}$$

Oxyhaemoglobin thus formed in the lungs then travels to different parts of the body through blood stream and delivers O_2 to the various tissues of the body. However, CO combines with haemoglobin irreversibly to form carboxyhaemoglobin which is about 300 times more stable than the oxyhaemoglobin.

Haemoglobin + CO → Carboxyhaemoglobin

As a result, the oxygen carrying capacity of haemoglobin is destroyed and the man dies of suffocation. Thus, the highly poisonous nature of CO arises due to its ability to form a complex with haemoglobin which is about 300 times more stable than the oxygen– haemoglobin complex.

11.18 How is excessive content of CO_2 responsible for global warming?

Ans. CO_2 is produced during combustion. It is utilized by plants during photosynthesis and O_2 is released into the atmosphere. As a result of this CO_2 cycle, a constant percentage of 21% O_2 in the atmosphere is maintained. However, if the concentration of CO_2 increases beyond a certain level due to excessive combustion, some of the CO_2 will always remain unutilized. This excess CO_2 absorbs heat radiated by the earth. Some of it is dissipated into the atmosphere while the remaining part is radiated back to the earth and other bodies present on the earth. As a result, temperature of the earth and other bodies on the earth increases. This is called greenhouse effect and CO_2 is called a green house gas.

As a result of greenhouse effect, global warming occurs which has serious consequences.

11.19 Explain structures of diborane and boric acid.

Ans. Refer theory

11.20 What happens when

(a) Borax is heated strongly,

(b) Boric acid is added to water

(c) Aluminium is treated with dilute NaOH

(d) BF_3 is reacted with ammonia?

Ans. (a) Refer theory

(b) Boric acid acts as a weak Lewis acid by accepting a hydroxide ion of water and releasing a proton into the solution.

$$H—OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$

(c) Refer theory

(d) BF_3 being a Lewis acid accepts a pair of electrons from NH_3 to form the corresponding complex.

$$\underset{\text{Lewis acid}}{F_3B} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{Complex}}{F_3B \longleftarrow NH_3}$$

11.21 Explain the following reactions

(a) Silicon is heated with methyl chloride at high temperature in the presence of copper

(b) Silicon dioxide is treated with hydrogen fluoride

(c) CO is heated with ZnO

(d) Hydrated alumina is treated with aqueous NaOH solution.

Ans. (a) A mixture of mono–, di– and trimethylchlorosilanes along with a small amount of tetramethylsilane is formed.

$$CH_3Cl + Si \xrightarrow[373\text{ K}]{\text{Cu power}} CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3\,SiCl + (CH_3)_4\,Si$$

(b) Refer theory

(c) Refer theory

(d) Alumina dissolves to form sodium meta-aluminate

$$\underset{\text{Hydrated alumina}}{Al_2O_3.H_2O(s)} + 2NaOH(aq) \xrightarrow{\text{Heat}} \underset{\text{Sod. meta aluminate of Bauxite}}{2NaAlO_2} + 3H_2O$$

or

$$Al_2O_3.2\,H_2O\,(\ell) + 2\,NaOH\,(aq) + H_2O\,(\ell) \longrightarrow \underset{\text{Sod. tetrahydroxoaluminate (III)}}{2\,Na[Al(OH)_4]\,(aq)}$$

11.22 Give reasons :

(i) Conc. HNO_3 can be transported in Aluminium container.

(ii) A mixture of dilute NaOH and Aluminium pieces is used to open drain.

(iii) Graphite is used as lubricant

(iv) Diamond is used as an abrasive.

(v) Aluminium alloys are used to make aircraft body.

(vi) Aluminium utensils should not be kept in water overnight.

(vii) Aluminium wire is used to make transmission cables.

Ans. (i) Refer theory

(ii) Refer theory

(iii) Refer theory

(iv) Refer theory

(v) Aluminium alloys such as duralumin is light, tough and resistant to corrosion and hence is used to make aircraft body.

(vi) Al reacts with H_2O and dissolved O_2 to form a thin film of Aluminium oxide.

$$2Al(s) + O_2(g) + H_2O(\ell) \longrightarrow Al_2O_3(s) + H_2(g)$$

A very small amount of Al_2O_3 may dissolve to give a few ppm of Al^{3+} ions in the solution. Since Al^{3+} ions are injurious to health, therefore, drinking water should not be kept in Aluminium utensils overnight.

(vii) On weight to weight basis, Aluminium conducts twice as Cu. Therefore, it is used in transmission cables.

11.23 Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon?

Ans. Refer theory

11.24 How would you explain the lower atomic radius of Ga as compared to Al ?

Ans. Due to poor shielding of the valence electrons of Ga by the inner 3*d*–electrons, the effective nuclear charge of Ga is greater in magnitude than that of Al. As a result, the electrons in gallium experience greater force of attraction by the nucleus than in Al and hence atomic size of Ga (135 pm) is slightly less than that of Al (143 pm).

11.25 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

Ans.. The phenomenon of existence of an element in two or more forms having different physical properties but identical chemical properties are called allotropy and the different forms are called allotropes. (For rest answers see Ans. 11.12 above)

11.26 (a) Classify following oxides as neutral, acidic, basic or amphoteric CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

(b) Write suitable chemical equations to show their nature.

Ans. (a) Neutral oxides: CO; Acidic oxides: B_2O_3, SiO_2, CO_2 Amphoteric oxides : Al_2O_3, PbO_2 Basic oxide : Tl_2O_3

(b) (i) Being acidic, B_2O_3, SiO_2 and CO_2 react with alkalis to form salts.

$$B_2O_3 + 2\,NaOH \longrightarrow 2NaBO_2 + H_2O$$
$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O$$
$$CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O$$

(ii) Being basic, Tl_2O_3 dissolves in acids

$$Tl_2O_3 + 6HCl \longrightarrow 2TlCl_3 + 3H_2O$$

(iii) Being amphoteric, Al_2O_3 and PbO_2 react with both acids and bases.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2\,(SO_4)_3 + 3H_2O$$
$$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$$
$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2$$

11.27 In some of the reactions, thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

Ans. Aluminium shows a uniform oxidation of +3. Like Aluminium, Tl also shows +3 oxidation state in some of its compounds like $TlCl_3$, Tl_2O_3, etc. Like Al, Tl also forms octahedral complexes: $[AlF_6]^{3-}$ and $[TlF_6]^{3\cdot}$ Group 1 metals shows +1 oxidation state. Tl also shows +1 oxidation state due to inert pair effect. Thus it resembles with group 1 metals.

11.28 When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

Ans. As the metal given in question on treatment with NaOH given a white ppt (A) which dissolves in excess of NaOH to given metal complex (B) therefore the given metal must be Al. the reactions may given as

$$2Al + 3NaOH \longrightarrow \underset{(A)}{Al(OH)_3} \downarrow + 3Na^+$$

$$\underset{(A)}{Al(OH)_3} + \underset{(\text{excess})}{NaOH} \longrightarrow \underset{(B)}{\underset{\text{sodium tetra Hydorxy aluminate (III)}}{Na^+[Al(OH)_4]^-}}$$

As $Al(OH)_3$ is amphoteric in nature, it reacts with dil HCl to form $AlCl_3$ (c).

$$\underset{(A)}{Al(OH)_3} + 3HCl \longrightarrow \underset{(C)}{AlCl_3} + 3H_2O$$

(A) when heated strongly give alumina which is used to extract meal.

$$\underset{(A)}{2Al(OH)_3} \xrightarrow{\Delta} \underset{(D)}{Al_2O_3} + 3H_2O$$

11.29 What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

Ans. **(a)** Refer theory

(b) Refer answer 11.25

(c) Refer theory

11.30 A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.

(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

Ans. (i) Since the aqueous solution of X is alkaline to litmus, here it must be a salt of strong base and weak acid.

$$\underset{\text{Borax(X)}}{Na_2B_4O_7.10H_2O} \xrightarrow{\text{Water}} \underset{\text{Strong alkali}}{2NaOH} + \underset{\text{weak acid}}{H_2B_4O_7} + BH_2O$$

(ii) Since (X) on strong heating swells up to a glassy material (Y). i.e. giving Borax Bead test thus it is now confirm that the compound X is Borax.

$$\underset{(X)}{Na_2B_4O_7.10H_2O} \xrightarrow{\Delta}$$

$$Na_2B_4O_7 + 10H_2O_2 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{(Y) Glassy material}}$$

(iii) When conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid separate out, thus Z must be ortho boric acid.

$$Na_2B_4O_7.10H_2O + H_2SO_4 \longrightarrow \underset{\text{boric acid}}{4H_3BO_3} + Na_2SO_4 + 5H_2O$$

(Z)

11.31 Write balanced equations for :

(i) $BF_3 + LiH \longrightarrow$

(ii) $B_2H_6 + H_2O \longrightarrow$

(iii) $NaH + B_2H_6 \longrightarrow$

(iv) $H_3BO_3 \xrightarrow{\Delta}$

(v) $Al + NaOH \longrightarrow$

(vi) $B_2H_6 + NH_3 \longrightarrow$

Ans. (i) $2BF_3 + 6LiH \longrightarrow \underset{\text{Diborane}}{B_2H_6} + 6LiF$

(ii) $\underset{\text{Diborane}}{B_2H_6} + 6H_2O \longrightarrow \underset{\text{Orthoboric acid}}{2H_3BO_3} + 6H_2$

(iii) $2NaH + B_2H_6 \longrightarrow \underset{\text{Sod. borohydride}}{2Na^+[BH_4]^-}$

(iv) $\underset{\text{Boric acid}}{H_3BO_3} \longrightarrow \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

$$\underset{\text{Meta boric acid}}{4HBO_2} \xrightarrow{\Delta} \underset{\text{Tetra boric acid}}{H_2B_4O_7} \xrightarrow{\Delta} \underset{\text{Boron trioxide}}{2B_2O_3} + H_2O$$

(v) $2Al + 2NaOH + 6H_2O \longrightarrow \underset{\text{Sodium tetrahydroxyaluminate (III)}}{2\overset{+}{Na}[Al(OH)_4]^-} + 3H_2$

(vi) $B_2H_6 + 2NH_3 \longrightarrow \underset{\text{Borane-ammonia complex}}{2BH_3.NH_3}$

11.32 Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

Ans. **Industrial method:**

$$2\,C\,(s) + O_2\,(g) \xrightarrow[\text{air}]{\text{Limited}} 2\,CO\,(g)$$

$$C\,(s) + O_2\,(g) \xrightarrow[\text{Air}]{\text{Excess}} CO_2(g)$$

Laboratory method: $HCOOH \xrightarrow{H_2SO_4} CO + H_2O$

$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2(aq) + CO_2\,(g) + H_2O\,(1)$

11.33 An aqueous solution of borax is

(a) neutral	**(b) amphoteric**
(c) basic	**(d) acidic**

Ans. Borax is a salt of a strong base (NaOH) and a weak acid (H_3BO_3), therefore, it is basic in nature, i.e., option (c) is correct.

11.34 Boric acid is polymeric due to

(a) its acidic nature

(b) the presence of hydrogen bonds

(c) its monobasic nature

(d) its geometry

Ans. Boric acid is polymeric due to the presence of H–bonds. Therefore, option (b) is correct.

11.35 The type of hybridisation of boron in diborane is

(a) *sp*	**(b) sp^2**
(c) sp^3	**(d) dsp^2**

Ans. In B_2H_6, B is sp^3–hybridized. Therefore, option (c) is correct.

11.36 Thermodynamically the most stable form of carbon is

(a) diamond	**(b) graphite**
(c) fullerenes	**(d) coal**

Ans. Thermodynamically the most stable form of carbon is graphite, i.e., option (b) is correct.

11.37 Elements of group 14.

(a) exhibit oxidation state of + 4 only

(b) exhibit oxidation state of +2 and +4

(c) form M^{2-} and M^{4+} ions

(d) form M^{2+} and M^{4+} ions.

Ans. Due to inert pair effect, elements of group 14 exhibit oxidation states of +2 and +4. Thus, option (b) is correct.

11.38 If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

Ans. Refer theory

Practice Questions

Very Short Answer Questions [1 Mark]

1. Name the element of group 13 which forms only covalent compounds.
2. Explain why silicon shows a higher covalency than carbon?
3. Why is diamond a bad conductor of electricity but a good conductor of heat?
4. Which oxide of carbon is an anhydride of carbonic acid ?
5. What are boranes?
6. Why boron forms electron deficient compounds?
7. Why boron halides do not exist as dimer while $AlCl_3$ exists as Al_2Cl_6?
8. Why B–X bond distance in BX_3 is shorter than theoretically expected value?
9. The +1 oxidation state is more stable than the + 3 oxidation state for thallium.
10. Why carbon forms covalent compounds whereas lead forms ionic compounds?
11. Why is boron used in nuclear reactors?
12. Why does boron resemble Si?
13. What name is given to the compounds formed by more electropositive elements with carbon?
14. Is carbon dioxide poisonous or not?
15. Between AlF_3 and $AlCl_3$ which one will have a higher melting point.
16. How are linear silicones obtained?
17. Graphite is used as solid lubricant but charcoal is not, why?
18. What are silicates?
19. BCl_3 exists but BH_3 does not. Explain.
20. Silanes gets hydrolysed by water whereas alkanes do not, why?
21. Explain the following statement with reason.
    The fullerene is considered as purest allotrope of carbon.
22. Explain why boron halides don't conduct electricity in the liquid state?
23. What is the use of boron nitride?
24. Give one example each of ionic and covalent carbides.
25 $(CH_3)_3N$ is basic but $(CF_3)_3N$ is not basic. Explain.

Short Answer Questions [2 & 3 Marks]

1. (a) Why BF_3 forms adduct with ammonia? Explain with reaction.
   (b) How does electron deficient compound BF_3 achieve electronic saturation, i. e., fully occupied outer electron shells?
2. What happens when borax solution is acidified? Write a balanced equations to support your answer.
3. (a) Complete and balance the following chemical equations.
   (i) $BF_3 + N(CH_3)_3 \longrightarrow$
   (ii) $BCl_3 + H_2O \longrightarrow$
   (b) Give the structure of anhydrous Aluminium chloride and boron trifluoride.
4. (a) Molten aluminium bromide is a poor conductor of electricity. Explain.
   (b) Anhydrous aluminium chloride is used as a catalyst. Explain.
   (c) White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.
5. (a) CO_2 is a gas while SiO_2 is a solid. Explain.
   (b) Give one chemical reaction to show that:
      (i) Tin (II) is a reducing agent whereas Pb (II) is not.
      (ii) Tin (II) reduces mercuric salt to mercurous salt.
6. (a) Carbon monoxide is readily absorbed by ammonical cuprous chloride solution but carbon dioxide is not. Explain.
   (b) Silanes are few in number whereas alkanes are large in number. Explain.
   (c) Diamond is covalent, yet it has high melting point. Why?
7. (a) Standard electrode potential values, E° of Al^{3+} / Al is – 1. 66 V and that of Tl^{3+}/Tl is 1.26 V. Predict about the formation of M $^{3+}$ ion in solution and compare the electropositive character of the two metals.
   (b) Why does not silicon form an analogue of graphite?
8. Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) is used as semiconductor(s).
9. (a) Which one is more soluble in diethyl ether, anhydrous $AlCl_3$ or hydrated $AlCl_3$?
   (b) Why BBr_3 is a stronger Lewis acid than BF_3?
10. How is carbon monoxide important in metallurgy?
11. Account for the following :
    (a) Aluminium sulphide gives a foul odour when it becomes damp.
    (b) Although aluminium is above hydrogen in the electrochemical series, still it is stable in moist air.
12. Give reason :
    (a) Silicon form compounds with coordination number of 5 and 6.
    (b) Si—F bond is stronger than C—F bond although Si is larger in size than C.
13. What are silicones? How are they manufactured?
14. Arrange the following in increasing order of the property indicated:
    (a) CCl_2, $SiCl_2$, $GeCl_2$, $SnCl_2$ and $PbCl_2$ (stability)
    (b) CO, SiO, SnO, GeO, PbO (basicity)
    (c) SiF_4, $SiCl_4$, SiI_4, $SiBr_4$ (stability)
15. Out of CCl_4 and $SiCl_4$ which one reacts with water?

16. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ is not. Give possible reasons.

Long Answer Questions [5 Marks]

1. (i) Compound X on reduction with $LiAlH_4$ gives a hydride Y. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced equations involved in the formation of Y and its reaction with air.

(ii) Assign reasons for each of the

(a) Gallium (+1) undergoes disproportionation reactions.

(b) Unlike In^+, Tl^+ is more stable with respect to disproportionation.

(c) InCl undergoes disproportionation but TlCl does not.

2. (i) C and Si are almost always tetravalent but Ge, Sn and Pb show bivalency. Why?

Or

Why the tendency to exhibit + 2 oxidation state increases with increasing atomic number in group 14.

Or

+ 2 oxidation of lead is more stable than + 4 oxidation state. Give reasons.

(ii) (a) Why $N(CH_3)_3$ is pyramidal but $N(SiH_3)_3$ is planar ?

(b) Why $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$?

(iii) Account for the following:

PbO_2 is a stronger oxidizing agent than SnO_2.

Or

PbO_2 can act as an oxidizing agent.

3. Write balanced equations for the following reactions :

(i) SnO is treated with dilute HNO_3.

(ii) Tin is heated with excess of chlorine gas.

(iii) An aqueous solution of sodium hydroxide is added dropwise to a solution of gallium chloride in water. A precipitate is formed initially which dissolves on further addition of NaOH solution.

(iv) Lead sulphide is heated in air.

(v) Lead tetrachloride is heated.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Name the elements of group 13 that form carbides on being heated with carbon above 1275 K. **[HOTS]**

2. Consider the reaction

$$BCl_3 + 6NH_3 \longrightarrow B(NH_2)_3 + 3NH_4Cl$$

What do you infer about acidic/basic character of BCl_3? **[HOTS]**

3. What type of bond would you expact when elements of the *p*-block combine with elements of *s*-block? **[HOTS]**

4. Why a silicon analogue of graphite does not exist? **[HOTS]**

5. What are the basic units of layer structure of orthoboric acid? How are they bonded to one another? **[HOTS]**

6. Name an oxide of carbon that is poisonous. Why is it poisonous? **[HOTS]**

7. Aluminium vessels should not be cleaned with cleansing agent containing washing soda. Explain. **[HOTS]**

8. The pπ-pπ back bonding occurs in the halides of boron but not in the halides of aluminium. Explain. **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. Why does aluminium become passive when dipped in concentrated nitric acid ? **[HOTS]**

2. Why $PbCl_4$ exists whereas $PbBr_4$ and PbI_4 do not ? Explain. **[HOTS]**

3. How would you explain the lower atomic radius of Ga as compared to Al? **[HOTS]**

4. SiF_6^{2-}, $[GeCl_6]^{2-}$ and $[Sn(OH)_6]^{2-}$ are known to exist. Give possible reason. **[HOTS]**

5. Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the rest tube, a pop sound indicates the evolution of hydrogen gas. The same activity when performed with concentrated nitric acid, reaction doesn't proceed. Explain the reason. **[Exemplar]**

6. Identify the compounds A, X and z in the following reactions:

(i) $A + 2HCl + 5H_2O \rightarrow 2NaCl + X$

$$X \xrightarrow[370K]{\Delta} HBO_2 \xrightarrow[>370K]{\Delta} Z$$ **[Exemplar]**

7. Complete the following chemical equations:

$Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3$

$X + 6H_2O \longrightarrow Y + 6H_2$

$3X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$ **[Exemplar]**

Long Answer Questions [5 Marks]

1. State with equations what happens when borax is heated on a platinum wire loop and to the resulting transparent mass, a minute amount of CuO is added and the mixture is again heated first in the oxidising flame and then in the reducing flame of a Bunsen burner ? **[HOTS]**

2. A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. Identify the compounds A, B and C. Give the reactions involved. **[Exemplar]**

CHAPTER TEST

Time : *30 min.* **Max. Marks :** *15*

Directions :
(i) *Attempt all questions*
(ii) *Questions 1 to 3 carry 1 mark each.*
(iii) *Questions 4 and 5 carry 2 marks each.*
(iv) *Question 6 carry 3 marks*
(v) *Question 7 carry 5 marks*

1. What is the general valence shell configuration of p– block elements?
2. How does non–metallic character vary down a group?
3. Glass made up of SiO_2 reacts with HF to form SiF_6^{2-} anion. The analogous CF_6^{2-} anion does not form. Why?
4. In what respect does the first member of a group differ from its congeners?
5. What is catenation? Why carbon shows remarkably the property of catenation?
6. (a) Why borazine is called inorganic benzene?
  (b) Why Ga has smaller atomic radii than aluminium?
  (c) Why aluminium is used as a structural material ?
7. (a) What are amphiboles? Give two examples with chemical formulae
  (b) Complete the following reactions:–
  (i) $Al_2O_3 + NaOH \longrightarrow$ (ii) $BF_3 + NaH \longrightarrow$ (iii) $SnCl_2 + HgCl_2 \longrightarrow$

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. B forms only covalent compounds.
2. Si because of the presence of vacant d–orbitals can show a covalency upto six while C because of the absence of d–orbitals cannot have a covalency of more than four.
3. In diamond all the valence electrons are involved in forming carbon-carbon bonds and does not have free electrons and, therefore, it is a bad conductor of electricity. Conduction of heat does not necessarily require movement of electrons thus diamond is a conductor of heat.
4. CO_2 is an anhydride of carbonic acid:
$H_2CO_3 \longrightarrow H_2O + CO_2$.
5. Refer theory
6. Boron has three electrons in the outermost shell which it can share with other atoms. Hence, in its compounds, only 6 electrons are present around B–atom, i.e., octet is not complete. Thus boron forms electron deficient compounds.
7. Boron atom being small in size is unable to accommodate four large sized halogen atoms around it to form dimer. Thus BCl_3 exists as a monomer whereas $AlCl_3$ exists as a dimer Al_2Cl_6.
8. This is due to $p\pi - p\pi$ back bonding of the fully filled *p*–orbital of halogen (X) atom with the empty *p*–orbital of boron atom.
9. Refer theory
10. Refer theory
11. Boron can absorb neutrons.
12. Both have similar charge over radius ratio, i.e., similar polarising power.
13. Ionic compounds.
14. No, it is not poisonous.
15. AlF_3 is more ionic, therefore, has higher melting point.
16. Refer theory
17. Graphite is soft due to which it can be used as solid lubricant whereas charcoal is hard due to which it cannot be used as lubricant.
18. Silicates are minerals which consist of SiO_4^{4-} units arranged in different ways.
19. In BCl_3, Cl donates lone pair of electrons to vacant p-orbital of boron (back-bonding) making it more stable whereas in BH_3 back-bonding is not possible, therefore, it exists as dimer. Secondly, in BCl_3, chlorine being bigger in size cannot form bridged bonds.
20. Silane gets hydrolysed because silicon has vacant *d*-orbital whereas alkane cannot due to non-availability of vacant *d*-orbital in carbon.
21. It is because it does not have edges, therefore, impurities cannot be adsorbed on it.
22. Boron halides don’t conduct electricity in the liquid state because they are covalent compounds.
23. Boron nitride is harder than diamond and is used as an abrasive.

24. CaC_2 is ionic carbide while SiC is the covalent carbide.

25. This is due to different electronegativities of H and F bonded to nitrogen. In $(CH_3)_3$ N, the lone pair on N is concentrated on N and so it can act as an electron pair donor (Lewis base). However in $(CF_3)_2$ N, the electron density on N is decreased due to strongly electronegative F atom attached to C. Hence, it cannot act as a Lewis base

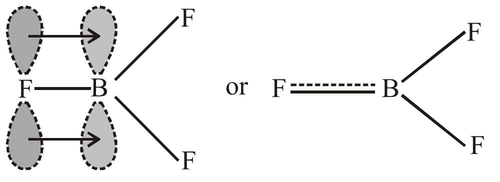
Short Answer Questions

1. (a) Refer answer 11.20 (d)

(b) By the following ways

(i) Multiple bonding there is one 2*p*-vacant orbital on B atom in BF_3 and 2*p*-orbital of each F atom is fully filled. Since the energies of these two 2*p*-orbitals (of B and F) are almost similar, one of the 2*p* filled orbital of F overlaps sidewise with the vacant 2*p*-orbital of B atom resulting in the transference of electrons from F atom to vacant 2*p* orbitals. Thus B—F bond acquires some double bond or $p\pi - p\pi$ bond.

The type of bond is called dative or back bonding.



Back bonding

(ii) Formation of complexes in which electrons are received from a donor molecule, e. g.,

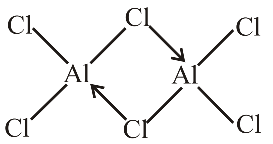
$F_3B \longleftarrow NH_3$. Boron compounds, thus, behave as Lewis acids.

2. Refer theory

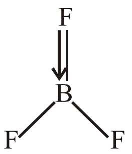
3. (a) (i) $BF_3 + :N(CH_3)_3 \longrightarrow [F_3B \longleftarrow N(CH_3)_3]$

(ii) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

(b)



Structure of anhydrous Al_2Cl_6



Structure of anhydrous BF_3

4. (a) Aluminium bromide is a covalent molecule. Even in the molten state, it ionizes only to a very small extent and hence is a poor conductor of electricity.

(b) The Al atom in $AlCl_3$, has only 6 electrons in its valence shell. It needs two more electrons to complete its octet. It is, therefore, acts as a lewis acid catalyst in Friedel–Crafts alkylation and acylation reactions of benzene and other aromatic compounds. In these reactions, it helps to generate the electrophile (R^+ or RCO^+) which attacks the benzene/aromatic ring.

(c) Anhydrous aluminium chloride is partially hydrolyzed by atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

$AlCl_3\,(s) + 3\,H_2O\,(\ell) \longrightarrow Al(OH)_3\,(s) + 3\,HCl\,(g)$

5. (a) Carbon atom has a small size and forms stable multiple covalent bonds because of close interaction between the 2*p* orbitals on carbon and 2*p* orbitals on oxygen. This is because the energy of 2*p* orbitals of carbon and 2*p* orbitals of oxygen are nearly the same and they can easily overlap. However, silicon has large size and so the 3*p*-orbitals of Si do not overlap effectively with 2*p* orbitals of oxygen. Therefore, Si – O are not formed. The tetravalency of silicon is satisfied by the formation of Si – O bonds which result in a network structure.

(b) (i) Both tin and lead show two oxidation states of +2 and +4. But the inert pair effect is more prominent in case of Pb than in Sn. In other words +2 oxidation state of Sn is less stable than its +4 oxidation state. Therefore, Sn (II) acts as a reducing agent and gets converted into more stable Sn (IV) by losing two electrons.

In contrast, + 2 oxidation state of Pb is more stable than its + 4 oxidation state. In other words, Pb (II) does not lose electrons easily and hence does not act as a reducing agent.

(ii) Being a reducing agent, tin (II) chloride reduces mercuric chloride ($HgCl_2$) to mercurous chloride (Hg_2Cl_2)

$SnCl_2 + 2\,HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2$

6. (a) Due to the presence of a lone pair of electrons on carbon in CO, it acts as a Lewis base (or ligand) and thus forms a soluble complex with ammonical cuprous chloride solution.

$$CuCl + NH_3 + :CO \longrightarrow \underset{\text{Soluble complex}}{[Cu(CO)NH_3]^+Cl^-}$$

On the other hand, CO_2 does not act as a Lewis base since it does have a lone pair of electrons on the carbon atom and hence does not dissolve in ammonical cuprous chloride solution.

(b) Carbon has the maximum tendency for catenation due to stronger C–C (355 $kJmol^{-1}$) bonds. As a result, it forms a large number of alkanes. Silicon, on the other hand, due to weaker Si–Si (200 kJ mol^{-1}) bonds has much lesser tendency for catenation and hence forms only a few silanes.

(c) Refer theory

7. (a) The negative value of E° for Al^{3+}/Al suggests that Al has a strong tendency to form Al^{3+} (aq) ions. On the other hand, the positive value of E° for Tl^{3+}/Tl suggests that Tl does not have high tendency to form Tl^{3+} ions. Since Al can form Al^{3+} ions more easily than Tl does to form Tl^{3+} ions, therefore, Al is more electropositive than Tl.

(b) In graphite, carbon is sp^2-hybridized and each carbon is linked to three other carbon atoms by forming hexagonal rings. Each carbon is now left with one unhybridized p–orbital which undergoes sideways overlap to form three $p\pi - p\pi$ double bonds. Thus, graphite has two dimensional sheet like (layered) structure consisting of a number of hexagonal rings fused together. Silicon, on the other hand, does not form an analogue of graphite because of the following reason: Due to bigger size and smaller electronegativity of Si than C, it does not undergo sp^2-hybridization and hence it does not form $p\pi - p\pi$ double bonds needed for graphite like structure. Instead, it prefers to undergo only sp^3–hybridization and hence silicon has diamond like structure.

8. (i) Carbon is the most non–metallic element of group 14 and hence its dioxide is most acidic.

(ii) Lead is most stable in +2 oxidation state due to inert pair effect.

(iii) Silicon and germanium are used as semiconductors.

9. (a) Anhyd.$AlCl_3$ is an electron deficient compound while hydrated $AlCl_3$ is not. Therefore, anhyd. $AlCl_3$ is more soluble in ether because the oxygen atom of ether donates a lone pair of electron to vacant p–orbital of Al atom in $AlCl_3$ forming a coordinate bond. In case of hydrated $AlCl_3$, Al is not electron deficient since H_2O has already donated a pair of electrons to it.

(b) The B atom in BF_3 and BBr_3 has only six electrons in its valence shell. Thus can accept a pair of electrons to complete its octet. Therefore both of them are Lewis acid. But in BF_3 , the sizes of empty $2p$– orbital of B and $2p$–orbital of F containing the lone pair of electrons are almost identical and are of equivalent energy hence effective $p\pi - p\pi$ bonding occurs due to which the electron deficiency of B atom decreases. While in BBr_3 , the size of $5p$–orbital of Br is much bigger than $2p$–orbital of B atom hence the back donation is not feasible. As a result the electron deficiency of B in BBr_3 is more than BF_3. Thus BBr_3 is stronger Lewis acid than BF_3.

10. Refer theory

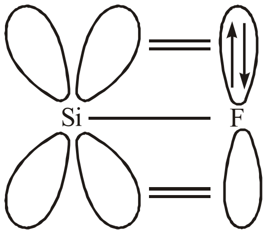
11. (a) The foul smell is due to the formation of H_2S.

$Al_2S_3 + 6H_2O \rightarrow 3H_2S + 2Al(OH)_3$

(b) In the presence of water and air, aluminium gets covered with a protective layer of aluminium oxide. Aluminium oxide does not allow further reaction. Therefore, aluminium is stable in moist air.

12. (a) Silicon shows a coordination number higher than four by using empty $3d$ atomic orbitals. Si can expand its octet beyond eight electrons.

(b) Si—F bond is stronger than C—F bond due to dative pi bonding involving filled p-atomic orbital of fluorine and empty d-atomic orbital of silicon.



13. Refer theory

14. (a) The stability of dihalides increasing down the group because divalent state becomes more and more stable as we move down the group.

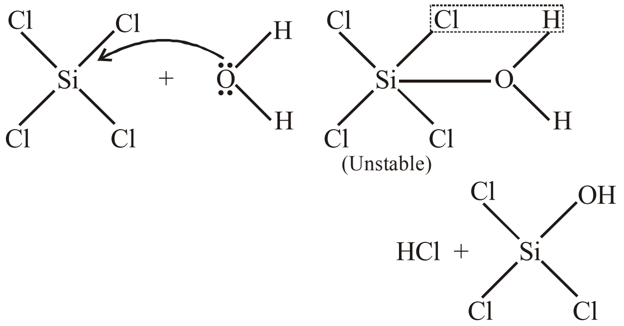
$CCl_2 < SiCl_2 < GeCl_2 < SnCl_2 < PbCl_2$

(b) Basicity of oxides increases down the group as metallic character increases.

$CO < SiO < GeO < SnO < PbO$

(c) Si — X bond strength decreases as the size of the halogen increases. The correct order is $SiI_4 < SiBr_4 < SiCl_4 < SiF_4$

15. Carbon has only s and p-orbitals. As a result carbon cannot increase its coordination number beyond four and therefore, it cannot accept electrons from water molecules. On the other hand, $SiCl_4$ is readily hydrolysed by water because silicon has vacant $3d$ orbitals in its outermost shell. As a result, silicon extends its coordination number beyond four. The vacant $3d$ orbitals of silicon accept electrons from water. and $SiCl_4$ can be hydrolysed as shown below :



16. The main reasons are:

(i) Due to smaller size of F as compared to Cl, six F atoms can be easily accommodated around Si atom but six large sized Cl atoms cannot.

(ii) The lone pair of electrons in F are present in a smaller $2p$–orbital but is Cl they are present in a larger $3p$–orbital. Therefore, interaction of F lone pair electrons with d–orbitals of silicon are stronger than that of Cl lone pairs of electrons.

Long Answer Questions

1. (i) $4BF_3 + 3\,LiAlH_4 \longrightarrow 2\,B_2H_6 + 3\,LiAlF_4$

The equation representing the reaction of Y with O_2 may be written as follows:

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

Thus $X = BF_3$ and $Y = B_2H_6$

(ii) (a) Due to inert pair effect, gallium shows both +1 and +3 oxidation states but its +3 oxidation state is more stable than +1 oxidation state. In other words, +1 gallium is less stable than +3 gallium and hence undergoes disproportionation to form gallium metal and the more stable +3 oxidation ions in aqueous solution as shown below:

$3GaX(s) \longrightarrow 2Ga(s) + Ga^{3+}(aq) + 3X^{-}(aq\}$

or $3\,Ga^{+}(aq) \longrightarrow 2\,Ga\,(s) + Ga^{3+}\,(aq)$

(b) Although both In and Tl can show oxidation states of + 1 and + 3, but inert pair effect is more prominent in Tl than in In. Therefore, + 1 oxidation of Tl is more stable than its + 3 oxidation state while + 3 oxidation state of In is more stable than its + 1 oxidation state. Consequently, in aqueous solution, less stable In^{+} undergoes disproportionation to more stable In^{3+} but + 1 thallium being more stable does not undergo dispro-portionation to + 3 thallium.

$3\,In^{+}\,(aq) \longrightarrow 2\,In\,(s) + In^{3+}\,(aq)$

(c) As stated above, + 3 oxidation state of In is more stable than its + 1 oxidation state, therefore, InCI undergoes disproportionation in aqueous solution.

$3\,InCl\,(aq) \longrightarrow 2\,In\,(s) + In^{3+}\,(aq) + 3\,Cl^{-}$

Since the +1 oxidation state of Tl is more stable than its +3 state, therefore, TlCl does not undergo disproportionation in aqueous solution.

2. (i) Refer theory

(ii) (a) In $N(CH_3)_3$, N is sp^3–hybridized with one lone pair of electrons and hence $N(CH_3)_3$ is pyramidal. In $N(SiH_3)_3$, Si is sp^3–hybridized and forms three –bonds with H and fourth with the N–atom. Further due to the presence of *d*–orbitals, Si has a strong tendency to form $p\pi–d\pi$ double bond with O or N–atoms. For this to occur, N must be sp^2–hybridized so that the *p*–orbital on N containing the lone pair of electrons overlaps with the empty *d*–orbital of Si. As a result, $N(SiH_3)_3$ is planar.

(b) This is because the lone pair of electrons present on N (present in the 2p orbital) is transferred to the empty d–orbital of Si (pπ – dπ overlapping) and hence is not available for protonation.

(iii) In PbO_2 and SnO_2 both lead and tin are present in + 4– oxidation state. But due to stronger inert pair effect, Pb^{2+} ion is more stable than Sn^{2+} ion. In other words, Pb^{4+} ions (i.e. PbO_2) is more easily reduce to Pb^{2+} ions than Sn^{4+} ions are reduced to Sn^{2+} ions. Thus, PbO_2 acts as a stronger oxidizing agent than SnO_2.

3. (i) $3SnO + 2HNO_3\,(dil) \rightarrow 2SnO_2 + 2NO + H_2O$

(ii) $Sn + 2Cl_2 \xrightarrow{\Delta} SnCl_4$

(iii) $GaCl_3 + 3NaOH \rightarrow \underset{\text{white ppt.}}{Ga(OH)_3} + 3NaCl$

$Ga(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{Na\,[Ga(OH)_4]}$

(iv) $2Pbs + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

(v) $PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. Boron and Aluminium.
They form B_2C_3 and Al_4C_3.
2. It shows the acidic character of BCl_3.
3. Such compounds will feature ionic bonds.
4. The graphite structure is considered to contain π-bonds with in planes. Since π-bonds are far weaker in lower member of a group as compared to top member so the silicon analogue of graphite does not exist.
5. The basic unit of layer structure of orthoboric acid is BO_3. They are bonded through hydrogen bonds.
6. CO (Carbon monoxide) is poisonous oxide of carbon.
It attaches more strongly, in comparison to oxygen, to the iron in the haemoglobin and so prevents the transport of sufficient oxygen. Thus a person who breathes in carbon monoxide is liable to suffocate.
7. Washing soda (Na_2CO_3) reacts with water to forms NaOH and Al is soluble in caustic soda.

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{sodium meta aluminate}}{2NaAlO_2} + 3H_2$$

8. The tendency to show pπ-pπ back bonding is maximum in boron halides and decreases very rapidly with increase in size of central atom and halogen atom. Since A1 is larger in size than B and thus do not show back bonding.

Short Answer Questions

1. Refer theory
2. Chlorine is a stronger oxidising agent and so can easily oxidise lead from +2 oxidation state to +4 oxidation state, therefore, $PbCl_4$ exists whereas $PbBr_4$ and Pbl_4 do not exist because bromine and iodine are weaker oxidising agents and so cannot oxidise Pb^{2+} to Pb^{4+}.
3. It is due to the poor shielding of the valence electrons of Ga by the inner 3*d*-electrons. As a result, the effective nuclear charge of Ga is somewhat greater in magnitude than that of Al. Thus, the electrons in gallium experience greater force of attraction by the nucleus than in aluminium. Hence atomic size of Ga (135 pm) is slightly less than that of Al (143 pm).
4. It is because of the presence of *d*-orbitals in Si. Ge and Sn. Due to this, they have the tendency to form complexes by accepting electron pairs from donor species.

$$SiF_4 + 2F^{-} \longrightarrow SiF_6^{2-}$$
$$GeCl_4 + 2Cl^{-} \longrightarrow [GeCl_6]^{2-}$$

Thus SiF_6^{2-},$[GeCl_6]^{2-}$ and $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

5. [***Hint :*** Conc HNO_3 renders aluminium passive by forming a protective oxide layer on the surface.]
6. A : $Na_2B_4O_7$ (Borax)
X : H_3BO_3
Z : B_2O_3
7. A : BF_3
X : B_2H_6
Y : H_3BO_3

Long Answer Questions

1. When borax is heated on a platinum wire loop, a transparent glassy bead is formed.

$$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow[-10H_2O]{\text{Heat}} Na_2B_4O_7$$

$$Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{\underset{\text{Sod. metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Transparent glassy bead}}$$

When this transparent glassy bead is heated with CuO in the oxidising flame, it imparts blue colour to the bead due to the formation of cupric metaborate

$$CuO + B_2O_3 \xrightarrow[\text{flame}]{\text{oxidising}} \underset{\text{Cupric metaborate (}\textit{blue}\text{)}}{Cu(BO_2)_2}$$

However, when cupric metaborate is heated in the reducing flame of the Bunsen burner, the blue cupric metaborate is reduced by carbon present in the flame first to colourless cuprous metaborate and then to metal which produces red scales.

$$\underset{\substack{\text{Cupric metaborate}\\(\textit{Blue})}}{2Cu(BO_2)_2} + C \longrightarrow \underset{\substack{\text{Cuprous metaborate}\\(\textit{Colourless})}}{2CuBO_2} + B_2O_3 + CO$$

2. $A = B_2H_6$, $B = BH_3.NMe_3$, $C = B(OH)_3$ i.e., H_3BO_3.

CHAPTER TEST

1. ns^2np^{1-6}.

2. Decreases.

3. Si has vacant *d*-orbitals and hence can expand its octet to bond with six F^- ions. C has only 2*s* and 2*p* valence orbitals. Therefore can form maximum of 4 bonds.

4. First member of a group is different from its congeners because of
- (i) small size
- (ii) absence of vacant *d*– orbitals
- (iii) ability to form π–bonds.

5. Refer theory

6. (a) Refer theory

(b) Ga is the first element which comes after filling up of d– block elements. As the d–orbitals have large size, the intervening electrons do not screen the nucleus effectively. Consequently, effective nuclear charge of Ga is greater in magnitude than that of Al. As a result, the electrons in Ga experience greater force of attraction by the nucleus than Al and hence atomic radius of Ga is slightly less than that of Al.

(c) Aluminium is light and a bright silvery white metal with high tensile strength. Due to protective oxide layer on its surface it is resistant to strong acids and this layer prevents further corrosion. Hence it is preferred as structural material.

7. (a) Amphiboles are double stranded chain silicates containing $(Si_4O_{11})_n^{6-}$.
Asbestos $CaMg_3O(Si_4O_{11})$ and Tremolite $Ca_2Mg_3(Si_4O_{11})_2(OH)_2$ belongs to this class.

(b) Refer theory

12

Chapter

Organic Chemistry - Some Basic Principles and Techniques

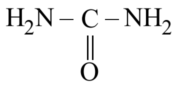
INTRODUCTION

We have learnt that catenation is the unique property of carbon which is responsible for forming C–C bonds and bonds of carbon with other elements like O, N, S, P and halogens. These compounds of carbon which are formed by its combination with itself and with elements mentioned previously are studied under a separate branch of chemistry called organic chemistry.

Virtually all plastics, synthetic and natural fibers, dyes and drugs, insecticides and herbicides, ingredients in perfumes and flavouring agents and all petroleum products are organic compounds. All the foods you eat consist chiefly of organic compounds in the families of the carbohydrates, fats and oils, proteins, and vitamins. The substances that make up furs and feathers, hides and skins, and all cell membranes are also organic.

When ammonium cyanate (obtained by double decomposition of ammonium sulphate and potassium cyanate) is heated, urea – a well known organic compound is obtained.

$$(NH_4)_2SO_4 + 2KCNO \longrightarrow \underset{\text{Ammonium Cyanate}}{2NH_4CNO} + K_2SO_4$$



$$NH_4CNO \xrightarrow[\text{Rearranges}]{\text{Heat}} H_2N-\underset{\underset{O}{\|}}{C}-NH_2$$

Urea

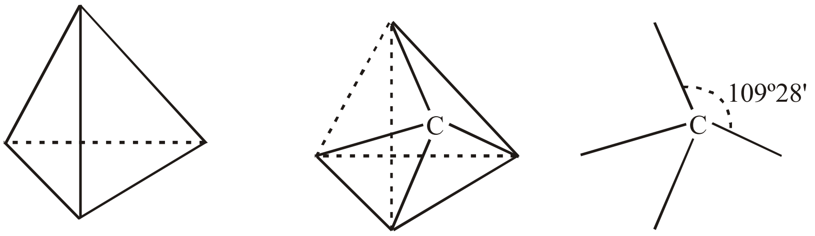
Berzilius, a Swedish chemist proposed a vital force theory. Organic compounds cannot be synthesized in the laboratory because they require the presence of a mysterious force (called vital force) which exists only in the living organisms. This theory got rejected when Wohler accidently discovered urea a well known organic compound found in the urine of humans and other mammals.

TETRAVALENCE OF CARBON

(a) The atomic number of carbon is 6 and it has four electrons in its valence shell. In order to acquire stable inert gas configuration, it can share its electrons with the electrons of other atom(s) to form four covalent bonds. Thus, carbon has a covalency of four or it is tetravalent.

(b) In 1874, Van't Hoff and Le Bel predicted that the four bonds of carbon in methane and other saturated compounds do not lie in a plane but are directed towards the four corners of a regular tetrahedron.

(c) It is because of this reason that Van't Hoff was awarded the first Noble Prize in chemistry in 1901.



A regular tetrahedron with 4 similar faces

Space model of carbon atom

The normal direction of valencies

Figure : Tetrahedral representation of carbon valencies

Carbon atoms present in organic compounds are either *sp*, sp^2 or sp^3 hybridised. Hybridisation influences the bond length and bond strength in organic compounds. The *sp* hybrid orbital contains more s-character than sp^2 and sp^3 and hence, it is closer to its nucleus and forms shorter and stronger bonds than sp^2 and sp^3 hybrid orbital.

The bond angles and geometry associated with the three types of hybridization are summarized below :

Hybridisation	sp^3	sp^2	sp
Angle	109°28′	120°	180°
Geometry	Tetrahedral	Trigonal	Linear
Example	Alkane, Cycloalkane and in saturated part of all organic molecules	Alkenes and other compounds containing C = C, C = I, C = N and C = S double bonds	Alkynes and all other compounds containing C ≡ C and C ≡ N triple bonds,
Bond	Four-σ	Three-σ One-π	Two-σ Two-π
s%	25	33.3	50
p%	75	66.7	50
Electronegativity	2.48	2.75	3.25

Bond dissociation energy for C in different hybridised state:

$C(sp)-H$	> $C(sp^2)$–H	> $C(sp^3)$–H
121 kCal mol^{-1}	106 kCal mol^{-1}	98.6 kCal mol^{-1}
$C(sp)-C(sp)$ >	$C(sp^2)-C(sp^2)$ >	$C(sp^3)-C(sp^3)$
200 kCal mol^{-1}	142 kCal mol^{-1}	80-85 kCal mol^{-1}

Note : (i) Greater is the s - character of the hybrid orbitals, greater is the electronegativity. Thus, a C - atom having an sp hybrid orbital with 50% s - character is more electronegative than sp^2 (33% s-character) or sp^3 (25% s-character) hybrid orbitals.

(ii) Since a bigger orbital forms a longer bond, therefore, C–C single bond length decreases in the order:

$C(sp^3)-C(sp^3) > C(sp^2)-C(sp^2) > C(sp)-C(sp)$

1.54 Å 1.34Å 1.20 Å

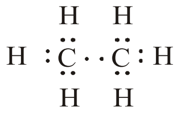
Some Characteristic Features of π–Bond

A pi–bond is formed by sideways or lateral overlap of two p–orbitals, Thus, alkenes contain one sp^2 — sp^2, C – C, σ–bond and one π–bond. In alkynes, the carbon atoms are sp–hybridized. Therefore, alkynes contain one sp–sp, C – C, σ–bond and two π–bonds which are mutually perpendicular to each other.

STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

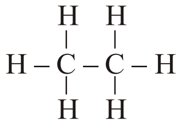
There are several ways of representation of organic comounds like Lewis structure, condensed structure, bond-line formula etc.

Lewis structure of ethane



$$\begin{array}{ccccc} & H & & H & \\ H & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{C}} & \cdot\cdot & \underset{\cdot\cdot}{\overset{\cdot\cdot}{C}}: & H \\ & H & & H & \end{array}$$

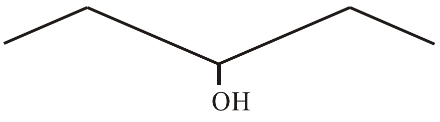
This structure can be simplified by representing the two-electron covalent bond by a dash (–). It can also be represented as :



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

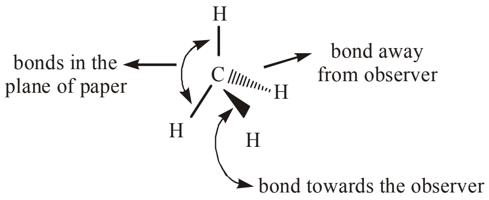
Condensed structural formula is represented by removing all of the dashes representing covalent bonds. For example, ethane, ethyne and ethyl amine can be represented as CH_3CH_3, $HC\equiv CH$, $CH_3CH_2NH_2$ etc.

In bond line structural formula, dashes representing carbon – carbon are drawn in a zig–zag manner without representing carbon and hydrogen. For example, Pentan –3– ol can be represented as,

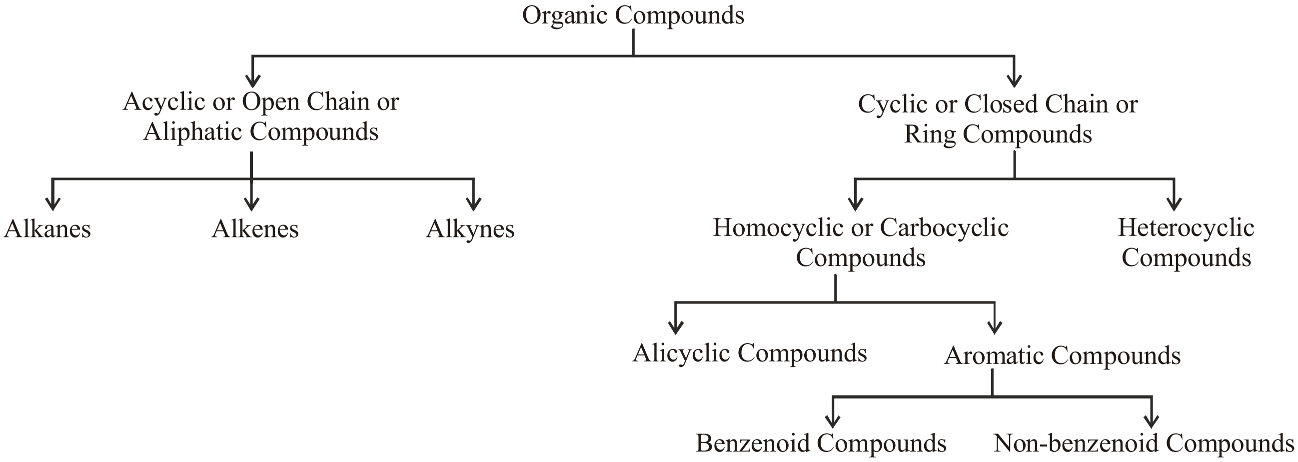


3–D Representation of Organic Molecules

By using solid (◢) and dashed (⦙⦙⦙) wedge formula, the 3–D image of a molecule from a 2–D picture can be perceived. The solid wedge indicates a bond projecting out of the plane of paper, towards the observer and dashed wedge indicates a bond projecting out of the plane of paper, away from the observer. For example, 3–D representation of CH_4 on paper is as follows:



CLASSIFICATION OF ORGANIC COMPOUNDS

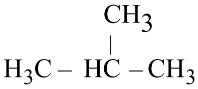


Acyclic or Open Chain Hydrocarbons

They consists of straight or branched chains. They are also called aliphatic compounds

$H_3C-C\equiv C-CH_2-CH_3$

Pentyne - 2

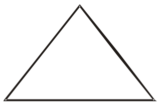


$$H_3C-\overset{\overset{\large CH_3}{|}}{HC}-CH_3$$

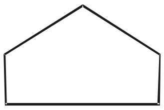
2Methyl propane

Cyclic or Closed Ring Hydrocarbons

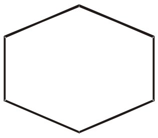
They contain closed chains or rings of carbon atoms.



Cyclopropane



Cyclopentane

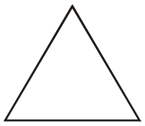


Cyclohexane

(i) Homocyclic or carbocylic compounds :

These compounds contain rings which are made up of only one kind of atoms.

(a) Alicyclic compounds : They resemble aliphatic compounds in most of their properties.



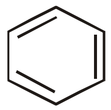
Cyclopropane

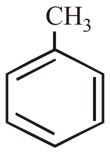
Cyclobutane

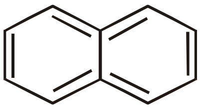
(b) **Aromatic compounds :** They contain benzene and other related ring compounds.

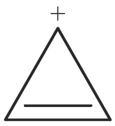
Benzenoids contain at least one benzene ring in their molecules, but if a non benzene ring is present it is termed as non benzenoid compound.

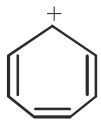
For example, Benzenoid aromatic compounds Non-benzenoid aromatic compounds

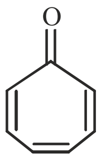

Benzene


Toluene


Naphthalene

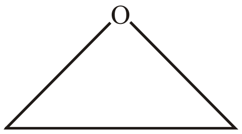

Cyclopropenyl cation

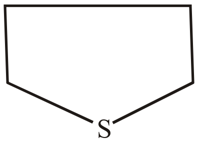

Cycloheptatrienyl cation


Tropone

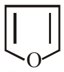
(ii) **Heterocyclic compounds:** Cyclic compounds containing one or more heteroatoms in their rings. Heterocyclic compounds are of two types :

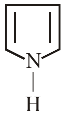
(a) **Aliphatic heterocyclic compounds.** For example,

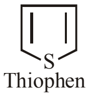

Oxirane

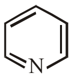

Thiacyclopentane

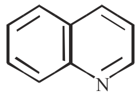
(b) **Aromatic heterocyclic compounds.** For example,


Furan


Pyrrole


Thiophene


Pyridine


Quinoline

Functional group: Functional group is an atom or group of atoms present in a molecule which is responsible for its chemical properties. For example, –C = O, $-NH_2$, –COOH etc.

Homologous series: A series of similarly constituted compounds in which two consecutive members differ in the molecular formula by a—CH_2 unit.

NOMENCLATURE OF ORGANIC COMPOUNDS

Nomenclature of Alkanes

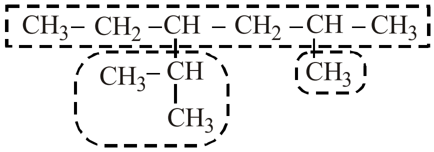
(i) **Straight chain hydrocarbons:**

The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of C - atoms present in the chain. The alkanes differ from each other by no. of – CH_2 groups in the chain. For example,

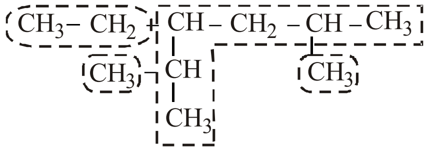
Methane	CH_4	Butane	C_4H_{10}
Ethane	C_2H_6	Pentane	C_5H_{12}
Propane	C_3H_8	Hexane	C_6H_{14}

(ii) **Branched chain hydrocarbons: The rules for naming are:**

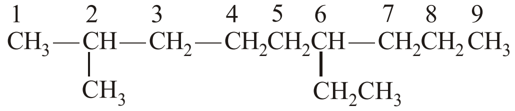
(a) The longest C - chain in the molecule is identified out of all the possible chains. If there are the possibilities of more than one longest chain, the chain which possesses more than one side chain is selected.

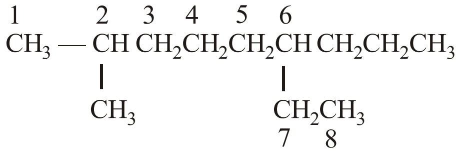

$$CH_3-CH_2-\underset{\substack{|\\CH_3-\underset{\substack{|\\CH_3}}{CH}}}{CH}-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

2 side chains (wrong)


$$CH_3-CH_2-\underset{\substack{|\\CH_3-\underset{\substack{|\\CH_3}}{CH}}}{CH}-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

3-side chains (correct)

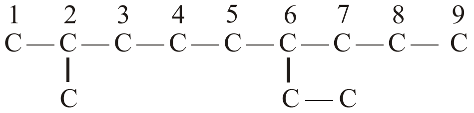

$$\overset{1}{CH_3}-\underset{\substack{|\\CH_3}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}\overset{5}{CH_2}\underset{\substack{|\\CH_2CH_3}}{\overset{6}{CH}}-\overset{7}{CH_2}\overset{8}{CH_2}\overset{9}{CH_3}$$ ✓ Correct



$$\overset{1}{CH_3}—\underset{CH_3}{\overset{2}{CH}}\,\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\underset{\underset{7\quad 8}{CH_2CH_3}}{\overset{6}{CH}}\,CH_2CH_2CH_3$$

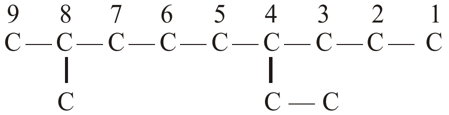
× Incorrect

(b) The numbering is done in such a way that branched carbon atoms get the lowest possible numbers.



$$\overset{1}{C}—\underset{C}{\overset{2}{C}}—\overset{3}{C}—\overset{4}{C}—\overset{5}{C}—\underset{C—C}{\overset{6}{C}}—\overset{7}{C}—\overset{8}{C}—\overset{9}{C}$$

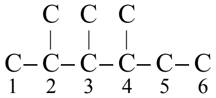
✓ Correct



$$\overset{9}{C}—\underset{C}{\overset{8}{C}}—\overset{7}{C}—\overset{6}{C}—\overset{5}{C}—\underset{C—C}{\overset{4}{C}}—\overset{3}{C}—\overset{2}{C}—\overset{1}{C}$$

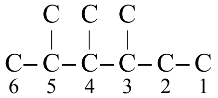
× Incorrect

In case, the parent chain has two or more substituents, numbering must be done in such a way that the sum of the locants on the parent chain is the lowest possible. Thus in following structures A and B numbering may be done in two ways : In (A), the sum of locants is 9 while in (B), it is 12, hence the former is correct while the latter is wrong.



$$\underset{1}{C}-\underset{2}{\overset{C}{C}}-\underset{3}{\overset{C}{C}}-\underset{4}{\overset{C}{C}}-\underset{5}{C}-\underset{6}{C}$$

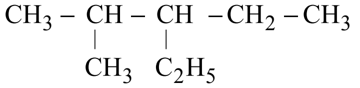
Sum of locants : 2 + 3 + 4 = 9 (A)
(correct)



$$\underset{6}{C}-\underset{5}{\overset{C}{C}}-\underset{4}{\overset{C}{C}}-\underset{3}{\overset{C}{C}}-\underset{2}{C}-\underset{1}{C}$$

Sum of locants : 3 + 4 + 5 = 12 (B)
(incorrect)

(c) The names of alkyl groups attached as a branch are prefixed to the name of parent alkane and position of substituents is indicated by appropriate numbers. If different alkyl groups are present they are listed in alphabetical order. For example

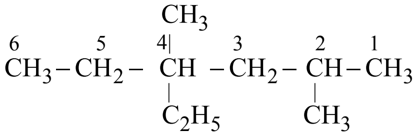


$$CH_3-\underset{CH_3}{CH}-\underset{C_2H_5}{CH}-CH_2-CH_3$$

3–Ethyl–2 methylpentane and not as 2–Methyl–3–ethylpentane

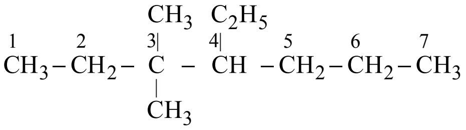
(d) If two or more identical substituent groups are present, then numbers are separated by commas. The names of identical substituents are indicated with prefixes such as di, tri, tetra, penta, hexa, etc. While writing names of substituents spelling of these prefixes are not considered.

For example :



$$\overset{6}{CH_3}-\overset{5}{CH_2}-\underset{C_2H_5}{\overset{\overset{CH_3}{4}}{CH}}-\overset{3}{CH_2}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_3}$$

4–Ethyl–2, 4–Dimethylhexane

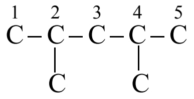


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{CH_3}{\overset{\overset{CH_3}{3}}{C}}-\overset{\overset{C_2H_5}{4}}{CH}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

4–Ethyl–3, 3–dimethylheptane

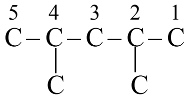
(e) If side chains are at same carbon from both sides, following rules are adopted :

(1) For same side chains, numbering may be given from any end. For example,



$$\overset{1}{C}-\underset{C}{\overset{2}{C}}-\overset{3}{C}-\underset{C}{\overset{4}{C}}-\overset{5}{C}$$

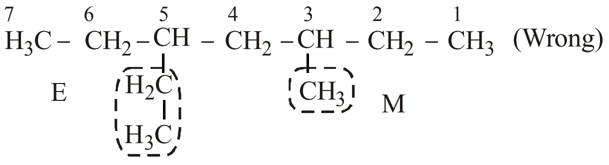
(Right)



$$\overset{5}{C}-\underset{C}{\overset{4}{C}}-\overset{3}{C}-\underset{C}{\overset{2}{C}}-\overset{1}{C}$$

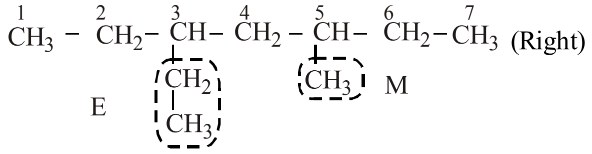
(Right)

(2) If side chains are different, numbering is given in alphabetical preference order. For example,



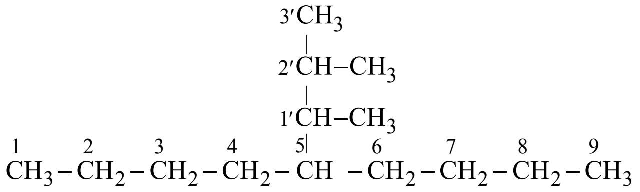
$$\overset{7}{H_3C}-\overset{6}{CH_2}-\underset{\boxed{\underset{H_3C}{H_2C}}}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{\boxed{CH_3}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

(Wrong)



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\boxed{\begin{matrix}CH_2\\ |\\ CH_3\end{matrix}}\ E}{\overset{3}{CH}}-\overset{4}{CH_2}-\underset{\boxed{CH_3}\ M}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_3}\ \text{(Right)}$$

(f) Naming the complex substituent : *In case the substituent on the parent chain is complex (i.e., it has itself branched chain) then it is named as a substituted alkyl group and its carbon chain is numbered from the carbon atom attached to the main chain.* The name of this complex substituent is written in bracket to avoid confusion with the numbers of the main chain. For example,

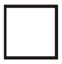
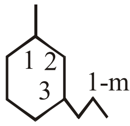


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{\begin{matrix}3'CH_3\\ |\\ 2'CH-CH_3\\ |\\ 1'CH-CH_3\\ 5|\end{matrix}}{CH}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_3}$$

5–(1′, 2′–dimethylpropyl)–nonane

Nomenclature of Cyclic Compounds

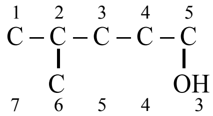
A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are given, then rules given above are applied.

For example : Cyclobutane   1-methyl-3-propylcyclohexane

Nomenclature of Organic Compounds Containing Functional Groups

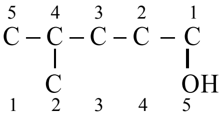
(a) Numbering is given from the end from which functional group is closest.

(b) If the functional group is situated at same carbon from both sides, follow the rules of saturated hydrocarbons. For example,



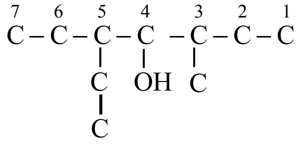
$$\overset{1}{C}-\underset{C}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\underset{OH}{\overset{5}{C}}$$

(Wrong)



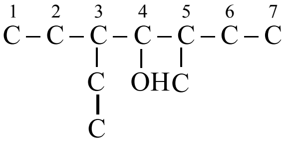
$$\overset{5}{C}-\underset{C}{\overset{4}{C}}-\overset{3}{C}-\overset{2}{C}-\underset{OH}{\overset{1}{C}}$$

(Right)



$$\overset{7}{C}-\overset{6}{C}-\underset{\begin{matrix}C\\ |\\ C\end{matrix}}{\overset{5}{C}}-\underset{OH}{\overset{4}{C}}-\underset{C}{\overset{3}{C}}-\overset{2}{C}-\overset{1}{C}$$

(Wrong)



$$\overset{1}{C}-\overset{2}{C}-\underset{\begin{matrix}C\\ |\\ C\end{matrix}}{\overset{3}{C}}-\underset{OH}{\overset{4}{C}}-\underset{C}{\overset{5}{C}}-\overset{6}{C}-\overset{7}{C}$$

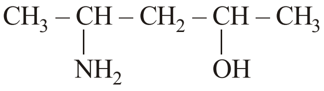
(Right)

(c) If the organic compound contains two or more functional groups, one of the group is selected as principal functional group containing longest possible chain of carbon atom and all the remaining functional groups are treated as substituents.

Order of preferance used while selecting the principal functional group

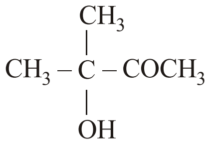
Carboxylic acids > Sulphonic acids > anhydrides > esters > acid chlorides > acid amides > nitriles > aldehydes > cyanides > isocyanides > ketones > alcohols > phenols > thiols > amines > ethers > alkenes > alkynes.

For example,



$$CH_3-\underset{NH_2}{CH}-CH_2-\underset{OH}{CH}-CH_3$$

4-Aminopentan–2–ol



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-COCH_3$$

3–hydroxy–3–methyl butan –2–one

(d) — R, — C_6H_5, halogens (F, Cl, Br, I), –NO_2, – OR etc. are always prefix substituents.

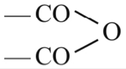
(e) If more than one functional group of same type is present, their number is indicated by adding di -, tri, etc. before the suffix.

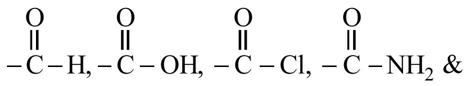
For examples,

(i) $CH_3CH_2COCH_2COCH_3$
Hexane - 2, 4 - dione

(ii) $CH \equiv C-CH=CH-CH=CH_2$
Hexa - 1, 3 - dien - 5 - yne

Table : Some functional groups and classes of organic compounds

Class of compounds	**Functional group structure**	**Functional group prefix**	**Functional group suffix**
Alkanes	–	–	-ane
Alkenes	$>C=C<$	–	-ene
Alkynes	$-C\equiv C-$	–	-yne
Arenes	–	–	-
Halides	$-X$ (X = F, Cl, Br, I)	halo	-
Alcohols	$-OH$	hydroxy	-ol
Aldehydes	$-CHO$	formyl, or oxo	-al
Ketones	$>C=O$	oxo	-one
Nitriles	$-C\equiv N$	cyano	nitrile
Ethers	R-O-R	alkoxy	-
Carboxylic acids	$-COOH$	carboxy	-oic acid
Carboxylate ions	$-COO^-$	–	-oate
Esters	$-COOR$	alkoxycarbonyl	-oate
Acyl halides	$-COX$ (X = F, Cl, Br, I)	halocarbonyl	-oyl halide
Amines	$-NH_2$, $>NH$, $>N-$	amino	-amine
Amides	$-CONH_2$, $-CONHR$, $-CONR_2$	carbamoyl	-amide
Nitro compounds	$-NO_2$	nitro	-
Sulphonic acids	$-SO_3H$	sulpho	sulphonic acid
Thio alcohol	$-SH$	Mercapto–	– thiol
Anhydride		—	– oic anhydride
Isocyanide	$-N\equiv C$	Carbylamine	– iso nitrile

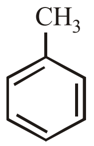


Note : $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-Cl$, $-\overset{O}{\overset{\|}{C}}-NH_2$ & $-C\equiv N$ the carbon atoms of the groups are also included in the longest chain. If these are alone in a compounds they comes on first carbon, if double, comes on first and last positions.

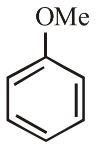
Nomenclature of Aromatic Compounds

(a) The substituent is placed as prefix to the word benzene.

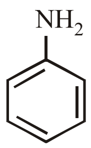
For examples,



Methyl benzene
(Toluene)



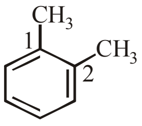
Methoxy benzene
(Anisole)



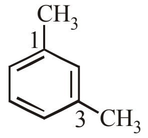
Amino benzene
(Aniline)

(b) If benzene ring is disubstituted, position of substituents is defined by numbering the C-atoms of ring such that substituents are located at lowest numbers as possible.

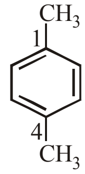
For example,



1,2-Dimethylbenzene
(*o*-Xylene)



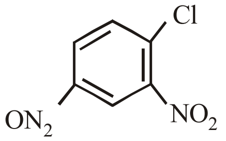
1,3-Dimethylbenzene
(*m*-xylene)



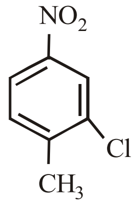
1,4-Dimethylbenzene
(*p*-xylene)

(c) For tri - or higher substituted benzene derivatives, the compounds are named by identifying substituent positions on the ring by following lowest locant rule. In some cases, common name of benzene derivatives is taken as base compound. Substituent of base compound is assigned no. 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents should be numbered according to alphabetical order.

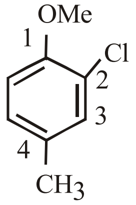
For example,



1-Chloro-2, 4-dinitrobenzene



2-Chloro-1-methyl-4-nitrobenzene



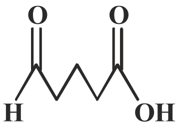
2-Chloro-4-methyl anisole

(d) When benzene ring is attached to an alkane with a functional group, it is considered as substituent instead of parent and its name as a substituent is phenyl.

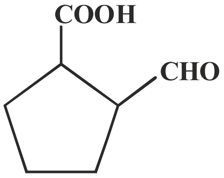
Illustration 1 :

Give the IUPAC names of the following bifunctional compounds

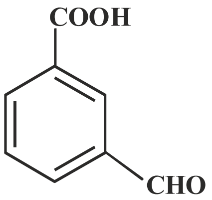
(*i*)



(*ii*)



(*iii*)



Sol. (i) 5-Oxopentanoic acid (ii) 2-Formylcyclopentane-1-carboxylic acid (iii) 3-Formylbenzoic acid.

ISOMERISM

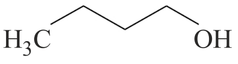
The existence of two or more chemical compounds with the same molecular formula but having different properties owing to different arrangement of atoms within the molecule is termed as isomerism.

Structural Isomerism

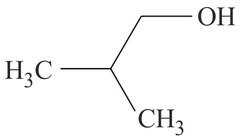
Compounds having same molecular formula but different structures fall in this category. It is further classified into different types.

(i) Chain isomerism: The isomers having same molecular formula but difference in the length of carbon chain are referred as chain isomers. Some examples are listed below :

(a) Molecular formula : C_4H_9OH

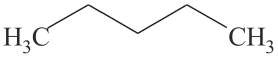


Butan-1-ol

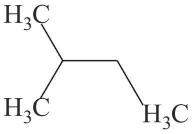


2-Methyl Propan-1-ol

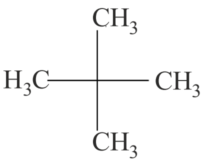
(b) Molecular formula : C_5H_{12}



Pentane

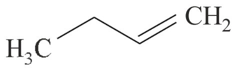


2-Methyl Butane

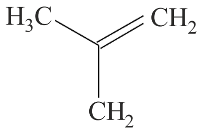


2,2-Dimethyl Propane

(c) Molecular formula : C_4H_8



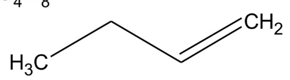
But-1-ene



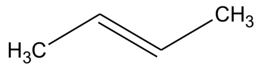
2-Methyl Prop-1-ene

(ii) Position isomerism : The isomers having same molecular formula but differ in the position of either substituent or the functional group on the same carbon skeleton. For examples,

(a) Molecular formula : C_4H_8

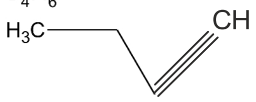


But-1-ene

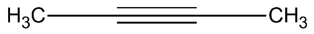


But-2-ene

(b) Molecular formula : C_4H_6

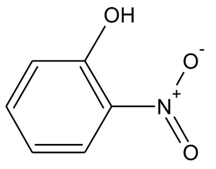


But-1-yne

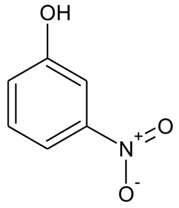


But-2-yne

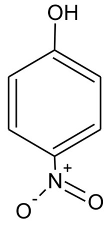
(c) Molecular formula : $C_6H_5O_3N$



o-nitrophenol



m-nitrophenol



p-nitrophenol

(iii) Functional isomerism: In these isomers, they have same molecular formula but different functional group present. These isomers are called functional isomers. For example,

(a) Alcohols and ethers are functional isomers.

Molecular Formula: C_2H_6O

CH_3CH_2OH	and	CH_3OCH_3
Ethanol		Methoxy methane

(b) Aldehydes and ketones are functional isomers.

Molecular Formula: C_3H_6O

CH_3CH_2CHO	and	CH_3COCH_3
Propanal		Propanone

(c) Carboxylic acid and ester are also functional isomers.

Molecular Formula: $C_2H_4O_2$

CH_3COOH	and	$HCOOCH_3$
Ethanoic acid		Methyl methanoate

(d) Nitro alkanes and alkyl nitrites are functional isomers.

Molecular Formula: $C_2H_5NO_2$

$CH_3CH_2NO_2$	and	CH_3CH_2ONO
Nitroethane		Ethyl nitrite

(e) Cyanides and isocyanides are functional isomers.

Molecular Formula : C_2H_3N

CH_3CN	and	CH_3NC
Ethane nitrile		Methane isonitrile.

(iv) Metamerism : It arises due to unequal distribution of alkyl groups on either side of functional group in the molecule . It is observed in ethers, thio–ethers, di–alkylamines.

(a) Molecular formula : $C_4H_{10}O$

$C_2H_5OC_2H_5$	$CH_3OC_3H_7$
Ethoxy ethane	Methoxy propane

(b) Molecular formula : $C_4H_{11}N$

$C_2H_5NHC_2H_5$ — N-ethyl ethanamine

$CH_3NHC_3H_7$ — N-methyl propanamine

Stereoisomerism

Isomers which have the same structural formula but different three dimensional structures (i.e. different relative arrangement of atoms of groups in space around the carbon atom) are known as stereomers or stereoisomers and the phenomenon as stereoisomerism. Since the spatial arrangement of atoms or groups is also referred as configuration of the molecule, we can say that stereoisomers have the same structural formulae but different configuration.

Stereoisomerism

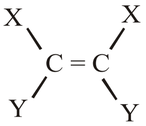
Two or more compounds which have the same molecular formula and the same connectivity of atoms but different three dimensional arrangement of their constituent atoms or groups are said to be stereoisomers and the phenomenon is termed as stereoisomerism.

(a) Geometrical isomerism : Arises due to different geometries of compounds, i.e. different arrangement of atoms or groups around doubly bonded C - atoms.

Two types:

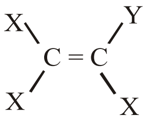
Cis-isomer

Two identical atoms or groups lie on same side of double bond i.e.



Trans-isomer

Two identical atoms or groups lie on opposite side of double bond, i,e.



If the two atoms or groups linked to same doubly linked carbon are similar as in the molecule aaC = Cab, the compound does not show geometrical isomerism.

(b) Optical isomerism : It is shown by compounds which rotates the plane of polarised light either towards right i.e clockwise or towards left, i.e., anti - clockwise.

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM:

A general reaction is depicted as:

$$\begin{tikzcd} \text{Organic molecule (Substrate)} \arrow[r] & \text{Attacking reagent} \arrow[r] & \text{[Intermediate]} \arrow[r] \arrow[dr] & \text{Product (s)} \\ & & & \text{By product(s)} \end{tikzcd}$$

A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products is referred as reaction mechanism.

The fission of covalent bond can be done by two ways :

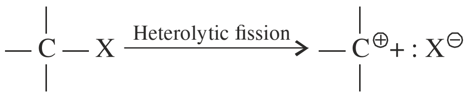
Heterolytic Cleavage

In this type of fission the electrons pair forming the covalent bond goes to a single atom or group and thus electrically charged fragments (ions) are formed. Thus the reactions involving heterolytic fission are known as ***ionic* or heteropolar or polar *reactions*** and are said to proceed via ***ionic (polar) mechanism***.

$$A:\overset{\curvearrowright}{B} \xrightarrow{\text{Heterolytic fission}} A^+ + :B^-$$

(when B is more electronegative than A) It results in formation of cations and anions

(i) Carbocation :



$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{Heterolytic fission}} -\overset{|}{\underset{|}{C}}{}^{\oplus} + :X^{\ominus}$$

If EN of X > EN of C

Organic species which has only six paired electons (i.e. three pairs of electrons) and a positive charge at its carbon centre is known as ***carbonium ion*** or ***carbocation***. Carbonium ions are generally symbolized as R^+. Carbon atom of a carbonium ion is sp^2 hybridised.

Their relative stability order of carbocation is $\underset{\text{tert}}{R_3\overset{+}{C}} > \underset{\text{sec.}}{R_2\overset{+}{C}H} > \underset{\text{Pri}}{R\overset{+}{C}H_2} > \underset{\text{methyl}}{\overset{+}{C}H_3}$

- Stability of carbocation $\propto +I \propto \frac{1}{-I}$

  For example,

  (1) $CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > NO_2-\overset{\oplus}{C}H_2$

  (2) $(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 > 3^{o} > 2^{o} > 1^{o} > \overset{\oplus}{C}H_3$
- Stability $\propto$ No. of resonating structures

(ii) Carbanion : Organic species which has eight electrons (i.e., four pairs of electrons) and a negative charge on one of its carbon centre is known as ***carbanion***. Carbanions are generally symbolized as R.

$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{Heterolytic fission}} -\overset{|}{\underset{|}{C}}:^{\ominus} + X^{\oplus}$$

If EN of C > EN of X

Carbanions follow the following stability order:

$$\underset{\text{Methyl}}{H_3C^-} > \underset{\text{pri}}{R\overset{-}{C}H_2} > \underset{\text{sec.}}{R_2\overset{-}{C}H} > \underset{\text{ter.}}{R_3\overset{-}{C}}$$

Stability of carbanion is due to following reasons

(a) Inductive effect

(b) Resonance

(c) *s*-character in Hybridisation

Stability of Carbanion $\propto -I, \propto \frac{1}{+I}$

For example,

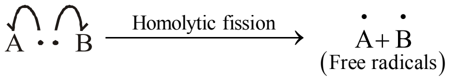
(a) $CH_3-\overset{\ominus}{\ddot{C}}H_2 < \overset{\ominus}{\ddot{C}}H_3 < NO_2-\overset{\ominus}{\ddot{C}}H_2$

(b) $\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

Note : Carbanions are nucleophiles.

Homolytic Cleavage

In homolytic bond fission one electron of the bonding pairs goes with each of the departing atom or group resulting in two electrically neutral fragments or atoms, known as free radicals. For example,



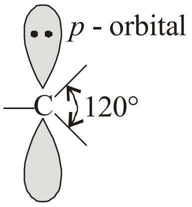
$$A \cdot\cdot B \xrightarrow{\text{Homolytic fission}} \underset{(\text{Free radicals})}{\dot{A}+\dot{B}}$$

Movement of a single electron is shown by a half headed curved arrow. The neutral chemical species (such as A and B) which contain an odd or unpaired electron and which are produced by homolytic fission of covalent bonds are called free radicals.

Thus a free radial may be defined as the atom or group of atoms having a single, odd or unpaired electron. Free radicals are electrically neutral and paramagnetic (due to the presence of odd electron) in nature. The stability of common free radicals is

benzyl > allyl > tert > sec > pri > methyl > vinyl

A free radical may have an sp^2-hybridised carbon in which odd electron remains in the p-orbital; the shape of this type of free radical will be planar.



Reactions which proceed by homolytic fission are called free radical or homopolar or non-polar reactions

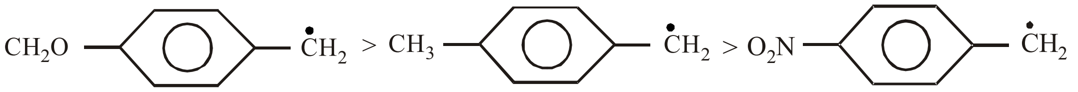
Decreasing order of stability of free radicals

(i) Benzylic free radical > allylic free radical > 3° > 2° > 1°

(ii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH\dot{C}H_2 > (CH_3)_3\dot{C} >$

$(CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3 > HC\equiv\dot{C}$

(iii)



Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a nucleophile i.e. nucleus seeking and the reaction is called nucleophilic.

They are of two types :

They are of two types :

(i) Charged nucleophiles :

All the negative ions qualify as nucleophiles.

$F^-, Cl^-, Br^-, I^-, OH^-, CN^-, RCOO^-$

$RO^-, R^-, R—C\equiv C^-, \overset{-}{N}H_2, \overset{-}{S}H$, etc.

(ii) Neutral nucleophiles : Central atom has electron pair.

$\ddot{N}H_3, R—\ddot{N}H_2, R-\ddot{N}HR, R_3\ddot{N}, H_2\ddot{O}:, R-\underset{\cdot\cdot}{\ddot{O}}-H,$

A reagent that takes away an electron pair is called an electrophile (E^+) i.e., electron seeking and the reaction is called electrophilic Electrophiles may be neutral or positively charged.

(i) Neutral electrophiles : Central atom has deficiency of electrons. For example, BF_3, BCl_3, $AlCl_3$, $BeCl_2$, $FeCl_3$, SO_3, etc..

(ii) Charged electrophiles :

All the positive ions behave like electrophiles.

$Cl^+, Br^+, I^+, NO_2^+, NO^+, H^+, H_3O^+, \overset{+}{N}H_4, R^+, R—\overset{+}{C}=O$, etc.

Electrophiles are generated by heterolysis of a covalent bond. Transition metal cations are electrophiles. For example :

$Fe^{3+}, Fe^{2+}, Ag^+, Hg^{2+}, Cd^{2+}$, etc.

Electron Displacement

The electron displacement in an organic molecule may take place either in ground state under the influence of an atom or a group or in presence of an appropriate attacking reagent.

Electron displacement due to influence of an atom or group present in molecule cause permanent polarisation of the bond. Example: Inductive effect and resonance effect. Temporary electron displacement effects are seen in a molecule when a reagent approaches attack it. Example: electromeric or polarisability effect.

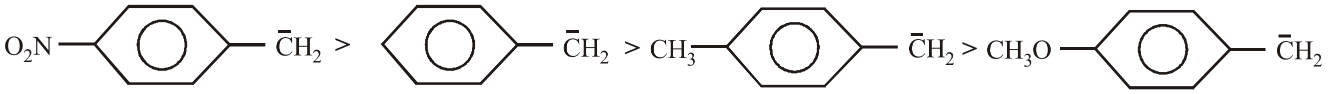
Inductive Effect

When there is a displacement of σ–electrons along a saturated carbon chain whenever an electron withdrawing or electron donating group is present at the end of the chain is called the inductive effect. This effect weakens after third carbon atom. This effect is permanent. Any atom or group, if attracts electrons more strongly than hydrogen, it is said to have a–I effect (election–attracting or electron–withdrawing or—I groups), viz. NO_2, Cl, Br, I, F, COOH, OCH_3, etc.; while if atom or group attracts electrons less strongly than hydrogen it is said to have a + I effect (electrons –repelling or electron–releasing or + I groups), viz. CH_3, C_2H_5 Me_2CH and Me_3C groups. The order of decreasing inductive effects of most common groups are

+ I groups: $(CH_3)_3C-, (CH_3)_2CH-, CH_3CH_2-, CH_3-, -H$

– I groups: $-\overset{+}{N}R_3 > -NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -\ddot{O}H > -\ddot{O}R > -C_6H_5 > -H$

Notes : The electron attracting groups increases the stability of carbanions.



The inductive effect in di-and tri-halogens substituted acids are progressively more stronger than the corresponding monohalogen substituted acid.

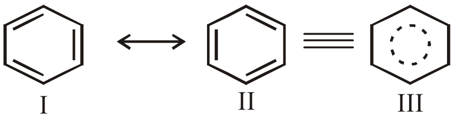
$$\underset{\text{Trichloroacetic acid}}{Cl_3CCOOH} > \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} > \underset{\text{Chloroacetic acid}}{ClCH_2COOH} > \underset{\text{Acetic acid}}{CH_3COOH}$$

Resonance Effect

Sometimes, it is not possible to assign a single electronic (Lewis) structure to a molecule which can satisfactorily explain all its properties. In such cases, it has been found that the molecule can often be represented by two or more Lewis structures each one of which can explain most of the properties but none of them can explain all the properties of the molecule. The real structure of the molecule lies somewhere in between all these electronic structures which differ in the position of electrons but not in the relative position of atoms. The various Lewis structures are called canonical or resonance structures.

The real structure of the molecule is not represented by any of the canonical structures but is actually a resonance hybrid of all these Lewis structures. The various resonance structures are separated by a double headed arrow (↔).

Thus in the light of resonance theory, benzene can be represented as a resonance hybrid of the following two Kekule (Lewis) structures, I and II.



I II III

Some important conditions for resonance are :

(a) The various resonance structures should differ only in position of electrons and not in the position of atoms.

(b) All the resonance structures should have the same number of paired and unpaired electrons. However distribution of electrons will be different.

(c) The energies of the various resonating structures must be same or nearly same.

(d) Resonating structures must be planar.

(e) All the canonical forms do not contribute equally towards the structure of a resonance hybrid. A more stable canonical structure contributes more to the resonance hybrid. The contribution depends upon the following factors :

   (i) Presence of isolated charges or increase in charge separation decreases the stability of a canonical form and hence its contribution is less in the hybrid structure.

   (ii) When all the structures have formal charge, the structure having negative charge on electronegative and positive charge on electropositive element (atom) will be more stable. For example, carbonyl group is a resonance hybrid of the following structures.

$$\underset{\text{I}}{>C=O} \leftrightarrow \underset{\text{II}}{>\overset{+}{C}-\overset{-}{O}} \leftrightarrow \underset{\text{III}}{>\overset{-}{C}-\overset{+}{O}}$$

   The polar structure (II) is more stable than (III) because in this structure negative charge resides on oxygen (more electronegative atom) and +ve charge is present on more electropositive carbon atom.

   (iii) Resonating structure having electron deficient positively charged atoms possess very high energy and hence are unstable.

   (iv) Resonating structures with a greater number of covalent bonds are more stable.

Effects of resonance:

(a) Resonance always increases the stability of molecule and lessens its reactivity. More the number of nearly similar reasonating structures, more will be its stability.

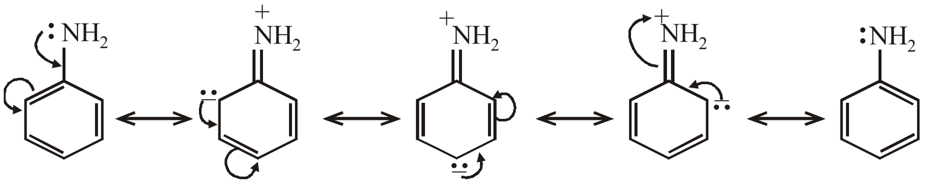
(b) Resonance leads to similar type of bonds between atoms involved in it. Thus in benzene all the carbon—carbon bonds are of same length, i.e. 1.39 Å (while the usual bond length of C—C in alkanes is 1.54 Å and of C—C in alkenes is 1.34Å).

There are two types of resonance or mesomeric effects designated as R or M effect.

(i) Positive resonance effect (+ R-effect)

In this effects transfer of electrons is a way from an atom or group attached to the conjugated system. In this effect, the electron displacement makes certain positions in the molecule of high-electron densities.

For example : Aniline



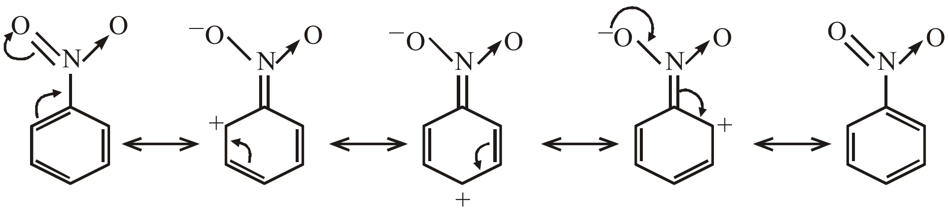
For example : halogen, – OH, – OR, –OCOR, – NH_2, – NHR, – NR_2, – NHR, – NR_2, – NHCOR

Decreasing order of activating (+R) groups – O –, –NH_2, –NHR, –NR_2, –OH, –OR, –NHCOR, –R, –Ar, –X (Till –OH they are very strong activating group)

(ii) Negative resonance effect (–R-effect)

In this effect, the electron displacement makes certain positions in the molecules of less electron density.

For ex : Nitrobenzene



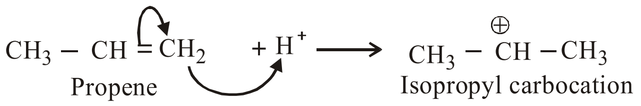
For examples : –COOH, – CHO, $>C = O$, – CN, – NO_2

The very strong deactivating (–R) groups are
$–NO_2$, $–CF_3$, $–NR_3^+$

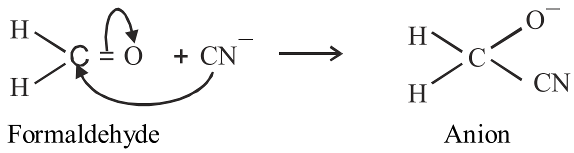
Electromeric Effect (E - Effect)

It is defined as the complete transfer of a shared pair of π - electrons to one of the atoms (more electronegative) joined by a multiple bond on demand of an attacking reagent. It is a temporary effect. There are two types of electromeric effect:

(i) + E effect :
In this, π – electrons of multiple bond are transferred to that atom to which reagent gets attached.
For example :



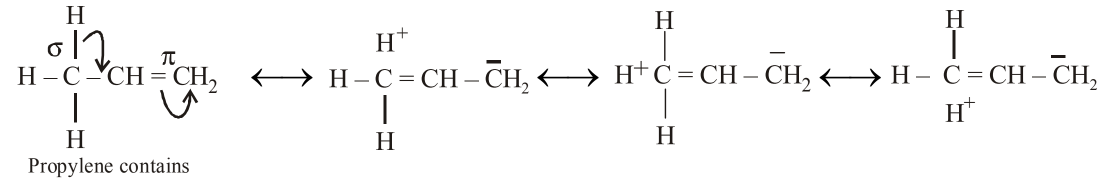
(ii) – E effect :
In this, π – electrons of multiple bond are transferred to that atom to which attacking reagent does not get attached
For example :



Oxygen being more electronegative pulls π electrons of multiple bond toward itself. Carbonyl C acquires positive charge thus got attacked by nucleophile.

Hyperconjugation

It involves delocalisation of σ – electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p* - orbital. It is a permanent effect. Hyperconjugation is also called no -bond resonance. For example, In propylene, there are three H—C sigma bonds in conjugation with the π bond. So, only three resonating forms can be written.



Propylene contains
3H – C hyperconjugated bond

Effects of hyperconjugation :

(a) Stability of alkenes :

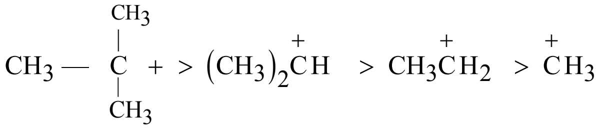
(i) Alkylated alkenes are more stable than others.
$R_2 - C = C - R_2 > R_2C = CHR. RCH = CHR > R_2C = CH_2 > R - CH = CH_2 > CH_2 = CH_2$
[Tetraalkyl ethylene] Least stable

(ii) Greater the number of α C – H bonds in an alkene, greater will be the number of hyperconjugated structures, hence greater will be the stability.

(b) Bond lengths : Hyperconjugation in a molecule results in a change in bond lengths.

(c) Stability of alkyl free radicals :
t–alkyl > *sec.* alkyl > primary alkyl > CH_3 (methyl radical)
Greater the number of hyperconjugative structures of an alkyl radical, higher is the stability.

(d) Stability of alkyl carbonium ions : Greater the number of alkyl groups attached to positively charged carbon atom, greater is the hyperconjugation interaction and stabilisation of the cation.
The relative stability of carbocations follows the order:



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}}{}^{+} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Types of Organic Reactions

(i) **Substitution or Displacement Reactions :** Substitution or displacement reactions are those reactions in which an atom or group of atoms attached to a carbon atom in a substrate molecule is replaced by another atom or group of atoms.

(ii) **Addition Reactions :** Addition reactions are those in which the attacking reagent adds up to the substrate molecule. Such reactions are given by those compounds which possess double or triple bonds.

(iii) **Elimination Reactions :** The reverse of addition reactions are termed as elimination reactions. In these reactions generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed.

(iv) **Rearrangement Reactions :** The reactions which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure are known as rearrangement reactions.

PURIFICATION OF ORGANIC COMPOUNDS

The organic compounds obtained from natural sources or synthesised in the lab are often contaminated with impurities. They are purified by specialised methods. The common method of purification are:

Sublimation

Some solids directly pass into vapour when heated and vapour directly pass into solid when cooled without the intermediate formation of liquid. This is known as sublimation. The substances which sublime can be purified by this method. Impurities left which can not sublimed.

For example, Camphor, napthalene, anthracene, benzoic acid, phthalic anhydride and anthraquinone are purified by sublimation.

Criteria of Purity

The purity of an organic compound can be ascertained by determining its some physical constants like m.p., b.p., specific gravity, refractive index and viscosity. In usual practice, sharp m.p. (in case of solids) and boiling point (in case of liquids) are used as criteria for purity because their determination is feasible in the laboratory.

Simple Crystallisation

This is the most common method for the purification of solid organic compounds. It is based on the fact that certain organic compounds are partly soluble in a solvent at room temperature and solubility increases with increase in temperature. Sometimes crystal formation can be initiated by the addition of a substance it is known as seeding. In practice, the excess of substance to be purified is heated to a higher temperature (nearly to boiling) with a suitable solvent. The hot solution is filtered to remove the insoluble substance, and the filtrate containing soluble organic compound is cooled when the fine crystals are obtained. The crystals are filtered out and dried

The solvent selected should have following characteristics.

(a) It should dissolve the substance to be purified and should not dissolve the impurity present.

(b) It should not react chemically with the compound to be purified.

(c) It should not be highly inflammable.

(d) Solvent should be of low viscosity.

Some of the common solvents are water, alcohol, ether, carbon tetrachloride, benzene, acetone etc.

For example :

(i) Benzoic acid mixed with naphthalene is purified by hot water.

(ii) Separation of a mixture of naphthalene and phthalic acid by using hot water.

Fractional Crystallisation

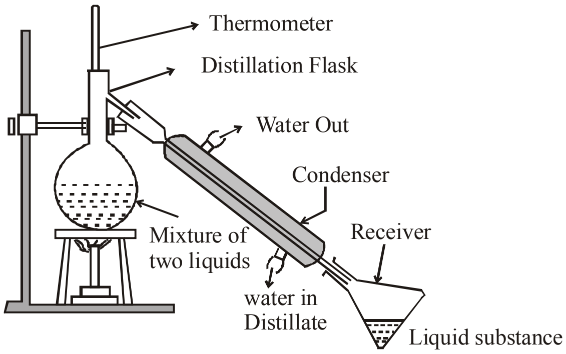
It is based on the differential solubilities of different compounds in a solvent. The compound having less solubility crystallises out first on cooling leaving behind others in solution.

The procedure involves the dissolution of mixture in small quantity of hot suitable solvent. When the concentrated solution is allowed to cool, the less soluble component separates out leaving the more soluble component in the mother liquor. For example, separation of *o*-nitro acetanilide and *p*-nitro acetanilide by crystallization with ethanol.

Distillation

Two liquids having different boiling points (with a difference of 10-20 K) can be separated by this method. When mixture of two such liquids is heated in a retort (or distillation flask) the low-boiling liquid component first distills over and the other component is left behind in the retort.

A simple experimental set up is shown in figure below



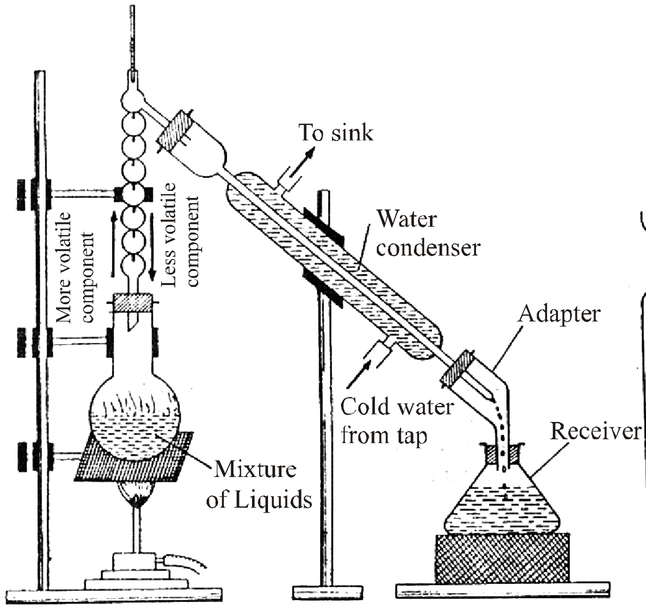
(a) Separation of benzene (B.P. 353 K) and toluene (B.P. 384 K)

(b) Separation of chlorobenzene and bromobenzene.

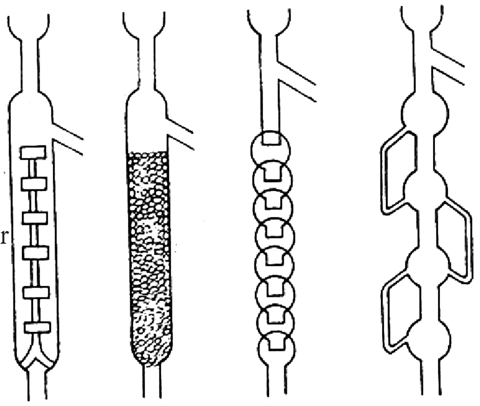
Fractional Distillation

It is employed for separating two or more volatile liquids having boiling points close to each other eg. acetone (bpt 60ºC) and methanol (bpt 65ºC). The vapours of the liquids pass through the fractionating column which provides greater space for their cooling. The vapours of high boiling fractions condense and fall back into distillation flask. The process is repeated till fractions of high volatility go up followed by of lower volatility. They are collected separately.

This method of distillation is applied for the separation of the mixture in which the components have a small difference in boiling points. In this method, the distillation flask is fitted with a large fractionating column having a large number of bulbs to increase the surface area as shown in figures (a) and (b). Cold water is circulated in the outer jacket of the condenser. On heating the flask, liquid vapourises and the vapours rise up the column. The vapours of less volatile component condense back in the flask while the vapours of only more volatile component escape from the top of fractionating column, condensed and collected in a receiver. For example, Separation of acetone and benzene from their mixture. As the difference in boiling points of acetone (329 K) and benzene (353K) is only 24 K, their mixture can be separated by the process of fractional distillation using fractionating column.



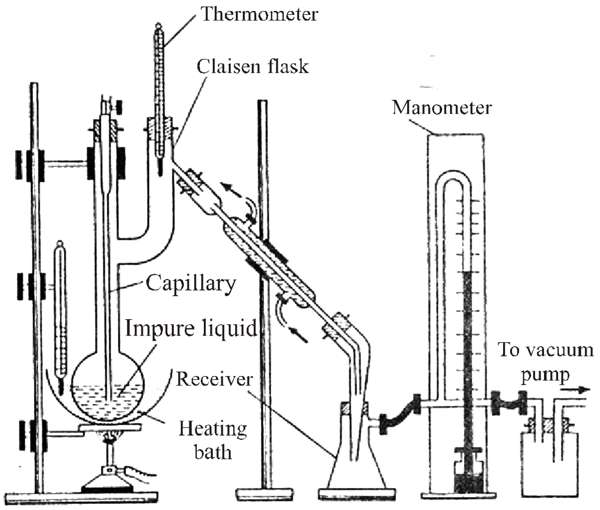
(a). Fractional distillation.



(b). Shapes of fractionating columns.

Vacuum Distillation or Distillation Under Reduced Pressure

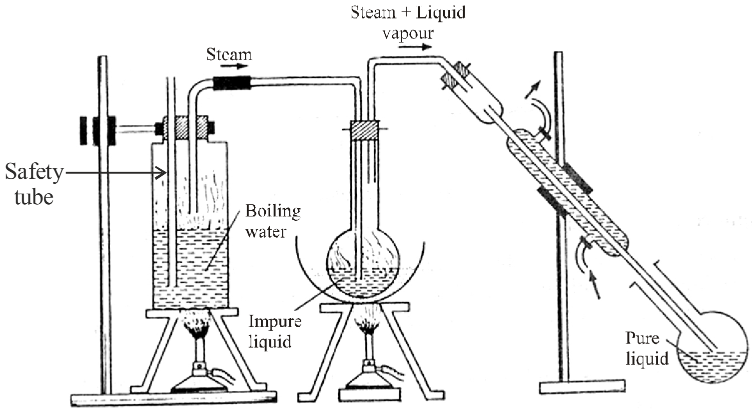
This technique of distillation is applied to liquids which decompose on heating to their boiling point. We know that the boiling point of a liquid varies with atmospheric pressure i.e., at reduced pressure the boiling point of liquid is also reduced and thus liquid distils at low temperature. The apparatus involves a vacuum pump connected with receiver as shown in figure to carryout distillation under reduced pressure. For example, glycerol is distilled at reduced pressure as it decomposes on heating to its boiling point.



Distillation under reduced pressure.

Steam Distillation

This is a convenient method for the separation and purification of organic compounds (solid or liquid) from non-volatile organic or inorganic impurities. This method is applicable to only those compounds which are *volatile in* steam, insoluble in water, possess a vapour pressure of about 10 – 15 mm of Hg at 373 K and contain non-volatile impurities. Some of the compounds which can be purified by this process are essential oils, oils, nitrobenzene, chlorobenzene, etc.



Steam distillation apparatus

The principle of steam distillation is based on Dalton's law of partial pressures. In steam distillation, a mixture of water and an organic liquid is heated by steam as shown in figure. The mixture boils when the combined vapour pressure of water (p_1) and that of the organic liquid (p_2) is equal to the atmospheric pressure (P) i.e.

$$P = p_1 + p_2$$

Evidently, the boiling temperature of the mixture would be lower than the boiling temperature of pure organic liquid and decomposition of organic compound is avoided.

The apparatus involves a steam generator connected to distillation flask. When steam passes through the impure organic compound the mixture starts boiling when the combined vapour pressure becomes equal to atmospheric pressure. At this temperature the vapours of the volatile liquid mixed with steam rise up and condense in condenser. The distillate contains the desired substance and water which can be easily separated with the help of a separating funnel to recover organic substance.

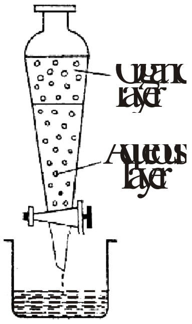
Differential Extraction

This method is applicable to recover one of the components from aqueous solution of the mixture by extracting the mixture with a suitable solvent. The solvent should be immiscible with water but should dissolve one of the components of the mixture.

The aqueous solution of the mixture is taken in a separating funnel as shown in figure. It is mixed with a small quantity of organic solvent and its contents are shaken well and then the funnel is allowed to stand for sometime. On standing, organic liquid forms a separate layer from aqueous layer. The two layers are collected separately by opening the stop cork. The extraction is further repeated with more quantity of organic solvent. Greater the number of extractions, more will be the amount of substance extracted. For example

(a) Extraction of nicotine from aqueous solution of tea leaves using ether.

(b) Extraction of benzoic acid from aqueous solution using benzene.



Chromatography

This technique was first discovered by a Russian botanist, Tswett in 1906. It is used for the separation of complex organic substances (solids, liquids or gases) such as amino acids, sugars, vitamins, hormones and plant pigments.

The technique depends on the distribution of the mixture between two phases, one fixed and the other mobile (moving). The fixed phase may be an adsorbent column (a solid chemical compound) or a paper strip. The moving phase may be a liquid or a gas. The mixture to be separated is dissolved in the moving phase and passed over the fixed phase.

Adsorption chromatography : The fixed phase is a solid e.g., alumina, magnesium oxide, silica gel, etc., and mobile phase is a liquid. Different constituents are adsorbed at different parts of the adsorbent, the component which has maximum adsorption affinity for the adsorbent is adsorbed at the nearest starting point and the component having minimum affinity is adsorbed at the farthest point of the adsorbent. Thus different bands, zones or chromatograms are formed at different parts of the column. The adsorbed components are then extracted (eluted) with the help of a suitable solvent.

Thin layer chromatography (TLC) : This is a particular case of adsorption chromatography in which a thin layer of adsorbent is coated on a glass plate.

Retardation factor (R_f value) : The relative adsorption of each component of the mixture is expressed in terms of its R_f value

$$R_f = \frac{\text{Distance travelled by the substance from base line(x)}}{\text{Distance travelled by the solvent from baseline } (v)}$$

Partition chromatography: Here the fixed phase may be solid or liquid strongly adsorbed on a solid support while the mobile phase is liquid. Paper chromatography is a special case of adsorption chromatography in which adsorbent column is a paper strip (solid).

QUALITATIVE ANALYSIS

The elements present in organic compounds are C and H. In addition to these, they may also contain O, N, S, halogens and P.

Detection of C and H: They are detected by heating the compound with copper (II) oxide. C is oxidised to CO_2 and H to H_2O. CO_2 turns lime water milky, while water formed turn white anhydrous $CuSO_4$ to blue hydrated $CuSO_4 : 5H_2O$

$$C + 2CuO \xrightarrow{\Delta} 2\,Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

$$\underset{\text{white}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{blue}}{CuSO_4.5H_2O}$$

Detection of other elements

Preparation of Lassaigne's extract : N, S, halogens and P are detected by Lassaigne's test. The elements present in organic compounds are converted to ionic form by fusing with Na-metal. The reactions involved are:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX \quad (X = Cl, Br, I)$$

They are extracted from fused mass by boiling with distilled water. The extract is known as sodium fusion extract (Lassaigne's extract).

(i) Test for N : The extract is boiled with $FeSO_4$ and then acidified with conc. H_2SO_4. Prussian blue colour confirms presence of nitrogen.

$$6\,CN^- + Fe^{2+} \longrightarrow \left[Fe(CN)_6\right]^{4-}$$

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{(prussian blue)}}{Fe_4\left[Fe(CN)_6\right]_3 . xH_2O}$$

But if sulphur is also present along with nitrogen one gets blood red colouration due to formation of ferric thiocyanate.

$$Na + C + S + N \longrightarrow NaSCN$$

$$Fe^{3+} + 2NaSCN \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)_3]^{2+}} + 3Na^+$$

(ii) Test for S:

(a) To extract, add CH_3COOH and lead acetate. A black ppt of PbS confirms S.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{\text{black}}{PbS\downarrow}$$

(b) Take small portion of Lassaigne's extract and add few drops of sodium nitroprusside solution, a violet colouration is obtained which fades away on standing.

$$2Na + S \longrightarrow Na_2S\,;$$

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{violet color}}{Na_4[Fe(CN)_5NOS]}$$

(iii) Test for halogens : The extract is acidified with HNO_3 and then treated with $AgNO_3$. A white ppt, soluble in NH_4OH indicates the presence of Cl. A yellowish ppt, sparingly soluble in NH_4OH indicates the presence of Br. A yellow ppt, insoluble in NH_4OH indicates the presence of I

$$X^- + Ag^+ \longrightarrow AgX\,(X = Cl, Br, I)$$

If N or S is also present, then extract is first boiled with conc. HNO_3 to decompose CN^- and S^{2-} (they would otherwise interfere with $AgNO_3$ test for halogens).

(iv) Test for P : Phosphorus is detected by fusing the organic compound with an oxidising agent like Na_2O_2 .P in the compound is oxidised to PO_4^{3-} which is then extracted with water. The solution is boiled with HNO_3 and then treated with ammonium molybdate. A yellow coloured ppt indicates presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3\,NaNO_3$$

$$5Na_2O_2 + 2\,P \longrightarrow 2\,Na_3PO_4 + 2\,Na_2O$$

$$H_3PO_4 + 12\,(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{phosphomolybdate}}}{(NH_4)_3PO_4.12\,MoO_3} + 21\,NH_4NO_3 + 12H_2O$$

QUANTITATIVE ANALYSIS

The percentage composition of elements present in an organic compound is determined in following ways:

Carbon and Hydrogen

A known mass of an organic compound is burnt in presence of excess of O_2 and CuO, when C and H are oxidised to CO_2 and H_2O. Let mass of organic compound be 'W' g, mass of H_2O and CO_2 produced be W_1 and W_2 g. Then,

$$\text{Percentage of C} = \frac{12 \times W_2 \times 100}{44 \times W}$$

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O$$

$$\text{Percentage of H} = \frac{2 \times W_1 \times 100}{18 \times W}$$

Illustration 2 :

20 ml. of gaseous hydrocarbon was exploded with excess of oxygen in an eudiometer tube. On cooling volume was reduced by 50 ml. On further treatment with KOH solution there was further contraction of 40 ml. What is the molecular formula of hydrocarbon ?

Sol. $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$

1 vol. $\left(x + \frac{y}{4}\right)$ vol. x vol. $\frac{y}{2}$vol.

20 vol. $20\left(x + \frac{y}{4}\right)$vol. 20x vol.

CO_2 produced is 40 ml. Therefore $20x = 40 \Rightarrow x = 2$

Contraction produced on explosion and cooling $20+20\left(x+\frac{y}{4}\right)-20x$

Contraction on explosion as given in question is 50.

$$\therefore 20+20\left(x+\frac{y}{4}\right)-20x=50$$

$$20\times\frac{y}{4}=30 \qquad \therefore y=6$$

Hence formula of hydrocarbon = C_2H_6.

Nitrogen

(i) **Dumas method:** The N-containing organic compound, when heated with CuO in an atmosphere of CO_2, yields free N_2 in addition to CO_2 and H_2O.

$$C_xH_yN_2+\left(2n+\frac{y}{2}\right)CuO \rightarrow xCO_2+\frac{y}{2}H_2O+\frac{z}{2}N_2+\left(2x+\frac{y}{2}\right)Cu$$

Let mass of organic compound = Wg

Volume of nitrogen collected = V_1 mL

Room temp = T_1 K

Volume of N_2 at STP = $\frac{P_1V_1\times 273}{760\times T_1}$ (Let it be V mL)

P_1 = Atm. pressure - Aqueous tension

22400 mL N_2 at STP weighs 28 g.

VmL N_2 at STP weighs = $\frac{28\times V}{22400}$ g

$$\%\text{ of }N_2=\frac{28\times V\times 100}{22400\times W}$$

(ii) **Kjeldhal's method:** The compound is heated with conc H_2SO_4 when nitrogen gets converted to $(NH_4)_2SO_4$. The mixture is then heated with excess of NaOH. The liberated NH_3 gas is absorbed in an excess of standard solution of H_2SO_4.

$$\text{N (from compound)}+\text{conc. }H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4+2\,NaOH \xrightarrow{\Delta} Na_2SO_4+2H_2O+2NH_3$$

$$2\,NH_3+H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The volume of the acid left unused is found by titration against a standard alkali solution.

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

The difference between initial amount of acid taken and that left after reaction gives the amount of acid reacted with NH_3.

$$\%\text{ of N}=\frac{14\times M\times 2\left(V-\frac{V_1}{2}\right)}{1000}\times\frac{100}{W}$$

Where $M \rightarrow$ molarity

$V \rightarrow$ Volume of H_2SO_4 taken

$V_1 \rightarrow$ Volume of NaOH used for titration of excess of H_2SO_4

$W \rightarrow$ Mass of organic compound

$2\left(V-\frac{V_1}{2}\right) \rightarrow$ Volume of NH_3 solution

Illustration 3 :

0.4422 gm. of an organic substance was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 cc of 1N H_2SO_4. The residual acid required 65.5 cc of N/2 alkaline solution. Find the percentage of nitrogen in the compound.

Sol. M_{eq} of the acid taken = 50 × 1 = 50

M_{eq} of the acid neutralised by alkaline solution = $65.5 \times \frac{1}{2} = 32.75$

M_{eq} of the acid neutralised by ammonia

$$= 50 - 32.75 = 17.25$$

Percentage of nitrogen

$$= \frac{1.4 \times N \times V}{\text{Wt. of substance}} = \frac{1.4 \times 17.25}{0.4422} = 54.61\%$$

Halogens

Carius method: A known mass of organic compound is heated with fuming HNO_3 in presence of $AgNO_3$. C and H in the compound are oxidised to CO_2 and H_2O. The halogen present forms Ag X which is filtered, washed, dried and weighed.

Let mass of organic compound = Wg

mass of AgX formed = W_1 g

1 mol of AgX contains 1 mol of X

$$\text{mass of X in } W_1 \text{ g of Ag} = \frac{\text{atomic mass of X} \times W_1\text{g}}{\text{molecular mass of AgX}}$$

$$\% \text{ of X} = \frac{\text{at. mass of X} \times W_1 \times 100}{\text{molecular mass if AgX} \times W}$$

Sulphur

A known mass of organic compound is heated with sodium peroxide or fuming HNO_3. S in the compound is oxidised to H_2SO_4. It is precipitated as $BaSO_4$ by adding excess $BaCl_2$ solution in water.

$$C + 2O\,(\text{from } HNO_3) \xrightarrow{\Delta} CO_2$$

$$2H + O\,(\text{from } HNO_3) \xrightarrow{\Delta} H_2O$$

$$S + H_2O + 3O\,(\text{from } HNO_3) \xrightarrow{\Delta} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{(white ppt)}}{BaSO_4} + 2HCl$$

The ppt is filtered, washed, dried and weighed.

The % of S is calculated from mass of $BaSO_4$.

Let mass of organic compound taken = Wg

mass of $BaSO_4$ formed = W_1 g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g S

$$W_1 \text{ g } BaSO_4 \text{ contains } \frac{32 \times W_1}{233} \text{ g S}$$

$$\% \text{ of S} = \frac{32 \times W_1 \times 100}{233 \times W}$$

Phosphorus

A known mass of an organic compound is heated with fuming HNO_3 Carbon and hydrogen are oxidised to CO_2 and H_2O respectively while P in compound is oxidised to H_3PO_4. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4$. 12 MoO_3 by adding ammonium molybdate. The precipitate of $(NH_4)_3PO_4 \cdot 12MoO_3$ is then filtered, washed, dried and weighed.

$$C + 2\,O\,(\text{from } HNO_3) \xrightarrow{\Delta} CO_2$$

$$2H + O\,(\text{from } HNO_3) \xrightarrow{\Delta} H_2O$$

$$2P + 5O\,(\text{from } HNO_3) \xrightarrow{\Delta} P_2O_5$$

$$P_2O_5 + 3H_2O \xrightarrow{\Delta} \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

$$H_3PO_4 + 12\,(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{\Delta} (NH_4)_3PO_4.12MoO_3 + 21\,NH_4NO_3 + 12H_2O$$

Let mass of organic compound = Wg

mass of ammonium phosphomolybdate = W_1 g

Molar mass of $(NH_4)_3PO_4$. 12 MoO_3 = 1877 g

$$\% \text{ of P} = \frac{31 \times W_1 \times 100}{1877 \times W}\%$$

If P is estimated as $Mg_2P_2O_7$.

$$\% \text{ of P} = \frac{62 \times W_1 \times 100}{222 \times W}\%$$

Oxygen

% of O_2 = 100 – (sum of % of all other elements)

$$\text{Compound} \xrightarrow[N_2 \text{ gas}]{\Delta} O_2 + \text{other gaseous products.}$$

$$2C + O_2 \xrightarrow{1373\text{ K}} 2\,CO\,] \times 5 \qquad \text{... (A)}$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5\,CO_2\,] \times 2 \qquad \text{... (B)}$$

On solving (A) and (B), we find that each mole of O_2 liberated produces 2 moles of CO_2.

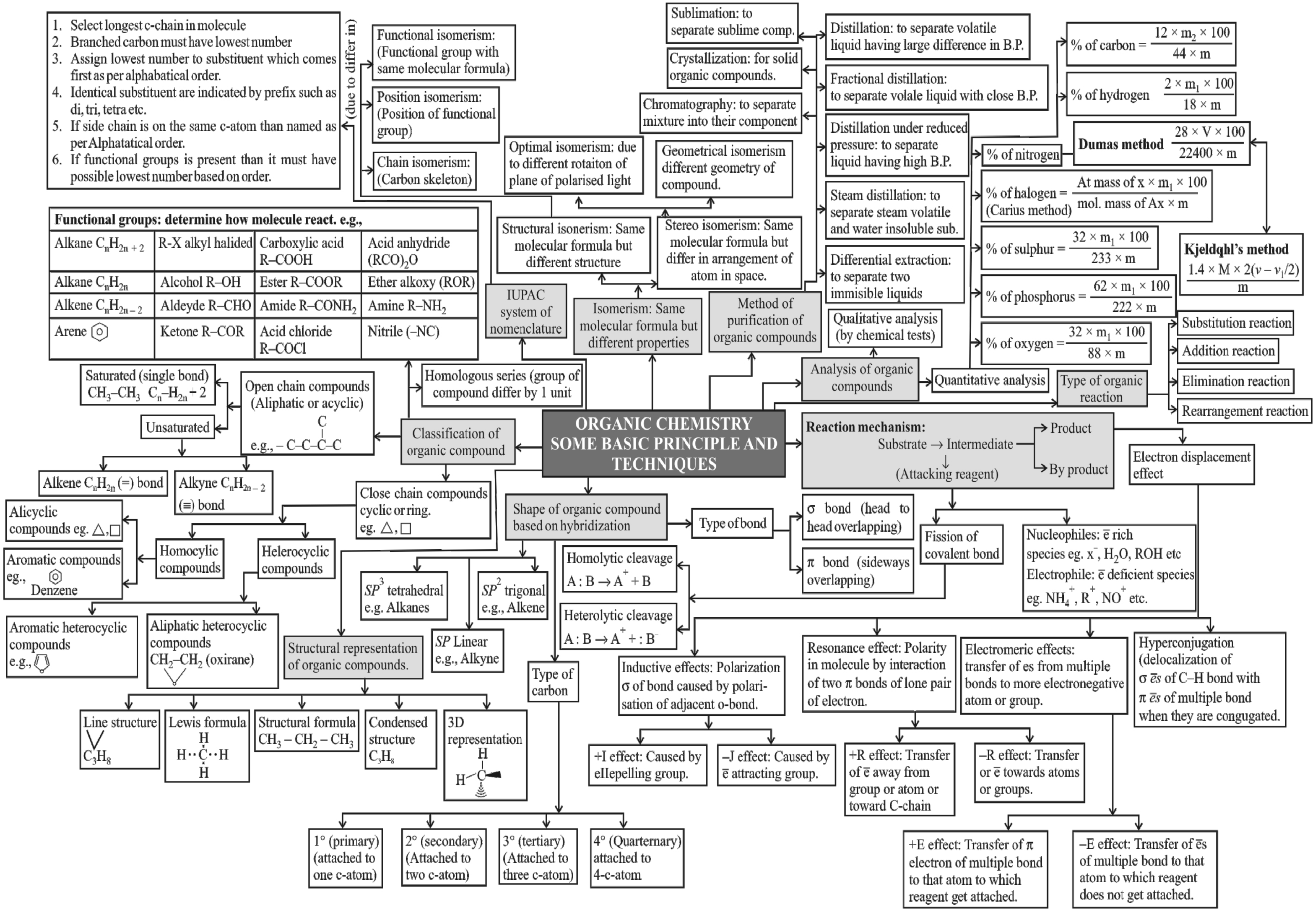
Let mass of organic compound = Wg

mass of CO_2 produced = W_1 g

$\therefore$ m_1 g of CO_2 is obtained from $\frac{32 \times W_1}{88}$ g O_2

$$\therefore \quad \% \text{ of } O_2 = \frac{32 \times W_1 \times 100}{88 \times W}\%$$

CONCEPT MAP



1. Select longest c-chain in molecule
2. Branched carbon must have lowest number
3. Assign lowest number to substituent which comes first as per alphabatical order.
4. Identical substituent are indicated by prefix such as di, tri, tetra etc.
5. If side chain is on the same c-atom than named as per Alphatatical order.
6. If functional groups is present than it must have possible lowest number based on order.

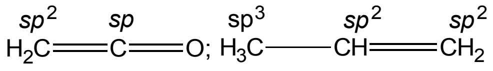
Functional groups: determine how molecule react. e.g.,

Alkane C_nH_{2n+2}	R-X alkyl halided	Carboxylic acid R–COOH	Acid anhydride $(RCO)_2O$
Alkane C_nH_{2n}	Alcohol R–OH	Ester R–COOR	Ether alkoxy (ROR)
Alkene C_nH_{2n-2}	Aldeyde R–CHO	Amide R–$CONH_2$	Amine R–NH_2
Arene ⌬	Ketone R–COR	Acid chloride R–COCl	Nitrile (–NC)

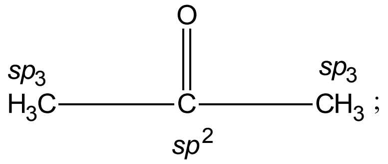
Textbook Exercises

12.1 What are hybridisation states of each carbon atom in the following compounds?
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6.

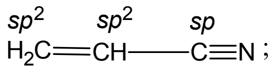
Ans.



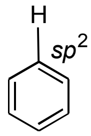
$\overset{sp^2}{H_2C}=\overset{sp}{C}=O$; $\overset{sp^3}{H_3C}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$



$\overset{sp_3}{H_3C}-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-\overset{sp_3}{CH_3}$;



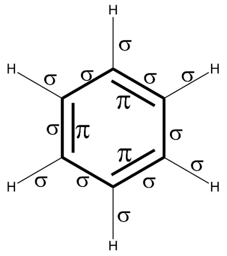
$\overset{sp^2}{H_2C}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv N$;



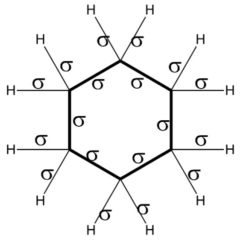
Each C is sp^2 hybridized

12.2 Indicate the σ– and π–bonds in the molecules:
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$

Ans. (i) C_6H_6 (ii) C_6H_{12}

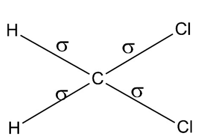


12 σ-bonds
3π-bonds

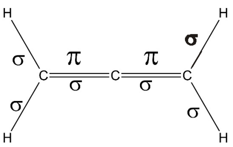


18 σ-bonds
0π-bonds

(iii) CH_2Cl_2 (iv) $CH_2=C=CH_2$

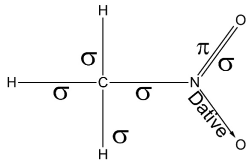


4 σ-bonds
0π-bonds

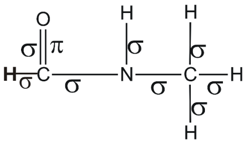


6 σ-bonds
2π-bonds

(v) CH_3NO_2 (vi) $HCONHCH_3$



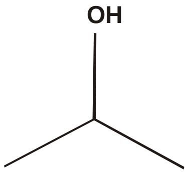
5 σ-bonds
1π-bond



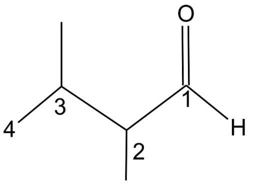
8 σ-bonds
1π-bond

12.3 Write bond line formulas for : Isopropyl alcohol, 2, 3-Dimethyl butanal, Heptan-4-one.

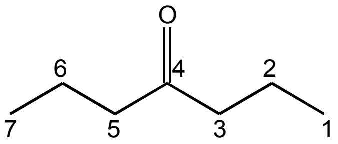
Ans.



Isopropyl alcohol ;



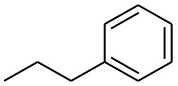
2, 3-Dimethylbutanal ;



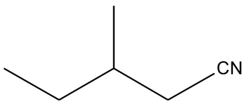
Heptan-4-one

12.4 Give the IUPAC names of the following compounds:

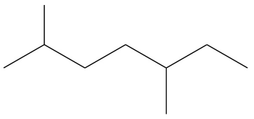
(a)



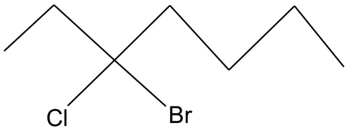
(b)



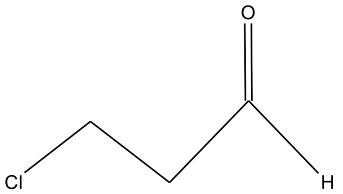
(c)



(d)



(e)



(f) Cl_2CHCH_2OH

Ans. (a) Propylbenzene
(b) 3–Methylpentanenitrile
(c) 2,5–Dimethylheptane
(d) 3–Bromo–3–chloroheptane
(e) 3–Chloropropanal
(f) 2, 2–Dichloroethanol

12.5 Which of the following represents the correct IUPAC name

for the compounds concerned?

(a) 2, 2–Dimethylpentane or 2–Dimethylpentane
(b) 2,4,7–Trimethyloctane or 2, 5, 7–Trimethyloctane
(c) 2–Chloro–4–methylpentane or 4–Chloro–2–methylpentane
(d) But–3–yn–1–ol or But –4–ol–1–yne.

Ans. (a) 2, 2 Dimethylpentane
(b) 2,4,7–Trimethyloctane.2,4, 7–locant set sum is lower than 2, 5, 7.
(c) 2–Chloro–4–methylpentane. Alphabetical order of substituents.
(d) But–3–yn–1–ol. Lower locant for principal functional group, i.e., alcohol.

12.6 Draw formulas for the first five members of each homologous series beginning with the following compounds.

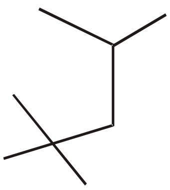
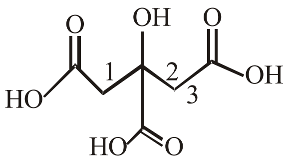
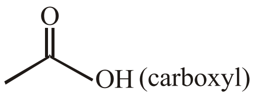
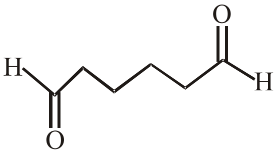
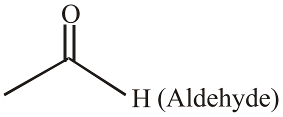
(a) H – COOH (b) CH_3COCH_3
(c) CH_2=CH_2

Ans. (a) HCOOH,CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH_2COOH$, $CH_3CH_2CH_2CH_2COOH$
(b) CH_3COCH_3,$CH_3CH_2COCH_3$, $CH_3CH_2CH_2COCH_3$, $CH_3CH_2CH_2CH_2COCH_3$, $CH_3CH_2CH_2CH_2CH_2COCH_3$
(c) CH_2=CH_2,CH_3CH=CH_2,CH_3CH_2CH=CH_2, $CH_3CH_2CH_2CH$=CH_2, $CH_3CH_2CH_2CH_2CH$=CH_2

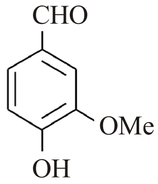
12.7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for:

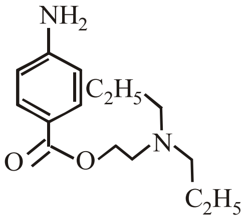
(a) 2,2,4–Trimethylpentane
(b) 2–Hydroxy–1,2,3–propanetricarboxylic acid
(c) Hexanedial

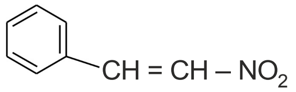
Ans.

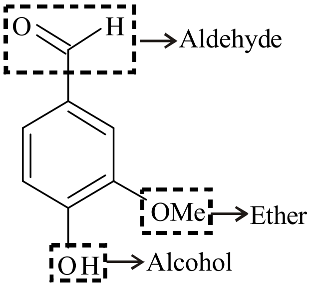
Condensed	Bond line	Functional Group
(a) $(CH_3)_3CCH_2CH(CH_3)_2$		–
(b) $HOOCCH_2CH(OH)COOH–CH_2COOH$		 and—OH (hydroxy)
(b) $OHC(CH_2)_4CHO$		

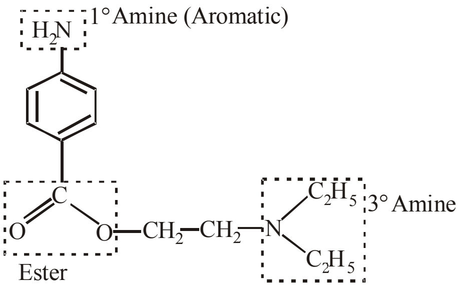
12.8 Identify the functional groups in the following compounds :

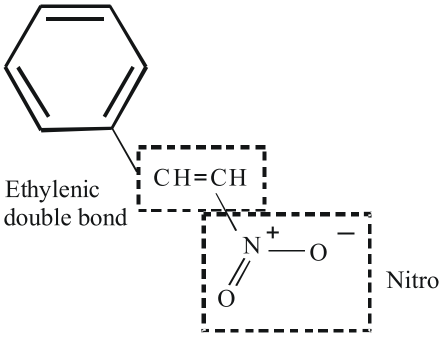
(a)


(b)


(c)


Ans. (a)


(b)


(c)


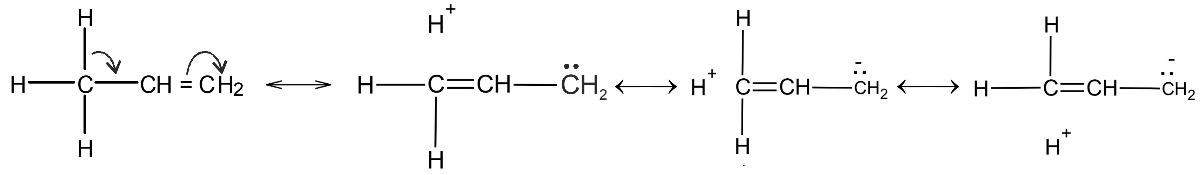
12.9 Which is expected to be more stable,

$O_2NCH_2\,CH_2O^-$ or $CH_3CH_2O^-$ and why?

Ans. $O_2N \longleftarrow CH_2 \longleftarrow CH_2 \longleftarrow O^-$ is more stable than $CH_3 \longrightarrow CH_2 \longrightarrow O^-$ because NO_2 group has –I effect and hence it tends to disperse the –ve charge on the O-atom. In contrast, CH_3CH_2 has +I effect. It therefore, tends to intensify the –ve charge and hence destabilizes it.

12.10 Explain why alkyl groups act as electron donors when attached to a π-system.

Ans. Due to hyper conjugation, alkyl group acts as electron donors when attached to π -system as shown below:

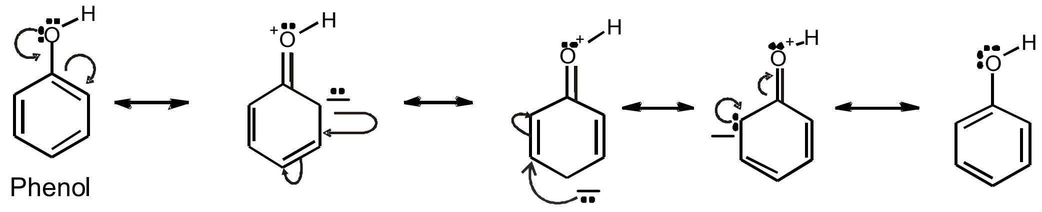


12.11 Draw the resonance structures for the following compounds. Show the electron shift using curved - arrow notation.

(a) C_6H_5OH **(b)** $C_6H_5NO_2$ **(c)** $CH_3\,CH=CHCHO$

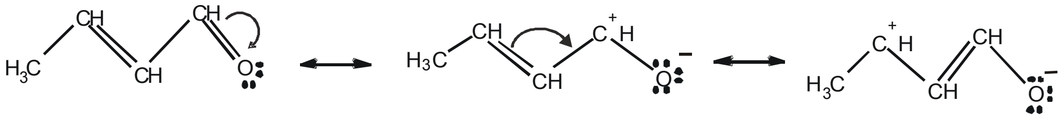
(d) C_6H_5-CHO **(e)** $C_6H_5-\overset{+}{C}H_2$ **(f)** $CH_3CH=CH\overset{+}{C}H_2$

Ans. (a)



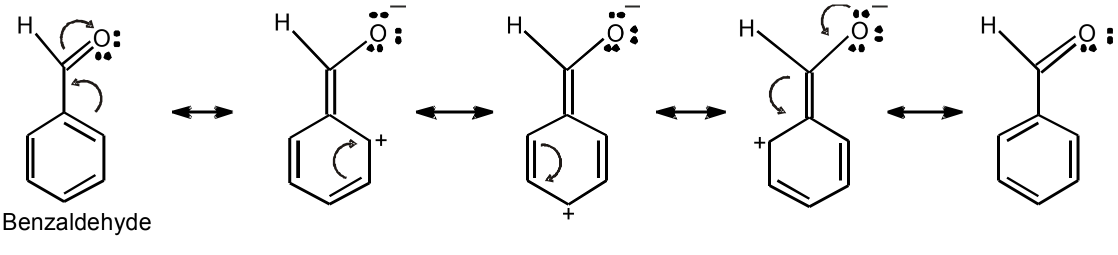
(b) Refer theory

(c)

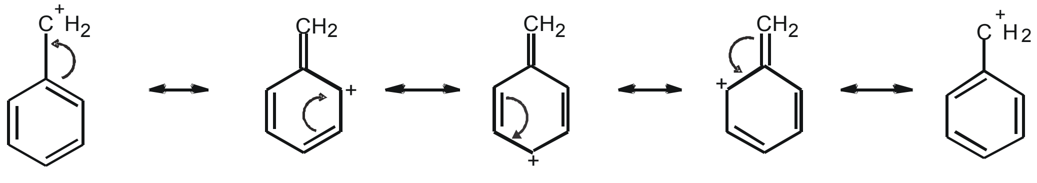


But-2-en-1-al

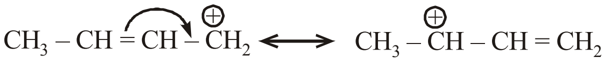
(d)



(e)



(f)



$$CH_3-CH=CH-\overset{\oplus}{C}H_2 \longleftrightarrow CH_3-\overset{\oplus}{C}H-CH=CH_2$$

12.12 What are electrophiles and nucleophiles? Explain with examples.

Ans. Refer theory

12.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles

(a) $CH_3COOH+HO^- \longrightarrow CH_3COO^-+H_2O$

(b) $CH_3COCH_3+{}^-CN \longrightarrow (CH_3)_2C(CN)(OH)$

(c) $C_6H_5+CH_3\overset{+}{C}O \longrightarrow C_6H_5COCH_3$

Ans. Nucleophiles: (a) and (b) and Electrophile: (c).

12.14 Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

(b) $(CH_3)_2C = CH_2 + HCl \longrightarrow (CH_3)_2CCl{-}CH_3$

(c) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O + Br^-$

(d) $(CH_3)_3C{-}CH_2OH + HBr \longrightarrow (CH_3)_2CBr\,CH_2CH_3 + H_2O$

Ans. (a) Nucleophilic substitution

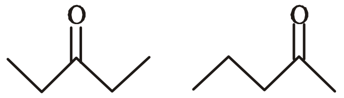
(b) Electrophilic addition

(c) Elimination

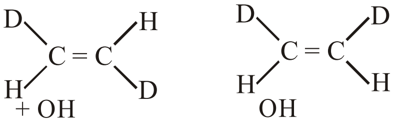
(d) Nucleophilic substitution with rearrangement.

12.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors?

(a)



(b)



(c)

Ans. (a) Structural isomers (actually position isomers as well as metamers)

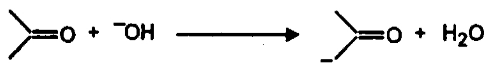
(b) geometrical isomers

(c) resonance contributors because they differ in the position of electrons but not atoms.

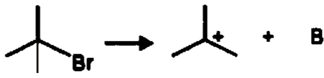
12.16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$

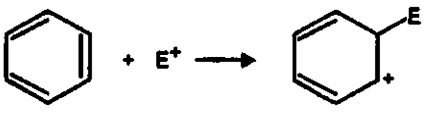
(b)



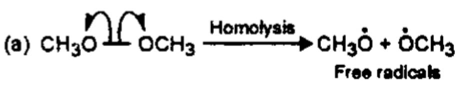
(c)

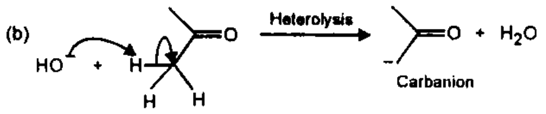


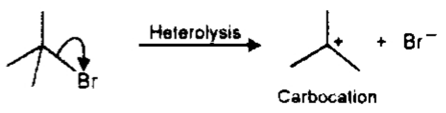
(d)

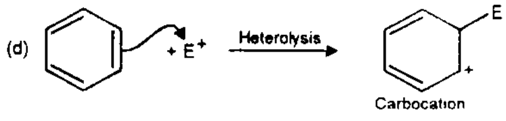


Ans









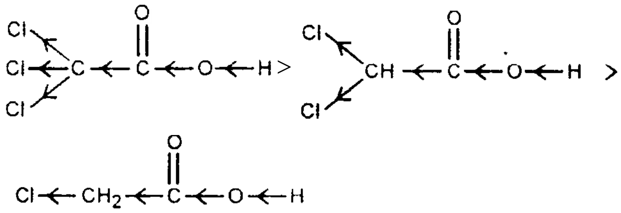
12.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids ?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

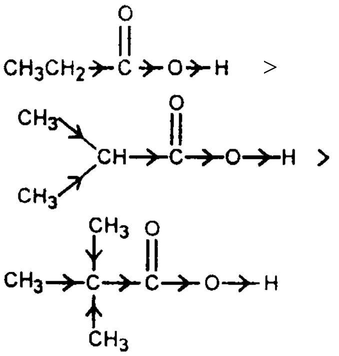
Ans. Refer theory

(a) -I-effect as shown below :



As the number of halogen atoms decreases, the overall –I effect decreases and the acid strength decreases accordingly,

(b) +I–effect as shown below :



As the number of alkyl groups increases, the + I-effect increases and the acid strength decreases accordingly.

12.18 Give a brief description of the principles of the following techniques taking an example in each case :

(a) Crystallisation

(b) Distillation

(c) Chromatography

Ans. Refer theory

12.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Ans. Refer theory

12.20 What is the difference between distillation, distillation under reduced pressure and steam distillation?

Ans. Refer theory

12.21 Discuss the Chemistry of Lassaigne's test.

Ans. During fusion, carbon and nitrogen of the organic compound combine to form sodium cyanide.

$$\underset{\text{(From organic compound)}}{Na+C+N} \longrightarrow \underset{\text{Sodium cyanide}}{NaCN}$$

On heating the filtrate with ferrous sulphate solution, sodium ferrocyanide, i.e. sodium hexacyanoferrate(II) is formed and at the same time some Fe^{2+} ions are oxidized to Fe^{3+} ions. These Fe^{3+} ions then react with sodium hexacyanoferrate (II) to produce iron(III) hexacyanoferrate(II) which is Prussian blue in colour.

$$2NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Fe(CN)_2$$
$$Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$$
$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12Na^+$$

If nitrogen and Sulphur both are present, they may combine during fusion to form sodium thiocyanate due to insufficient sodium. This when heated with ferrous sulphate produces a blood red coloration due to ferric thiocyanate.

$$Na + C + N + S \rightarrow NaSCN$$
$$Fe^{3+} + 3NaSCN \longrightarrow \underset{\text{Blood red coloration}}{Fe(SCN)_3} + 3Na^+$$

12.22 Differentiate between the principle of estimation of nitrogen in an organic compound by
(i) Duma's method (ii) Kjeldahl's method.

Ans. Refer theory

12.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Ans. Refer theory

12.24 Explain the principle of paper chromatography.

Ans. Refer theory

12.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

Ans. Sodium extract is boiled with nitric acid to decompose NaCN and Na_2S, if present, otherwise these will react with $AgNO_3$ and hence will interfere with the test.

$$NaCN + AgNO_3 \longrightarrow NaNO_3 + AgCN \text{ (white ppt)}$$
$$Na_2S + AgNO_3 \longrightarrow 2NaNO_3 + Ag_2S \text{ (black ppt)}$$

Hence to remove them i.e. NaCN and Na_2S, HNO_3 is added.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

12.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, Sulphur and halogens.

Ans. The organic compound is fused with sodium metal to convert these elements which are present in the covalent form to ionic form.

12.27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Ans. A mixture of camphor and $CaSO_4$ can be separated by the following methods:

(i) Camphor is a sublimable solid while $CaSO_4$ is not, therefore, sublimation of mixture gives camphor on the sides of funnel while $CaSO_4$ is left in the china dish.

(ii) Camphor is soluble in organic solvents like $CHCl_3$,CCl_4 etc while $CaSO_4$ is not. Therefore, when the mixture is shaken with the solvent, camphor goes into solution while $CaSO_4$ remains as residue. It is filtered and evaporation of solvent gives camphor.

12.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Ans. In steam distillation, the mixture consisting of the organic liquid and water boils at a temperature when the sum of the vapour pressure of organic liquid (p_1) and that of water (p_2) becomes equal to the atmospheric pressure (p), i. e, $p = p_1 + p_2$. Since the vapour pressure of water around the boiling point of the mixture is quite high and that of liquid is quite low (10–15 mm), therefore, the organic liquid distils at a pressure much lower than the pressure. In other words, the organic liquid vapourizes at a temperature much lower than its normal boiling point.

12.29 Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate ? Give reason for your answer.

Ans. When CCl_4 is heated with $AgNO_3$ solution, white ppt. of AgCl will not be formed. The reason being that CCl_4 is a covalent compound, therefore, it does not ionize to give Cl^- ions needed for the formation of ppt. of Ag Cl.

12.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound ?

Ans. CO_2 is acidic in nature, therefore, it reacts with the strong base KOH to form K_2CO_3.

$$2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

The increase in the mass of U-tube containing KOH then gives the mass of CO_2 produced and from its mass the percentage of carbon in the organic compound can be estimated by using the equation % of C = 12/44 × (Mass of CO_2 formed) /(Mass of substance taken) × 100

12.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test ?

Ans. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If H_2SO_4 were used, lead acetate itself will react with H_2SO_4 to form white ppt. of lead sulphate which will interfere with the test.

$$\underset{\text{Lead acetate}}{Pb(OCOCH_3)_2} + H_2SO_4 \longrightarrow \underset{\text{(White ppt.)}}{PbSO_4\downarrow} + 2CH_3COOH$$

12.32 An organic compound contains 69% carbon and 4. 8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Ans. We know that %C = 12/44 × (Mass of CO_2 formed)/(Mass or substance taken) × 100

Substituting the values of % of C and mass of the substance taken, we have,

$$69 = \frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed} \times 100}{\text{mass of substance taken}}$$

$$\text{or Mass of } CO_2 \text{ formed} = \frac{69 \times 44 \times 0.2}{12 \times 100} = 0.506 \text{ g}$$

Similarly, % H = 2/18 × (Mass of H_2O formed)/ mass of substance taken ×100

Substituting the values of % H and the mass of substance taken, we have,

$$4.8 = \frac{2 \times \text{mass of water formed}}{18 \times 0.2} \times 100 \text{ or}$$

$$\text{mass of water formed} = \frac{4.8 \times 18 \times 0.2}{2 \times 100} = 0.0864 \text{ g}$$

12.33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Ans. **Step 1.** To determine the volume of H_2SO_4 used.

Volume of acid taken = 50 ml of 0. 5 M H_2SO_4 = 25 ml of 1 M H_2SO_4

Volume of alkali used for neutralization of excess acid = 60 ml of 0.5 M NaOH = 30 ml of 1M NaOH.

Now 1 mole of H_2SO_4 neutralizes 2 moles of NaOH

(i. e. $H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$)

30 ml of 1 M NaOH = 15 ml of 1 M H_2SO_4

∴ Volume of acid used by ammonia

= 25 – 15 = 10 ml

Step 2. To determine percentage of nitrogen.

Again 1 mole of H_2SO_4 neutralizes 2 moles of NH_3

$$\left(\text{i.e. } 2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4\right)$$

10 ml of 1 M $H_2SO_4 \equiv$ 20 ml of 1 M NH_3

But 1000 ml of 1 M NH_3 contain nitrogen = 14 g

20 ml of 1M NH_3 will contain nitrogen

= 14/1000 ×20 g

But this much amount of nitrogen is present in 0. 5 g of the organic compound.

Percentage of nitrogen = 14/1000 × 20/0.5 × 100 = 56. 0.

Alternatively, % of N can be determined by applying the following equation,

$$\%N = \frac{\begin{array}{c}1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \\ \text{Vol. of the acid used}\end{array}}{\text{Mass of substance taken}}$$

Substituting the values of all the items in the above equation, we have,

$$\%N = \frac{1.4 \times 1 \times 2 \times 10}{0.5} = 56.0$$

12.34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Ans. Here, the mass of the substance taken = 0. 3780 g

Mass of AgCl formed = 0. 5740 g

Now 1 mole of AgCl ≡ 1 g atom of Cl or

(108 + 35. 5) = 143.5 g of AgCl ≡ 35 .5 g of Cl

Applying the relation, Percentage of chlorine

$$= \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = 37.56\%$$

12.35 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

Ans. Here, the mass of the substance taken = 0. 468 g

Mass of $BaSO_4$ formed = 0. 668 g

Now 1 mole of $BaSO_4 \equiv$ 1g atom of S

or (137 + 32 + 4 × 16) = 233g of $BaSO_4 \equiv$ 32 g of S

Applying the relation, Percentage of Sulphur

$$= \frac{32}{233} \times \frac{\text{Mass of BaSO}_4\text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{32}{233} \times \frac{0.668}{0.468} \times 100 = 19.603\%$$

12.36 In the organic compound $CH_2 = CH–CH_2–CH_2–C \equiv CH$, the $C_2–C_3$ bond is the pair of hybridised orbitals involved in the formation of

(a) $sp–sp^2$ **(b) $sp – sp^3$**

(c) $sp^2 – sp^3$ **(d) $sp^3– sp^3$**

Ans. When both double and triple bonds are present, double bond is given preference while numbering the carbon chain. Thus,

$$\underset{sp^2}{\overset{1}{CH_2}} = \underset{sp^2}{\overset{2}{CH}} - \underset{sp^3}{\overset{3}{CH_2}} - \underset{sp^3}{\overset{4}{CH_2}} - \underset{sp}{\overset{5}{C}} \equiv \underset{sp}{\overset{6}{CH}}$$

∴ $C_2–C_3$ bond is formed by overlap of $sp^2 – sp^3$ orbital. Thus, option (c) is correct.

12.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ **(b) $Fe_4[Fe(CN)_6]_3$**

(c) $Fe_2[Fe(CN)_6]$ **(d) $Fe_3[Fe(CN)_6]_4$**

Ans. The prussian blue colour is due to the formation $Fe_4[Fe(CN)_6]_3$. Thus, option (b) is correct.

12.38 Which of the following carbocation is most stable ?

(a) $(CH_3)_3CC^+H_2$ **(b) $(CH_3)_3C^+$**

(c) $CH_3CH_2C^+H_2$ **(d) $CH_3C^+HCH_2CH_3$**

Ans. The order of stability of carbocation is:

3° > 2° > 1°

(a) $(CH_3)_3C - \overset{+}{C}H_2$ 1° Carbocation

(b) $(CH_3)_3C^+$ 3° Carbocation

(c) $CH_3CH_2CH_2^+$ 1° Carbocation

(d) $CH_3\,\overset{+}{C}HCH_2CH_3$ 2° Carbocation

Thus, option (b) is correct.

12.39 The best and latest technique for isolation, purification and separation of organic compounds is;

(a) Crystallisation **(b) Distillation**

(c) Sublimation **(d) Chromatography**

Ans. Chromatography. Thus, option (d) is correct.

12.40 The following reaction is classified as :

$CH_3CH_2I + KOH\,(aq) \longrightarrow CH_3CH_2OH + KI$

(a) electrophilic substitution

(b) nucleophilic substitution

(c) elimination

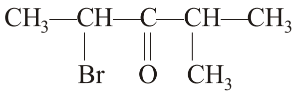
(d) addition.

Ans. This is an example of nucleophilic substitution reaction since the nucleophile $I^–$ is replaced by the nucleophile $OH^–$ ion. Thus, option (b) is correct.

Practice Questions

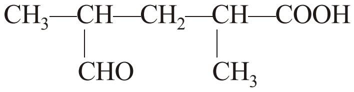
Very Short Answer Questions [1 Mark]

1. What type of isomerism is shown by butane and isobutane?
2. Write the metamer of diethyl ether. What is its IUPAC name ?
3. What is the functional group of (i) an aldehyde and (ii) a nitro compound?
4. What primary and secondary suffixes are as applied to IUPAC nomenclature?
5. Give the IUPAC name of the compound:
   $CH_2=CH-CH(CH_3)_2$
6. An organic liquid decomposes below its boiling point. How will you purify it ?
7. Two volatile compounds A and B differ in their boiling points by 15K. Suggest a suitable method for their separation.
8. How will you separate a mixture of *o*– and *p*– nitro phenols?
9. Name two methods which can be safely used to purify aniline.
10. What type of organic compounds cannot be Kjeldahlised?
11. Define the term 'elution' as applied to column chromatography.
12. Define homologous series.
13. Give the IUPAC names of the following compound:



$CH_3-\underset{Br}{\underset{|}{CH}}-\underset{O}{\underset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

14. Write the IUPAC name of

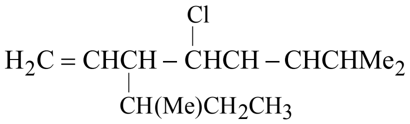


$CH_3-\underset{CHO}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-COOH$

15. Name the process of separating benzoic acid and naphthalene.
16. What is the suitable adsorbent in the process of column chromatography?
17. Which gas is liberated in Kjeldahl's method?
18. What is the value of 'x' in an organic compound with molecular formula C_xH_{12} with vapour density 42?
19. Which gas is liberated in Duma's method?
20. Why are melting point and refractive index used as the criteria of purity of organic compounds?
21. Name the gas displaced in Victor Meyer's method.
22. In order to determine the molecular mass of benzene, which method would you use?
23. Why does hydrazine not give test for Lassaigne's extract?
24. Complete the following :
    $(CH_3COO)_2\,Pb + Na_2S \rightarrow$
25. Is neopentyl radical, 4°?
26. It is advisable to prepare Lassaigne's extract in distilled water. Why?

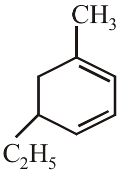
Short Answer Questions [2 & 3 Marks]

1. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible ?
2. Arrange the following:
   (i) $-NO_2$, $-COOH$, $-F$, $-CN$, $-I$, in increasing order of–I effect.
   (ii) $-CH_3$, $-D$, $-C(CH_3)_3$, $-CH(CH_3)_2$, $-CH_2CH_3$ in decreasing order of +I effect.
3. What do you mean by (i) Homolytic fission (ii) Heterolytic fission.
4. What are carboanions? Discuss their types.
5. Explain the relative stabilities of primary, secondary and tertiary free radicals.
6. Arrange the following:
   (i) $C_6H_5\dot{C}HCH_3$, $C_6H_5CHCH=CH_2$, $C_6H_5CH_2\dot{C}H_2$, $C_6H_5\dot{C}(CH_3)_2$ in order of increasing stability.
   (ii) $CH_3CH_2^+$, $C_6H_5CH_2^+$, $(CH_3)_3C^+$, $CH_2=CHCH_2^+$ in order of decreasing stability.
   (iii) $HC\equiv C^-$, $CH_2=CH^-$, $CH_3CH_2^-$, CH_3^-, $(CH_3)_2CH^-$, $C_6H_5CH_2^-$ in order of increasing stability.
7. What are carbocations (carbonium ion)? Discuss their types.
8. What are free radicals ? Discuss their types.
9. Give IUPAC names for
   (i) $CH_3-CH=C(NO_2)\,CH_2CH_3$
   (ii)



$H_2C=\underset{CH(Me)CH_2CH_3}{\underset{|}{CH}}CH-\overset{Cl}{\overset{|}{C}}HCH-CHCHMe_2$

   (iii)



   (iv) $(H_2C=CH)_2\,CHCH_2CH=CHCH_3$
10. Write the condensed structural formula of
    (i) 4-ethyl-3-methyl heptane
    (ii) 3, 3-dimethyl octane
11. Write the structural formula of
    (i) *o*-methoxyethylbenzene
    (ii) 2,3-dibromo-1-phenylpentane
    (iii) 4-ethyl-1-fluoro-2-nitrobenzene
12. In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 of AgBr. Find the percentage of bromine in the compound.
13. An alcohol with no carbon-carbon double bond has the formula C_4H_8O. What are the possible structures?
14. How does (i) an electron with drawing group (EWG) and (ii) an electron donating group (EDG) influence the acid strength of carboxylic end?
15. Draw all possible isomers for a compound with molecular formula C_8H_{10} containing benzene ring. Also, give IUPAC name to these isomers.
16. An aliphatic amine has a molecular mass of 59. Draw all its possible isomers.
17. Which of the following species behaves as (i) a nucleophile, (ii) an electrophile, (iii) both, or (iv) neither?

    $:\!\ddot{\underset{\cdot\cdot}{I}}\!:^-$ $H_3N:$, $BeCl_2$, NO_2^+, $CH_3C\equiv N:$, H_2, $H_2C=\ddot{C}:$, CH_4
18. Explain why an organic liquid vapourizes at a temperature below its boiling point in its steam distillation?

19. What type of compounds are purified by sublimation?

20. How will you separate iodine from sodium chloride?

21. What are the advantages of using the chromatography method over other methods of separation?

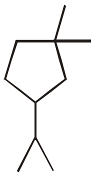
Long Answer Questions [5 Marks]

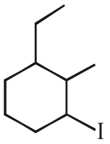
1. What are reaction intermediates ? How are they generated by bond fission ?

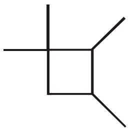
2. (i) Select electrophiles out of the following:
H^+, Na^+, Cl^-, C_2H_5OH, $AlCl_3$, SO_3, CN^-, $CH_3CH_2^+$,: CCl_2, R–X

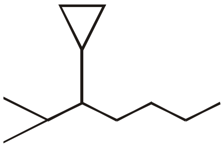
(ii) Select nucleophiles from the following: BF_3, NH_3, ^-OH, R–X, C_2H_5OH.

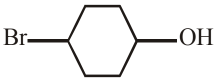
3. Name each of the following :

(i) 

(ii) 

(iii) 

(iv) 

(v) 

4. Draw all possible isomers of a compound with molecular formula, $C_4H_{10}O$. Classify them as chain and position isomers.

5. (i) On combustion, 0.3650 g of compound (A) gave 0.88 g CO_2 and 0.495 g H_2O. Further, 0.1186 g of the same compound gave, on combustion by Dumas' method, 20 ml of nitrogen measured at 27°C and 779 mm Hg pressure. (Aqueous tension at 27°C = 19 mm Hg). What is the percentage composition of the compound?

(ii) A 3.87 mg sample of organic compound give 5.80 mg CO_2 and 1.58 mg H_2O on combustion. What is the percentage composition of this compound? The organic compound contains only C, H and O.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Can we estimate oxygen in an organic compound? **[HOTS]**

2. Lassaigne's test is not shown by diazonium salts. Why? **[HOTS]**

3. Why do carbocations undergo a variety of reactions ? **[HOTS]**

4. A student was given the compound $H_2N - C_6H_4 - SO_3H$ for elemental analysis. While performing Lassaigne's test for N, what colour will he get and why? **[HOTS]**

5. Write the structural formula of the compound 4-formyl -3-methylbutanoic acid. **[HOTS]**

Short Answer Questions [2 & 3 Marks]

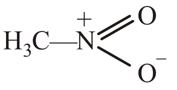
1. Suggest a method to purify:

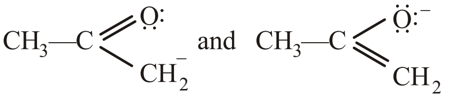
(i) Camphor containing traces of common salt.

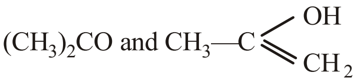
(ii) Kerosene oil containing water.

(iii) A liquid which decomposes at its boiling point. **[HOTS]**

2. Which of the following pairs of structures do not constitute resonance structures?

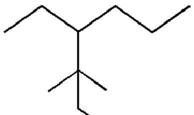
(a) 
$H_3C—\overset{+}{N}(=O)—O^-$ and $H_3C—O—N=O$

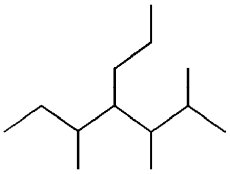
(b) 
$CH_3—C(=\ddot{O}:)—\overset{-}{C}H_2$ and $CH_3—C(—\ddot{O}:^-)=CH_2$

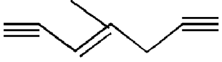
(c) 
$(CH_3)_2CO$ and $CH_3—C(OH)=CH_2$

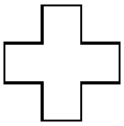
(d) $CH_3CH=CHCH_3$ and $CH_3CH_2CH=CH_2$ **[HOTS]**

3. Give IUPAC names for the following compounds.

(*a*) 

(*b*) 

(*c*) 

(*d*)  **[HOTS]**

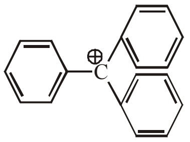
4. Pick up the species which can act as **[HOTS]**

(*a*) both *i.e.* electrophile as well as nucleophile and

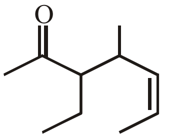
(*b*) neither electrophile or nucleophile.

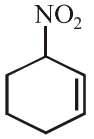
H^+, H_2, H_2O, Cl^+, Cl^-, Cr^{3+}, CH_4, NO_2^+, $BeCl_2$, CH_2O, $CH_3CH=CH_2$, $SnCl_4$, CH_3CN, SiF_4 **(3 marks)**

5. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation. **[Exemplar]**



6. Name the compounds whose line formulae are given below: **[Exemplar]**

(i) 

(ii) 

7. Identify the most stable species in the following set of ions giving reasons: **[Exemplar]**

(i) $\overset{+}{C}H_3, \overset{+}{C}H_2Br, \overset{+}{C}HBr_2, \overset{+}{C}Br_3$

(ii) $\overset{\ominus}{C}H_3, \overset{\ominus}{C}H_2Cl, \overset{\ominus}{C}HCl_2, \overset{\ominus}{C}Cl_3$

8. Why does SO_3 act as an electrophile? **[Exemplar]**

9. In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons. **[Exemplar]**

10. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability. **[Exemplar]**

11. Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaignes extract (L.E.) independently by the fusion of the compound with sodium metal. then they added solid $FeSO_4$ and dilute sulphuric acid to a part of Lassaigne's extract. Manish and Rajni obtained prussian blue colour but Ramesh got red colour. Ramesh repeated the test with the same Lassigne's extract, but again got red colour only. They were surprised and went to their teacher and told him about their observation. Teacher asked them to think over the reason for this. Can you help them by giving the reason for this observation. Also, write the chemical equations to explain the formation of compounds of different colours. **[Exemplar]**

Long Answer Questions [5 Marks]

1. 0.25g of an organic compound containing carbon, hydrogen and oxygen was analysed by the combustion method. The increase in mass of calcium chloride tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.1837g respectively. Calculate the percentage composition of the compound. **[HOTS]**

2. (*a*) Give structures of all the C_5H_{11} alkyl groups and identify them as primary, secondary, or tertiary alkyl groups.

(*b*) Give the structure of the simplest hydrocarbon having all the four types of carbon atoms. Write down its IUPAC name too. **[HOTS]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
- ***(i) Attempt all questions***
- ***(ii) Questions 1 to 3 carry 1 mark each.***
- ***(iii) Questions 4 and 5 carry 2 marks each.***
- ***(iv) Question 6 carry 3 marks***
- ***(v) Question 7 carry 5 marks***

1. Categorise the following species as electrophiles or nucleophiles

HS^-, BF_3, ROH

2. Give reaction for test of sulphur with sodium nitroprusside in organic compound.

3. Write the aci-form of nitro methane.

4. What is the role of

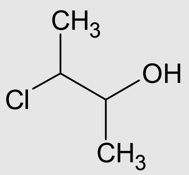
(a) K_2SO_4 in Kjeldahl solution during digestion.

(b) Dil. HNO_3 in Lassaigne's extract.

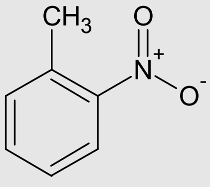
5. Write the resonance structures of $CH_2 = CH–CHO$ and arrange them in order of decreasing stability.

6. Give IUPAC names of

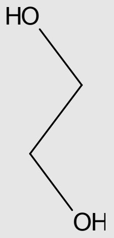
(a)



(b)



(c)



7. (i) 0.30g of an organic compound gave 50 cc of nitrogen collected at 300K and 715 mm pressure in Duma's method. Calculate the percentage of nitrogen in the compound.(Vapour pressure of water at 300K is 15 mm).

(ii) Is benzyl carbocation is *o*, *p*– directing or *m*–directing. Prove it with resonance diagram.

Solutions

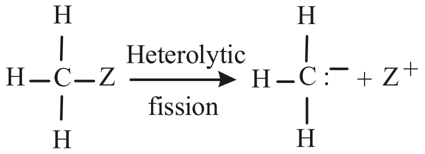
PRACTICE QUESTIONS

Very Short Answer Questions

1. Chain or nuclear isomerism.
2. 1-Methoxypropane, $CH_3OCH_2CH_2CH_3$ or 2-methoxypropane, $CH_3\text{-}OCH(CH_3)_2$.
3. (i) –CHO (II) $-NO_2$
4. The primary suffix indicates whether the carbon chain is saturated or unsaturated while the secondary suffix indicates the functional group present in the molecule.
5. 3-Methylbut-l-ene.
6. Distillation under reduced pressure, i. e., vacuum distillation.
7. By fractional distillation.
8. *o*–nitro phenol is steam volatile while *p*–nitro phenol is not and hence these can be separated by steam distillation.
9. Vacuum distillation and steam distillation.
10. Compounds containing nitrogen atom in the ring and those compounds in which nitrogen is directly linked either to oxygen or to another nitrogen atom such as in nitro ($-NO_2$) and azo (–N = N) compounds.
11. It is the process of extraction of different compounds adsorbed on the column by means of a suitable solvent called eluent.
12. Refer theory
13. 2-Bromo-4-methylpentan-3-one.
14. 2, 4-dimethyl-5-oxopentanoic acid.
15. Fractional crystallisation using benzene as a solvent.
16. Al_2O_3 (alumina).
17. Ammonia gas (NH_3).
18. V.D. is 42, Mol. wt. = 2 × V.D. = 2 × 42 = 84 therefore, molecular formula is C_6H_{12}.
19. N_2.
20. Every pure substance has fixed melting point and refractive index. Impurities reduce the melting point and change refractive index.
21. Air.
22. Victor-Meyer's method because it is volatile liquid.
23. It does not contain carbon, therefore, it is not an organic compound.
24. $(CH_3COO)_2Pb + Na_2S \rightarrow \underset{\text{(black ppt.)}}{PbS} + 2CH_3COONa$
25. No. It is 1°.
26. Tap water usually contains dissolved chlorine which gives test for halogens.

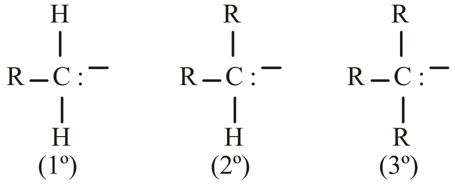
Short Answer Questions

1. Four: 1, 1–dichloropropane ($CH_3CH_2CHCl_2$), 1, 2–dichloropropane ($CH_3CHClCH_2Cl$), 2, 2–dichloropropane ($CH_3CCl_2CH_3$) and 1, 3–dichloropropane ($ClCH_2CH_2CH_2Cl$).
2. (i) $-NO_2 > -CN > -COOH > -F > -I$
   (ii) $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > -D$.
3. Refer theory
4. Carbanion is defined as a group of atoms in which a carbon atom carries a negative charge. For example, when group Z attached to the carbon leaves without electron pair, the methyl anion (carbanion) is formed Carbanions are unstable and highly reactive species.



$$H_3C{-}Z \xrightarrow[\text{fission}]{\text{Heterolytic}} H_3C:^- + Z^+$$

Types of carboanions. Carbanions are of three types namely primary (1°), secondary (2°) and tertiary (3°) carbanions.

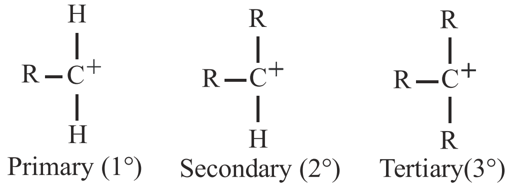


5. Refer theory
6. (i) $C_6H_5CH_2\dot{C}H_2 < C_6H_5\dot{C}HCH_3 < C_6H_5\dot{C}(CH_3)_2 < C_6H_5\dot{C}H{-}CH{=}CH_2$.
   (ii) $(CH_3)_3C^+ > C_6H_5CH_2^+ > CH_2=CHCH_2^+ > CH_3CH_2^+$
   (iii) $(CH_3)_2CH^- < CH_3CH_2^- < CH_3^- < CH_2=CH^- < C_6H_5CH_2^- < HC \equiv C^-$.
7. Carbocation is defined as the group of atoms in which a carbon atom carries a positive charge i. e., has only six electrons in its valence shell. For example, in the heterolytic fission of a carbon halogen bond in alkyl halides an alkyl carbocation is formed.

$$CH_3Cl \longrightarrow CH_3^+ + Cl^-$$

Types of carbocations

Carbocations are classified as primary (1°, secondary (2°) and tertiary (3°)

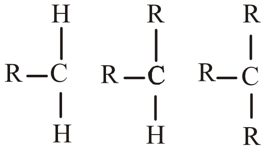


On the basis of number of alkyl groups present on central carbon atom. Carbocations are short lived and highly reactive species as they have a strong tendency to complete their octet.

8. Free radical is defined as an atom or group of atoms having an odd or unpaired electron. Due to the presence of unpaired electron, free radicals are paramagnetic in character. Free radicals are highly reactive and short lived due to their tendency to pair up the odd electron. Free radicals are formed due to the homolytic fission of covalent bond by the effect of heat or UV light.

$$R{-}X \xrightarrow{\text{HeatLight}} \dot{R} + \dot{X}$$

Types of Free radicals. Free radicals are classified as primary (1°), secondary (2°) and tertiary (3°) free radicals depending upon whether the carbon carrying the odd electron is primary, secondary or tertiary respectively.



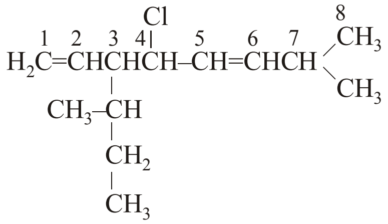
$$\mathrm{R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}} \qquad \mathrm{R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}} \qquad \mathrm{R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}}$$

(1°) (2°) (3°)

The structure of free radical is planar due to sp^2 -hybridization of carbon atom carrying odd electron.

9. (i) 3-Nitro-2-pentene

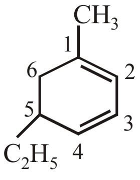
(ii)



$$\overset{1}{H_2C}=\overset{2}{C}H\overset{3}{C}H\overset{4}{C}H(Cl)-\overset{5}{C}H=\overset{6}{C}H\overset{7}{C}H(\overset{8}{CH_3})CH_3 ;\ C_3:\ CH(CH_3)CH_2CH_3$$

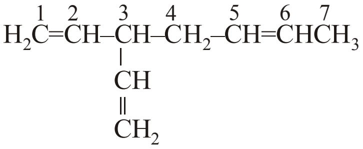
4-Chloro-3-(1-methyl propyl or sec-butyl) -7-methyl-1, 5-octadiene

(iii)



1-Methyl-5-ethylcyclohexa-1, 3-diene

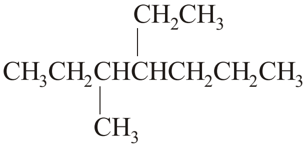
(iv)



$$\overset{1}{H_2C}=\overset{2}{C}H-\underset{\underset{\underset{CH_2}{\|}}{CH}}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H=\overset{6}{C}H\overset{7}{C}H_3$$

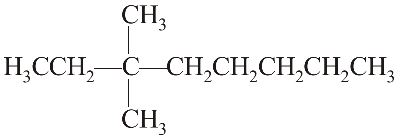
3-ethenyl (or vinyl) Hepta-1, 5-diene

10. (i)



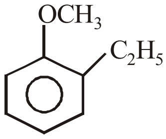
$$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

(ii)

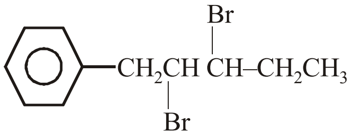


$$H_3CCH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2CH_2CH_2CH_3$$

11. (i)

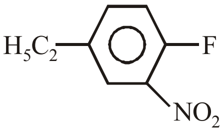


(ii)



$$C_6H_5-CH_2\underset{\underset{Br}{|}}{C}H\ \overset{\overset{Br}{|}}{C}H-CH_2CH_3$$

(iii)



12. Mass of the organic compound = 0.15 g
Mass of AgBr obtained = 0.12 g

Molecular mass of AgBr = 108 + 80
= 188 g mol^{-1}

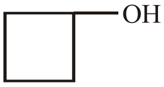
Percentage of Br

$$=\frac{(\text{at. mass of Br})}{\text{MW(AgBr)}}\times\frac{\text{mass of AgBr}}{\text{mass of org. compound}}\times 100$$

$$=\frac{80}{188}\times\frac{0.12}{0.15}\times 100 = 34.04\%$$

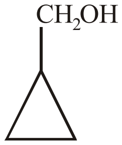
13. The possible structures of an alcohol with molecular formula, (C_4H_8O) and with no carbon-carbon double bond are

(i)



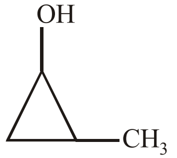
cyclobutanol

(ii)



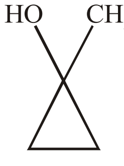
cyclopropyl methanol

(iii)



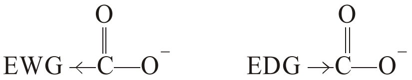
2-methyl cyclopropanol

(iv)



1-methyl cyclopropanol

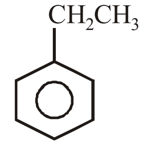
14. The influence of the inductive effect on acidity is best understood in terms of the conjugate base, $RCOO^-$, and can be summarized as follows:



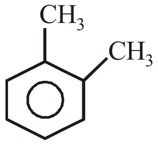
$$\text{EWG} \leftarrow \overset{\overset{O}{\|}}{C}-O^- \qquad \text{EDG} \rightarrow \overset{\overset{O}{\|}}{C}-O^-$$

(i) EWG stabilizes $RCOO^-$ and strengthens the acid	(i) EDG destabilizes $RCOO^-$ and weakens the acid.

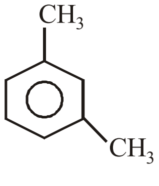
15. The possible isomers are:



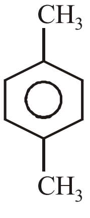
Ethyl benzene



1,2-dimethyl benzene



1,3-dimethyl benzene



1,4-dimethyl benzene

16. $C_nH_{2n+1}\ NH_2$ or $C_nH_{2n+3}N$ is the molecular formula of aliphatic amine. Molecular mass is 59.

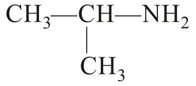
$\therefore$ $12n + 2n + 3 + 14 = 59$

$$n=\frac{59-17}{14}=\frac{42}{14}=3$$

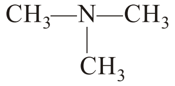
Thus, the molecular formula is C_3H_9N.

The possible isomers are:

(i) $CH_3—CH_2—CH_2—NH_2$

(ii) 
$CH_3—\underset{\underset{CH_3}{|}}{CH}—NH_2$

(iii) $CH_3—CH_2NHCH_3$

(iv) 
$CH_3—\underset{\underset{CH_3}{|}}{N}—CH_3$

17. (i) Nucleophiles : $:\ddot{\underset{..}{I}}:^{-}$, $H_3N:$

(ii) Electrophiles : $BeCl_2$ (Be has vacant π-atomic orbital available) and NO_2^+ (the electrophilic character completely masks the potential nucleophilic behaviour of the unshared electron-pairs on the O's).

(iii) *Both :* $CH_3C\equiv N:$, $H_2C=\ddot{C}:$, since C in each of these species is π-bonded to an electrophilic site. The electronegative N and O also have unshared e^--pairs and are the nucleophilic sites.

(iv) Neither : CH_4, H_2.

18. Refer theory

19. Substances whose vapour pressures become equal to the atmospheric pressure much below their melting points.

20. Either by sublimation or by extraction with CCl_4 followed by evaporation.

21. Advantages of using chromatography over other methods of separation are as follows:

(i) It is used to separate the complex mixture of substances.

(ii) It is also used in biology to separate the plant pigments.

(iii) It is more accurate and efficient.

Long Answer Questions

1. The highly reactive species formed from the reactants during the reaction are called reaction intermediates. The moment these are formed in the reaction, they get consumed. The high reactivity of reaction intermediates is due to the fact that these are charged species and moreover have incomplete octet. These are (i) free radicals (ii) carbocations (iii) carbanions.

Generation of reaction intermediates

(i) Free radicals. Refer short ans. 8

(ii) Carbocations. Refer short ans. 7

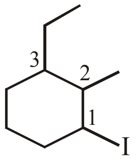
(iii) Carbanions. Refer short ans. 4

2. (i) H^+, Na^+, $AlCl_3$, SO_3, $CH_3CH_2^+$: CCl_2, R–X.

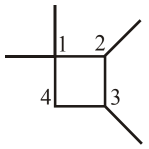
In $SO_3, O=\overset{\overset{O}{\|}}{S}—O^-$, S atom carries a positive charge and hence acts as an electrophile. In $AlCl_3$, Al atom has six and in: CCl_2, C atom has six electrons in the valence shell and hence each one of these needs two more electrons to complete their respective octets. As a result, both $AlCl_3$ and: CCl_2 act as electrophiles. In R–X, due to greater electro negativity of X, R carries a partial positive charge and hence acts as an electrophile.

(ii) NH_3, ^-OH, C_2H_5OH.

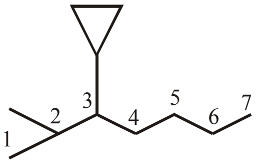
3. (i) 1, 1-Dimethyl-3-isopropylcyclopentane

(ii) 

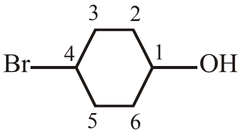
3-Ethyl-1-iodo-2-methyl cyclohexane

(iii) 

1, 1, 2, 3-tetramethyl cyclobutane

(iv) 

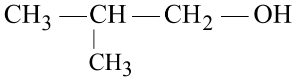
3-cyclopropyl-2-methly heptane

(v) 

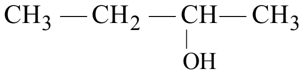
4-Bromo cyclohexanol

4. (i) $CH_3—CH_2—CH_2—CH_2—OH$

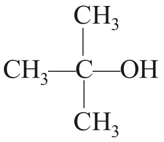
Butanol-1

(ii) 
$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—OH$

2-methyl propanol-1

(iii) 
$CH_3—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3$

Butanol-2

(iv) 
$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—OH$

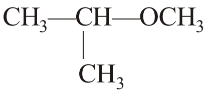
2-methyl propanol-2

(v) $CH_3—CH_2—O—CH—CH_3$

Ethoxy ethane

(vi) $CH_3—CH_2—CH_2—O—CH_3$

Methoxy propane

(vii) 
$CH_3—\underset{\underset{CH_3}{|}}{CH}—OCH_3$

2-methoxy propane

Chain isomers: [I and II], [III and IV]

Position isomers : [I and III], [II and IV]

and [VI and VII]

5. (i) Calculation of percentage of C and H mass of organic compound = 0.3650 g

mass of CO_2 = 0.88 g

mass of H_2O = 0.495 g

$$\%C=\frac{12x}{44w}\times100=\frac{12\times0.88}{44\times0.3650}\times100$$
$$=65.75\%$$

$$\%H=\frac{2y}{18w}\times100=\frac{2\times0.495}{18\times0.3650}\times100$$
$$=15.07\%.$$

Calculation of percentage of nitrogen
$T=27+273=300\,K$ $w=0.1186\,g$
P of dry gas $=779-19=760$ mm Hg
V at 300 K $=20$ ml
V of N_2 of STP

$$=\frac{760\text{mm Hg}\times20\text{ml}\times273\text{K}}{760\text{mmHg}\times300\text{K}}$$
$=18.2$ ml

$$\%N=\frac{28\times V_{STP}}{22,400\times w}\times100$$

$$\frac{28\times18.2\times100}{22,400\times0.1186}=19.18\%.$$

(ii) Mass of organic compound = 3.87 mg
mass of carbon dioxide = 5.80 mg
mass of water = 1.58 mg

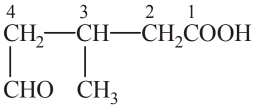
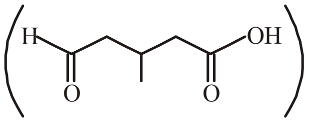
$$\%C=\frac{12x}{44w}.100=\frac{12\times5.80\text{mg}}{44\times3.87\text{mg}}\times100$$
$$=40.87\%$$

$$\%H=\frac{2y}{12w}.100=\frac{2\times1.58\text{mg}}{18\times3.87\text{mg}}\times100$$
$$=4.54\%$$

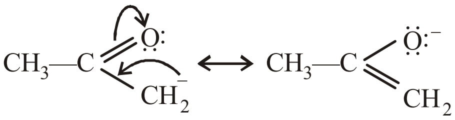
$\therefore$ % of Oxygen $=100-(40.87+4.54)$
$=54.59\%$

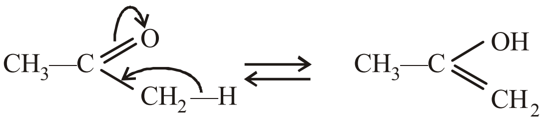
HOTS/EXEMPLAR QUESTIONS

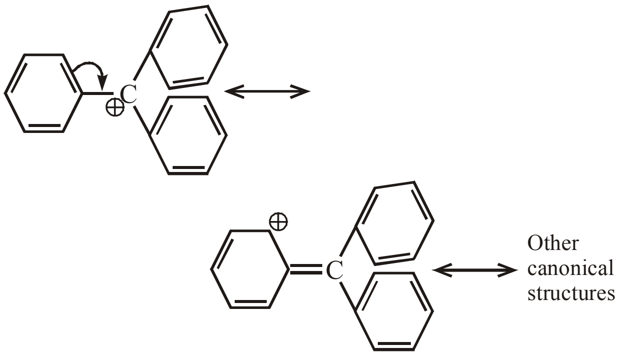
Very Short Answer Questions

1. Yes. But usually it is indirectly estimated by subtracting the percentage of all the elements present in an organic compound from 100.
2. Diazonium salts usually lose N_2 on heating much before they have a chance to react with fused sodium metal. Therefore, diazonium salts do not show positive Lassaigne's test for nitrogen.
3. Because carbocations are highly reactive species. This reactivity is due to its tendency to complete the octet of electron deficient carbon. Hence carbocations undergo a variety of reactions.
4. Blood red, because compound contains both N and S.
5. 
$\underset{CHO}{\overset{4}{C}H_2}-\underset{CH_3}{\overset{3}{C}H}-\overset{2}{C}H_2\overset{1}{C}OOH$


Short Answer Questions

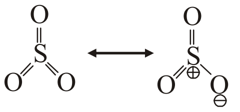
1. (i) Sublimation. Camphor sublimes while common salt remains as residue in the china dish.
(ii) Solvent extraction using a separatory funnel. The lower water layer is run off when kerosene oil is obtained. It is dried over anhydrous $CaCl_2$ and then distilled to give pure kerosene oil.
(iii) Distillation under reduced pressure.
2. (a) The two structures differ in the position of atoms and hence they are not resonance structures. In fact, these are functional isomers.
(b) 

These two are resonance structures because they differ in the position of electrons only and not atoms.
(c) These are not resonance structures since they differ in the position of atoms. They are, in fact, tautomers.


(d) These are not resonance structures since these differ in the position of double bond. In fact, these are position isomers.
3. (a) 4-Ethyl-3,3-dimethylheptane.
(b) 2,3,5-Trimethyl-4-propylheptane
(c) Hept-3-ene-1,6-diyne (-ene is written first because it comes first in alphabetic order).
(d) Cyclododecane (it is having 12 C's)
4. (a) **Both (Ambiphile).** $CH_2=\ddot{O}:$, $CH_3C\equiv N:$ (In these, C is electrophilic ; while O/N is nucleophilic).
(b) H_2, CH_4 (absence of charge, π electrons, lone pair of electrons or $\delta+$ and $\delta-$ charges).
5. Stabilised due to nine possible canonical structures.


6. (i) 3-Ethyl-4-methylheptan-5-en-2-one
(ii) 3-Nitrocyclohex-1-ene.
7. (i) $\overset{\oplus}{C}H_3$, The replacement of hydrogen by bromine increases positive charge on carbon atom and destabilises the species.

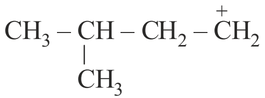
(ii) $\overset{\ominus}{C}-Cl_3$ is most stable because electro-negativity of chlorine is more than hydrogen. On replacing hydrogen by chlorine, negative charge on carbon is reduced and species is stabilised.

8. 

Three highly electronegative oxygen atoms are attached to sulphur atom. It makes sulphur atom electron deficient. Due to resonance also, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.

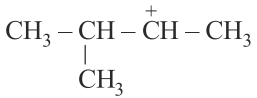
9. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in rings, azo groups and nitro groups cannot be removed as ammonia.

10. Four possible carbocations are



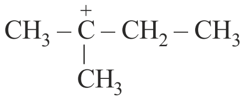
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{+}{C}H_2$

(I)



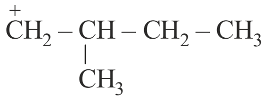
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{+}{C}H-CH_3$

(II)



$CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_2-CH_3$

(III)



$\overset{+}{C}H_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

(IV)

Order of increasing stability I < IV < II < III

11. In Lassaigne's test SCN^- ions are formed due to the presence of sulphur and nitrogen both. These give red colour with Fe^{3+} ions. This happens when fusion is not carried out in the excess of sodium. With excess of sodium the thiocyanate ion, if formed is decomposed as follows:

$$NaSCN + 2Na \rightarrow NaCN + Na_2S$$

Long Answer Questions

1. (i) Percentage of carbon.

Increase in mass of potash bulbs = 0.1837 g i.e., mass of CO_2 formed = 0.1837 g

$$\therefore \text{ Percentage of C } = \frac{12}{44}\times\frac{\text{Mass of } CO_2}{\text{Mass of compound}}\times 100 = \frac{12}{44}\times\frac{0.1837\times 100}{0.25} = 20.04$$

(ii) Percentage of hydrogen

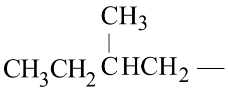
Increase in mass of calcium chloride = 0.15 g i.e. mass of water formed = 0.15 g

$$\therefore \text{ Percentage of hydrogen} = \frac{2}{18}\times\frac{\text{Mass of } H_2O}{\text{Mass of compound}}\times 100 = \frac{2}{18}\times\frac{0.15\times 100}{0.25} = 6.66$$

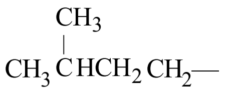
(iii) Percentage of oxygen.

Percentage of oxygen = 100 – (Percentage of C + Percentage of H) = 100 – (20.04 + 6.66) = 73.30

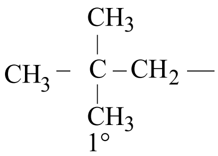
2. (a) (i) $\underset{1^\circ}{CH_3CH_2CH_2CH_2CH_2}—$

(ii) 

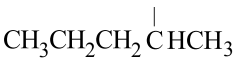
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2—$ 1°

(iii) 

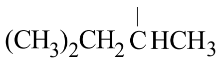
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2—$ 1°

(iv) 

$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2—$ 1°

(v) 

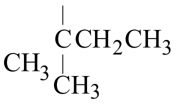
$CH_3CH_2CH_2\overset{|}{C}HCH_3$ 2°

(vi) 

$(CH_3)_2CH_2\overset{|}{C}HCH_3$ 2°

(vii) 

$CH_3CH_2\overset{|}{C}H\,CH_2CH_3$ 2°

(iv) 

$CH_3\underset{CH_3}{\underset{|}{\overset{|}{C}}}CH_2CH_3$ 3°

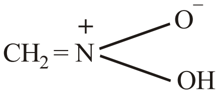
CHAPTER TEST

1. Electrophile BF_3

Nucleophiles : HS^-, ROH

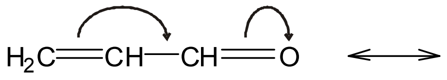
2. On heating sodium fusion extract with sodium nitroprusside appearance of a violet color further indicates the presence of sulphur.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5(NOS)]$$

3. 

4. (a) K_2SO_4 is added to increase the boiling point of H_2SO_4 so that proper digestion of solution takes place.

(b) Sodium extract is boiled with nitric acid to decompose NaCN and Na_2S, if present, otherwise these will react with $AgNO_3$ and hence will interfere with the test. Hence to remove them i.e. NaCN and Na_2S, HNO_3 is added.

5. 

I

$$\underset{\text{II}}{H_2\overset{+}{C}-CH=CH-O^{-}} \longleftrightarrow \underset{\text{III}}{H_2\overset{-}{C}-CH=CH-\overset{+}{\underset{\cdot\cdot}{O}}:}$$

Structure (I) is most stable since each C and O atom has an octet of electrons and none of these atoms carries any charge. Structures (II and III) both involve separation of charge and both are less stable than structure (I). however structure (II) is more stable than structure (III) since it carries a –ve charge on the more electronegative O atom and +ve charge on the less electronegative C atom while in structure (III) , the more electronegative O atom carries +ve charge while less electronegative C atom carries the –ve charge. Thus the decreasing order of stability is : I > II > III.

6. (a) 3–chloro butan –2–ol
(b) 1–methyl, 2–nitro benzene
(c) ethane 1,2 di–ol

7. (i) Here, mass of the substance taken is = 0.30g
Volume of nitrogen collected = 50 cc
Atmospheric pressure = 715 mm Hg
Room temperature = 300K
Vapour pressure of water at 300K = 15 mm
Actual pressure of dry gas = 715 –15 = 700 mm Hg
Step 1.To convert the volume at experimental conditions to volume at STP.

Experimental conditions	At STP
$P_1 = 700$ mm	$P_2 = 760$ mm
$V_1 = 50$ cc	$V_2 = ?$
$T_1 = 300$K	$T_2 = 273$K

Now we know that $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Substituting the values in above equation

$$\frac{700\times 50}{300} = \frac{760\times V_2}{273}$$

Hence $V_2 = \frac{273\times 700\times 50}{300\times 760} = 41.9\text{cc}$

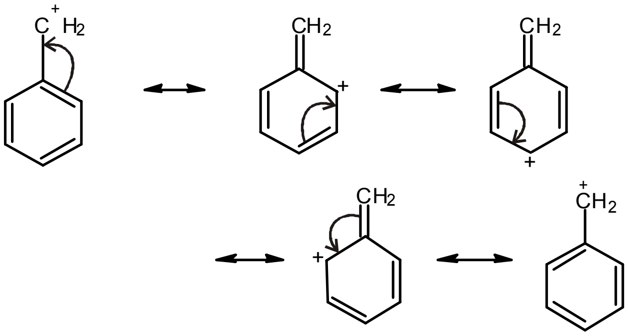
Step 2. To calculate %age of nitrogen

$$= \frac{28\times \text{Volume of } N_2 \text{ at STP} \times 100}{22400\times \text{ mass of substance taken}} = \frac{28\times 41.9\times 100}{22400\times 0.30}$$

$= 17.46\%$

(ii) Benzyl carbocation is meta directing this can be proved by observing the resonance structure given below where + charge appears on the ortho and para position of benzene ring while *m*–position has rich electron density.

Benzyl carbocation



13

Chapter

Hydrocarbons

INTRODUCTION

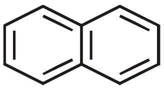
Hydrocarbons are the compounds of carbon and hydrogen. Both these elements readily undergo combustion. Therefore, hydrocarbons are the major source of fuel. The hydrocarbons have solved most of our problems. LPG (Liquefied petroleum gas) and CNG (Compressed natural gas) are extremely popular names with which every one is familiar. Another fuel, LNG (Liquid natural gas) has been developed quite recently.

All of them are obtained either directly or indirectly during the mining of petroleum as well as by carrying out its fractional distillation. Unsaturated hydrocarbons like ethylene and propylene upon polymerisation form a number of useful polymers like low density and high density polyethene, polyproprene, polystyrene etc. which have a wide range of applications. Aromatic hydrocarbons are used in the synthesis of many dyes and drugs.

CLASSIFICATION OF HYDROCARBONS

Depending upon the types of carbon-carbon bonds present, hydrocarbons are classified as

Hydrocarbons

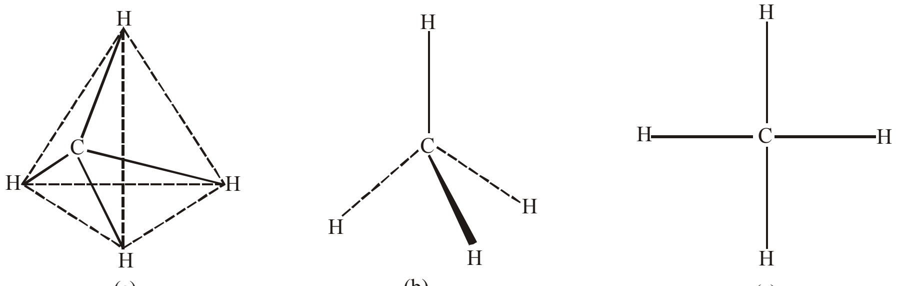
- **Acyclic or open chain hydrocarbons**
  These compounds contain open chains of carbon atoms in their molecules
  - **Saturated hydrocarbons**
    Those compounds which contain C–C and C–H single bonds.
    For example :
    C_2H_6, $CH_3CH_2CH_3$, etc.
    Ethane Propane
  - **Unsaturated hydrocarbons**
    Those compounds which contain C–C multiple bonds i.e. double bond, triple bond or both
    For example :
    $CH_3-C\equiv CH$,
    Propyne
    $CH_2=CH_2$, etc.
    Ethylene
- **Cyclic hydrocarbons**
  These compounds contain closed chains or rings of carbon atoms in their molecules
  - **Aromatic hydrocarbons**
    Hydrocarbons which contain either fused or isolated benzene rings in their molecules
    
    Benzene
    
    Naphthalene
  - **Alicyclic hydrocarbons**
    Hydrocarbons having ring of three or more carbon atoms and properties similar to aliphatic hydrocarbons.

ALKANES

They are saturated hydrocarbons containing C–C single bonds. Their general formula is C_nH_{2n+2}.
They exhibit structural and chain isomerism. All carbon atoms of alkanes are sp^3 hybridized.

Structure of Alkanes

Each carbon atom of alkanes is in sp^3 state of hydridisation with its four bonding orbitals directed towards the four corners (or vertices) of a regular tetrahedron. All the bond angles are tetrahedral angles i.e., $H-C-H$ or $H-C-C$ bond angle is 109°28′ or 109.5°. Alkane molecules are non planar because all the carbon atoms possess sp^3 hybridisation state.



(a) (b) (c)

NOMENCLATURE AND ISOMERISM IN ALKANES

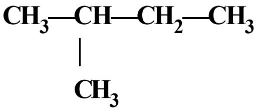
Alkanes are represented by the general formula C_nH_{2n+2} (here $n = 1, 2, 3, 4.....$ etc.). The IUPAC and common names of a few members of the family are listed:

Formula of the Compound	IUPAC name	Common name
CH_4	Methane	Methane
$CH_3—CH_3$	Ethane	Ethane
$CH_3—CH_2—CH_3$	Propane	Propane
$CH_3—CH_2—CH_2—CH_3$	Butane	*n*-Butane
$CH_3—(CH_2)_3—CH_3$	Pentane	*n*-Pentane

Illustration 1 :

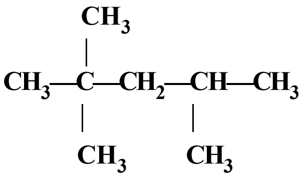
Write the IUPAC names of the following compounds.

(i)



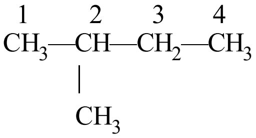
$$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CH_3$$

(ii)



$$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—\underset{\underset{CH_3}{|}}{CH}—CH_3$$

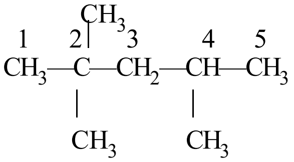
Solution: (i)



$$\overset{1}{CH_3}—\underset{\underset{CH_3}{|}}{\overset{2}{CH}}—\overset{3}{CH_2}—\overset{4}{CH_3}$$

2-Methylbutane

(ii)



$$\overset{1}{CH_3}—\overset{\overset{CH_3}{2|}}{\underset{\underset{CH_3}{|}}{C}}—\overset{3}{CH_2}—\underset{\underset{CH_3}{|}}{\overset{4}{CH}}—\overset{5}{CH_3}$$

2, 2, 4-Trimethylpentane

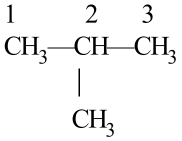
Illustration 2 :

Write the chain isomers of butane (C_4H_{10}) and pentane (C_5H_{12}). Give their IUPAC names.

Solution: Chain isomers of butane (C_4H_{10})

$CH_3—CH_2—CH_2—CH_3$

Butane



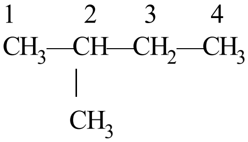
$$\overset{1}{CH_3}—\underset{\underset{CH_3}{|}}{\overset{2}{CH}}—\overset{3}{CH_3}$$

2-Methylproppane

Chain isomers of pentane (C_5H_{12})

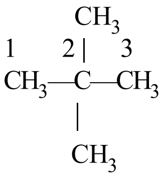
$CH_3—CH_2—CH_2—CH_2—CH_3$

Pentane



$$\overset{1}{CH_3}—\underset{\underset{CH_3}{|}}{\overset{2}{CH}}—\overset{3}{CH_2}—\overset{4}{CH_3}$$

2-Methylbutane



$$\overset{1}{CH_3}—\overset{\overset{CH_3}{2|}}{\underset{\underset{CH_3}{|}}{C}}—\overset{3}{CH_3}$$

2, 2-Dimethylpropane

Methods of Preparation

(i) From unsaturated hydrocarbons :

$$\underset{\text{Ethene}}{H_2C = CH_2} + H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{Ethene}}{H_3C — CH_3}, \quad \underset{\text{Ethyne}}{HC \equiv CH} + 2H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{Ethene}}{H_3C—CH_3}$$

Hydrogenation can also be done in presence of other catalysts like Pt or Pd.

$$\underset{\text{ethyne}}{H - C \equiv C - H} + 2H_2 \xrightarrow{\text{Ni|Pd|Pt}} \underset{\text{ethane}}{H_3C - CH_3}$$

When the catalyst is Pt or Pd, the hydrogenation proceeds smoothly at ordinary temperature and pressure. With nickel as catalyst, higher temperature (250° – 300°C) and pressure are needed. With Raney nickel, the reaction takes place at 473 – 573 K. Raney nickel is an alloy containing equal amount of Ni and Al leached with NaOH. Methane can not be prepared by this method.

(ii) From Alkyl Halides

(a) Reduction of alkyl halides :

$$\underset{\text{Alkyl halide}}{R - X} \xrightarrow{\text{Reductant}} \underset{\text{Alkane}}{R - H} + HX$$

Reductants : Zn–Cu couple/EtOH, Na–EtOH, Zn–HCl, Zn – CH_3COOH, Pt or Pd or Ni/H_2, Al–Hg/EtOH, $LiAlH_4$ etc.

Ex. : $CH_3I + Zn - Cu / \text{alcohol} \rightarrow CH_4 + H - I$

(b) Wurtz reaction :

$$R - Br + 2Na + Br - R \xrightarrow[\text{Dry Ether}]{\Delta} \underset{\text{Alkane}}{R - R} + 2NaBr$$

Ex. $CH_3 - I + 2Na + I - CH_3 \xrightarrow[\text{Ether}]{\Delta,\ \text{Dry}} \underset{\text{Ethane}}{CH_3 - CH_3} + \underset{\text{Methyl iodide}}{2NaI}$

Methane cannot be prepared by this method. The alkane produced is higher and symmetrical i.e., it contains double the number of carbon atoms present in the alkyl halide taken.

When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. The Wurtz reaction is not useful for preparing unsymmetrical alkanes.

$$C_2H_5I + CH_3I \longrightarrow C_2H_6 + C_3H_8 + C_4H_{10}$$

The separation of these alkanes is not always easy because of little difference in their boiling points.

Wurtz reaction generally fails with tertiary alkyl halides.

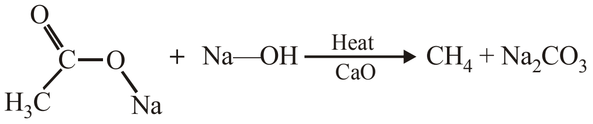
$$3^\circ \text{ halide} + \text{ base} \xrightarrow[\text{Elimination}]{} \text{alkene}$$

In presence of moist ether, the product is alcohol

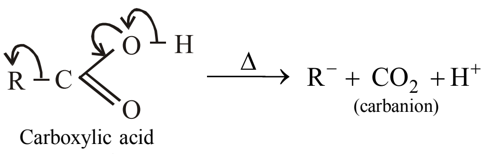
$$Na + H_2O \longrightarrow NaOH \xrightarrow{R-X} \underset{\text{alcohol}}{ROH}$$

(iii) From Carboxylic acids

(a) Decarboxylation



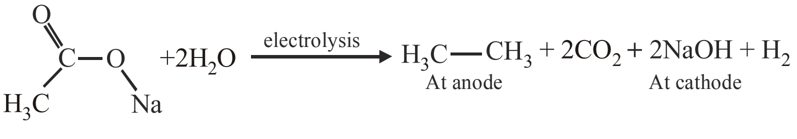
The reaction is employed for stepping down a homologous series. De-carboxylation proceeds via the formation of carbanion as follows.



Carboxylic acid

$$R^- + H^+ \longrightarrow \underset{\text{Alkane}}{RH}$$

(b) Kolbe's electrolysis



Methane cannot be prepared by this method. The side products are olefins, alcohols (particularly in alkaline solution) and esters. Presence of alkyl groups in α-position decreases the yield of alkane.

Mechanism :

$2CH_3COONa + 2H_2O \longrightarrow CH_3{-}CH_3 + 2CO_2 + 2NaOH + H_2$

$2CH_3COONa \xrightarrow{\text{Ionization}} 2CH_3COO^- + 2Na^+$

At anode :

$2CH_3COO^- \longrightarrow 2CH_3COO^{\bullet} + 2e^-$

$2CH_3COO^{\bullet} \longrightarrow 2CH_3^{\bullet} + 2CO_2$

$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6$

At cathode :

$$2H^+ + 2e^- \longrightarrow \underset{H_2(\uparrow)}{\underset{\downarrow}{[2H]}}$$

(iv) From Grignard reagent :

$RMgX \xrightarrow{Z-H} RH + Mg(Z)X$

ZH [compound containing active hydrogen]. Ex :

HOH, NH_3, $RC \equiv CH$, C_6H_5OH, CH_3COOH, RNH_2, R_2NH, Pyrrole, C_2H_5OH etc.

Ex. $C_2H_5MgI + HOH \longrightarrow C_2H_6 + Mg(OH)I$

$C_2H_5MgI + RC \equiv CH \longrightarrow C_2H_6 + Mg\,(C \equiv CR)I$

If heavy water, D_2O, is used, then the product is deuteroalkane (R – D).

$R - MgX + DOD \longrightarrow R - D + Mg(OD)X$

Physical properties :

(i) Physical State: Alkanes are colourless and odourless gases. Alkanes from $C_1 - C_4$ are gases. $C_5 - C_{17}$ are colourless liquids, C_{18} – onwards are waxy, white solids.

(ii) Boiling Points : Boiling points of alkanes are the lowest of all the groups of organic compounds. The forces of attraction among the alkane molecules are the weakest vander Waal's forces of attraction.

Among isomeric alkanes, the boiling point decreases with increasing branching.

Ex. *n*-Pentane > iso-Pentane > neo-Pentane

With the increase in branching, surface area decreases and hence intermolecular forces become weaker.

$\text{B.P} \propto \text{mol. wt.}$ (for homologous)

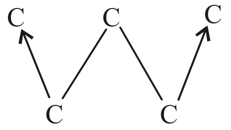
$\text{B.P} \propto \dfrac{1}{\text{lateral chain}}$ (for Isomers)

$\text{B.P} \propto$ vander Waal's forces of attraction

(iii) Melting Points

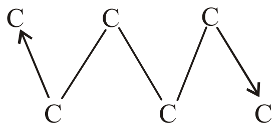
Unbranched alkanes containing even number of carbon atoms have higher melting points than the unbranched alkanes containing odd number of carbon atoms.

Ex.



n-pentane

(both methyl groups are directed on same side)



n-hexane

(both methyl group are adversely directed)

M.P. with even no. of carbon atoms > M.P. with odd no. of carbon atoms

$\text{M.P.} \propto \text{mol.wt.} \propto \text{packing efficiency.}$

(iv) Fuel Capacity : Decreasing order of fuel capacity is more branched > less branched > unbranched and lower mol.wt. > higher mol. wt.

(v) **Solubility :** Alkanes are insoluble in water. The reason is that water molecules are polar whereas alkanes are non-polar (C – C and C – H bonds are nearly purely covalent). Alkanes are soluble in non-polar solvents like benzene, ether, chloroform etc.

Chemical properties

Alkanes are chemically unreactive under ordinary conditions due to the presence of strong and non-polar C – C and C – H bonds and hence electrophilies (E^+) and nucleophilies (Nu^-) do not attack them. They do not react with acids, bases and oxidising agents. However they react with X_2 or HNO_3 when heated.

(i) Substitution reactions : Reactions in which an atom or group in a compound is replaced by another atom or group is known as substitution reaction and the product formed is known as substituted product.

(a) Halogenation :

$$R-H+X_2 \xrightarrow{h\nu} R-X+HX$$

Reactivity order of hydrogen atoms in alkanes is

$$3^o > 2^o > 1^o$$

Reactivity order of halogens is

$$F_2 > Cl_2 > Br_2 > I_2$$

Fluorine can react even in dark. Cl_2 and Br_2 require light energy. I_2 does not show any reaction at room temperature. On heating, it shows iodination.

Fluorination :

Direct-fluorination of alkanes is usually explosive.

$$CH_4+2F_2 \longrightarrow C+4HF$$

It is carried out successfully by diluting fluorine with nitrogen and carrying out the reaction in a metal tube packed with copper gauze at a temperature of 150ºC–350ºC. Product of fluorination is usually a complex mixture.

$$CH_4+F_2 \longrightarrow CH_3F+HF$$

Chlorination :

$$R-H+Cl_2 \longrightarrow \underset{\text{Alkyl chloride}}{R-Cl+HCl}$$

The monochloro derivative of alkane is obtained by taking alkane in large excess.

Ex. $\underset{\text{Ethane (Excess)}}{C_2H_6} + Cl_2 \xrightarrow{h\nu} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + HCl$

When chlorine is in excess, a mixture of mono, di, tri and tetra derivatives is obtained.

Ex. $CH_4 \xrightarrow{h\nu, Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$

Chlorination of alkanes takes place under the following conditions :

At 300ºC, in darkness.

At 100ºC, in the presence of organic peroxides.

At 150ºC, in the presence of tetra ethyl lead(TEL).

⇒ Chlorination of methane is based on free radical mechanism and it is completed in the following three steps :

(a) Chain initiating (first) step

$$Cl_2 \longrightarrow Cl^\bullet + Cl^\bullet$$

(b) Chain propagation (second) step

$$Cl^\bullet + CH_4 \longrightarrow CH_3^\bullet + HCl$$
$$CH_3^\bullet + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$$

(c) Chain terminating (third) step

$$CH_3^\bullet + {}^\bullet Cl \longrightarrow CH_3Cl$$
$$CH_3^\bullet + {}^\bullet CH_3 \longrightarrow CH_3-CH_3$$
$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$$

Bromination : Bromination of alkanes is similar to chlorination but not so vigorous.

Iodination : Iodination of alkanes is reversible.

$$CH_4+I_2 \overset{\Delta}{\rightleftharpoons} CH_3-I+HI$$

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HNO_3, HgO, etc. which destroys the HI as it is formed and so drives the reaction to the right.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Iodination of alkanes is very slow because iodine free radical is not formed (due to high activation energy)

(ii) Complete oxidation or combustion: Alkanes, when burnt is excess of air of oxygen, form carbon dioxide and water, e.g.,

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 212.8 \text{ kcal/mole}$$

The general combustion equation for any alkane is:

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

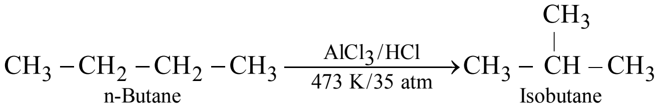
Incomplete combustion of alkanes result in the formation of carbon black which is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_4(g) + O_2(g) \xrightarrow[\text{combustion}]{\text{incomplete}} (cs) + 2H_2O(l)$$

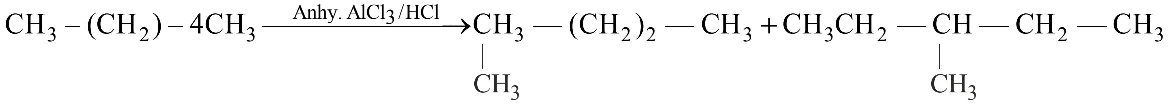
(iii) Thermal decomposition: The decomposition of a compound by heat is known as pyrolysis or cracking.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + \underset{\text{Methane}}{CH_4} \xleftarrow{675-875K} \underset{\text{Propane}}{CH_3.CH_2CH_3} \xrightarrow{675-875K} \underset{\text{Propene}}{CH_3CH = CH_2} + H_2$$

(iv) Isomerisation:- The process of conversion of one isomer of a compound to another isomer is known as isomerisation. Straight chain alkanes are converted into their branched chain isomers when heated in presence of $AlCl_3$/HCl at 300°C.

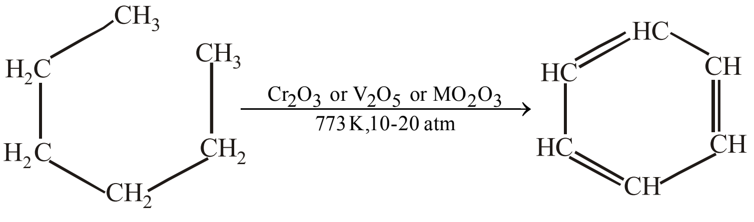


$$\underset{\text{n-Butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow[473\text{ K}/35\text{ atm}]{AlCl_3/HCl} \underset{\text{Isobutane}}{CH_3 - \overset{\overset{\large CH_3}{|}}{C}H - CH_3}$$



$$CH_3 - (CH_2) - 4CH_3 \xrightarrow{\text{Anhy. } AlCl_3/HCl} \underset{\underset{\large CH_3}{|}}{CH_3} - (CH_2)_2 - CH_3 + CH_3CH_2 - \underset{\underset{\large CH_3}{|}}{CH} - CH_2 - CH_3$$

(v) Aromatisation :- The conversion of aliphatic compound into aromatic compound is known as aromatisation or reforming. *n*-Alkanes with six or more carbon atoms are required.



n-Hexane Benzene

CONFORMATIONS OF ALKANES

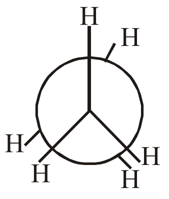
This happens due to rotation along the σ-bond. In ethane molecule, the two carbon atoms are connected by σ-bond. If one of the methyl groups in ethane molecule is kept fixed and the other is rotated about C – C bond, a large number of momentary arrangements of the hydrogen atoms on one carbon atom with respect to the hydrogen atoms of the other carbon atoms in space are obtained. Out of infinite number of possible conformations of ethane, only two extreme conformations are important.

(i) One extreme conformation will be such in which the rear methyl group is completely eclipsed by the front methyl group and thus, only the front methyl group, i.e., hydrogen atoms of the methyl group nearer to the eye is visible. Such conformation is known as eclipsed conformation.

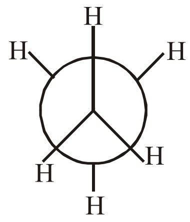
(ii) Another extreme conformation will be such in which the rear methyl group has been rotated upside down and thus both the methyl groups, i.e., all the six hydrogen atoms are visible and are as far apart from each other as possible. Such conformation is known as staggered.

(iii) The infinite number of possible intermediate conformation between the two extreme conformations are referred to as skew conformations. In these conformations, hydrogen atoms are closer than in staggered but away than in eclipsed conformation. The relative stabilities of the various conformation of ethane are in the following order.

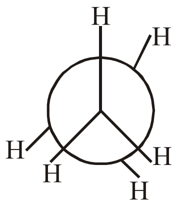
Staggered > Skew > Eclipsed



Eclipsed



Staggered

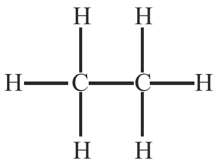


Skew

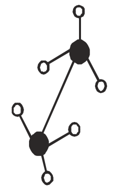
Staggered form of ethane is more stable because the e⁻ clouds of C – H bonds are as far apart as possible and thus, the repulsions are minimum. In eclipsed form, e⁻ clouds come closer thus causing increase in repulsions. Thus, staggered form is more stable than eclipsed form.

Notes : In all the confirmations, the bond angles and the bond lengths remain the same.

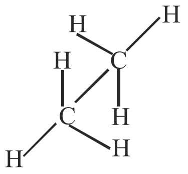
The conformations of a molecule are usually represented by the following Projections:



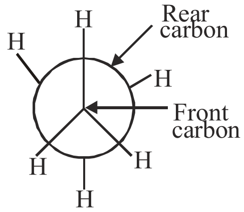
Planar projection



Ball and stick model



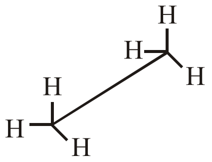
Perspective projection or Sawhorse formula



Newmann projection formula

Sawhorse and Newman Projections

(i) Sawhorse projections : In this projection, the molecule is viewed along the molecular axis.



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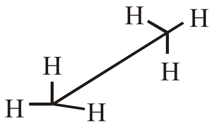
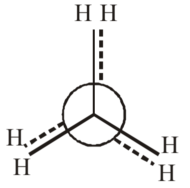


Staggered

(ii) Newman projections : In this projection, the molecule is viewed at the C – C bond head on.



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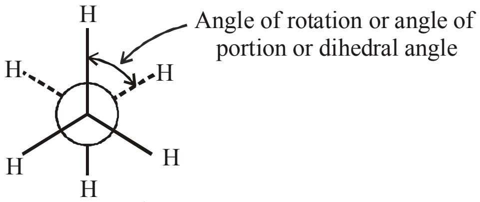


Staggered

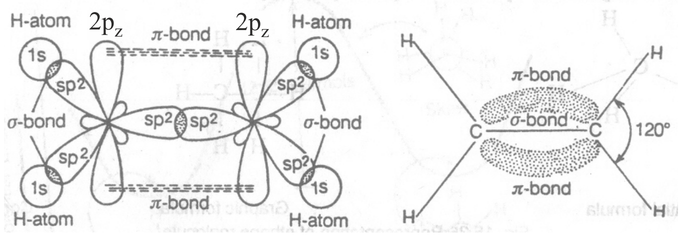
Out of these the Newman projection formulae are generally considered to be the best since eclipsing of hydrogen atoms can best represented by the Newman projection.

ALKENES

Alkenes are those unsaturated hydrocarbons which contain at least one carbon-carbon double bond (C = C) in their molecules. Their general formula is (C_nH_{2n})

Structure of Alkenes

Each of the doubly bonded carbon atom is in sp^2 hybridised state. The complete orbital picture of the formation of the ethylene can be represented as below.



NOMENCLATURE

In IUPAC system of nomenclature longest chain of carbon atoms containing double bond is selected. Numbering of the chain is done from the end which is nearest to the double bond. Suffix-ene is used in nomenclature. For example,

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

IUPAC name of the compound is But-1-ene

ISOMERISM IN ALKENES

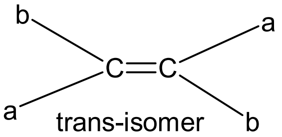
Alkenes show *chain* (1-butene and isobutene), *position* (butene –1 and butene-2) and *geometrical isomerism.*

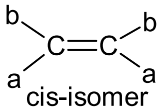
$$\underbrace{\underset{\text{Butene-1}}{CH_3CH_2CH=CH_2} \text{ and } \underset{\text{Isobutene}}{(CH_3)_2C=CH_2}}_{\text{Chain isomers}} \; ; \; \underbrace{\underset{\text{Butene-1}}{CH_3CH_2CH=CH_2} \text{ and } \underset{\text{Butene-2}}{CH_3CH=CHCH_3}}_{\text{Position isomers}}$$

Geometrical Isomerism in Alkenes: The necessary condition - for a molecule to show geometrical isomerism are

(i) the molecule must contain double bond

(ii) each of the two carbon atoms of the double bond must have different substituents which may be same or different.

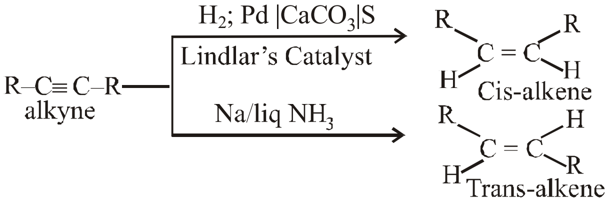




The isomer having the similar groups. I, on the same sides was called cis and the other having similar groups on the opposite sides was called *trans* and the phenomenon on the whole was known as *cis-trans*-isomerism commonly known as *geometrical isomerism*. In short, the isomers which possess the same structural formula but differ in the spatial arrangement of the groups around the double bond are known as geometrical isomers and the phenomenon is known as geometrical isomerism. Geometrical isomerism is due to the restricted rotation around the double bond. Compounds containing C = N and N = N also show geometrical isomerism.

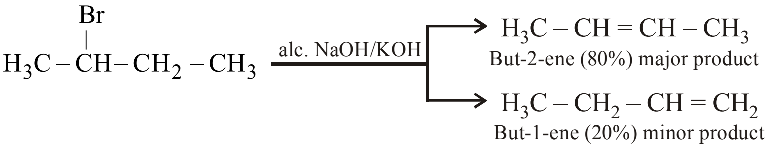
Methods of Preparation

(i) Partial reduction on alkynes



Lindlar's catalyst is a Pd supported over $CaCO_3$ or $BaSO_4$ and partially poisoned by the addition of S or quinoline.

(ii) Dehydrohalogenation of haloalkanes



$$H_3C-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2-CH_3 \xrightarrow{\text{alc. NaOH/KOH}} \begin{cases} \underset{\text{But-2-ene (80\%) major product}}{H_3C-CH=CH-CH_3} \\ \underset{\text{But-1-ene (20\%) minor product}}{H_3C-CH_2-CH=CH_2} \end{cases}$$

This reaction is also called β-elimination reaction.

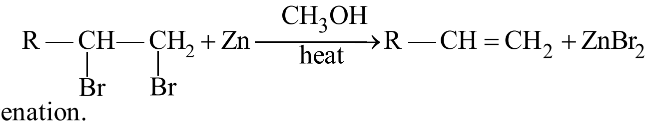
The ease of dehydrohalogenation follows the order:

Tertiary alkyl halide > sec. alkyl halide > Pri. alkyl halide.

Further the ease of dehydrohalogenation for different halogens is in the order.

Iodide > Bromide > Chloride.

(iii) From vicinal dihalides



$$R-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH_2}+Zn \xrightarrow[\text{heat}]{CH_3OH} R-CH=CH_2+ZnBr_2$$

This reaction is known as dehalogenation.

(iv) Dehydration of alcohol

Alcohols when dehydrated in presence of catalyst give alkenes.

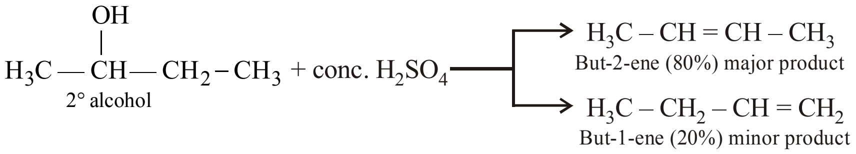
The ease of dehydration follows the following order which is evident by the conditions required for the dehydration of the three types of alcohols.

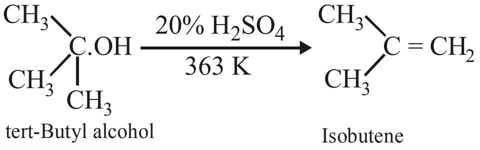
Tertiary > Secondary > Primary

$$n\text{-}CH_3.CH_2.CH_2OH \xrightarrow[413-434K]{75\%\ H_2SO_4} CH_3CH=CH_2 + H_2O$$

Propyl alcohol (a primary alcohol) 1° alcohol

Propene





Physical Properties

(i) From $C_2 - C_4$ they are colourless, odourless gases, from $C_5 - C_{17}$ they are colourless liquids, C_{18} onwards alkenes are solids. Ethylene (C_2H_4) is a sweet smelling gas.

(ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H_2O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl_4, petroleum ether., etc.

(iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond. Alkenes are therefore, less volatile than the corresponding alkanes.

Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

$$\text{MP and BP} \propto \text{mol. wt.}$$

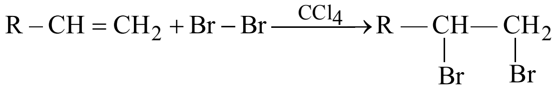
$$\propto \frac{1}{\text{branching in alkenes}}$$

Chemical Properties

(i) Addition reaction

(a) $R-CH=CH_2 + H_2 \xrightarrow[473\text{–}573\,K]{\text{Raney Ni}} R-CH_2-CH_3$

(b)

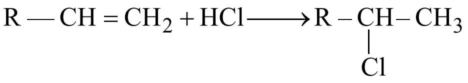


$$R-CH=CH_2 + Br-Br \xrightarrow{CCl_4} R-\underset{\substack{|\\Br}}{CH}-\underset{\substack{|\\Br}}{CH_2}$$

Vicinal Bromide

The order of reactivity for halogen addition is $Cl_2 > Br_2 > I_2$.

(c) **Markovnikov reaction :**

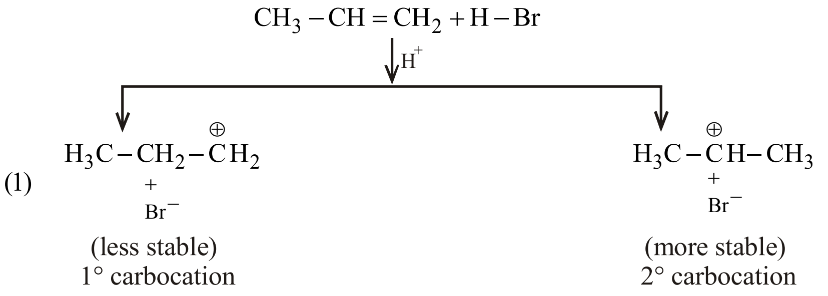


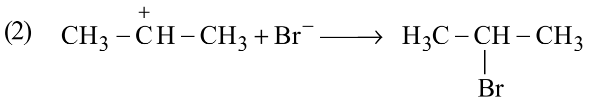
$$R-CH=CH_2 + HCl \longrightarrow R-\underset{\substack{|\\Cl}}{CH}-CH_3$$

The order of reactivity among hydrogen halides is HI > HBr > HCl > HF

In such cases addition of HX is governed by **Markovnikoff's rule** according to which *"when an unsymmetrical reagent (such as HX, H_2SO_4, HOCl, etc.) adds to an unsymmetrical alkene, then the negative (or more negative) part of the reagent is added to that carbon atom of the double bond which bears the least number of hydrogen atom (s), i.e., which bears more substituents.*

Mechanism




(2) $CH_3-\overset{+}{C}H-CH_3+Br^- \longrightarrow H_3C-\underset{\underset{Br}{|}}{C}H-CH_3$

2-Bromopropane (major)

$CH_3-CH_2-\overset{\oplus}{C}H_2+Br^- \longrightarrow CH_3CH_2CH_2Br$

1-Bromopropane (minor)

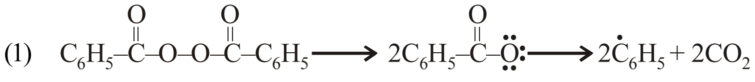
(d) Anti Markovnikov reaction : It has been observed that addition of hydrogen bromide to propene in presence of, peroxide yields mainly *n*-propyl bromide, i.e., under these conditions the reagent adds on to the olefin in a manner contrary to Markownikoff's rule.

$$R-CH=CH_2+HBr \xrightarrow{H_2O_2} R-CH_2-CH_2-Br$$

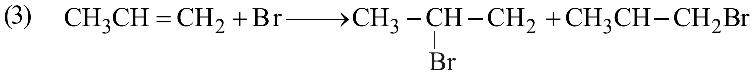
Anti markonikov's addition

It is also called Peroxide effect or Kharash effect.

Mechanism :


(1) $C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow 2C_6H_5-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}\!\!: \longrightarrow 2\dot{C}_6H_5+2CO_2$

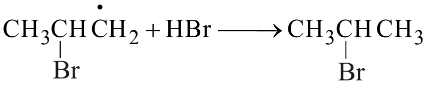
(2) $\dot{C}_6H_5+H-Br \longrightarrow C_6H_6+\dot{B}r$


(3) $CH_3CH=CH_2+\dot{B}r \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}H-\dot{C}H_2+CH_3\dot{C}H-CH_2Br$

1° free radical (less stable) 2° free radical (more stable)

(4) $CH_3\dot{C}HCH_2Br+H-Br \longrightarrow CH_3CH_2CH_2Br$

(major)

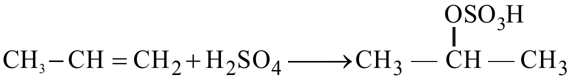

$CH_3\underset{\underset{Br}{|}}{C}H\dot{C}H_2+HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{C}HCH_3$

(minor)

(e) With Conc. H_2SO_4 :

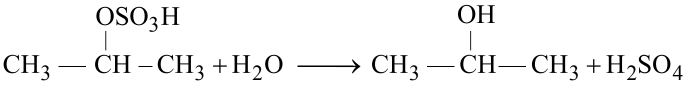
$$CH_2=CH_2+H_2SO_4 \longrightarrow CH_3CH_2HSO_4$$

Ethylene Ethyl hydrogen sulphate


$CH_3-CH=CH_2+H_2SO_4 \longrightarrow CH_3-\overset{\overset{OSO_3H}{|}}{C}H-CH_3$

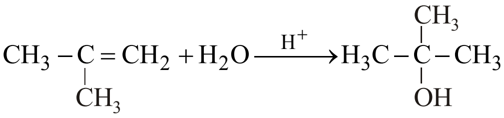
Propylene Isopropyl hydrogen sulphate

The alkyl hydrogen sulphates decompose on heating with water to give alcohols.


$CH_3-\overset{\overset{OSO_3H}{|}}{C}H-CH_3+H_2O \longrightarrow CH_3-\overset{\overset{OH}{|}}{C}H-CH_3+H_2SO_4$

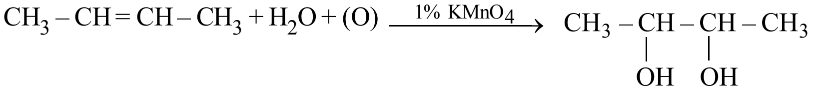
Isopropyl hydrogen sulphate Isopropyl alcohol

(f) Addition of water :

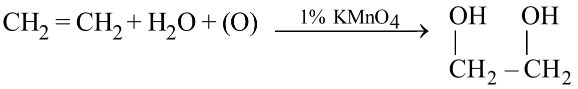

$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2+H_2O \xrightarrow{H^+} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

(ii) Oxidation:

(a) With 1% alkaline $KMnO_4$(Baeyer reagent) :


$CH_3-CH=CH-CH_3+H_2O+(O) \xrightarrow{1\%\ KMnO_4} CH_3-\underset{\underset{OH}{|}}{C}H-\underset{\underset{OH}{|}}{C}H-CH_3$

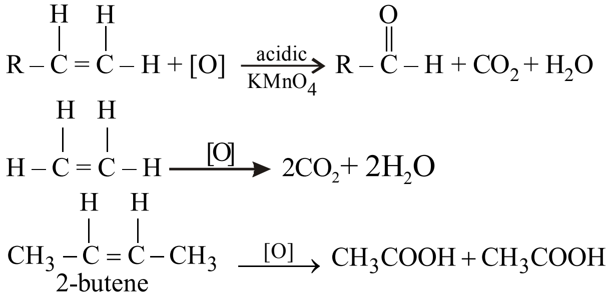
cis-glycol


$CH_2=CH_2+H_2O+(O) \xrightarrow{1\%\ KMnO_4} \overset{\overset{OH}{|}}{C}H_2-\overset{\overset{OH}{|}}{C}H_2$

Ethylene Ethylene glycol

The pink colour of $KMnO_4$ solution is discharged and a brown ppt of MnO_2 is formed. It is used as a test for the presence of unsaturation in organic compounds (Baeyer's test).

(b) With Acidic $KMnO_4$/Hot $KMnO_4$:

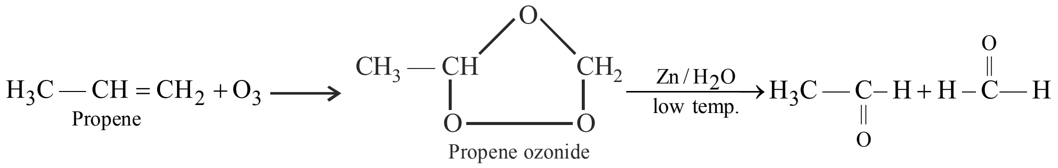


$$R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H+[O]\xrightarrow[KMnO_4]{acidic} R-\overset{O}{\overset{\|}{C}}-H+CO_2+H_2O$$

$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H\xrightarrow{[O]} 2CO_2+2H_2O$$

$$\underset{\text{2-butene}}{CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3}\xrightarrow{[O]} CH_3COOH+CH_3COOH$$

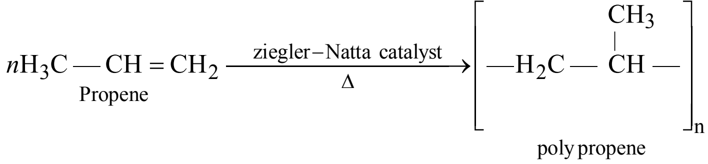
(iii) Ozonolysis :



The overall reaction (formation of ozonide followed by hydrolysis) is the replacement of an olefinic bond, > C = C <, by two carbonyl groups, > C = O, and is known an ***ozonolysis***.

(iv) Polymerization: The process in which simple molecules combine to form large molecule is called polymerisation; the starting simple molecule is called monomer while the large final product is called a polymer. Polymers are used as plastics, rubber and several other important products. For example

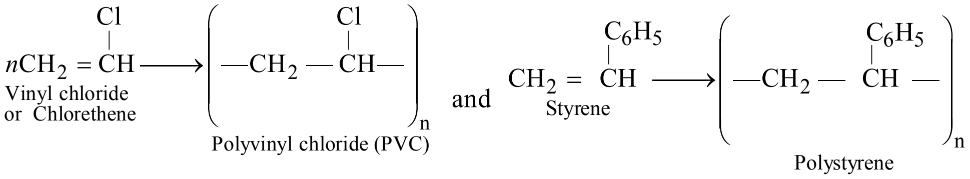
(a)



$$\underset{\text{Propene}}{nH_3C—CH=CH_2}\xrightarrow[\Delta]{\text{ziegler–Natta catalyst}}\underset{\text{poly propene}}{\left[—H_2C—\overset{CH_3}{\overset{|}{CH}}—\right]_n}$$

(b) $$\underset{}{nCH_2=CH_2}\xrightarrow[\text{high pressure, }O_2]{473–673K}\underset{\text{Polyethene}}{(-CH_2-CH_2-)_n}$$

Certain substituted ethenes can be polymerised to give important polymers. For example.



$$\underset{\substack{\text{Vinyl chloride}\\ \text{or Chlorethene}}}{nCH_2=\overset{Cl}{\overset{|}{CH}}}\longrightarrow\underset{\text{Polyvinyl chloride (PVC)}}{\left(—CH_2—\overset{Cl}{\overset{|}{CH}}—\right)_n}\quad\text{and}\quad\underset{\text{Styrene}}{CH_2=\overset{C_6H_5}{\overset{|}{CH}}}\longrightarrow\underset{\text{Polystyrene}}{\left(—CH_2—\overset{C_6H_5}{\overset{|}{CH}}—\right)_n}$$

$$\underset{\text{Tetrafluoro ethene}}{F_2C=CF_2}\longrightarrow\underset{\text{poly tetrafluoro ethene}}{(-F_2C-CF_2-)_n}$$

ALKYNES

Alkynes are characterised by the presence of a triple bond between two carbon atoms, i.e., $—C\equiv C—$. They contain four hydrogen atoms less than the corresponding alkane and hence correspond to the general formula C_nH_{2n-2}.

Structure of Alkynes

In the formation of ethyne (e.g. acetylene) each carbon atom undergoes *sp* hybridisation leaving $2p_y$ and $2p_z$ orbitals unhybridised. One *sp* hybridised orbital of each carbon atom overlap axially to produce a stable C–C sigma bond. The remaining *sp* hybrid orbital of each carbon atom overlaps with the half filled 1*s* orbital of H atoms forming 2C – H bonds as shown in figure.

The unhybridised parallel $2p_y$ orbitals of each carbon atom overlaps sidewise to form a weak pi(π) bond. Similarly, unhybridised parallel $2p_z$ orbitals of each carbon atom overlaps and form second pi (π)

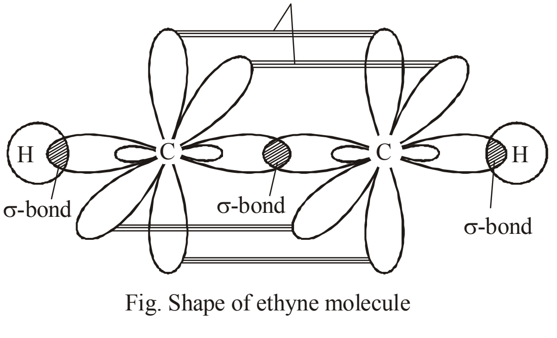
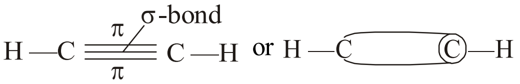


Fig. Shape of ethyne molecule

bond. Thus a triple bond between two carbon atom in ethyne is formed which is composed of 1σ and 2π bonds. Molecule of acetylene has all carbon and hydrogen atoms arranged linearly. The electron cloud of π-bonds are all around the internuclear axis giving it a cylindrical shape.



Observed bond lengths between C – C and C– H in ethyne molecule are as follows.

$C \equiv C = 1.20\,\text{Å}$ $\qquad$ $C — H = 1.08\text{Å}$

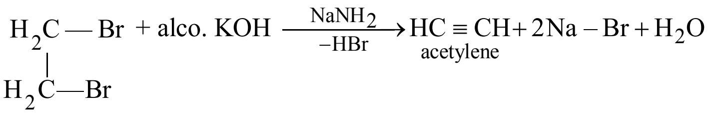
Total $C \equiv C$ bond dissociation energy = 811 kJ/mole.

METHODS OF PREPARATION

(i) Lab method

$$CaC_2 + 2H_2O \longrightarrow HC \equiv CH + Ca(OH)_2$$

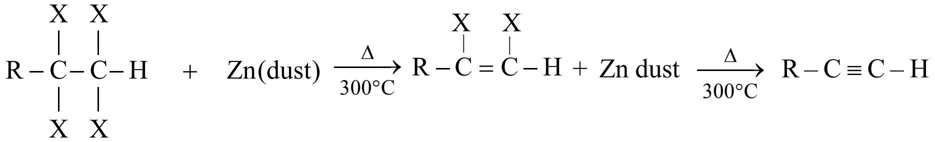
(ii) By dehydrohalogenation



$$\begin{array}{l} H_2C — Br \\ \quad | \\ H_2C — Br \end{array} + \text{alco. KOH} \xrightarrow[-HBr]{NaNH_2} \underset{\text{acetylene}}{HC \equiv CH} + 2Na - Br + H_2O$$

Vicinal dihalides when treated with alcoholic KOH and sodamide yields alkynes.

(iii) From tetrahaloalkanes (dehalogenation)



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H + Zn(dust) \xrightarrow[300°C]{\Delta} R-\overset{X}{C}=\overset{X}{C}-H + Zn\ dust \xrightarrow[300°C]{\Delta} R-C \equiv C-H$$

Note: In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends, then cycloalkene is obtained.

Physical Properties

- **(a)** Alkynes are colourless, odourless and tasteless.
- **(b)** Lower alkynes are partially soluble in H_2O. (It is due to their polarizability)
- **(c)** Higher alkynes are insoluble in water due to more % of covalent character.
- **(d)** Completely soluble in organic solvents.
- **(e)** Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.
- **(f)** Upto C_4 alkynes are gaseous. $C_5 - C_{11}$ liquids, C_{12} & above are solids.
- **(g)** Acetylene & 1–alkyne are acidic in nature. It is due to presence of active H.
- **(h)** Order of solubility, density, B.P., M.P. and acidic nature :

  Alkyne > Alkene > Alkane

Chemical Properties

(i) Acidic character of alkynes

Hydrogen atom or atoms attached to the triply bonded atoms can be easily removed by means of a strong base, and hence acetylenes or 1-alkynes are considered as weak acids.

Terminal alkynes (1-alkynes) are acidic in nature.

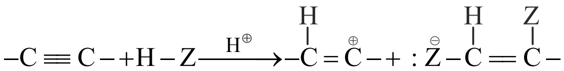
$$HC \equiv CH + 2Na \longrightarrow \underset{\text{white ppt.}}{NaC \equiv CNa} + H_2$$

$$HC \equiv CH + Na^{+}–NH_2^{-} \longrightarrow H—C \equiv C^{-}\,Na^{+} + NH_3$$

The H–atoms are attached to *sp*-hybridised carbon atoms. Due to 50% s-character, the C-atoms in alkynes have high electronegativity. Hence, they attract the shared electron pair of C–H bond strongly and hence, the H-atoms can be liberated as protons.

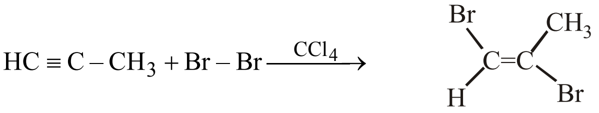
(ii) Addition reactions

Formation of the addition product in alkynes take place according to following steps.



$$-C \equiv C - + H - Z \xrightarrow{H^{\oplus}} -\overset{H}{C} = \overset{\oplus}{C} - + \overset{\ominus}{:Z} - \overset{H}{C} = \overset{Z}{C} -$$

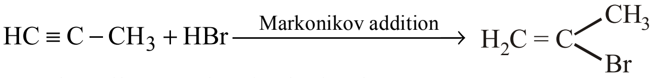
(a) Addition of halogens



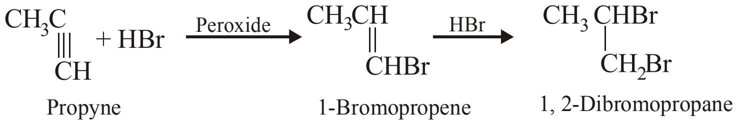
trans-1, 2 dibromopropene

Reddish orange colour of bromine in CCl_4 is decolourised. This is used as a test for unsaturation.

(b) Addition of hydrogen halides

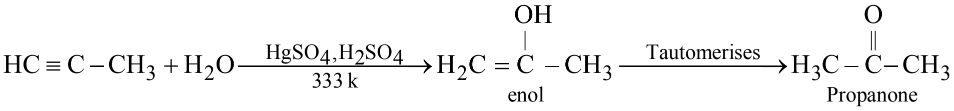


In presence of peroxides, anti-Markovnikov product is obtained.



$$\underset{\text{Propyne}}{\begin{matrix}CH_3C\\ |||\\ CH\end{matrix}} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromopropene}}{\begin{matrix}CH_3CH\\ \|\\ CHBr\end{matrix}} \xrightarrow{HBr} \underset{\text{1, 2-Dibromopropane}}{\begin{matrix}CH_3\,CHBr\\ |\\ CH_2Br\end{matrix}}$$

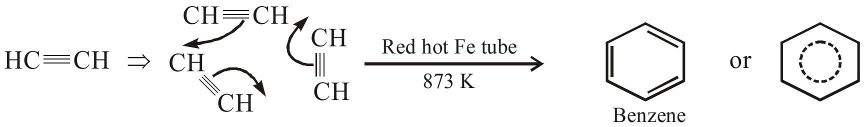
(c) Addition of water



$$HC \equiv C - CH_3 + H_2O \xrightarrow[333\text{ k}]{HgSO_4, H_2SO_4} H_2C = \underset{\text{enol}}{\overset{\overset{OH}{|}}{C}} - CH_3 \xrightarrow{\text{Tautomerises}} \underset{\text{Propanone}}{H_3C - \overset{\overset{O}{\|}}{C} - CH_3}$$

(iii) Polymerization

(a) Cyclic polymerisation : If three moles of acetylene is passed into red hot iron or Cu or quartz tube at 900 K then a cyclic trimer is formed which is called benzene.



Benzene

(b) Linear polymerisation : Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called **trimerisation.**

$$HC \equiv CH + HC \equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinylacetylene}}{CH_2 = CH - C \equiv CH}$$

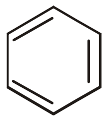
AROMATIC HYDROCARBONS (ARENES)

Aromatic compounds have structure having at least one unsaturated ring in which π-electrons are continuously delocalised in cyclic fashion. Most of the aromatic compounds contain benzene ring. However there are other aromatic hydrocarbons also which do not contain a benzene ring but instead contain other highly unsaturated ring.

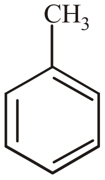
Aromatic compounds containing benzene ring are called benzenoids while those not containing benzene ring are called non-benzenoids.

Some Examples of Arenes

(i) Monocyclic arenes. These contain one benzene ring. Examples are benzene, toluene, xylenes etc.

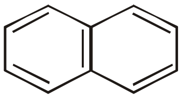


Benzene



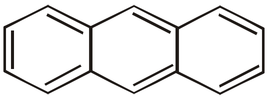
Toluene

(ii) Bicyclic arenes. These contain two benzene rings. Common example is naphthalene.



Naphthalene

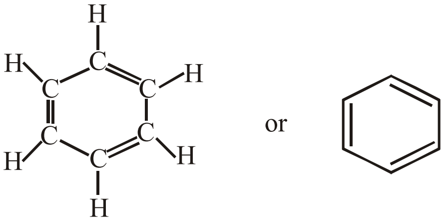
(iii) Tricyclic arenes. These contain three benzene rings. The first and common member is anthracene.



Anthracene

Structure of Benzene

Kekule in 1865 proposed that the six carbon atoms of benzene are joined to each other by alternate single and double bonds to form a hexagonal ring. Each carbon is further attached to a hydrogen atom. Thus benzene structure as proposed by Kekule can be drawn as below

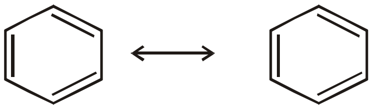


Benzene

Kekul structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which would later on explained by resonance.

Resonance

The phenomenon in which two or more structures can be written for the true structure of a molecule, but none of them can be said to represent it uniquely, is referred to as ***resonance or mesomerism***. The true structure of the molecule is said to be a resonance hybrid of the various possible alternative structures which themselves are known as resonating structures or canonical structures.



or

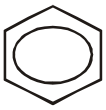


Fig. Resonating structures of benzene

Fig. Resonance hybrid* benzene

The resonance hybrid is more stable (i.e. has less energy) than any one of the various resonating structures. The difference in energy between the hybrid and the most stable canonical structure is referred to as the resonance energy of the molecule. It is observed that larger the number of the possible canonical structures, greater will be the resonance energy and hence stability of the compound. The resonance energy of a resonance hybrid is the difference between the theoretical and experimental heats of hydrogenation of the compound.

Aromaticity

Benzene and other organic compounds which resemble benzene in certain characteristic properties are called ***aromatic compounds***. These characteristics properties constitute what is commonly known as **aromatic character** or **aromaticity**.

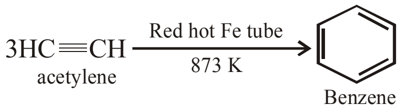
(a) Aromatic compound has planar structure.

(b) An aromatic compound must have cyclic clouds of delocalised π electrons above and below the plane of the molecule.

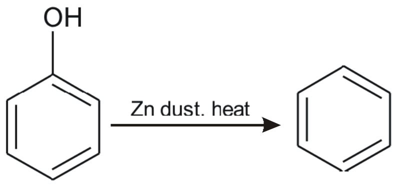
(c) The π clouds must contain a total of $(4n+2)$ π electrons. Where π is an integer i.e., its value may be 0, 1, 2, 3, 4... This rule is known as $(4n+2)\pi$ rule or ***Huckel rule***.

Methods of Preparation

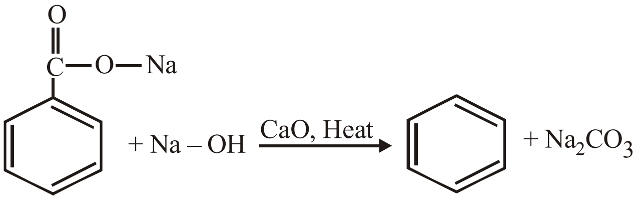
(i) Cyclic polymerization of ethyne



(ii) Reduction of phenol

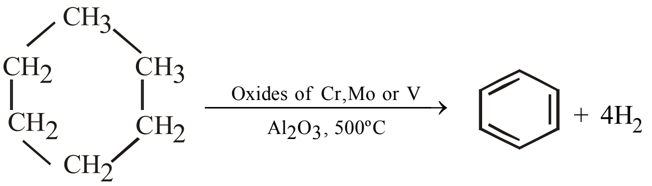


(iii) Decarboxylation



(iv) By catalytic reforming aromatisation

Reforming or aromatisation is the process of converting straight chain alkanes and cyclic alkanes into corresponding aromatic hydrocarbons under suitable conditions.



Physical Properties

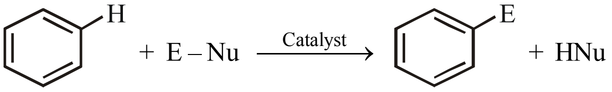
Colourless liquid (B.P. = 80ºC) having specific smell. Lighter than water (relative density = 0.879) and is immiscible with water. Non-polar in nature and its dipole moment is zero. Insoluble in water, soluble in organic solvents like alcohol, ether, acetone, acetic acid, CCl_4, CS_2 etc. It is itself a good solvent. It is highly inflammable and burns with smoky flame.

Chemical Properties

(i) Electrophilic substitution reaction :

Arenes undergo electrophilic substitution reactions like nitration, halogenation, sulphonation, Friedal craft reaction in which the attacking reagent is an electrophile (E^+)

The reaction can be represented by :

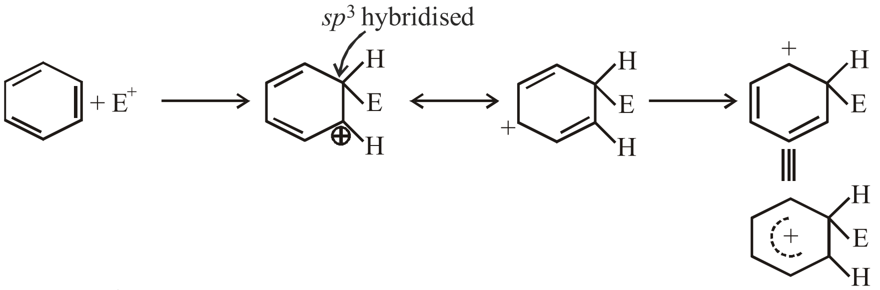


Mechanism of Electrophilic Substitution Reactions

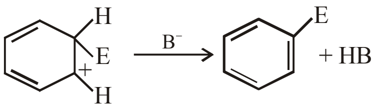
(a) Generation of electrophile : A Lewis acid helps in generation of electrophile E^+.

- $Cl - Cl + AlCl_3 \rightarrow \overset{\oplus}{Cl} + [AlCl_4]^-$
- $CH_3 - Cl + AlCl_3 \rightarrow \overset{\oplus}{CH_3} + [AlCl_4]^-$

(b) Formation of carbocation

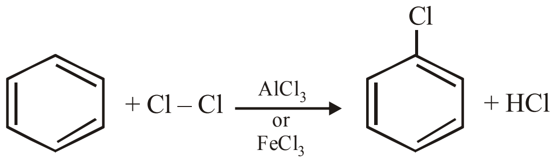


(c) Removal of proton



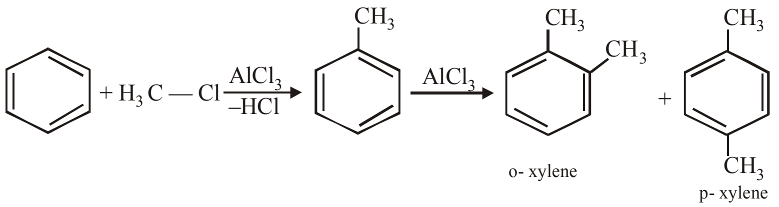
Example

(i) Friedel craft halogenation

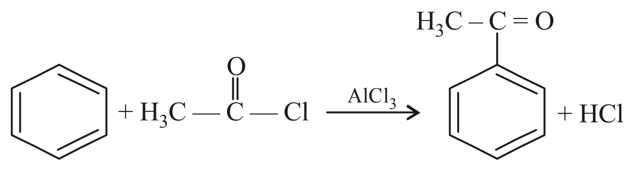


Chlorobenzene

(ii) Friedel craft alkylation

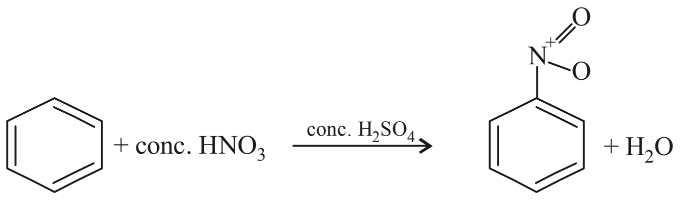


(iii) Friedel craft acylation

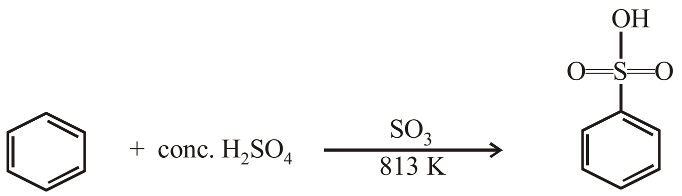


acetophenone

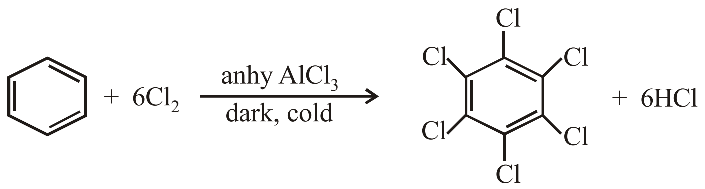
(iv) Nitration



(v) Sulphonation



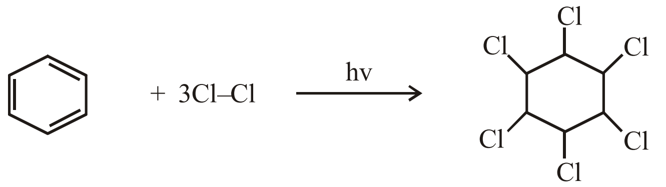
Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark yields hexachloro benzene (C_6Cl_6)



Hexachlorobenzene

(ii) Addition Reaction

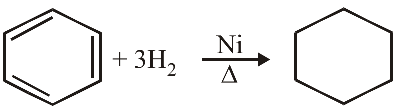
(a) Halogenation :



Benzene hexachloride (BHC)

The reaction follows free radical addition mechanism. BHC is a well known insecticide.

(b) Hydrogenation:



Cyclohexane

(iii) Combustion

When heated in air, benzene burns with flame producing CO_2 and H_2O

$$C_6H_6 + \frac{15}{2}SO_2 \rightarrow 6CO_2 + 3H_2O$$

General combustion reaction for any hydrocarbon may be given as

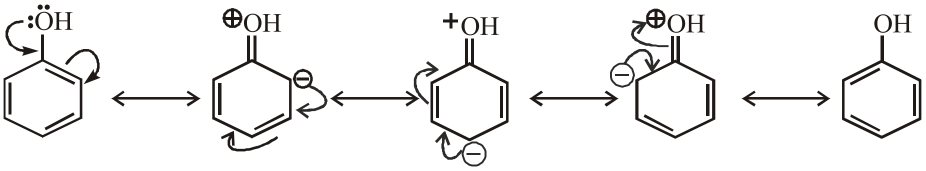
$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

Directive Influence of Functional Groups

The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the ring towards electrophilic substitution of the incoming group.

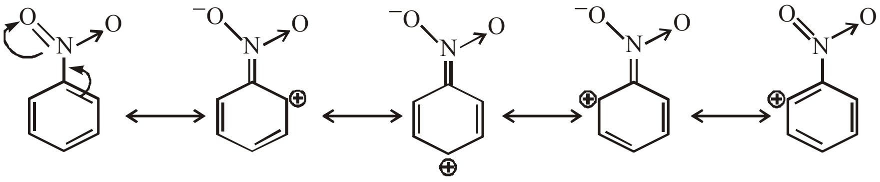
(1) Ortho and para directing groups

These are those groups which direct the incoming group to *o*– and *p*-positions. There occurs an increase in electron density at *o*- and *p*- positions. So, these groups are called activating groups. For ex : $–NH_2$, –NHR, $–NHCOCH_3$, $– OCH_3$, $–CH_3$, $–C_2H_5$, –OH, etc.



(2) Meta directing groups :

These groups direct incoming group towards meta position. The electron density at o- and p-positions is less due to which the $E^{\oplus}$ attacks at the meta position. They are also called deactivating groups. For example $–NO_2$, –CN, – CHO, –COR, – COOH, – COOR, $– SO_3H$, etc.



The electron donating ability of some substituents in benzene follows the order:

$$–O^- > –NH_2 > NR_2 > –OH > –OCH_3 > –NHCOCH_3 > –F > –Cl > –Br > –I$$

The electron-withdrawing ability of some substituents in benzene follows the order:

$$(CH_3)_3N^+ > – NO_2 > –CN > –SO_3H > –CHO > –COCH_3 > –COOH$$

CONCEPT MAP

HYDROCARBONS

Aromatic Hydrocarbons

- Contain at least one unsaturated ring

Aromaticity :

- Aromatic compound must have planer structure
- must contain (4n+2) π electrons
- must have cyclic clouds of delocalised π es

PREPARATION

- $3HC \equiv CH \xrightarrow[\text{Fe tube}]{\text{Red hot}} \text{Benzene}$
- $\text{phenol} \xrightarrow[\Delta]{\text{Zn dust}} \text{Benzene}$
- $C_6H_5COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} \text{Benzene}$

PROPERTIES

Electrophilic substitution

- $C_6H_6 + Cl_2 \xrightarrow{AlCl_3} \text{Chlorobenzene} + HCl$
- $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} \text{toluene}$
- $C_6H_6 + \text{Conc. } HNO_3 \xrightarrow[H_2SO_4]{\text{Conc.}}$  $+H_2O$

Addition reaction

- $C_6H_6 + 3Cl_2 \rightarrow \text{BHC}$
- $C_6H_6 + 3H_2 \xrightarrow[\Delta]{Ni} \text{Cyclohexane}$

Ortho directing groups :

- $-NH_2, -NHR, -NHCOCH_3$
- $-OCH_3, -CH_3, -C_2H_5, -OH$ etc.

Meta directing groups :

- $-NO_2, -CN, -CHO, -COR, -COOH$, etc.

ALKYNES

- General formula : C_nH_{2n-2}
- C-atom is in *sp* hybridised state.

PREPARATION

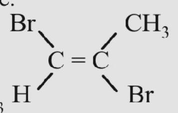
$CaC_2 + 2H_2O \rightarrow HC\equiv CH + Ca(OH)_2$

- **Dehydrohalogenation:**

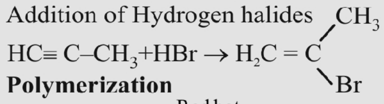
$H_2CBr-CH_2Br \xrightarrow{NaNH_2} HC\equiv CH + 2NaBr$

PROPERTIES

- Terminal alkynes are acidic in nature.
- **Addition reactions**

$HC\equiv CH-CH_3 + Br_2 \xrightarrow{CCl_4}$ 

- Addition of Hydrogen halides

$HC\equiv C-CH_3 + HBr \rightarrow$ 

- **Polymerization**

$3CH\equiv CH \xrightarrow[\text{Fe tube}]{\text{Red hot}} \text{Benzene}$

Liner Polymerization

$2HC\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl} CH_2\equiv CH-C\equiv CH$

ALKANES

- General formula : C_nH_{2n+2}
- C atom posses sp^3 hybridised state.

PREPARATION

- **Hydrogenation**

$CH_2=CH_2+H_2 \xrightarrow{Pt/Pd/Ni} CH_3-CH_3$

- **Wurtz reaction**

$R-Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} R-R+2NaBr$

- **Decarboxylation**

$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{Cao} CH_4 + Na_2CO_3$

- **Kolbe's electrolytic method**

$2CH_3COO^-Na^+ + 2H_2O \rightarrow CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$

PROPERTIES

- Boiling points decrease with increasing branching
- Melting point with even no of C-atom > odd no. of C-atoms
- Halogenation

$R-H+X_2 \xrightarrow{hv} R-X+HX$

Compound with even number of C-atom

- **Aromatisation**

$n\text{–Hexane} \xrightarrow{Cr_2O_3 \text{ or } V_2O_5} \text{Benzene}$

- **Conformation**

Stability **order:** staggered > skew > eclipsed

ALKENES

- General formula : C_nH_{2n}
- C-atom is in sp^2 hybridised state.

PREPARATIONS

$R-C\equiv C-R \xrightarrow[\text{catalyst}]{\text{Lindlar's}} RCH=CHR$

- **Dehydrohalogenation**

$H_3C-CHBr-CH_2CH_3 \rightarrow H_3C-CH=CH-CH_3$

- **Dehydration of alcohol**

$H-CH_3CH_2CH_2OH \xrightarrow{75\% H_2SO_4} CH_3-CH=CH_2+H_2O$

PROPERTIES

- **Addition reaction**

$R-CH=CH_2+H_2 \xrightarrow[Ni]{Raney} RCH_2-CH_3$

- Markovnikov reaction

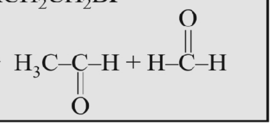
$R-CH=CH_2+HCl \rightarrow RClCH-CH_3$

Reactivity : HI > HBr > HCl > HF

- **Antimarkovnikov reaction** (Kharasch effect)

$R-CH=CH_2+HBr \xrightarrow{H_2O_2} RCH_2CH_2Br$

- **Ozonolysis**

$H_3C-CH=CH_2+O_3 \xrightarrow{zn/H_2O}$ 

$H_3C-\underset{\underset{O}{\|}}{C}-H + H-\overset{\overset{O}{\|}}{C}-H$

Textbook Exercises

13.1 How do you account for the formation of ethane during chlorination of methane ?

Ans. Chlorination of methane is a free radical reaction which occurs by the following mechanism:

Initiation : $Cl-Cl \xrightarrow{\text{Homolytic fission}} \underset{\text{Chlorine free radical}}{2Cl^{\bullet}}$

Propagation: $CH_3-H+Cl\bullet \longrightarrow {}^{\bullet}CH_3+HCl$

$\bullet CH_3+Cl-Cl \longrightarrow CH_3-Cl+{}^{\bullet}Cl$ ... (i)

Termination: $\bullet CH_3+{}^{\bullet}CH_3 \longrightarrow \underset{\text{ethane}}{CH_3-CH_3}$ ... (ii)

$\bullet CH_3+{}^{\bullet}Cl \longrightarrow CH_3-Cl,\ \bullet Cl+{}^{\bullet}Cl \longrightarrow Cl-Cl$ ... (iii)

From the above mechanism, it is evident that during propagation step, CH_3 free radicals are produced which may undergo three reactions, i. e. (i)–(iii). In the chain termination step, the two CH_3 free radicals combine together to form ethane (CH_3–CH_3) molecule.

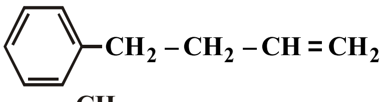
13.2 Write IUPAC names of the following compounds:

(a) $CH_3CH=C(CH_3)_2$

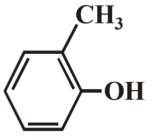
(b) $CH_2=CH-C\equiv C-CH_3$

(c)

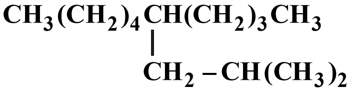
(d)



(e)

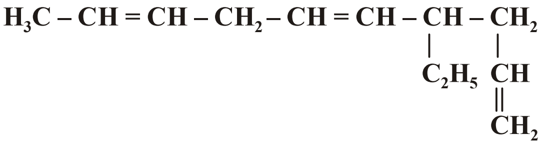


(f)



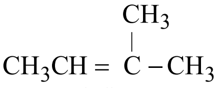
$$CH_3(CH_2)_4\underset{\underset{CH_2-CH(CH_3)_2}{|}}{CH}(CH_2)_3CH_3$$

(g)



$$H_3C-CH=CH-CH_2-CH=CH-\underset{\underset{C_2H_5}{|}}{CH}-\underset{\underset{\underset{\underset{CH_2}{||}}{CH}}{|}}{CH_2}$$

Ans. (a)



$$CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$

2–Methylbut–2–ene

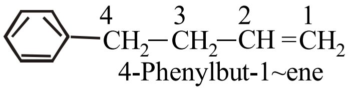
(b) $CH_2=CH-C\equiv C-CH_3$

Pent -1-en-3-yne

(c)

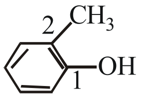
Buta–1, 3–diene

(d)



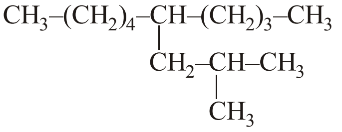
4-Phenylbut-1~ene

(e)



2-Methylphenol

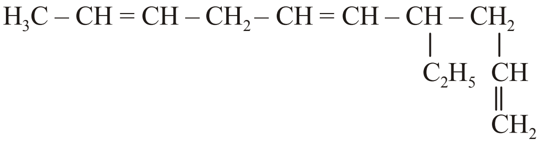
(f)



$$CH_3-(CH_2)_4-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2-CH-CH_3}}{|}}{CH}-(CH_2)_3-CH_3$$

5-(2-Methylpropyl)-decane

(g)



$$H_3C-CH=CH-CH_2-CH=CH-\underset{\underset{C_2H_5}{|}}{CH}-\underset{\underset{\underset{\underset{CH_2}{||}}{CH}}{|}}{CH_2}$$

4-Ethyldeca-1, 5, 8-triene

13.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated:

(a) C_4H_8 **(one double bond)**

(b) C_5H_8 **(one triple bond)**

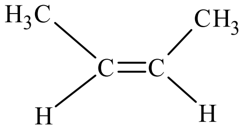
Ans. (a) Isomers of C_4H_8 having one double bond are:

(a) C_4H_8

(i) $H_3C-CH_2-CH=CH_2$

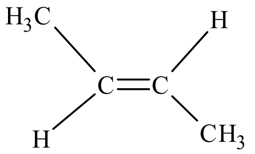
But-1-ene

(ii)



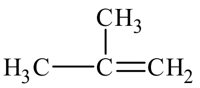
cis-But-2-ene

(iii)



trans-But-2-ene

(iv)



$$H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2$$

2-Methylprop-1-ene

(b) C_5H_8

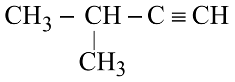
(i) $\overset{5}{CH_3}\ \overset{4}{CH_2}-\overset{3}{CH_2}\equiv \overset{2}{C}-\overset{1}{CH}$

Pent-1-yne

(ii) $\overset{5}{CH_2}\ \overset{4}{CH_2}-\overset{3}{C}\equiv \overset{2}{C}-\overset{1}{CH_3}$

Pent-2-yne

(iii)



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv CH$$

3–Methylbut–1–yne

13.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds: (i) Pent–2–ene (ii) 3, 4–Dimethylhept–3–ene (iii) 2–Ethylbut–l–ene (iv) 1–Phenylbut–l–ene.

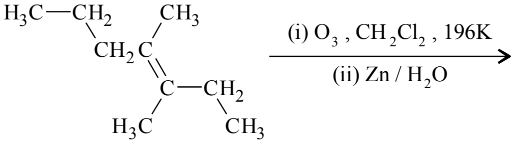
Ans. (i) $\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$

Pent-2-ene

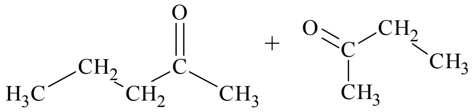
$$\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3/\text{CH}_2\text{Cl}_2, 196\text{K}}$$

$$\underset{\text{Propanal}}{CH_3-CH_2-CH=O}+\underset{\text{Ethanal}}{O=CH-CH_3}$$

(ii)

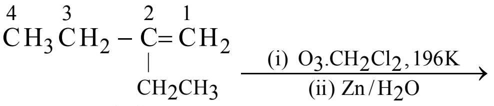


3,4-Dimethylhept-3-ene

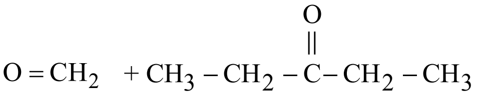


Pentan-2-one Butan-2-one

(iii)



$$\overset{4}{C}H_3\overset{3}{C}H_2-\underset{\underset{\text{2-Ethylbut-1-ene}}{CH_2CH_3}}{\overset{2}{C}}=\overset{1}{C}H_2\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3.\text{CH}_2\text{Cl}_2, 196\text{K}}$$



$$\underset{\text{Methanal}}{O=CH_2}+\underset{\text{Pentan-3-one}}{CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3}$$

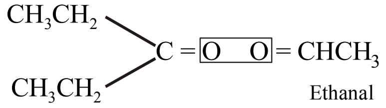
(iv) $\overset{4}{C}H_3\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H-C_6H_5\xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3,\text{CH}_2\text{Cl}_2, 196\text{K}}$

1–Phenylbut–1–ene

$$\underset{\text{Propanal}}{CH_3CH_2CH=O}+\underset{\text{Benzaldehyde}}{O=CH-C_6H_5}$$

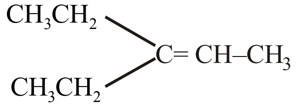
13.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

Ans. **Step 1:** Write the structure of the products side by side with their oxygen atoms pointing towards each other.



Pentan-3-one

Step 2 : Remove the oxygen atoms and join the two ends by a double bond, the structure of the alkene 'A' is



3-Ethylpent-2-ene (A)

13.6 An alkene 'A' contains three C–C, eight C–H σ–bonds, one C–C π–bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write the IUPAC name of 'A'.

Ans.. (i) An aldehyde with molar mass of 44 u is ethanal, $CH_3CH=O$

(ii) Write two moles of ethanal side by side with their oxygen atoms pointing towards each other.

$$\underset{\text{Ethanal}}{CH_3CH=}\boxed{O\quad O}\underset{\text{Ethanal}}{=CHCH_3}$$

(iii) Remove the oxygen atoms and join them by a double bond, the structure of alkene 'A' is

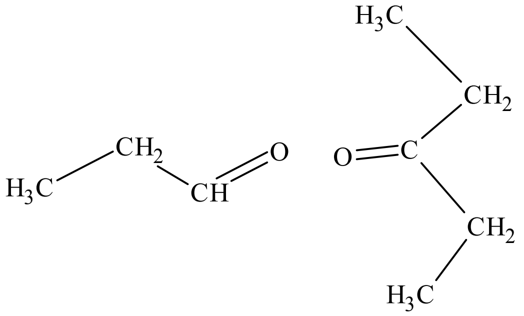
$CH_3–CH=CH–CH_3$

But–2–ene

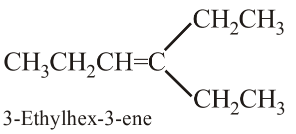
As required, but–2–ene has three C–C, eight C–H and one C–C π–bond.

13.7 Propanal and pentan-3-one are the ozonolysis products of an alkene. What is the structural formula of the alkene?

Ans. (i) Write the structures of propanal and pentan-3-one with their oxygen atoms facing each other, we have,



(ii) Remove oxygen atoms and join the two fragments by a double bond, the structure of the alkene is



3-Ethylhex-3-ene

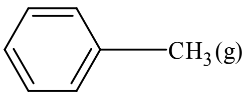
13.8 Write chemical equations for the combustion reaction of the following hydrocarbons.
(i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene

Ans. (i) $\underset{\text{Butane}}{C_4H_{10}(g)}+13/2\,O_2(g)\xrightarrow{\Delta}4\,CO_2(g)+5\,H_2O(g)$

(ii) $\underset{\text{Pentene}}{C_5H_{10}(g)}+15/2\,O_2(g)\xrightarrow{\Delta}5\,CO_2(g)+5\,H_2O(g)$

(iii) $\underset{\text{Hexyne}}{C_6H_{10}(g)}+17/2\,O_2(g)\xrightarrow{\Delta}6\,CO_2(g)+5\,H_2O(g)$

(iv)

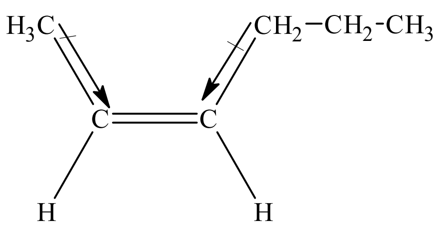


Toluene

or $C_7H_8(g)+9\,O_2(g)\xrightarrow{\Delta}7\,CO_2(g)+4\,H_2O(g)$

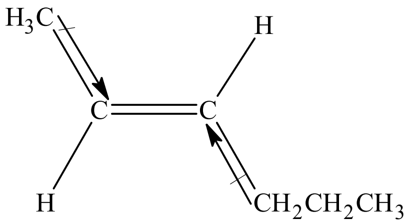
13.9 Draw the *cis*–and *trans*–structures for hex–2–ene. Which isomer will have higher b. p. and why ?

Ans. The structure of cis–and trans–isomer of hex–2–ene are:



cis–Hex–2–ene

(Higher dipole moment, higher b.p.)



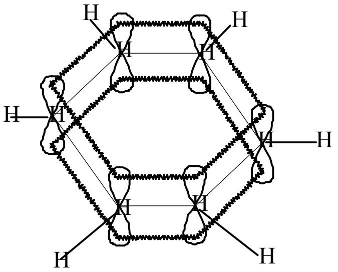
trans–Hex–2–ene

(Lower dipole moment, lower b. p.)

The dipole moment of a molecule depends upon dipole-dipole interactions. Since cis-isomer has higher dipole moment, therefore, it has higher boiling point.

13.10 Why is benzene extra ordinarily stable though it contains three double bonds ?

Ans. Resonance or delocalization of electrons usually leads to stability. Since in benzene all the six π–electrons of the three double bonds are completely delocalized to form one lowest energy molecular orbital which surrounds all the carbon atoms of the ring, therefore, it is extra–ordinarily stable.

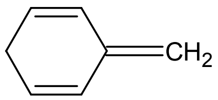


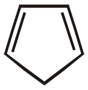
Delocalization of 6π-electrons in benzene

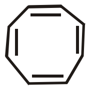
13.11 What are the necessary conditions for any system to be aromatic ?

Ans. Refer theory

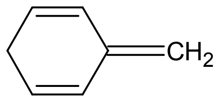
13.12 Explain why the following systems are not aromatic?

(i) 

(ii) 

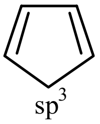
(iii) 

Ans. (i) sp^3



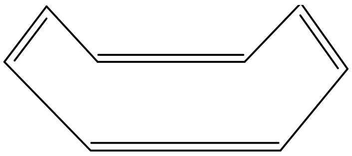
Due to the presence of a sp^3–hybridized carbon, the system is not planar. It does contain six π-electrons but the system is not fully conjugated since all the six π-electrons do not form a single cyclic electron π cloud which surrounds all the atoms of the ring. Therefore, it is not an aromatic compound.

(ii)



Due to the presence of a sp^3-carbon, the system is not planar. Further, it contains only four π electrons, therefore, the system is not aromatic because it does not contain planar cyclic cloud having (4n + 2) π-electrons.

(iii)



Tub shaped

Cyclooctatetraene is not planar but is tub shaped. It is, therefore, a non–planar system having 8 pi-electrons. Therefore, the molecule is not aromatic since it does not contain a planar cyclic cloud having (4n + 2)π-electrons.

13.13 How will you convert benzene into

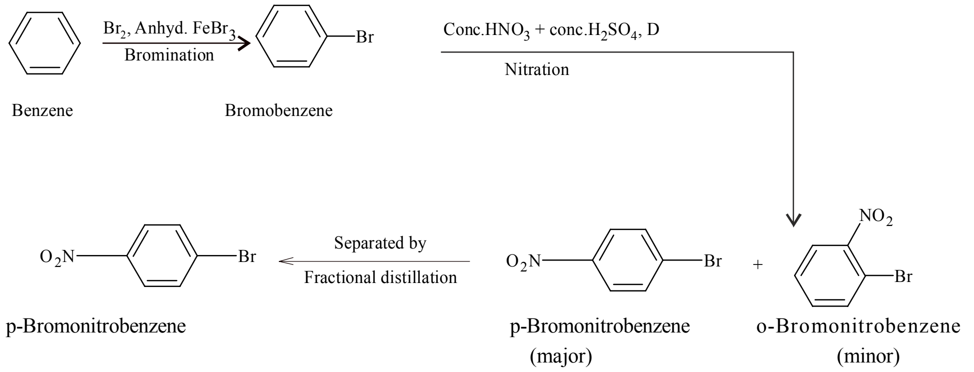
(i) *p*-nitrobromobenzene

(ii) *m*-nitrochlorobenzene

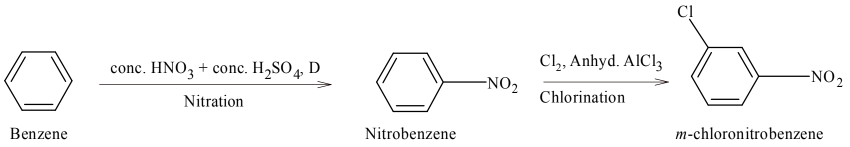
(ii) *p*-nitrotoluene

(iv) acetophenone ?

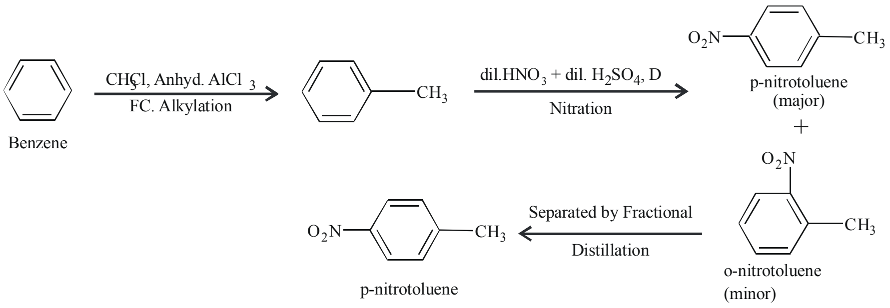
Ans. (i) The two substituents in the benzene ring are present at *p*-positions. Therefore, the sequence of reactions should be such that first an o, p-directing group, i.e., Br atom should be introduced in the benzene ring and this should be followed by nitration. Thus,



(ii) Here since the two substituents are at m– position w. r. t each other, therefore, the first substituent in the benzene ring should be a m–directing group (i. e., NO$_2$) and then the other group (i. e. Cl) should be introduced. Therefore, the sequence of reactions is:



(iii) Here since the two substituents are at p–position w. r. t. each other, therefore, the first substituent in the benzene ring should be a o, p-directing group (i.e., CH_3) and then the other group (i.e., NO_2) should be introduced.

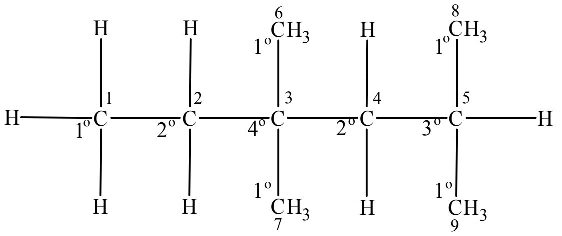


(iv) Refer theory

13.14 In the alkane,

$CH_3CH_2 - C(CH_3)_2 - CH_2 - CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the number of H – atoms bonded to each one of these.

Ans. The expanded formula of the given compound is:



The number of H-atoms bonded to each carbon are:

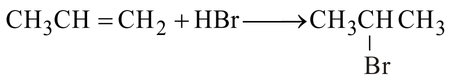
C_1 : 3 H-atoms
C_2 : 2 H-atoms
C_3 : 0 H-atoms
C_4 : 2 H-atoms C_8 : 3 H-atoms
C_5 : 1 H-atoms C_9 : 3 H-atoms
C_6 : 3 H-atoms
C_7 : 3 H-atoms

13.15 What effect does branching of an alkane chain has on its boiling point?

Ans. Refer theory

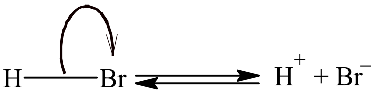
13.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

Ans. **Addition of HBr to propene :**



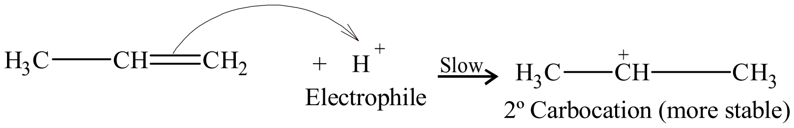
$$CH_3CH = CH_2 + HBr \longrightarrow CH_3\underset{\substack{|\\ Br}}{C}HCH_3$$

Mechanism :

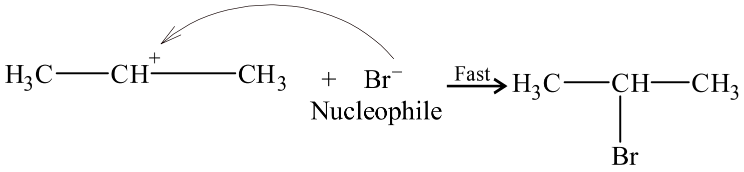


$$H—Br \rightleftharpoons \overset{+}{H} + Br^-$$

Step I :



Step II :



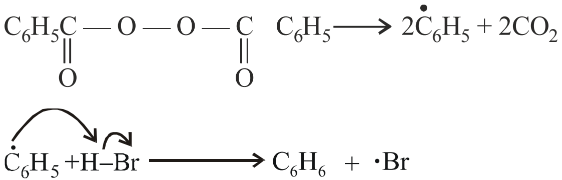
$$H_3C-\overset{+}{C}H-CH_3 + Br^- \xrightarrow{\text{Fast}} H_3C-\underset{\underset{Br}{|}}{CH}-CH_3$$

2-Bromopropane

Addition of HBr to propene in presence of benzoyl peroxide :

$$CH_3CH=CH_2+HBr\xrightarrow[(C_6H_5CO)_2O]{}CH_3CH_2CH_2Br$$

Mechanism :

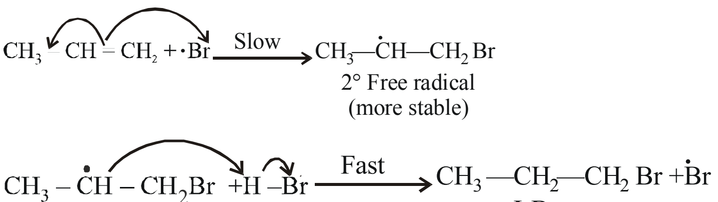


$$C_6H_5\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}\;C_6H_5\longrightarrow 2\dot{C}_6H_5+2CO_2$$

$$\dot{C}_6H_5+H-Br\longrightarrow C_6H_6+\cdot Br$$

Benzene

In the first step, $\dot{B}r$ radical adds to propene in such a way so as to generate the more stable 2° free radical. In the second step, the free radical thus obtained rapidly abstracts a hydrogen atom from HBr to give 1– bromopropane.



$$CH_3-CH=CH_2+\cdot Br\xrightarrow{\text{Slow}}CH_3-\dot{C}H-CH_2Br$$

2° Free radical (more stable)

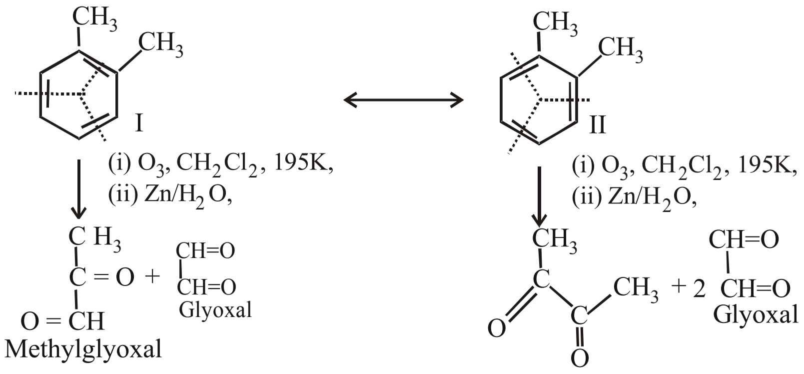
$$CH_3-\dot{C}H-CH_2Br+H-Br\xrightarrow{\text{Fast}}CH_3-CH_2-CH_2Br+\dot{B}r$$

I-Bromopropane

From the above discussion, it is evident that although both reactions are electrophilic addition reactions but it is due to different orientation of addition of H and Br atoms which gives different products.

13.17 Write down the products of ozonolysis of 1, 2-dimethylbenzene (o–xylene). How does the result support Kekule structure of benzene ?

Ans. o–Xylene may be regarded as a resonance hybrid of the following two Kekule structures. Ozonolysis of each one these gives two products as shown below:



1, 2-Dimethylglyoxal

Thus, in all, three products are formed. Since all the three products cannot be obtained from any one of the two Kekule structures, this shows that o–xylene is a resonance hybrid of the two Kekule structures (I and II).

13.18 Arrange benzene, *n*–hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

Ans. The hybridization state of carbon in these three compounds is;

	Benzene	**n-hexane**	**ethyne**
Type of orbital :	sp^2	sp^3	sp
s-Character :	33.3%	25%	50%

since, s–electrons are closer to the nucleus, therefore, as the s–character of the orbital making the C–H bond increases, the electrons of C–H bond lie closer and closer to the carbon atom. In other words, the partial positive charge on the H-atom increases and hence the acidic character increases as the s-character of the orbital increases. Thus, the acidic character decreases in the order.

Ethyne > Benzene > Hexane

13.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

Ans. Due to the presence of an electron cloud containing 6 π–electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophilic (electron–deficient) reagents towards it and repels nucleophilic (electron–rich) reagents. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

13.20 How would you convert the following compounds into benzene?

(i) Ethyne **(ii) Ethene** **(iii) Hexane**

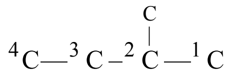
Ans. (i) Refer theory

(ii) Ethene is first converted into ethyne and then to benzene as shown above.

$$CH_2=CH_2 \xrightarrow{Br_2/CCl_4} Br-CH_2-CH_2-Br \xrightarrow[\substack{\text{1,2-Dibromoethane}\\ \text{(Dehydro bromination)}}]{KOH(alc),\Delta} HC\equiv CH \xrightarrow[873\text{ K}]{\text{Red hot Fe tube}} \text{Benzene}$$

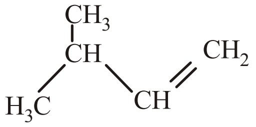
(iii) Refer theory

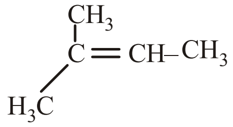
13.21 Write structures of all the alkenes which on hydrogenation give 2–methylbutane?

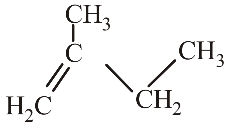
Ans. The basic skeleton of 2–methylbutane is 

$${}^4C-{}^3C-{}^2\overset{\overset{C}{|}}{C}-{}^1C$$

Putting double bonds at various different positions and satisfying the tetracovalency of each carbon, the structures of various alkenes which give 2–methylbutane on hydrogenation are:


3-methyl but-1-ene


2-methyl but-2-ene


2-methyl but-1-ene

13.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.

(a) Chlorobenzene, 2, 4–dinitrochlorobenzene , *p*–nitrochlorobenzene

(b) Toluene , $p-H_3C-C_6H_4-NO_2$, $p-O_2N-C_6H_4-NO_2$

Ans. (a) The typical reactions of benzene are electrophilic substitution reactions. Higher the electron density in the benzene ring, more reactive is the compound toward these reactions. Since NO_2 is more powerful electron–withdrawing group than Cl, therefore, more the number of nitro groups, less reactive is the compound. Thus, the overall reactivity decreases in order.

Chlorobenzene > *p*-nitrochlorobenzene > 2, 4-dinitrochlorobenzene.

(b) Here, CH_3 group is electron donating but NO_2 group is electron–withdrawing. Therefore, the maximum electron–density will be in toluene, followed by *p*–nitro toluene followed by *p*-dinitrobenzene.

Thus, the overall reactivity decreases in the order :

Toluene > p–H_3C–C_6H_4–NO_2 > p– O_2N–C_6H_4–NO_2

13.23 Out of benzene, *m*–dinitrobenzene and toluene which will undergo nitration most easily and why ?

Ans. CH_3 group is electron–donating while –NO_2 group is electron–withdrawing. Therefore, maximum electron density will be in toluene, followed by benzene and least in m–dinitrobenzene. Therefore, the ease of nitration decreases in the order: toluene > benzene > *m*–dinitrobenzene.

13.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

Ans. Anhydrous $FeCl_3$, $SnCl_4$, BF_3, etc.

13.25 Why is Wurtz reaction not preferred for the preparation of the alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

Ans. For preparation of alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. Since two alkyl halides can react in three different ways, therefore, a mixture of three alkanes instead of the desired alkane would be formed. For example, Wurtz reaction between 1–bromopropane and 1– bromobutane gives a mixture of three alkanes, i. e., hexane, heptane and octane as shown below:

$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2-Br} + 2Na + Br\,CH_2CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3} + 2\,NaBr$$

$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2-Br} + 2Na + \underset{\text{1–Bromopropane}}{Br-CH_2CH_2CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Heptane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaBr$$

$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2-Br} + 2Na + Br-CH_2CH_2CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaBr$$

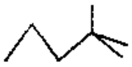
Practice Questions

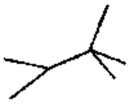
Very Short Answer Questions [1 Mark]

1. What is halogen carrier? Give one example.
2. Arrange the following in the increasing order of C–C bond length C_2H_6, C_2H_4, C_2H_2
3. Name the products formed when an ethereal solution containing ethyl iodide and methyl iodide is heated with sodium metal.
4. Out of ethylene and acetylene which is more acidic and why ?
5. How can ethylene be converted into ethane ?
6. Arrange the following: HCl, HBr, HI, HF in order of decreasing reactivity towards alkenes.
7. Give the structure of the alkene (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br
8. Name two reagents which can be used to distinguish between ethene and ethyne.
9. Can eclipsed and staggered conformations of ethane be isolated? Give reason.
10. What is Lindlar's catalyst? What is it used for?
11. What are the requirements for geometrical isomerism?
12. Why is dipole moment of trans-1, 2-dichloroethene zero?
13. What happens when benzene is treated with excess of Cl_2 in presence of sunlight? Give chemical reaction.
14. Arrange the three isomers of pentane in increasing order of their boiling points.
15. How will you distinguish between
   $CH_3CH_2C \equiv CH$ and $CH_3—C \equiv C—CH_3$

Short Answer Questions [2 & 3 Marks]

1. Arrange the following in increasing order of their release of energy on combustion.

   (i) 

   (ii) 

   (iii) 

   (iv) 

2. Write all the possible isomers for a benzene derivative having the molecular formula C_8H_{10}.
3. How will you demonstrate that double bonds of benzene are somewhat different from that of olefines?
4. Describe iodination of methane.
5. Explain briefly the process of aromatization (or reforming).
6. Define the terms conformation and conformational isomerism.
7. Why is cyclopropane is more reactive as compared to cyclohexane?
8. How are alkenes obtained from alkyl halides ?
9. Which of the following shows geometrical isomerism ?
   (i) $CHCl=CHCl$ (ii) $CH_2=CCl_2$
   (iii) $CCl_2=CHCl$
   Give the structures of its cis. –and trans –forms.
10. What happens when
    (i) A mixture of steam and methane is passed over heated nickel (supported over catalyst at 1273 K)
    (ii) Methane is heated to high temperature (1500 K).
    (iii) Isobutane is treated with alkaline $KMnO_4$.

11. Out of staggered and eclipsed confirmations of ethane, which is more stable and why?

12. What happens when (give chemical equation)

(i) Sodium ethanoate is heated with sodalime,

(ii) Sodium cyclohexane carboxylate is heated with sodalime?

13. What happens when

(i) bromoethane is treated with zinc and hydrochloric acid

(ii) hydrogen is passed into 2-bromopropane in the presence of palladium?

14. What is the role of red phosphorus in the reduction of alkyl halide using hydroiodic acid?

15. Give the structure and number of structural isomers that are possible when

(i) a symmetrical X_2 adds to

(a) $CH_3CH=CHCH_3$

(b) $CH_3CH=CH_2$

(ii) an unsymmetrical HX adds to

(a) $CH_3CH=CHCH_3$

(b) $CH_3CH=CH_2$

16. List the following alkenes in decreasing order of reactivity towards electrophilic addition:

(i) $Cl\,CH_2CH=CH_2$ (ii) $(CH_3)_2\,C=CH_2$

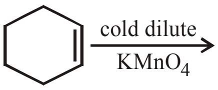
(iii) $CH_3CH=CH_2$ (iv) $CH_2=CHCl$

Explain your answer.

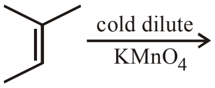
17. Hydrocarbon A (MF is C_5H_8) gave a white precipitate with ammonical silver nitrate. Oxidation of A with hot alkaline $KMnO_4$ gave 2-methyl propanoic acid. What is the structural formula of A?

18. Write down the structural formulae of the product obtained in the following reaction:

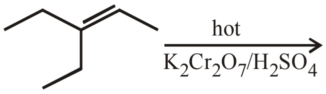
(i)



(ii)



(iii)



19. Explain why alkynes are less reactive than alkenes toward addition of Br_2.

20. How will you make the following conversions?

(i) Propene into propyne

(ii) 1, 1-dibromopentane into pentyne-1

21. Supply structures for the products of the reaction of Methyl benzene with

(i) chlorine in the presence of light

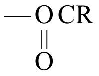
(ii) chlorine in the presence of $FeCl_3$

(iii) $K_2Cr_2O_7\,/\,H_2SO_4$

22. Classify the following substituent groups by their orientation and reactivity :

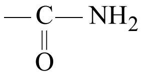
(i) $—CH=CHNO_2$

(ii)



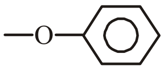
$—O\underset{\underset{O}{\|}}{C}R$

(iii)



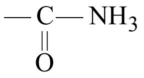
$—\underset{\underset{O}{\|}}{C}—NH_2$

(iv)



(v) $—CH_2OH$

(vi)



$—\underset{\underset{O}{\|}}{C}—NH_3$

23. How will you make the following conversions?

(i) Benzene to benzoic acid

(ii) Benzoic acid to ethylbenzene

(iii) Benzoic acid to benzene sulphonic acid

24. Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

25. What do you mean by cracking or pyrolysis?

Long Answer Questions [5 Marks Qs.]

1. Discuss the different conformations of ethane.

2. (i) Why is the Wurtz synthesis not a good method for preparing propane?

(ii) What alkanes would be expected from the reaction of sodium with 50 : 50 mixture of 1-chloropropane and 2-chloropropane ?

3. (i) Arrange the following compounds according to the increasing order of boiling point: Hexane, heptane, 3-methyl pentane, 2, 2-dimethyl butane.

(ii) Account for the following :

(a) The boiling points of hydrocarbon decreases with increase in branching.

(b) Hydrocarbons with odd number of carbon atoms have a melting point lower than expected.

(c) Boiling point of *n*-pentane is greater than that of neo-pentane but melting point of neo-pentane is greater than that of *n*-pentane.

4. List alkanes, alkenes and terminal alkynes in order of decreasing acidity of their terminal C—H. Also, account for the order of acidities. Give two reactions to show acidic nature of terminal alkynes.

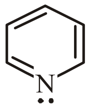
5. The ring systems having following characteristics are aromatic.

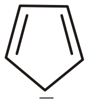
(i) Planar ring containing conjugated π bonds.

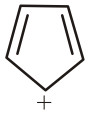
(ii) Complete delocalisation of the π-electrons in ring system i.e, each atom in the ring has unhybridised *p*-orbital, and

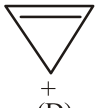
(iii) Presence of $(4n + 2)$ π-electrons in the ring where *n* is an integer ($n = 0, 1, 2$ ....) [Huckel's rule]

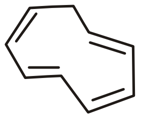
Using this information classify the following compounds as aromatic/non-aromatic.


(A)


(B)


(C)


(D)


(E)

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Although alkenes are more reactive than alkynes towards addition reaction, reverse is true regarding catalytic hydrogenation. Explain. **[HOTS]**

2. Can you separate the two conformations of ethane ? **[HOTS]**

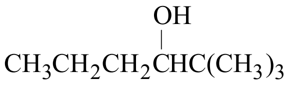
Short Answer Questions [2 & 3 Marks]

1. Account for the fact that the chain-initiating step in thermal chlorination of CH_4 is

$$Cl_2 \xrightarrow{\text{heat}} 2Cl^{\bullet} \text{ and not } CH_4 \xrightarrow{\text{heat}} CH_3^{\bullet} + H^{\bullet}$$

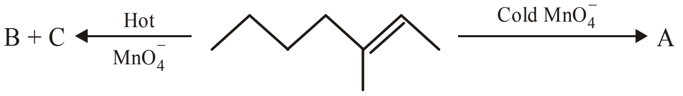
[HOTS]

2. Give the major product formed when each of the following alcohol is heated in presence of conc. H_2SO_4.

(a) 
$CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HC(CH_3)_3$

(b) $CH_3CH_2CH_2CH_2CH_2OH$ **[HOTS]**

3. Identify A, B and C in the following set :



[HOTS]

4. Alkenes are more reactive than alkynes toward addition of electrophilic reagents (e.g. Br_2, HBr, etc.) yet it is easy to stop the reaction at the alkene stage when 1 molar equivalent of the reagent is used. Explain. **[HOTS]**

5 How will you prepare 3-methylbut-1-yne by starting with ethyne? **[HOTS]**

6. Explain the following :

(a) Alkanes are inert

(b) Pyrolysis of alkanes leads to cleavage of C–C bonds rather than C–H bonds

(c) Although combustion of alkanes is a strongly exothermic process, it occurs only at high temperatures. **[HOTS]**

7. Which member of each pair is more reactive toward addition of HBr?

(a) 1-Propene or 2-methylpropene **[HOTS]**

(b) Cyclohexene of 1-methylcyclohexene

(c) 1-Butene or 1,3-butadiene

8. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane. **[Exemplar]**

9. Rotation around carbon-carbon single bond of ethane is not completley free. Justify the statement. **[Exemplar]**

10. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide. **[Exemplar]**

Long Answer Questions [5 Marks]

1. Ethyne reacts with dil. H_2SO_4 in presence of mercury salts to give acetaldehyde but with dil. HCl under similar conditions, it gives vinyl chloride. Explain why? **[HOTS]**

2. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. ON treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved. **[Exemplar]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

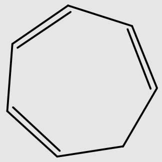
1. Give IUPAC name for tert. butanol and Isopropyl chloride.

2. What happens when propene is treated with cold $KMnO_4$?

3. Give the IUPAC name of the lowest molecular weight alkane that contains a quaternary carbon.

4. How would you differentiate between:
  (a) ethane and ethene.
  (b) ethene and ethyne.

5. Will the following compound be aromatic. Explain.



6. Give mechanism of Markovnikov addition.

7. Correct the following :
  (a) Ethyne to ethanal
  (b) Tert. butyl chloride to 2,2,3,3 tetra methyl butane.
  (c) Ethyne to benzene.
  (d) Benzoic acid to benzene
  (e) But 1–ene to butane 1,2– diol.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. A halogen compound used during halogenation of benzene is called halogen carrier e.g. $FeCl_3$.

2. $C_2H_2 < C_2H_4 < C_2H_6$.

3. A mixture of ethane, propane and butane is formed.

4. Acetylene, due to greater electronegativity of the sp–hybridized carbon.

5. By catalytic reduction with H_2 in presence of nickel at 523–573 K.

6. $HI > HBr > HCl > HF$

7. 2–Butene $H_3C—CH = CH—CH_3$ (being symmetrical gives the same product i. e., 2–bromobutane).

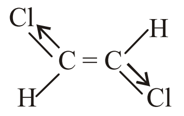
8. Tollens' reagent and ammonical CuCl solution.

9. No, because the difference of energy between these two conformations is very small, so even at room temperature these two interconverts rapidly and hence cannot be isolated.

10. Pd deposited over $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of lead acetate or sulphur or quinoline. This is used for partial reduction of alkynes to cis–alkenes.

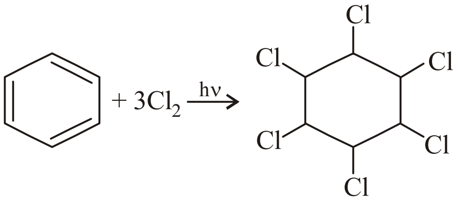
11. Refer theory

12. The two Cl's of the trans-isomer have equal and opposite bond moments bearing a net zero molecular dipole moments.



trans-1, 2-Dichloroethene

13.



Benzene Hexachlorocyclohexane

14. Isomers are 2-methyl pentane, 2, 3-dimethyl butane and 2, 2-dimethyl butane.
All three are isomers with the same molecular formula but one with least branching will have the highest boiling point, this is due to large surface area and more dispersion, forces.

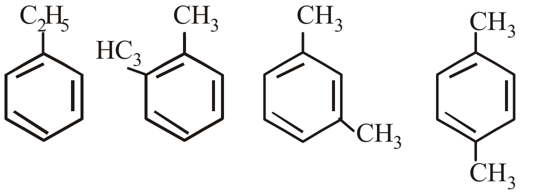
15. $CH_3-C\equiv C-CH_3 + NaNH_2 \longrightarrow$ No reaction

$$CH_3CH_2\equiv CH + NaNH_2 \longrightarrow CH_3CH_2C\equiv \overset{-}{C}\overset{+}{Na}$$

Short Answer Questions

1. More the number of C–atoms having maximum hydrogens, i. e., CH_3 groups, greater is the heat of combustion.
Thus the increasing order of heat of combustion is (iii) < (iv) < (i) < (ii).

2. Four isomers; ethylbenzene (1), *o*–xylene (2), *m*–xylene (3) and *p*–xylene (4).



ethylbenzene *o*-xylene *m*-xylene *p*-xylene

3. The double bonds of olefines decolorize Br_2 in CCl_4 and discharge the pink colour of Baeyer's reagent with simultaneous formation of a brown ppt. of MnO_2 while those of benzene do not.

4. Refer theory

5. Refer theory

6. Conformation of a molecule refers to different three dimensional positions of atoms relative to each other, arising from rotation about single (s) bonds. The energy required for rotation about C–C bond is very low and such rotation usually occur readily. So, the various conformations of a molecule are freely interconvertible. This phenomenon of getting different conformations arising from rotation about a single or sigma bond is called conformational isomerism.

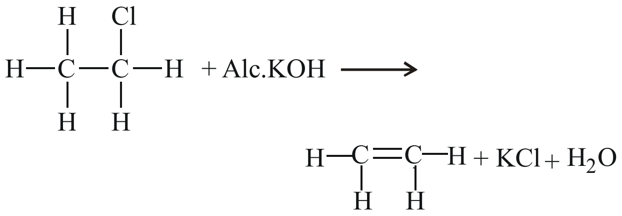
7. Cyclopropane is planar having bond angle of 60°. Cyclohexane does not have all the carbon atoms in one plane and bond angle is 109°.28'. Due to deviation from normal tetrahedron cyclopropane is very strained and hence very reactive. On the other hand, cyclohexane is free from angle strain hence known as strainless rings and hence is quite stable and unreactive.

8. By heating alkyl halides with alcoholic solution of potassium hydroxide. A molecule of halogen acid is eliminated. The reaction is known as dehydrohalogenation reaction.

$$\underset{}{RCH_2-CH_2-X} \xrightarrow[\text{Heat}]{\text{Alc.KOH}} \underset{\text{Alkene}}{RCH=CH_2} + HX$$

(X = Cl, Br, I)

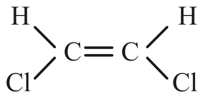
e.g.



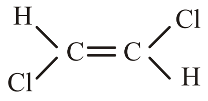
$$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-H + \text{Alc.KOH} \longrightarrow H-\underset{H}{C}=\underset{H}{C}-H + KCl + H_2O$$

This is an elimination reaction. The ease of dehydrohalogenation for different halogens is Iodine > Bromine > Chlorine, while for carbons it is tertiary > secondary > primary i. e., tertiary alkyl iodide is the most reactive.

9. Only (i) i. e. ClCH = CHCl has two different substituents on each carbon atom of the double bond and hence shows geometrical isomerism. The other two compounds, i. e., (ii) and (iii) do not show geometrical isomerism because one of the carbon atoms of the double bond in each case has two identical atoms, i.e., Cl atoms as structure of cis and trans form of CHCl = CHCl, 1, 2-dichloroethene



cis



trans

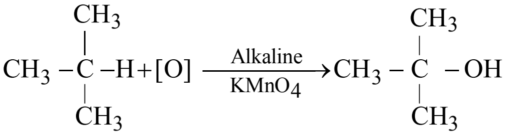
10. (i) Methane is oxidized to carbon monoxide and hydrogen is evolved.

$$CH_4 + H_2O \xrightarrow[1273\,K]{Ni} CO + 3H_2$$

(ii) It breaks down to its elements.

$$CH_4 \xrightarrow[\text{Carbon}]{1500\,K} C + 2H_2$$

(iii) Tert–butyl alcohol is formed.



$$\underset{\text{Isobutane}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H} + [O] \xrightarrow[KMnO_4]{\text{Alkaline}} \underset{\text{tert–Butyl alcohol}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH}$$

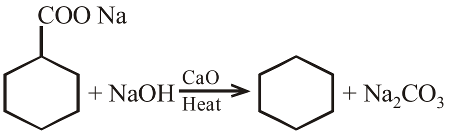
Isobutane tert–Butyl alcohol

11. Refer theory

12. (i) Methane is formed.

$$\boxed{CH_3\,COONa + NaO}\,H \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(ii)

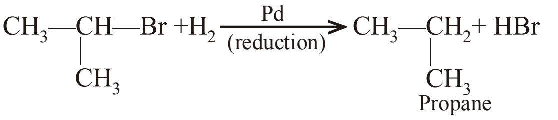


Cyclohexane

13. (i) Ethane is formed

$$CH_3CH_2-Br + 2[H] \xrightarrow[\text{(reduction)}]{Zn/HCl} CH_3CH_3 + HBr$$

(ii) Propane is obtained.



$$CH_3-\underset{CH_3}{CH}-Br + H_2 \xrightarrow[\text{(reduction)}]{Pd} CH_3-\underset{CH_3}{CH_2} + HBr$$

Propane

14. Alkyl halides can be reduced to alkanes by using red phosphorus and hydroiodic acid.

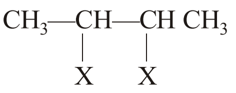
For example,

$$\underset{\text{bromoethane}}{CH_3CH_2}-Br+2HI\rightarrow \underset{\text{ethane}}{CH_3CH_3}+HBr+I_2$$

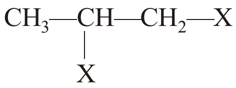
The function of the red phosphorus is to remove the iodine liberated in this reaction as it can react further with the alkane.

$$3I_2+2P\longrightarrow 2PI_3$$

15. (i) There is only one product in each case:

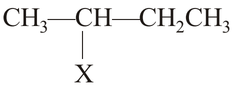
(a) 

$CH_3-\underset{X}{CH}-\underset{X}{CH}\,CH_3$

(b) 

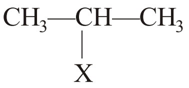
$CH_3-\underset{X}{CH}-CH_2-X$

(ii) (a) one product



$CH_3-\underset{X}{CH}-CH_2CH_3$

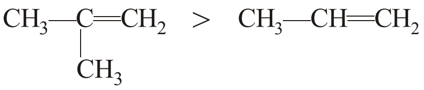
(b) two product



$CH_3-\underset{X}{CH}-CH_3$

and $CH_3-CH_2-CH_2-X$

16. Electron-donating alkyl groups make the π-bond more electron-rich and more reactive. Conversely, electron withdrawing groups such as Cl make the π-bond more electron deficient and less reactive. The order is

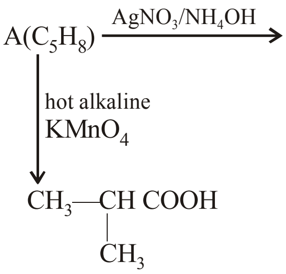


$CH_3-\underset{CH_3}{C}=CH_2 > CH_3-CH=CH_2$

(two CH_3 groups) (one CH_3 groups)

$> Cl-CH_2CH=CH_2 > CH_2=CH-Cl$

(one alkyl group with Cl atom) (Cl is directly bonded to double bonded carbon)

17. 

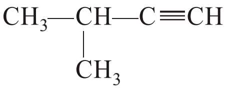
$A(C_5H_8)\xrightarrow{AgNO_3/NH_4OH}$ white ppt indicates the presence of triple bond at the terminal position.

$\downarrow$ hot alkaline $KMnO_4$

$CH_3-\underset{CH_3}{CH}\,COOH$

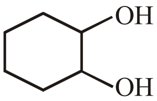
2-Methyl propanoic acid

Therefore, the structural formula of A is

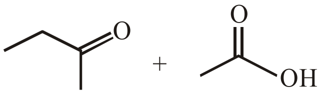


$CH_3-\underset{CH_3}{CH}-C\equiv CH$

3-Methy-1-butyne

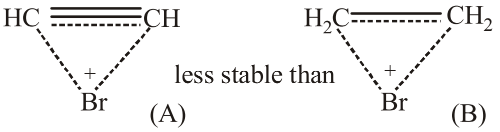
18. (i)  (Hydroxylation)

(ii) 

(iii) 

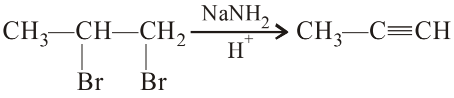
Butanone Ethanoic acid

19. The three-membered ring bromonium ion formed from the alkyne (A) has a full double bond causing it to be more strained and less stable than the other from the alkene (B).

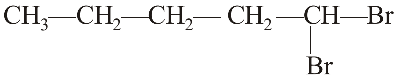


Also, the carbon's of (A) that are part of the bromonium ion have more *s*-character than (B), further making (A) less stable than (B).

20. (i) $CH_2=CH-CH_2+Br_2\longrightarrow$

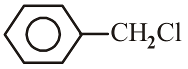


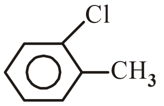
$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}\xrightarrow[H^+]{NaNH_2}CH_3-C\equiv CH$

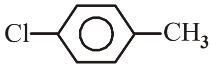
(ii) 

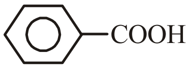
$CH_3-CH_2-CH_2-CH_2-\underset{Br}{CH}-Br$

$\xrightarrow[H^+]{NaNH_2}CH_3-CH_2-CH_2-C\equiv CH$

21. (i) 

(ii) a mixture of 

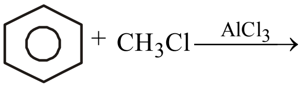
and 

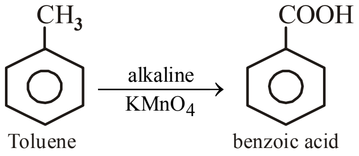
(iii) 

22. ⇒ (ii), (iv), (v) ⟶ activating and *o, p*-directing.

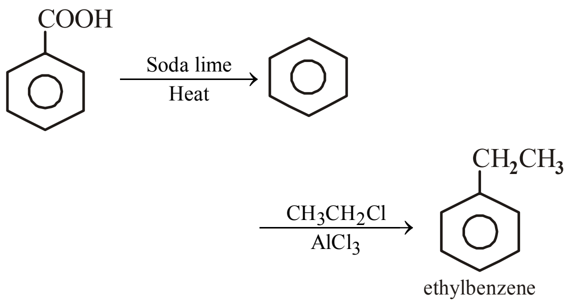
⇒ (iii) and (vi) ⟶ deactivating and *m*-directing.

⇒ (i) is deactivating (by NO_2 group) but *o, p*-directing (due to $C=C$ group).

23 (i) 

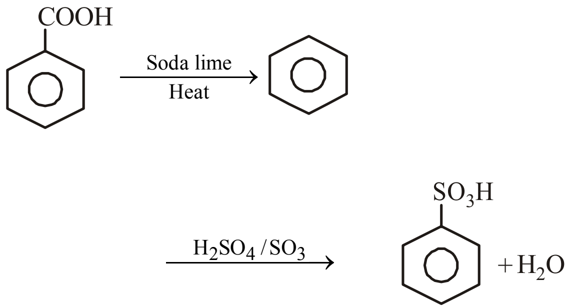


(ii) Benzoic acid to ethylbenzene



ethylbenzene

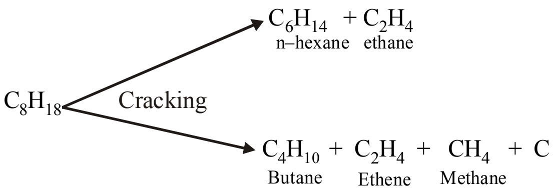
(iii) Benzoic acid to benzene sulphonic acid



benzene sulphonic acid

24. Both alkenes and arenes are electron-rich. Therefore undergo electrophilic reactions. Olefins undergo addition reactions because addition of a reagent to an olefin gives a more stable product as sp^2 hybridisation changes to sp^3 hybridisation. Addition to the double bond of arene would give a product with less or no resonance stability hence addition is difficult in arenes. On the other hand in substitution reaction, resonance stabilisation is retained therefore, arenes undergo substitution reaction.

25. Cracking is the process of breaking down the less volatile higher molecular mass hydrocarbon from petroleum into different types of more volatile lower molecular mass hydrocarbon. The cracking of alkanes involve the cleavage of C–C and C–H bonds. For example

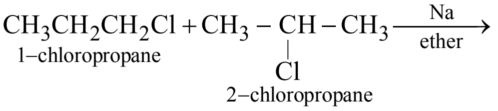


Long Answer Questions

1. Refer theory

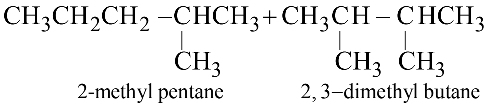
2. (i) Refer text book ans. 13.25

(ii) Three alkanes are obtained from the reaction of sodium with equimolar mixture of 1-chloropropane and 2-chloropropane.



$$\underset{\text{1–chloropropane}}{CH_3CH_2CH_2Cl} + \underset{\text{2–chloropropane}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3} \xrightarrow[\text{ether}]{\text{Na}}$$

$$\underset{\text{hexane}}{CH_3CH_2CH_2-CH_2CH_2CH_3}$$



$$\underset{\text{2-methyl pentane}}{CH_3CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3} + \underset{\text{2, 3–dimethyl butane}}{CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3}$$

3. (i) The increasing order of boiling points is 2, 2- dimethyl butane < 3- methyl pentane < hexane < heptane.

Hexane, 3-methyl pentane and 2, 2-dimethyl butane are isomers. As we know that increase in branching reduces the extent of contact between the neighbouring molecules. The van der Waals forces decreases, boiling point also decreases. Heptane has the highest boiling point due to its high molecular mass.

(ii) (a) Branched chain alkanes have lower boiling points than their straight chain isomers, and as branching increases, the boiling point decreases still further. The explanation is that increased branching gives the molecule a more spherical shape and reduces the extent of contact between neighbouring molecules. Consequently, the attractive forces are reduced and the boiling point decreases.

(b) Hydrocarbon with odd number of carbon atoms have lesser melting point than expected. This is because, in the crystalline state the molecule adopt a highly ordered arrangement in which the carbon chains form a zig-zig pattern. For the even members, different chains peak closer together than for the odd numbered members, so that the attractive forces are larger for the even membered hydrocarbon than for odd membered hydrocarbons of similar size. Therefore, relatively more energy must be applied to separate the molecules with even numbers of carbon atoms and enable them to adopt the more random arrangement of the liquid state than to separate the molecules with odd numbers of carbon atoms.

(c) The *n*-pentane, due to large surface area, the extent of contact between neighbouring molecules is more. Therefore, the attractive forces are more and the boiling point increases. But the melting point of neo-pentane is greater than that of n-pentane because neo-pentane has a highly symmetrical structure and reduced surface area. Therefore, it is packed in the crystal systems more closely than *n*-pentane. So more energy is required to break the neo-pentane lattice than the *n*-pentane. Hence, neo-pentane has a higher melting point *n*-pentane.

4. The order of decreasing acidic strength

Alkyne > alkene > alkane

The acidic character of acetylene may be explained in terms of the *s*-character of the *sp* hybridised orbital. An electron in an *s*-orbital is more tightly held than in a *p*-orbital because the *s*-electrons are closer to the nucleus. Since there is more *s*-character in *sp* orbitals, the electrons in *sp* orbitals are held more strongly by the nucleus than sp^2 and sp^3 electrons. In other words, the *sp* hybridised carbon is more electronegative than sp^2 and sp^3 hybridised carbon atoms. Due to this, the hydrogen of acetylenic carbon develops a more positive charge and is acidic in character.

$$CH \equiv C-H + NaNH_2 \longrightarrow \underset{\text{sodium acetylide}}{CH \equiv C^-Na^+} + NH_3$$

$$CH \equiv CH + 2AgNO_3 \xrightarrow{2NH_4OH}$$

$$\underset{\text{silver acetylide}}{Ag^+C \equiv C^-Ag^+} + \underset{\text{(white ppt)}}{2NH_4NO_3} + 2H_2O$$

5. A = Planar ring, all atoms of the ring sp^2 hybridised, has six delocalised π electrons, follows Huckel rule. It is aromatic.

B = Six delocalised π-electrons (4π electrons +2 unshared electrons on negatively charged carbon) in a planar ring, follows Huckel's rule. It is aromatic.

C = Has only four-delocalised π-electrons. It is non-aromatic.

D = Follows Huckel's rule, has 2π electrons i.e., $(4n+2)\pi$-electrons where (n = 0), delocalised π-electrons. It is aromatic.

E = 8π electrons, does not follow Huckel's rule i.e, $(4n+2)\pi$-electrons rule. It is not aromatic.

HOTS/EXEMPLAR QUESTIONS

Very Short Answer Questions

1. Alkenes are adsorbed on the surface of the catalyst only when the plane of the π bond approaches perpendicularly (head on). Because of cylindrical nature of the π bonds. Any approach along the axis of the cylinder can be successful.

2. The two conformations of ethane cannot be separated but are readily convertible.

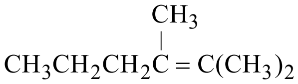
Short Answer Questions

1. We know that the value of E_{act} of reactions involving only bond-breaking is equal to ΔH, then

$$\underset{(58\ \text{kCal})}{Cl-Cl} \xrightarrow{\text{heat}} 2Cl\bullet \qquad \Delta H = 58, E_{act} = 58\ \text{kCal}$$

$$\underset{(104\ \text{kCal})}{CH_3-H} \xrightarrow{\text{heat}} CH_3\bullet + H\bullet\ \Delta H = 104, E_{act} = 104\ \text{kCal}$$

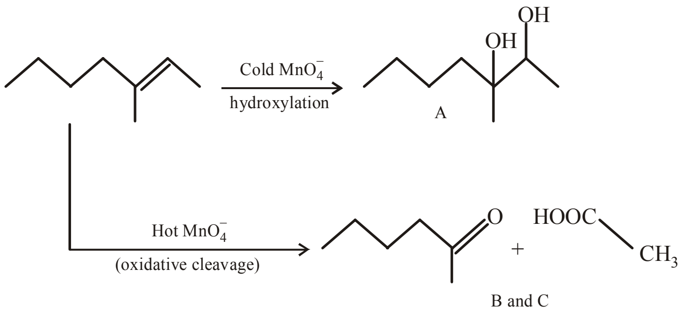
2. (a)



$$CH_3CH_2CH_2\overset{\overset{\large CH_3}{|}}{C} = C(CH_3)_2$$

(b) $CH_3CH_2CH=CHCH_3$

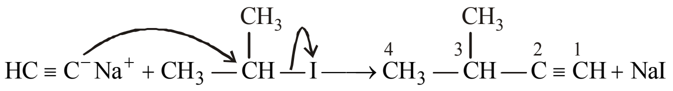
3.



4. The high reactivity of alkynes than alkenes toward electrophiles can be explained on the basis of stability of their corresponding intermediate cyclic bromonium ion or carbocation.

$$\underset{\text{from alkyne}}{CH_2 = \overset{+}{C}H} \text{ less stable than } \underset{\text{(from alkene)}}{CH_3 - \overset{+}{C}H_2}$$

5. $$\underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[196\ K]{Na, NH_3(l)} \underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+}$$



$$HC \equiv C^-Na^+ + \underset{\text{Isopropyl iodide}}{CH_3 - \overset{\overset{\large CH_3}{|}}{CH} - I} \longrightarrow \underset{\text{3-Methylbut -1-yne}}{\overset{4}{CH_3} - \overset{\overset{\large CH_3}{3|}}{CH} - \overset{2}{C} \equiv \overset{1}{CH}} + NaI$$

6. (*a*) A reactive site in a molecule generally has at least one of the following features : (*i*) one or more unshared pair of electrons, (*ii*) a polar bond, (*iii*) an electron deficient atom, (*iv*) an atom with an expandable octet. Alkanes have none of these features, hence these are inert.

(*b*) The C—C bond has a lower average bond energy ($\Delta H = +347\ \text{kJ mol}^{-1}$) than the C—H bond ($\Delta H = +415\ \text{kJ mol}^{-1}$).

(*c*) The reaction is very slow at moderate temperatures because of a very high activation energy.

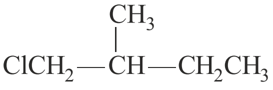
7. Species with more stable intermediate (carbocation) will be more reactive

(a) 2-Methylpropene (3° carbocation as intermediate)

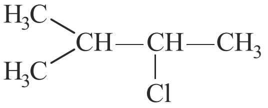
(b) 1-Methylcycloehexene (3° carbocation as intermediate)

(c) 1, 3-Butadiene (Allylic carbocation as intermediate)

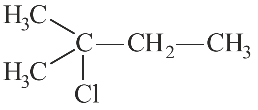
8. 2-Methyl butane is $CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$. Possible compounds are A, B and C given below:


A(1°)

None possibilities for compound 'A' because nine methyl hydrogens are present in 2-methylbutane.


B(2°)

Two possibilities for 'B' compound because two CH hydrogens are present in 2-methylbutane.


C(3°)

Only one possibility for 'C' compound because one CH hydrogens is present in 2-methylbutane.

Relative amounts of A, B and C compounds =

Number of hydrogen × relative reactivity

	A(1°)	**B(2°)**	**C(3°)**
Relative amount	$9 \times 1 = 9$	$2 \times 3.8 = 7.6$	$1 \times 5 = 5$

Total amount of monohaloginated compounds = 9 + 7.6 + 5 = 21.6

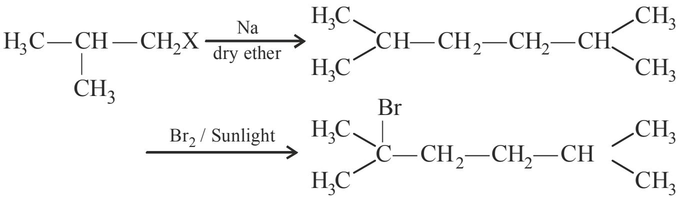
$$\text{Perentage of A} = \frac{9}{21.6} \times 100 = 41.7\%$$

$$\text{Perentage of B} = \frac{7.6}{21.6} \times 100 = 35.2\%$$

$$\text{Perentage of C} = \frac{5}{21.6} \times 100 = 23.1\%$$

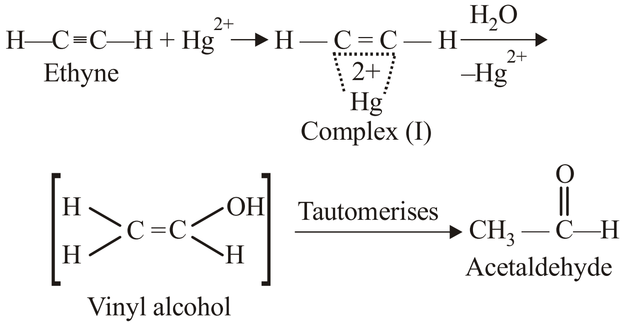
9. The rotation about C–C bond is restricrted because of repulsioin between electron cloud of C–H bonds on either carbon atoms.

10.

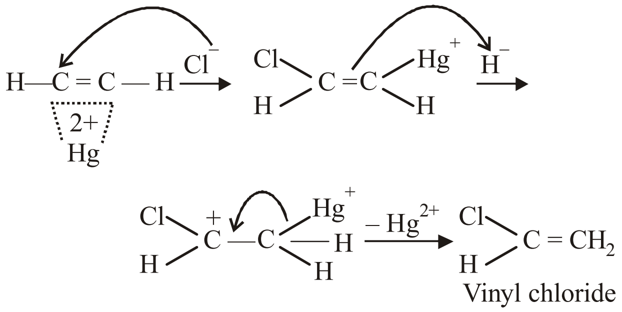


Long Answer Questions

1. First of all, mercury ions form a complex (I) with acetylene. Since H_2O is more nucleophilic than SO_4^{2-} ion, it attacks the complex (I) to form first vinyl alcohol which then tautomerises to give acetaldehyde



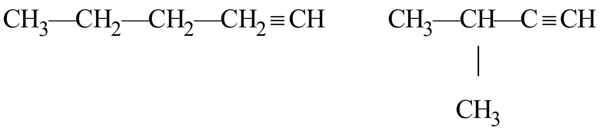
In case of dil. HCl, since Cl^- ion is more nucleophilic than H_2O, it reacts with complex (I) to form vinyl chloride.



2.
$$\underset{(A)}{C_5H_{11}Br} \xrightarrow{\text{alc.KOH}} \underset{(B)}{\text{Alkene}(C_5H_{10})} \xrightarrow{Br_2 \text{ in } CS_2} \underset{(C)}{C_5H_{10}Br_2}$$

$$\xrightarrow[-2HBr]{\text{Alc.KOH}} \underset{\text{D (Alkyne)}}{C_5H_8} \xrightarrow{Na-liq.NH_3} \underset{\text{Sodium alkylide}}{C_5H_7-Na+\frac{1}{2}H_2}$$

The reactions suggest that (D) is a terminal alkyne. This means triple bond is at the end of the chain. It could be either (I) or (II).


I II

Since alkyne 'D' on hydrogenation yields straight chain alkane, therefore structure I is the structure of alkyne (D).

Hence, the structures of A, B and C are as follows:

(A) $CH_3—CH_2—CH_2—CH_2—CH_2Br$

(B) $CH_3—CH_2—CH_2—CH=CH_2$

(C) $CH_3—CH_2—CH_2—CH(Br)—CH_2Br$

CHAPTER TEST

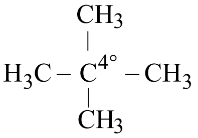
1. (i) 2-methyl propan 2-ol

(ii) 2-chloropropane

2. $H_2C=CH-CH_3 + \text{cold. } KMnO_4 \longrightarrow$

$HO-CH_2-CH(OH)-CH_3$ (propan 1,2 di–ol)

3. 2, 2–Dimethylpropane.



$$H_3C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{C^{4^\circ}}}-CH_3$$

4. (a) Ethane and ethene can be differentiated by adding bromine water. Ethene decolorizes bromine water but ethane doesn't.

(b) Ethene and ethyne can be differentiated by adding Tollen's reagent. Ethyne gives silver mirror test while ethene does not.

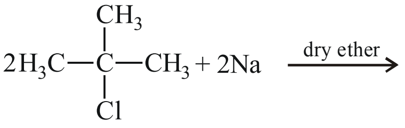
5. It is not aromatic.

Although it has 6π – electrons but it is not conjugated.

6. Refer theory

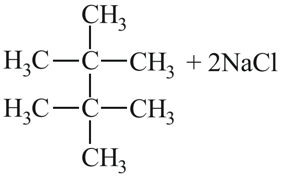
7. (a) $\underset{\text{ethyne}}{3HC \equiv CH} + H_2O \xrightarrow{H^+ \text{and } Hg^{2+}}$

$H_2C = CHOH \xrightarrow{\text{isomerisation}} \underset{\text{ethanal}}{H_3CCHO}$

(b) 

$$2H_3C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-CH_3 + 2Na \xrightarrow{\text{dry ether}}$$

t-butyl chloride



$$H_3C-\overset{\overset{\Large CH_3}{|}}{C}-CH_3 \quad + 2NaCl$$
$$H_3C-\underset{\underset{\Large CH_3}{|}}{C}-CH_3$$

2, 2, 3, 3-tetramethyl butane

(c) Refer theory

(d) $\underset{\text{Benzoic acid}}{C_6H_5COOH} + 2NaOH \xrightarrow{\text{CaO, Heat}} \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3 + H_2O$

(e) $\underset{\text{But–1–ene}}{H_3CCH_2CH = CH_2} + \text{cold dil.}KMnO_4 \rightarrow$

$\underset{\text{butan-1, 2-diol.}}{H_3CCH_2CH(OH)CH_2(OH)}$

14

Chapter

Environmental Chemistry

INTRODUCTION

Pollutants are substances introduced into the environment that has undesirable effects. The pollutants may be inorganic, biological or radiological in nature.

(i) Bio-degradable pollutants are domestic wastes which are rapidly decomposed by micro-organisms.

(ii) Non-biodegradable pollutants include chemicals, mercuric salts, lead compounds, pesticides, etc.

(iii) Natural pollution is caused by radioactive substances, volcanic eruptions, forests and mines fires, floods, etc.

(iv) Artificial pollution is caused by industries, thermal plants, automobile exhausts, sewage, etc.

ENVIRONMENT

The conditions existing around animal or human life.The gaseous envelop surrounding the earth is called atmosphere. It has been classified into following regions:

- **Stratosphere :** The layer of the earth's atmosphere above the troposphere and below the mesosphere.
- **Troposphere :** The lowest region of the atmosphere extending from earth's surface to the lower boundary of the stratosphere. In this region, human beings along with other organisms live. It contains water vapour and is greatly affected by air pollution.

Note : The other two layers are Thermosphere and Mesosphere.

AIR POLLUTION

Air pollution is the introduction of harmful substances into air that can have adverse effects on humans and the ecosystem. The major air pollutants are

Carbon Monoxide (CO)

It is produced by incomplete combustion of gasoline in motor vehicles, wood, coal, inceneration and forest fires. It is treacherous and deadly poisonous gas. It induces headache, visual difficulty, coma and death. It blocks the normal transport of oxygen from the lungs to other parts of the body.

Sulphur Dioxide (SO_2)

It is produced by petrol combustion, coal combustion, petrol refining and smelting operations. It hinders the movement of air in and out of lungs. It is particularly poisonous to trees causing chlorosis and dwarfing. In presence of air it is oxidised to SO_3 which is also irritant.

$$2\,SO_2 + O_2\ (\text{air}) \longrightarrow 2\,SO_3$$

In presence of moisture SO_3 is converted into highly corrosive sulphuric acid.

$$SO_3 + H_2O\ (\text{moisture}) \longrightarrow H_2SO_4$$

It attacks marble, limestone,vegetation, paper and textiles and injurious to human beings.

Oxides of Nitrogen

NO_2 and NO, Source - combustion of coal, gasoline, natural gas, petroleum refining, chemical plants, manufacturing explosives and fertilizers, tobacco smoke.

Breathing NO_2 causes chlorosis to plants and chronic lung conditions leading to death. NO_2 reacts with moisture to form acids.

$$2\,NO_2 + H_2O \longrightarrow HNO_2 + HNO_3\,,\ 3\,HNO_2 \longrightarrow 2\,NO + HNO_3 + H_2O$$

Smoke, Dust

Sources : cement works, iron and steel works, gas works, power generating stations.

Smog

It is a mixture of smoke and fog in suspended droplet form. It is of two types :

(i) **London smog or classical smog :** It is a mixture of coal smoke and fog. The fog part is mainly SO_2 and SO_3. It has sulphuric acid aerosol. It causes bronchial irritation and acid rain. It is reducing in nature.

(ii) **Photochemical smog or Los Angeles smog :** The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.

Hydrocarbons + O_2, NO_2, NO, O, $O_3 \rightarrow$ Peroxides, formaldehyde, peroxyacetylnitrate (PAN), acrolein etc.

It is oxidising in nature and causes irritation to eyes, lungs, nose, asthamatic attack and damage plants.

Acid Rain

The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids and lower the pH of water below 5.5.

$$H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

$$2H_2O + 2SO_2 + O_2 \rightarrow 2H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$2H_2O + 4NO_2 + O_2 \rightarrow 4HNO_3 \rightleftharpoons 4H^+ + 4NO_3^-$$

The acids are toxic to vegetation, react with marble and damage buildings.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Acids corrode water pipes and produce salts with heavy metals ions viz Cu, Pb, Hg and Al which are toxic in nature.

Green House Effect

The retention of heat by the earth and atmosphere from the sun and its prevention to escape into the outer space is known as green house effect.

Global warming is average increase in the temperature of earth due to increase in concentration of green house gases (CO_2, O_3, NO_x etc.)

Consequences of global warming :

(i) Global warming is due to rise in sea level due to increased rate of melting of glaciers and floods.

(ii) Increase in infectious diseases like malaria, dengue, etc.

Ozone Layer and Its Depletion

The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful U. V. radiations from the sun. The U. V. radiations cause skin cancer, cataract of eye, and harm to vegetation.

Depletion of ozone is caused by oxides of nitrogen

$$N_2O + h\upsilon \longrightarrow \underset{\text{(reactive nitric oxide)}}{NO + N}$$

$$NO + O_3 \longrightarrow NO_2 + O_2,$$

$$O_3 + h\upsilon \longrightarrow O_2 + O,$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$2O_3 + h\upsilon \longrightarrow 3O_2 \text{ (Net reaction)}$$

The presence of chlorofluorocarbons also increase the decomposition of O_3.

$$CF_2Cl_2 + H\upsilon \longrightarrow CF_2Cl + Cl$$

$$CFCl_3 + H\upsilon \longrightarrow CFCl_2 + Cl,$$

$$Cl + O_3 \longrightarrow ClO + O_2,$$

$$ClO + O \longrightarrow Cl + O_2$$

$$O_3 + O \longrightarrow 2O_2 \text{ (Net reaction)}$$

Control of air pollution : It can be controlled by

(i) Dissolving HCl, HF, SiF_4 in water and SO_2, Cl_2, H_2S in alkaline solution.

(ii) Adsorbing gas and liquid molecules over activated charcoal and silica gel.

(iii) Chemical reactions

(iv) Use of precipitators to settle charge particles

(v) Use of settling chambers under the action of gravity
(vi) Use of natural gas in place of diesel, petrol, etc.

WATER POLLUTION

The contamination of water by foreign substances which would constitute a health hazard and make it harmful for all purposes (domestic, industrial or agriculture etc.) is known as water pollution. The polluted water may have offensive odour, bad taste, unpleasant colour, murky, oily, etc.

Sources of Water Pollution

(i) **Domestic sewage :** Discharges from kitchens, bathrooms, laboratories, etc.
(ii) **Industrial wastes :** Wastes from manufacturing processes which include acids, alkalies, pesticides, insecticides, metals like copper, Zinc, lead, mercury, fungicides, etc.
(iii) **Oil :** from oil spills or washings of automobiles
(iv) **Atomic explosion** and processing of radioactive materials
(v) **Suspended particles** (organic or inorganic) viruses, bacterias, algae, protozoa, etc.
(vi) **Wastes from fertilizer** plants such as phosphates, nitrates ammonia, etc.
(vii) **Clay :** Ores, minerals, fine particles of soil.

Aerobic and Anaerobic Oxidation

The oxidation of organic compounds present in sewage in presence of good amount of dissolved or free oxygen (approx. 8.5 ml/l) by aerobic bacterials is called *aerobic oxidation*. When dissolved or free oxygen is below a certain value, the sewage is called *stale* anaerobic bacterias bring out putrefaction producing H_2S, NH_3, CH_4, $(NH_4)_2S$, etc. This type of oxidation is called *anaerobic* oxidation.

Biological Oxygen Demand (BOD)

It is defined as the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/l or ppm. An average sewage has BOD of 100 to 150 mg/l.

Chemical Oxygen Demand (COD)

It is a measure of all types of oxidisable impurities present in the sewage. COD values are higher than BOD values.

SOIL OF LAND POLLUTION

The addition of substances in an indefinite proportion changing the productivity of the soil is known as soil or land pollution.

Sources of Soil Pollution

(i) **Agricultural pollutants :** Chemicals like pesticides, fertilizers, bacteriacides, fumigants, insecticides, herbicides, fungicides.
(ii) **Domestic refuge** and industrial wastes.
(iii) **Radioactive wastes** from research centres, and hospitals.
(iv) **Soil conditioners** containing toxic metals like Hg, Pb, As, Cd, etc.
(v) **Farm wastes** from poultries, dairies and piggery farms.
(vi) **Improper disposal** of human and animal exreta.
(vii) **Pollutants** present in air from chemical works

PESTICIDES

The chemical substances used to kill or stop the growth of unwanted organisms are called pesticides. They are further classified as

(i) **Insecticides :** They are used to kill insects. The most common insecticides are
- (a) D.D.T
- (b) BHC, gamexene
- (c) Baygon
- (d) Sevin Carbaryl
- (e) Parathion
- (f) Methoxychlor
- (g) Aldrin

(i) **Herbicides :** They are used to kill weeds, e.g.
- (a) 2, 4-dichlorophenoxy acid
- (b) Triazines
- (c) $NaClO_3$ Sodium chlorate
- (d) Na_3AsO_3 Sodium arsenite

The (iii) and (iv) are not used nowadays.

Addition of phosphate fertilizers to water leads to nutrient enrichment (eutrophication).

CONCEPT MAP

Environmental Chemistry

Pollutants are

- Bio-degradable: decomposed by micro-organisms
- Non-biodegradable: includes chemicals, mercuric salts etc.
- Natural emitted in radioactivity, Volcanoes, etc.
- Artificial: emitted by industries, automobiles, etc.

Major air pollutants are:

- CO: emitted mainly by automobiles. Blocks normal transport of oxygen in the bodies.
- SO_2: produced by petrol, coal combustion, etc. causes acid rain

  NO_x ($x = 1$ or 2): produced in combustion of coal, natural gas, etc. causes acid rain.
- Smoke, dust: Sources are cement works, power generating stations, etc.
- Smog: Smoke + fog

Two important air pollution phenomena are:

(a) Green House effect: Retention of heat in the atmosphere of the earth leading to Global warming. It is causing due to rise in the sea level by melting .

(b) Ozone layer depletion: Depletion of the ozone layer above the earth's surface by NO_x ($x=1,2$) and CFCs, etc. Ozone layer cuts the harmful UV radiations from reaching the earth

Water Pollution: is contamination of water by making it unfit for drinking and other purposes. Presence of substances causing reduction in soil productivity are called soil pollution. There are many sources of air & soil pollution. Pesticides cause both – soil & water pollution.

Biological Oxygen Demand (BOD) is the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days.

Chemical Oxygen Demand (COD) is a measure of all types of oxidisable impurities present in the sewage. COD values are always greater than BOD values.

Textbook Exercises

14.1 Define environmental chemistry.

Ans. Environmental chemistry is defined as that branch of science which deals with the chemical phenomenon occurring in the environment, i. e., study of origin, transport, reactions, effects and the fates of chemical species in the environment.

14.2 Explain tropospheric pollution in 100 words.

Ans. Tropospheric pollution occurs due to the presence of undesirable gases and the solid particles in the air.

The major gaseous and the particulate pollutants present in the troposphere are as follows:

(i) Gaseous air pollutants. These include mainly oxides of sulphur (SO_2, SO_3), oxides of nitrogen (NO, NO_2) and oxides of carbon (CO, CO_2) in addition to hydrogen sulphide (H_2S), hydrocarbons, ozone and other oxidants.

(ii) Particulate pollutants. These include dust, mist, fumes, smoke, smog, etc.

14.3 Carbon monoxide gas is more dangerous than carbon dioxide gas. Why ?

Ans. CO binds to haemoglobin for which it has 200 times more affinity than oxygen and forms carboxyhaemoglobin. In blood, when the concentration of carboxyhaemoglobin reaches 3. 4%, the oxygen carrying capacity of the blood is greatly reduced. In other words, the body becomes oxygen–starved. This results into headache, nervousness, cardiovascular disorder, weak eye–sight etc. On the other hand,CO_2 does not combine with haemoglobin and hence is less harmful as pollutant. CO_2 is the main contributor towards green–house effect and global warming.

14.4 Which gases are responsible for green–house effect? List some of them.

Ans. CO_2 is the main gas responsible for green–house effect. Other green–house gases are methane, nitrous oxide, water vapors, chlorofluorocarbons (CFC's) and ozone.

14.5 Statues and monuments in India are affected by acid rain. How?

Ans. The air around the statues and monuments in India contains fairly high levels of the oxides of sulphur and nitrogen. This is mainly due to a large number of industries and power plants in the nearby areas. The problem has been further aggravated due to use of poor quality of coal, kerosene and firewood as fuel for domestic purposes. The resulting acid rain attacks the marble of these statues and monuments

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

As a result, these monuments are being slowly eaten away and marble is getting discolored and lusterless.

14.6 What is smog? How are classical and photochemical smog different?

Ans. Smog is a combination of smoke and fog. Difference between Classical and photochemical smog

Classical Smog	Photochemical Smog
1. This was first time observed in London in 1952.	1. This was observed in Los Angeles in 1950.
2. It is formed due to presence of SO_2 and humidity in the air which combine to form H_2SO_4 fog which deposits on the particulates.	2. It is formed due to photochemical reaction when air contains NO_2 and hydrocarbons.
3. It involves smoke and fog.	3. It does not involve any smoke or fog.
4. It is formed in the months of winter particularly in the morning hours when the temperature is low.	4. It is formed in the months of summer during afternoon when there is a bright sunlight so that photochemical reactions can take place.
5. It causes bronchitis i.e. irritation in lungs.	5. It causes irritation in the eyes.
6. It is reducing in character.	6. It is oxidizing in character.

14.7 Write down the reactions involved during the formation of photochemical smog.

Ans. In the presence of sunlight, NO_2 undergoes photolysis to form NO and atomic oxygen. Atomic oxygen then combines with the molecular oxygen in the presence of some molecule which acts as a source of transfer of energy to form ozone, O_3. The ozone formed reacts with NO to form NO_2 and O_2. Thus NO_2 cycle is completed.

Reactions:– $NO_2 \xrightarrow{hv} NO + O,$

$$O + O_2 \longrightarrow O_3,\ O_3 + NO \longrightarrow NO_2 + O_2$$

When hydrocarbons are present, they combine with oxygen atom, produced in the first step during photolysis of NO_2, to form highly reactive free radicals as intermediates. These free radicals initiate a variety of reactions:

$$RCO + O_2 \longrightarrow RCO_3,\ RCO_3 + NO \longrightarrow RCO_2 + NO_2,$$

$$RCO_3 + O_2 \longrightarrow O_3 + RCO_2,\ RCO_3 + NO_2 \longrightarrow RCO_3NO_2$$

(peroxoacrylnitrates –PAN)

As a result concentration of ozone, PAN and aldehydes and ketones is a build up in the atmosphere.

14.8 What are the harmful effects of photochemical smog and how can they be controlled?

Ans. The harmful effects of smog are:

(i) All these compounds like ozone, PAN etc. cause irritation in our eyes.

(ii) They damage many materials such as metals, stones , building materials.

(iii) Ozone destroys rubber.
(iv) It is also harmful to fabrics, crops and ornamental plants.
(v) NO_2 present in photochemical smog , reduces visibility. Hence pilots experience problems due to this smog.

14.9 What are the reactions involved for ozone layer depletion in the stratosphere ?

Ans. NO which may be produced at the ground level due to human activity react with ozone and form different oxides of nitrogen & oxygen

$$NO + O_3 \longrightarrow NO_2 + O_2,\ \dot{N}O_2 + O \longrightarrow NO + O_2$$

Chlorofluorocarbons(CFC) are commonly known as freons which introduced in the atmosphere from aerosol sprays, refrigerating equipments and others. These compounds decompose to form Cl free radical

$$CF_2Cl_2 \longrightarrow CF_2Cl + \dot{C}l,\ \dot{C}FCl_3 \longrightarrow CFCl_2 + \dot{C}l$$

The reactive chlorine atoms then destroys the ozone layer through the following sequence of reactions.

$$\dot{C}l + O_3 \longrightarrow Cl\dot{O} + O_2, Cl\dot{O} + O \longrightarrow \dot{C}l + O_2$$

14.10 What do you mean by ozone hole? What are its consequences?

Ans. Due to depletion of ozone in the atmosphere, large ozone holes are created in the ozone layer.

Effects of Ozone depletion

(i) The U.V. rays coming from the sun passes through the stratosphere and reach the surface of earth. This radiation is the cause of cancer in skin.
(ii) Exposure of eyes to the U.V. radiation can cause cataract or even blindness.
(iii) Exposure of plants to the U.V. radiations can adversely affect the plant proteins and results in destruction of chlorophyll and harmful mutation.
(iv) It has a very strong effect on our climate. It upsets the heat balance of the earth.
(v) If it is not controlled, it would cause ecological disturbances.

14.11 What are the major causes of water pollution? Explain.

Ans. The main causes for pollution in water are:

(i) Sewage and domestic wastes causes pathogens which are disease causing bacteria and also result in gastro–intestinal diseases.
(ii) The industrial effluents contain toxic and hazardous chemicals cause lead poisoning, kidney damage, etc.
(iii) The agricultural discharge includes fertilizers, pesticides, etc., causing harm to men and animals.
(iv) Siltation produces turbidity in water thereby hindering the free movement of aquatic organisms and their growth and productivity.
(v) The thermal pollutants increase the temperature of water adversely affecting the aquatic lives present in them.
(vi) The radioactive discharge from nuclear reactors are highly hazardous.

14.12 Have you ever observed any water pollution in your area ? How can you control it ?

Ans. We have water pollution due to sewage disposal in our area. It is controlled by spraying insecticides in the drains. Some places have been earmarked for water harvesting.

14.13 What do you mean by Biochemical Oxygen Demand (BOD) ?

Ans. The total amount of oxygen consumed by micro–organisms in decomposing the waste present in a certain volume of a sample of water is called Biochemical Oxygen Demand (BOD) of water.

14.14 Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution ?

Ans. Yes, we do observe soil pollution in our neighbourhood due to dumping of non–biodegradable waste like plastic bags and cans along with biodegradable wastes.

The best way to manage waste from house–hold is to keep two garbage bins, one for the biodegradable waste and the other for the non–biodegradable waste. Many combustible wastes can be burned and the ashes can be used for land–fill. However care must be taken for the toxic gases which can emit during combustion.

14.15 What are pesticides and herbicides ? Explain giving examples.

Ans. **Pesticides.** These are synthetic toxic chemicals which are used in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. Their repeated use gives rise to pests that are resistant to that group of pesticides. As a result, these pesticides become ineffective for those pests.

Earlier DDT was used. As insect resistance towards DDT increased, other organic toxins such as Aldrin and Dialdrin were introduced for use as pesticides. But these were non–biodegradable and slowly transferred to human being through food chain causing metabolic and physiological disorders, Conse quently, a new series of pesticides, organophosphates and carbamates have been introduced. These are biodegradable but are severe nerve toxins and hence more harmful to humans and have caused even deaths. Thus, the insecticide industry is engaged in developing new insecticides.

Herbicides. These are the chemicals used to control weeds. Earlier, inorganic compounds such as sodium chlorate ($NaClO_3$) and sodium arsenite (Na_3AsO_3) were used but arsenic compounds, being toxic to mammals, are no longer preferred. Instead, organic compounds such as triazines, are now considered as better herbicides, especially for the corn–fields.

14.16 What do you mean by green chemistry? How will it help decrease environmental pollution?

Ans.. Producing chemicals of our daily needs using such reactions and chemical processes which neither use toxic chemicals nor emit such chemicals into the atmosphere. It is evident that if concerted efforts are made to develop green chemical products, it will certainly help us to keep our environment pollution free.

14.17 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere ? Discuss.

Ans. The solar energy radiated back from the earth surface is absorbed by the greenhouse gases (i.e., CO_2, CH_4, O_3, CFC's and water vapour) present near the earth's surface. Thus, they heat up the atmosphere near the earth's surface and keep it warm. As a result, they keep the temperature of the earth constant and help in the growth of plants and existence of life on the earth. If there were no greenhouse gases, there would have no vegetation and life on the earth.

14.18 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

Ans. Excessive phytoplankton (organic pollutants such as leaves, grass, trash etc.) present in water is biodegradable. A large population of bacteria decomposes this organic matter in water. During this process, they consume the oxygen dissolved in water. Water has already limited dissolved oxygen (10 ppm). Thus, it is further depleted. When the level of dissolved oxygen falls below 6 ppm, the fish cannot survive. Hence, they die and float dead on the lake.

14.19 How can domestic waste be used as manure?

Ans. Domestic waste comprises of two types of materials, biodegradable such as leaves, rotten food etc. and non–biodegradable such as plastics, glass, metal scrap etc. The non–biodegradable waste is sent to industry for recycling. The biodegradable waste should be deposited in the land fills. With the passage of time, it is converted into manure (compost).

14.20 For your agricultural field or garden, you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Ans. The compost producing pit should be set up at a suitable place or in a tin to protect ourselves from bad odour and flies. It should be kept covered so that flies cannot make entry into it and the bad odour is minimized. The recyclable material like plastics, glass, newspapers etc. should be sold to the vendor who further sells it to the dealer. The dealer further supplies it to the industry involved in recycling process.

Practice Questions

Very Short Answer Questions [1 Mark]

1. Name the different regions of the atmosphere alongwith their altitudes.
2. In what regions of the atmosphere, the temperature increases with altitude and in which regions it decreases?
3. What gas leaked to bring havoc in Bhopal tragedy?
4. What is the %age of CO_2 in the pure dry air?
5. Name three gases which are major air pollutants.
6. What is the most important sink of CO pollutant?
7. What is the compound formed when CO combines with blood?
8. What is anoxia or asphyxiation?
9. How are NO and NO_2 formed in the atmosphere?
10. How are fuel gases from industries freed from oxides of nitrogen and sulphur?
11. What is chlorosis?
12. What is the size range of particulates?
13. What type of aromatic compounds are present as particulates in the air?
14. Who are the people who usually suffer from 'black lung disease' and who are those who suffer from 'white lung disease'?
15. How particulates help in the cloud formation?
16. Which zone is called ozonosphere?
17. Which main compounds are causing damage to ozone layer?
18. Which gaseous species are present in the mesosphere and thermosphere?
19. Which disease is caused due to hole in the ozone layer and why?
20. What is the composition of 'London smog or reducing smog'?
21. In which season and of what time of the day, there is 'London smog or reducing smog' ?
22. What is the nature of 'London smog' ?
23. In which season and what time of the day, there is photochemical smog?
24. Which acids are present in the acid rain?
25. Name two important sinks of CO_2.
26. What is marine pollution?
27. What type of pollution affects the sea–birds?
28. What are the main sources of thermal pollution?
29. Why COD is preferred over BOD ?
30. What is humification?
31. What should be the tolerable limit of fluoride ions in drinking water? What happens if it is higher than 10 ppm ?
32. Name any four methods for waste management.
33. What is the nature of 'photochemical smog'?
34. Name of source of energy which does not create pollution.
35. What are PCBs?
36. What are polar stratospheric clouds (PSCs)?
37. What is meant by polar vortex?
38. What is effect of excess of SO_4^{2-} ion in drinking water?
39. Write the name of gas produced in Mathura refineries which can damage the great historical monument "Taj Mahal"?
40. What type of radiations are absorbed by CO_2 in the atmosphere?

Short Answer Questions [2 & 3 Marks]

1. Name two natural sources of air pollution.
2. What are 'asbestosis' and 'silicosis'?
3. What is the composition of 'photochemical smog'?
4. What is the role of CO_2 in the 'greenhouse effect'?
5. What is COD ? Which chemical substance is generally used in its measurement?
6. What are viable and non–viable particulates?
7. (i) Why there is ozone depletion mainly over Antarctica ?
(ii) In which season the depletion of ozone on Antarctica takes place and when is it replenished?

8. Give three examples in which green chemistry has been applied.
9. Define environmental pollution. Give the causes of pollution.
10. What are primary and secondary pollutants? Explain with suitable examples.
11. What are biodegradable and non-biodegradable pollutants?
12. Depending upon the nature of pollutants, how can the pollution be classified into different types ?
13. What is the composition of pure dry air? What do you mean by the terms 'sink' and 'target' with respect to pollution?
14. How can SO_x pollution be controlled?
15. How plant nutrients and pesticides acts as water pollutants?
16. Why is acid rains considered a threat to Taj Mahal?
17. Discuss the importance of dissolved oxygen in water. What processes are generally responsible for the deoxygenation of the water?
18. On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.
19. What are the sources of dissolved oxygen in water?
20. How can lead poisoning be cured?
21. Oxygen plays a key role in the troposphere while ozone in the stratosphere. Elucidate.
22. What is BOD and COD?

Long Answer Questions [5 Marks]

1. What is the strategy for control of Environmental pollution?
2. List industrial wastes which contaminate water.

HOTS/Exemplar Questions

Very Short Answer Questions [1 Mark]

1. Why does rain water normally have a pH of about 5.6? When does it become acid rain? **[HOTS]**
2. How particulates help in the cloud formation? **[HOTS]**

Short Answer Questions [2 & 3 Marks]

1. What is PAN? **[HOTS]**
2. What is Pneumoconiosis? How does it occur? **[HOTS]**
3. Green house effect leads to global warming. Which substances are responsible for green house effect. **[Exemplar]**
4. During an educational trip, a student of botany saw a beautiful lake in a village. She collected many plants from that area. She noticed that villagers were washing clothes around the lake and at some places waste material from houses was destroying its beauty.
   After few years, she visited the same lake again. She was surprised to find that the lake was covered with algae, stinking smell was carring out and its water had beccome unusable. Can you explain the reason for this condition of the lake? **[Exemplar]**
5. What is the importance of measuring BOD of a water body? **[Exemplar]**

CHAPTER TEST

Time : ***30 min.*** **Max. Marks :** ***15***

Directions :
(i) Attempt all questions
(ii) Questions 1 to 3 carry 1 mark each.
(iii) Questions 4 and 5 carry 2 marks each.
(iv) Question 6 carry 3 marks
(v) Question 7 carry 5 marks

1. What is siltation?
2. How can one control photochemical smog?
3. Why 'photochemical smog' is given this name?
4. How can you explain that builders in detergents act as pollutants in water?
5. What is the cause of acid rain?
6. What are the harmful effects of NO_x pollution?
7. List five major water pollutants giving their sources.

Solutions

PRACTICE QUESTIONS

Very Short Answer Questions

1. Troposphere (0-10 km, stratosphere (10-50 km), mesosphere (50-85 km), thermosphere (85 - 500 km).

2. Temperature increases with altitude in stratosphere and thermosphere while it decreases in troposphere and mesosphere.

3. Methyl isocyanate (MIC).

4. About 0. 032%.

5. CO_x, NO_x, and SO_x

6. Soil micro–organism.

7. Carboxyhaemoglobin (HbCO).

8. Acute oxygen starvation in the body (due to CO poisoning) is called anoxia or asphyxiation.

9. NO is formed due to reaction between N_2 and O_2 during lightning or combustion of fossil fuels. It is further oxidized to NO_2.

10. By scrubbing them with conc. H_2SO_4 or with alkaline solutions like $Ca(OH)_2$ and $Mg(OH)_2$.

11. Slowing down the formation of chlorophyll in plants due to presence of SO_2 as pollutant is called chlorosis.

12. 5 nm to 500,000 nm.

13. Polycyclic aromatic hydrocarbons (PAH).

14. Coal miners suffer from black lung disease and textile workers suffer from white lung disease.

15. They act as nuclei for cloud formation.

16. Stratosphere.

17. NO and freons.

18. Gaseous ions like NO^+, O_2^+, N_2^+, O^+ and atoms of N and O.

19. Ultraviolet rays will reach the earth after passing through the hole and cause skin cancer.

20. Fog of H_2SO_4 droplets deposited on the particulates.

21. In winter during the morning hours.

22. Reducing.

23. In summer, in the afternoon.

24. H_2SO_4, HNO_3 and HCl.

25. Oceans (which dissolve it) and plants (which use it for photosynthesis).

26. Pollution of sea water due to discharge of wastes into it is called marine pollution.

27. Oil water pollution.

28. Thermal power plants and nuclear plants.

29. COD can be found in a few minutes whereas BOD requires at least 5 days.

30. The decomposition of organic material (leaves, roots etc.) in the soil by microorganism to produce humus is called humification.

31. 1 ppm or 1 mg dm^{-3}. Higher concentration is harmful to bones and teeth.

32. Recycling, burning, incineration and sewage treatment.

33. It is oxidizing in nature.

34. Sun is source of energy which does not create pollution.

35. PCBs are **polychlorinated biphenyls**

36. **Polar stratospheric clouds.** PSC's are formed over Antarctica. They are of two types:
Type I clouds contain some solidified nitric acid trihydrate (HNO_3, $3H_2O$) formed at –77°C.
Type II clouds contain some ice, formed at –85°C
These clouds play an important role in ozone depletion.

37. **Polar vortex.** When polar stratospheric clouds are formed over Antarctica during winters, stable wind patterns in the stratosphere are called **polar vortex** which encircle the continent.

38. Excess of SO_4^{2-} in drinking water (>500 ppm) may cause a laxative effect.

39. Sulphur dioxide.

40. Infrared radiations.

Short Answer Questions

1. (i) Volcanic eruptions
(ii) Forest fires

2. The lung disease caused by particulates of asbestos is called 'asbestosis' and that caused by those of silica is called 'silicosis'.

3. It is a mixture of a number of irritation causing compounds like NO_2, O_3, peroxyacylnitrates (PAN), aldehydes, ketones, hydrocarbons and CO.

4. Heat from the sun after being absorbed by the earth is remitted by the earth and absorbed by CO_2 and then radiated back to the earth, thereby resulting in the increase of temperature of earth.

5. COD stands for Chemical Oxygen Demand. It is a measure of all types of oxidisable impurities present in the sewage. COD values are higher than BOD values.
It is measured by treating the given sample of water with an oxidizing agent, generally $K_2Cr_2O_7$ in presence of dilute H_2SO_4.

6. Viable particulates are small size living organisms such as bacteria, fungi, moulds, algae etc.
Non–viable particulates are formed by disintegration of large size materials or condensation of small size particles or droplets, e. g., mist, smoke, fume and dust.

7. (i) This is because in other parts of the stratosphere, chlorine free radicals combine to form compounds which goes away but in Antarctica, the compounds formed are converted back into chlorine free radicals which deplete the ozone layer.
(ii) During spring season (i. e., in the months of September and October), depletion of ozone takes place and after spring (i. e., in the month of November), it is replenished.

8. (i) In dry cleaning, use of liquefied CO_2 in place of tetrachloroethene ($Cl_2C = CCl_2$).
(ii) In bleaching of paper by using H_2O_2 in place of chlorine.
(iii) In the manufacture of chemicals like ethanal using environment–friendly chemicals and conditions.

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{Pd(II)/Cu(II)(in water)}]{\text{Catalyst}} CH_3CHO(90\%)$$

9. The addition of undesirable material to air, water and soil by a natural sources or due to human activity which adversely affects the quality of environment is called environmental pollution. The undesirable material thus added to the environment are called pollutants. Environmental pollution model includes:

(i) Atmospheric pollution
(ii) Water pollution
(iii) Land pollution

The main causes of pollution are

(i) Fast population growth
(ii) Use of excessive pesticides in agriculture
(iii) Rapid urbanization
(iv) Excessive industrialization

10. Primary pollutants are those which after their formation enter into environment and remain as such. For example, NO formed by bacterial decay or by lightning flashes becomes pollutant if present in excessive amount.

Secondary pollutants are those which are formed due to chemical reactions between the primary pollutants in the atmosphere or hydrosphere. For example, hydrocarbons and oxides of nitrogen which are primary pollutants react together in the presence of sunlight to form certain compounds like PAN which are also harmful. Thus the harmful compounds formed from primary pollutants are called secondary pollutants.

11. Bio-degradable pollutants are materials such as domestic sewage, cow dungs etc. which are easily decomposed by the micro-organisms either by nature or by suitable treatment and thus are not harmful but if these are present in excess in the environment, they do not undergo degradation completely and thus become pollutants.

Non-biodegradable pollutants are materials such as mercury, DDT etc. which do not undergo degradation or degrade very slowly but may react with the compound present in the environment and produce even more toxic product.

12. It can be classified in two different ways:

(a) Depending upon the part of the environment polluted. For example
    (i) Air pollution
    (ii) Water pollution
    (iii) Soil pollution
(b) Depending upon the nature of the pollutant added into the environment. A few common examples are:
    (i) Radioactive pollution
    (ii) Plastic pollution
    (iii) Soap and detergent pollution
    (iv) Oil pollution
    (v) Chemical pollution
    (vi) Noise pollution
    (vii) Acid rain pollution
    (viii) Smog pollution
    (ix) Effluent pollution and many others

13. The composition of the pure dry air is as follows: N_2(78.1%), O_2(20.95%), Ar(0.93%), CO_2(0.032%), Ne (18 ppm), He (5.2ppm), CH_4(1.3 ppm), Kr(1 ppm), H_2(0.5 ppm), N_2O (0.25 ppm), CO (0.10 ppm), O_3 (0.02 ppm), SO_2 (0.001 ppm), NO_2(0.001 ppm).

In nature, some amount of certain pollutants is taken up by medium present in the environment. Such medium is called 'sink' for that pollutant. Ocean acts as sink for SO_2 and CO_2. The living organisms like animals and plants or the materials like metals and buildings which are affected by pollutants are called targets.

14. (i) By use of low sulphur or sulphur free fuels like natural gas.
(ii) By removing sulphur from fuel before burning.
(iii) By making sulphur free liquefied gaseous fuels from coal.
(iv) By using alternate source of energy rather then sulphur containing fossil fuels.

15. The plant nutrients containing N and P, which flows into lakes where they support the growth of aquatic plants. These plants on decay produce unpleasant odour . Further, the micro-organisms in decomposing these plants consume oxygen. As a results, the amount of dissolved oxygen in the water decreases which proves that these are fatal for aquatic life. Pesticides are organic compounds which are used to protect plants from pests. These are used to stop the growth of weeds. These are mild poisons. When plants are watered or during rain, these chemicals flow down into lakes or rivers and cause problems to aquatic as well as human lives.

16. Oxides of N and S released by the Mathura refinery and by the automobile causes acid rain formation over Agra. This acidic rain water reacts with marble of Taj Mahal causing pitting, therefore acid rain is a threat to Taj Mahal.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

17. Dissolved oxygen is very important for the support of aquatic life. The phytoplanktons and zooplanktons will die and their growth will be inhibited if the dissolved O_2 concentration decreases.

Processes of deoxygenation of water

1. Micro-organisms consume oxygen and oxidises the organic matter
   $$\text{Carbohydrate} + O_2\,(aq) \longrightarrow CO_2\,(aq) + H_2O\,(l)$$
2. By biochemical oxidation
   $$4Fe^{2+}(aq) + O_2(aq) + 10H_2O(l) \longrightarrow 4Fe(OH)_3(aq) + 8H^+(aq)$$
3. Mediated oxidation of organic matters, it also consumed by the bioxidation of nitrogenous materials.
   $$NH^+{}_4(aq) + 2O_2(aq) \longrightarrow 2H^+(aq) + NO_3^-(aq) + H_2O(l)$$

18. CFC's are stable compounds. These undergo decompositions in presence of sunlight, as shown below :

Reactions

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + \dot{C}F_2Cl(g)$$
$$\dot{C}l(g) + O_3(g) \longrightarrow Cl\dot{O}(g) + O_2(g)$$
$$Cl\dot{O}(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$$

Chain reactions continue in which ozone layer is depleted.

19. Sources of dissolved oxygen in water

(i) Photosynthesis
(ii) Natural aeration
(iii) Mechanical aeration

20. Lead poisoning can be cured by feeding the patient with an aqueous solution of calcium complex of EDTA.

$$Ca - EDTA + Pb^{2+} \longrightarrow Ca^{2+} + Pb - EDTA$$

The soluble Pb–EDTA is excreted through urine.

21. The portion of the atmosphere closest to the earth up to the height of ~ 10 km from the sea level is called troposphere. Oxygen plays an important role in this sphere to support animal life and other chemical processes such as combustion etc. Beyond 11 km up to the altitude of 50 km is stratosphere. Ozone is the important chemical compound of this region which absorbs ultraviolet radiations and raised the temperature in this zone. This act of ozone protects us from the harmful effects of sun's ultraviolet radiations.

22. BOD gives the idea of extent of organic waste present in water. It is defined as the amount of oxygen in milligrams dissolved in water needed to break down the organic matter present in one litre of water for five days at 20°C.
COD is a parameter for measuring the amount of oxygen in ppm that would be required to oxidize the organic and inorganic waste present in the water.

Long Answer Questions

1. The management of waste for control of environmental pollution can be done by:

(a) **Recycling.** For example :
   (i) the collection and recycling of glass.
   (ii) the use of scrap metal in the manufacture of steel.
   (iii) The recovery of energy by burning combustible waste.

(b) **Sewage treatment.** It can be carried out in three steps.
   (i) Removal of solid matter.
   (ii) Degradation of the organic content by microbial oxidation.
   (iii) Application of various physical and chemical processes like coagulation, filtration and disinfection using chlorine.

(c) **Incineration.** It is the conversion of organic materials to CO_2 and H_2O at 1000°C and in excess of oxygen.

(d) **Digestion.** It is the anaerobic digestion when micro-organisms degrade wastes in the absence of oxygen.

$$2(CH_2O) \longrightarrow CO_{2(g)} + CH_{4(g)}$$

(e) **Dumping.** The controlled dumping of wastes in ocean and soil is a useful practice.

2. Industrial wastes which contaminate water are following :

(a) **Detergents and fertilizers.** They may contain phosphates additives, which encourage the formation of algae and reduces the dissolved oxygen. This process is called Eutrophication.

(b) **Heavy metals.** The industrial or mining waste may contain Cd, Pb, Hg etc. These metals can damage the kidneys, liver, brain and central nervous system.

(c) **Acid polluted water.** The water having pH less than 3 is deadly to most forms of aquatic life.

(d) **Polychlorinated biphenyls** (PCBs) PCBs used in transformers, capacitors are resistant to oxidation and can cause skin disorders promote cancer.

HOTS/EXEMPLAR QUESTIONS

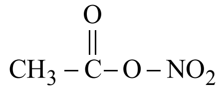
Very Short Answer Questions

1. Normally rain has a pH of about 5.6 due to dissolution of CO_2 of the atmosphere into it ($CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$). When the pH of rain falls below 5.6, it becomes acid rain.

2. They act as nuclei for cloud formation.

Short Answer Questions

1. It is peroxyacylnitrate.



$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O - NO_2$$

2. Pneumoconiosis is a disease of lungs such as lung cancer, bronchital asthma, chronic bronchitis etc. It is caused by small sized particulates which enter into lung through nose and provide a large surface area for adsorption of carcinogenic compounds such as polynuclear hydrocarbons, asbestos etc.

3. Trapping of heat by green house gases, namely carbon dioxide, methane, nitrous oxide, ozone and chlorofluorocarbons.

4. [**Hint :** Process of eutrophication is responsible for this. Explain the effect of accumulation of phosphate from detergents and organic matter entering into the lake along with domestic waste.]

5. BOD is the mesure of level of pollution caued by organic biodegradable material. Low value of BOD indicates that water contains less organic matter.

CHAPTER TEST

1. Siltation is the mixing of soil or rock particles in water.

2. Installation of efficient catalytic converters in automobiles as it prevents the release of oxides of nitrogen and hydrocarbons to the atmosphere.

3. Because it is formed as a result of photochemical reaction (i. e., in presence of sunlight) between oxides of nitrogen and hydrocarbons.

4. The builders polyphosphate undergo bio-degradation by hydrolysis, the hydrolysis products do not pose any threat to aquatic life but serve as nutrients for plants leading to their excessive growth in ponds, lakes and rivers. These excessive plants decomposed by microorganism and this decomposition requires oxygen thus resulting into decrease of dissolved oxygen level in water body. Therefore, they act as pollutant in water.

5. Acid rain is caused by the presence of oxides of nitrogen and sulphur in the atmosphere. Oxides of nitrogen are released into the environment largely from automobile exhausts and combustion of fossil fuel. Oxides of sulphur are emitted into the atmosphere mainly because of fossil fuel combustion, ore smelting and sulphur based industries. The oxides of nitrogen and sulphur react with water vapours present in the atmosphere to form HNO_3 and H_2SO_4 which comes down along with water droplets in the form of acid rain.

6. (i) NO_2 is extremely toxic to living tissues and harmful to paints, textiles and metals.

(ii) NO_2 results in respiratory problems in human beings and lead to bronchitis.

(iii) NO_2 in the presence of sunlight produces highly active oxygen atoms.

$$NO_2 \xrightarrow{\text{Sunlight}} NO + O$$

The active oxygen immediately reacts with the traces of hydrocarbons in the air and produces irritants called photochemical smogs.

7.

Pollutant	**Source**
Micro-organism	Domestic sewage
Organic waste	Domestic sewage, Animal waste, and discharge from food processing industries.
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Radioactive substances	Nuclear reactors

VALUE BASED QUESTIONS

1. Two friends Heena and Shikha were discussing which term is better for expressing the concentration of a solution Molality or Molarity ? Shikha told Heena that Molality is considered better for expressing the concentration as compared to Molarity and also gave justification to her answer

(i) What would be the explanation of Shikha?

(ii) What is the difference between molality & molarity?

(iii) Mention the values shown by Shikha.

2. Shivam, a student of class XIth had difficulty to understand rules for writing the electronic configuration of the elements. Shivam is a very shy boy and hesitate to ask questions in class. Shravan one of his classmates discussed this problem with his teacher. The teacher called Shivam to staffroom and explained the concept in detail. Shivam, then got satisfied.

(i) What rules were told to Shivam by his teacher?

(ii) Write the electronic configuration of Cu.

(iii) What values are displayed by Shravan.

3. Ana and Isha , two students of class XIth were discussing about the allotropes of carbon. Ana asked Isha , why one allotrope of carbon is very hard and use to make jewellery whereas other is very soft and used to make pencils. Isha explained her that this is due to difference in their molecular structure.

(i) Name the above two allotropes of carbon.

(ii) Why one allotrope is conductor and other is not?

(iii) What values are associated with Isha?

4. Saurabh and Sandeep were discussing the difference between NF_3 and NH_3 and both got confused.Saurabh and Sandeep asked their subject teacher, why NF_3 and NH_3 have different dipole moment while both are having same hybridization states and same number of lone pair of electrons.

(i) Draw the structure of NF_3 and NH_3

(ii) Why NF_3 and NH_3 have different dipole moment?

(iii) What values are displayed by Saurabh and Sandeep?

5. In a school trip to Shimla one day Siya and Smita decided to cook Rice . Siya took a pan to cook while Smita took a pressure cooker for cooking at the same place. Smita advised Siya not to cook in pan and suggest her to use pressure cooker.

(i) Who will cook rice faster?

(ii) What is the effect of pressure on boiling point?

(iii) What value are associated with Smita?

6. The teacher gave the samples of milk, black coffee, tomato juice, lemon juice and egg white to two groups of students and asked them to find the pH value of each sample and arrange them in the order of decreasing pH values. They reported the PH values as given

Group A : Egg white ,Milk ,Black Coffee ,Tomato Juice, Lemon Juice

Group B: Egg white ,Black Coffee ,Tomato Juice, Lemon Juice

(a) Which group of students reported the correct decreasing order?

(b) How pH depends upon hydrogen ion concentration?

(c) Mention the value associated with the group shown the correct order.

7. The teacher asked Arjun, a student of class XIth is it possible to store silver nitrate in copper vessel. Arjun explained the teacher; it is not possible to store silver nitrate in copper vessel. He also gave justification for his answer.

(a) What justification did Arjun gave to his teacher.

(b) Define electrochemical series?

(c) What values displayed by Arjun?

8. Quicklime is an important compound. It is prepared by thermal decomposition of limestone in kiln. During such an operation the top of the Chimney of the kiln was closed. After one week when the kiln was opened it was observed that very little lime was formed. The workers reported the poor result to the Production engineer who suggested them to increase the height of the chimney. This time also there was no improvement in the production of lime. Then he suggested workers to keep the top of the chimney opened. This helped.

(a) Represent the thermal decomposition of lime stone by a chemical equation.

(b) Why was the production of lime not satisfactory when the top of the chimney was closed?

(c) Mention the associated values with the production engineer.

9. A botany student Riya saw a beautiful lake in a village during a school trip. Riya noticed that around the lake villagers washing their clothes and at the same time wastes from houses was destroying the lake beauty. She visited there again after few years and was surprised to find that the lake was covered with algae, stinking smell.

(i) What is the reason for this condition of the lake?

(ii) What will be the effect of this condition on animal kingdom?

(iii) What values are associated with Riya?

10. A Laboratory attendant got an instruction from a chemistry teacher to store a particular chemical in the dark room and add some urea in it and keep it away from the dust. In both acidic and alkaline medium this chemical acts as reducing as well as oxidising agent and very useful in pollution control .

(i) Write the name of this compound.

(ii) Explain why such precautions are taken for storing this chemical.

(iii) Write the use of this compound.

11. Sameer resides near Yamuna Bank .He observed that families from nearby localities bring loads of laundry to wash in the river every day and many others bring their cars, taxis and rickshaws and wash them by using water from the river. The same water was being consumed by people living in nearby areas. When he tried to stop people from washing clothes and cleaning vehicles Amir a local resident raised objection. He said "It makes no difference if we wash our cars and clothes here. It is a natural resource and everyone has right to use it" . After reading the above passage, answer the following questions

(a) Who do you think is right Sameer or the Amir?Give a reason for your answer.

(b) What are the values associated with the answer?

12. Drycleaners of your local market frequently use tetrachloroethane for the purpose of drycleaning. Rohan one of the member of the RWA of society advised him to use liquefied carbon dioxide with suitable detergent as an alternative solvent. Answer the following questions:

(i) By avoiding the use of tetrachloroethane what type of harm to the environment can be prevented ?

(ii) Will the use of liquefied carbon dioxide and detergent be completely safe from the point of view of pollution? Comment.

(iii) What are the values associated with the Rohan's action?

13. Tanya and Riya are best friends. One evening Tanya went to Riya's house and found her working in the kitchen. She saw that the burner was emitting yellow flame and a black soot was getting deposited on the bottom of the cooking vessel .She advised Riya to put off the gas and clean the holes of the burner. After cleaning the holes they found that the burner was now emitting clean blue flame.

(i) Why was the burner emitting yellow flame?

(ii) What was the purpose of cleaning the holes of the burner?

(iii) What value is expressed by Tanya?

14. Skanda and Shyam two students of class 12 participated in a seminar about hazardous effects of tobacco. While in discussion they came to know that "combustion of carbon containing compounds with limited supply of oxygen yields polycyclic aromatic hydrocarbons which are carcinogenic as well as mutagenic. Some polycyclic aromatic hydrocarbons have been isolated from tobacco smoke." After the seminar they decided that they will share this valuable information with their classmate.

Answer the following questions:

(i) Give examples of any two polycyclic aromatic hydrocarbons.

(ii) Explain why tobacco smoking is injurious to health?

(iii) What are the values shown by both?

15. An organic compound on heating changes directly into vapors without undergoing into liquid state, it is insoluble in water and is commonly used to prevent clothes against moths. It is contaminated with cinnamaldehyde. suman, a student of class XI was asked by his teacher how to purify it. Now answer the following questions

(i) Which method of purification would suman apply?

(ii) Name the compound and write it's another use.

(iii) Write the value associated with this.

SOLUTIONS

1. (i) According to Shikha molality is considered better for expressing the concentration. As it involve mass of solvent and we know that mass of substance does not change with temperature.

(ii) Molarity is temperature dependent whereas molality is temperature independent.

(iii) Keen to learn, critical thinking ability are some of the values shown by Shikha.

2. (i) Three rules (i) Aufbau's Principle (ii) Pauli exclusion principle and (iii) Hund's rule were told to Shivam by his teacher.

(ii) Electronics configuration Cu (29) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

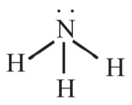
(iii) Helping nature, Problem solving skill are some values displayed by Shravan.

3. (i) Two allotropes of carbon are Diamond and Graphite.

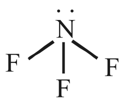
(ii) Graphite due to presence of free electron is a good conductor of electricity whereas there is no such free electron in carbon atom of diamond to conduct electricity.

(iii) Helping, Problem Solving etc. are some values associated with Isha.

4. (i)



$\mu = 1.46$ D



$\mu = 0.24$ D

(ii) Since flourine is more electronegative than hydrogen. It is expected that the net dipole moment of NF_3 (μ = 0.24 D) is less than that of NH_3 (μ = 1.46 D)

(iii) Eager to know, discussing ability, raising doubts with confidence etc. are some values displayed by Saurabh and Sandeep.

5. (i) Smita will cook rice faster.

(ii) The vapour pressure increase with temperature, because at higher temperature the molecules are moving faster and more able to overcome the attractive intermolecular forces that tend to bind them together.

(iii) Observational ability , Scientific Thinking, Knowledge etc. are the values associated with Smita.

6. (a) Group A students reported the correct decreasing order of pH.

(b) The relation between pH and hydrogen ion pH = – log $[H^+]$ concentration is

(c) Keen observation, problem solving and accuracy are the values associated with group A students.

7. (a) Copper is in higher position than silver in electrochemical series thus displaces silver from solution of its salt.

(b) Electrochemical series is a series of chemical elements arranged in order of their standard reduction potential

(c) Problem solving, Analysing, Scientific thinking are the values displayed by Arjun.

8. (a) $CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$

Calcium Carbonate	Calcium oxide	Carbon dioxide

(b) When the top of chimney is closed CO_2 formed due to decomposition will not escape out. Hence this will recombine with quicklime and form $CaCO_3$
Hence production of lime was not satisfactory

(c) Scientific thinking, decision making and problem solving etc. are the values associated with production.

9. (i) This is due to Eutrophication in which waste materials and detergents used in washing of clothes contain lot of phosphate in them, these phosphate in water increases growth of algae.

(ii) This leads to anaerobic condition resulting the death of animals.

(iii) Observational ability, awareness etc are some values displayed by Riya.

10. (i) The compound is hydrogen peroxide (H_2O_2)

(ii) H_2O_2 decomposes slowly when exposed to air

$$2H_2O_2(l) \xrightarrow{\text{sunlight}} 2H_2O(l) + O_2(g) \text{ Dust}$$

Dust also causes explosive decomposition of H_2O_2 therefore it is kept in dark coloured wax lined glass bottles or in plastic bottles.

(iii) It is useful in treatment of domestic and industrial effluents

11. (a) Sameer is right as he knows that detergents are surface-active agents, which tend to produce stable, copious foams in rivers. These foams generally form a thick and dense layer over the surface of the water, extending over several hundred yards of the river water. The foamy water is unsafe for both humans and fish.

(b) Sameer is concerned for water pollution and its effects to life of living beings. he is aware that chemicals in soaps and detergents are harmful for humans and also threatening to aquatic life.

12. (i) The major cause of ozone layer depletion in the stratosphere is the excessive use of chlorofluorocarbon compounds . Thus, avoiding indiscriminate use of such compounds can save us from the harmful effects of ozone layer depletion.

(ii) Use of liquefied carbon dioxide solvent is not absolutely safe. The excessive concentration of CO_2 in the atmosphere leads to greenhouse effect.

(iii) Rohan is concerned towards pollution and spreading awareness of its hazardous effects to others.

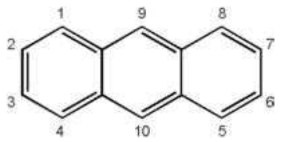
13. (i) Yellow flame was emitting due to incomplete combustion of the fuel .

(ii) By cleaning the holes of the burner the deposits were removed which led to the complete combustion of the fuel.

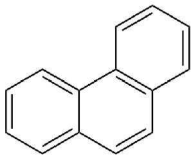
(iii) Tanya helped her friend in saving fuel and in preventing wastage of gas.

14.

(i)



Anthracene



Phenanthrene

(ii) Tobacco smoke contains many polycyclic aromatic hydrocarbons which are carcinogenic and mutagenic.

(iii) Both are inquisitive and friendly .they are concerned towards social problems and hence they want to spread this information to all.

15. (i) Sublimation

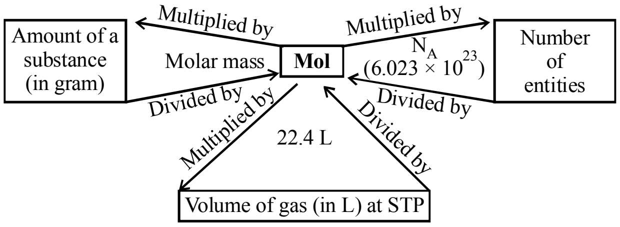
(ii) Naphthalene and can be used as air freshener

(iii) Scientific attitude

IMPORTANT FORMULAE, TERMS AND DEFINITIONS

PHYSICAL CHEMISTRY

SOME BASIC CONCEPTS OF CHEMISTRY

- 

- Molecular mass
$$=\frac{\text{Average relative mass of one molecule}}{\frac{1}{12}\times\text{mass of C-12 atom}}$$
- Molecular mass = 2 × VD
- Eq. wt. of metal
$$=\frac{\text{wt. of metal}}{\text{wt. of } H_2 \text{ displaced}}\times 1.008$$
- Eq. wt. of metal $=\frac{\text{wt. of metal}}{\text{wt. of oxygen combined}}\times 8$
$$=\frac{\text{wt. of metal}}{\text{wt. of chlorine combined}}\times 35.5$$
- Molecular formula = $(\text{Empirical formula})_n$

ATOMIC STRUCTURE

- Energy of electron in species with one electron.
$$E_n=\frac{-2\pi^2me^4Z^2}{n^2h^2}$$
For energy in SI system,
$$E_n=\frac{-2\pi^2me^4Z^2}{n^2h^2(4\pi\varepsilon_0)^2}$$
$$E_n=\frac{-1312Z^2}{n^2}\text{kJ mol}^{-1}$$
$$mvr=\frac{nh}{2\pi}$$
- $r=\frac{n^2h^2}{4\pi^2mZe^2}=0.529\left(\frac{n^2}{Z}\right)$ Å
- Total energy of electron in the nth shell
$$=\text{K.E.}+\text{P.E.}=kZ\frac{e^2}{2r_n}+\left(-\frac{kZe^2}{r_n}\right)=-\frac{kZe^2}{2r_n}$$
- $\bar{\upsilon}=\frac{1}{\lambda}=RZ^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$, $[R=1.0968\times10^7\ m^{-1}]$
$$E=h\nu=\frac{hc}{\lambda}$$
$$\lambda=\frac{h}{\sqrt{2m\times\text{K.E.}}}$$
- No. of spectral lines produced when an electron drops from n^{th} level to ground level $=\frac{n(n-1)}{2}$
- Heisenberg's Uncertainty Principle $(\Delta x)(\Delta p)\ge h/4\pi$
- Nodes $(n-1)$ = total nodes, ℓ = angular nodes, $(n-\ell-1)$ = Radial nodes
- Orbital angular momentum : $\sqrt{\ell(\ell+1)}\frac{h}{2\pi}=\sqrt{\ell(\ell+1)}h$

CHEMICAL BONDING

- (i) % ionic character
$$=\frac{\text{Actual dipole moment}}{\text{Calculated dipole moment}}\times 100$$
(ii) Dipole moment is helpful in predicting geometry and polarity of molecule.
- **Fajan's Rule :** Following factors are helpful in increasing covalent character in ionic compounds
(i) Small cation (ii) Big anion
(iii) High charge on cation/anion
(iv) Cation having pseudo inert gas configuration ($ns^2p^6d^{10}$)
e.g. Cu^+, Ag^+, Zn^{+2}, Cd^{+2}
- **M.O. theory :**
(i) Bond order = $\frac{1}{2}(N_b-N_a)$
(ii) Higher the bond order, higher is the bond dissociation energy, greater is the stability, shorter is the bond length.
- Formal charge (F.C.) on an atom in a Lewis structure
= [total number of valence electrons in the free atoms]
– [total number of non-binding (lone pair) electrons]
$-\frac{1}{2}$[total number of bonding (shared) electrons]
- **Relative bond strength :** $sp^3d^2 > dsp^2 > sp^3 > sp^2 > sp > p\text{-}p$ (Co-axial) > s - p > s - s > p - p (Co-lateral)

- **VSEPR theory**
  (i) (LP-LP) repulsion > (LP-BP) > (BP-BP)
  (ii) $NH_3 \rightarrow$ Bond Angle 106° 45' because (LP-BP) repulsion > (BP-BP) $H_2O \rightarrow$ 104° 27' because (LP-LP) repulsion > (LP-LB) > (BP-BP)
- **Hybridisation :**

$$= \frac{1}{2}\begin{pmatrix} \text{number of valence electrons of central atom} \\ + \text{number of monovalent atoms attached to it} \\ + \text{negative charge if any} - \text{positive charge if any} \end{pmatrix}$$

CHEMICAL EQUILIBRIUM

- $K_p = K_c (RT)^{\Delta n_g}$ where $\Delta n_g = n_P - n_R$
- Free Energy Change (ΔG)
  (a) If $\Delta G = 0$ then reversible reaction would be in equilibrium, $K_c = 0$
  (b) If $\Delta G = (+)$ ve then equilibrium will be displaced in backward direction; $K_c < 1$
  (c) If $\Delta G = (-)$ ve then equilibrium will shift in forward direction; $K_c > 1$
- (a) K_c unit $\rightarrow (\text{moles/lit})^{\Delta n}$,
  (b) K_p unit $\rightarrow (\text{atm})^{\Delta n}$
- **Reaction Quotient and Equilibrium Constant**
  Consider the following reversible reaction

$$A + B \rightleftharpoons C + D$$

$$\therefore \quad Q_c = \frac{[C][D]}{[A][B]}$$

Case I : If $Q_c < K_c$ then : [Reactants] > [Products] then the system is not at equilibrium
Case II : If $Q_c = K_c$ then : The system is at equilibrium.
Case III : If $Q_c > K_c$ then : [Products] > [Reactants] The system is not at equilibrium.

- A relationship between the equilibrium constant K_C, reaction quotient and Gibb's energy.

$$\Delta G = \Delta G° + RT \ln Q$$

At equilibrium $\Delta G = 0$ and $Q = K$ then

$$\Delta G° = -RT \ln K_c$$

$$\therefore \quad \Delta G° = -RT \ln K_p$$

- Le-Chatelier's principle
  (i) Increase of reactant conc. (Shift reaction forward)
  (ii) Decrease of reactant conc. (Shift reaction backward)
  (iii) Increase of pressure (from more moles to less moles)
  (iv) Decrease of pressure (from less moles to more moles)
  (v) For exothermic reaction decrease in temp. (Shift forward)
  (vi) For endothermic increase in temp. (Shift backward)

IONIC EQUILIBIRIUM

- (i) Lewis Acid (e^- pair acceptor) $\rightarrow$ CO_2, BF_3, $AlCl_3$, $ZnCl_2$, normal cation
  (ii) Lewis Base (e^- pair donor) $\rightarrow$ NH_3, ROH, ROR, H_2O, RNH_2, normal anions
- Dissociation of Weak Acid and Weak Base
  (i) Weak Acid, $K_a = Cx^2/(1-x)$ or $K_a = Cx^2$; $x << 1$
  (ii) Weak Base, $K_b = Cx^2/(1-x)$ or $K_b = Cx^2$; $x << 1$
- Buffer solution {Henderson equation} :
  (i) Acidic, $pH = pK_a + \log \{\text{Salt/Acid}\}$.
  For maximum buffer action $pH = pK_a$
  Range of buffer $pH = pK_a \pm 1$
  (ii) Alkaline $\rightarrow pOH = pK_b + \log \{\text{Salt/Base}\}$ for max. buffer action $pH = 14 - pK_b$
  Range $pH = 14 - pK_b \pm 1$
  (iii) Buffer Capacity $= \dfrac{\text{Moles / lit of Acid or Base Mixed}}{\text{Change in pH}}$
- Relation between ionisation constant (K_i) and degree of ionisation(α):-

$$K_i = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{(1-\alpha)} \text{ (Ostwald's dilution law)}$$

It is applicable to weak electrolytes for which $\alpha << 1$ then

$$\alpha = \sqrt{K_i V} = \sqrt{\frac{K_i}{C}} \text{ or } V\uparrow C\downarrow \alpha\uparrow$$

- **Common ion effect :** By addition of X mole/L of a common ion, to a weak acid (or weak base) α becomes equal to $\dfrac{K_a}{X}\left(\text{or } \dfrac{K_b}{X}\right)$ [where α = degree of dissociation]
- (i) If solubility product > ionic product then the solution is unsaturated and more of the substance can be dissolved in it.
  (ii) If ionic product > solubility product the solution is super saturated (principle of precipitation).
- Salt of weak acid and strong base :

$$pH = 0.5\,(pK_w + pK_a + \log c);\; h = \sqrt{\frac{K_h}{c}}\;;\; K_h = \frac{K_w}{K_a}$$

(h = degree of hydrolysis)

Salt of weak base and strong acid :

$$pH = 0.5\,(pK_w - pK_b - \log c);\; h = \sqrt{\frac{K_w}{K_b \times c}}$$

Salt of weak acid and weak base :

$$pH = 0.5\,(pK_w + pK_a - pK_b);\; h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

OXIDATION - REDUCTION

- Oxidant itself is reduced (gives O_2)
  Or Oxidant $\longrightarrow e^-$ (s) Acceptor
  Reductant itself is oxidised (gives H_2)
  Or reductant $\longrightarrow e^-$ (s) Donor
- (i) Strength of acid $\propto$ O.N
  (ii) Strength of base $\propto$ 1/ O.N
- (i) Electrochemical Series:- Li, K, Ba, Sr, Ca, Na, Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H_2, Cu, Ag, Pt, Au.
  (ii) As we move from top to bottom in this series
  (a) Standard Reduction Potential ↑
  (b) Standard Oxidation Potential ↓
  (c) Reducing Capacity ↓
  (d) IP ↑
  (e) Reactivity ↓

THERMO-DYNAMICS

- First Law of Thermodynamics :

$$\Delta E = Q + W$$

Expression for pressure volume work

$$W = -P\Delta V$$

Maximum work in a reversible expansion :

$$W = -2.303n\,RT \log \frac{V_2}{V_1}$$

$$= -2.303\,nRT\log\frac{P_1}{P_2}$$

$$W_{rev} \geq W_{irr}$$

- $q_v = c_v\Delta T = \Delta U,\ q_p = c_p\Delta T = \Delta H$

Enthapy changes during phase transformation

(i) Enthalpy of Fusion
(ii) Heat of Vapourisation
(iii) Heat of Sublimation

- **Enthalpy :** $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$
- **Kirchoff's equation :**

$$\Delta E_{T_2} = \Delta E_{T_1} + \Delta C_V\ (T_2 - T_1)\ \text{[constant V]}$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_P\ (T_2 - T_1)\ \text{[constant P]}$$

- **Entropy(s) :** Measure of disorder or randomness
$\Delta S = \Sigma S_p - \Sigma S_R$

$$\Delta S = \frac{q_{rev}}{T} = 2.303\ nR\log\frac{V_2}{V_1} = 2.303\ n\,R\log\frac{P_1}{P_2}$$

- Free energy change : $\Delta G = \Delta H - T\Delta S,\ \Delta G^o = -nFE^o_{cell}$
$-\Delta G = W(\text{maximum}) - P\Delta V,\ \Delta G_{system} = -T\Delta S_{total}$

ΔH	ΔS	ΔG	Reaction characteristics
–	+	Always negative	Reaction is spontaneous at all temperature.
+	–	Always positive	Reaction is nonspontaneous at all temperature
–	–	Negative at low temperature but positive at high temperature	Spontaneous at low temp. & non spontaneous at high temperature
+	+	Positive at low temp. but negative at high temperature	Non spontaneous at low temp. & spontaneous at high temp.

GASEOUS STATE

- Ideal gas equation : PV = nRT
(i) $R = 0.0821$ liter atm. $deg^{-1}\ mole^{-1}$
(ii) $R = 2$ cals. $deg.^{-1}\ mole^{-}$
(iii) $R = 8.314\ JK^{-1}\ mole^{-1}$
- Velocities related to gaseous state

$$\text{RMS velocity} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{M}}\ \ \&\ \text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

Average speed = 0.9213 × RMS speed
RMS speed = 1.085 × Average speed
MPS = .816 × RMS; RMS = 1.224 MPS
MPS : A.V. speed : RMS = 1 : 1.128 : 1.224

- Rate of diffusion $\propto \dfrac{1}{\sqrt{\text{density of gas}}}$
- van der Waal's equation

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad \text{for n moles}$$

- Z (compressibility factor) $= \dfrac{PV}{nRT}$; Z = 1 for ideal gas

$$T_C = \frac{8a}{27Rb},\ P_C = \frac{a}{27b^2},\ V_C = 3b,\ T_b = \frac{a}{bR}$$

SOLID AND LIQUID STATE

- Surface tension and viscosity of liquid decreases with increase in temperature.

INORGANIC CHEMISTRY

PERIODIC TABLE

- General electronic configuration (of outer orbits)

s-block	ns^{1-2}
p-block	ns^2np^{1-6}
d-block	$(n-1)d^{1-10}\ ns^{1-2}$
f-block	$(n-2)f^{1-14}s^2p^6d^{10}$ $(n-1)s^2p^6d^{0\text{ or }1}\ ns^2$

Property	**Pr (L To R)**	**Gr (T to B)**
(i) Atomic radius	↓	↑
(ii) Ionisation potential	↑	↓
(iii) Electron affinity	↑	↓
(iv) Electronegativity	↑	↓
(v) Metallic character or electropositive character	↓	↑
(vi) Alkaline character of hydroxides	↓	
(vii) Acidic character	↑	↓
(viii) Reducing property	↓	↑
(ix) Oxidising property	↑	↓
(x) Non metallic character	↑	↓

- $IP \propto \dfrac{1}{\text{Metallic character}} \propto \dfrac{1}{\text{Reducing character}}$
- $EA \propto \dfrac{1}{\text{size}} \propto$ nuclear charge.
Second electron affinity is always negative.
Electron affinity of chlorine is greater than fluorine (small atomic size).
- The first element of a group has similar properties with the second element of the next group. This is called diagonal relationship. The diagonal relationship disappears after IV group.

s-BLOCK ELEMENTS

- Atomic radii : Li < Na < K < Rb < Cs
- Electronegativity : Li > Na > K > Rb > Cs
- First ionization potential : Li > Na > K > Rb > Cs
- Melting point Li > Na > K > Rb > Cs
- Colour of the flame Li - Red, Na - Golden, K - Violet, Rb - Red, Cs - Blue, Ca - Brick red, Sr - Blood red, Ba-Apple green

- Rb and Cs show photoelectric effect.
- Stability of hydrides : $LiH > NaH > KH > RbH > CsH$
- Basic nature of hydroxides : $LiOH < NaOH < KOH < RbOH < CsOH$
- **Hydration energy :** $Li > Na > K > Rb > Cs$
- **Reducing character :** $Li > Cs > Rb > K > Na$

BORON FAMILY

- Stability of +3 oxidation state : $B > Al > Ga > In > Tl$
- Stability of +1 oxidation state : $Ga < In < Tl$
- Basic nature of the oxides and hydroxides : $B < Al < Ga < In < Tl$
- Relative strength of Lewis acid : $BF_3 < BCl_3 < BBr_3 < BI_3$
- **Ionisation energy : $B > Al < Ga > In < Tl$**
- **Electronegativity :** Electronegativity first decreases from B to Al and then increases marginally.

CARBON FAMILY

- Reactivity : $C < Si < Ge < Sn < Pb$
- Metallic character : $C < Si < Ge < Sn < Pb$
- Acidic character of the oxides : $CO_2 > SiO_2 > GeO_2 > SnO_2 > PbO_2$
  Weaker acidic (amphoteric)
- Reducing nature of hydrides $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
- Thermal stability of tetrahalides $CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$
- Oxidising character of M^{+4} species $GeCl_4 < SnCl_4 < PbCl_4$
- Ease of hydrolysis of tetrahalides $SiCl_4 < GeCl_4 < SnCl_4 < PbCl_4$

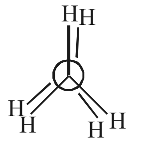
ORGANIC CHEMISTRY

GENERAL ORGANIC CHEMISTRY

- The order of decreasing electronegativity of hybrid orbitals is $sp > sp^2 > sp^3$.
- Conformational isomers are those isomers which arise due to rotation around a single bond.
- A meso compound is optically inactive, even though it has asymmetric centres (due to internal compensation of rotation of plane polarised light)
- An equimolar mixture of enantiomers is called racemic mixture, which is optically inactive.
- Reaction intermediates and reagents :
  Homolytic fission → Free radicals
  Heterolytic fission → Ions (Carbonium ions, carbanions etc.)
- Nucleophiles – Electron rich
  Two types : (i) Anions (ii) Neutral molecules with lone pair of electrons (Lewis bases)
  Electrophiles : Electron deficient.
  Two types : (i) Cations (ii) Neutral molecules with vacant orbitals (Lewis acids).
- Inductive effect is due to σ electron displacement along a chain and is permanent effect.
- +I (inductive effect) increases basicity, – I effect increases acidity of compounds.
- Resonance is a phenomenon in which two or more structures can be written for the same compound but none of them actually exists.

ALKANES

- Pyrolytic cracking is a process in which alkane decomposes to a mixture of smaller hydrocarbons, when it is heated strongly, in the absence of oxygen.
- Ethane can exist in an infinite number of conformations. They are



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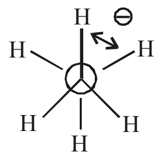
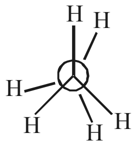
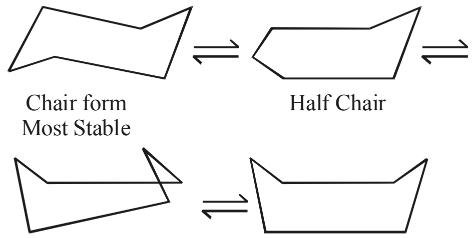


θ = 60° Staggered



θ < 60° > 0 Skew

- **Conformations of Cyclohexane :** It exists in two nonplanar, strainless forms, the boat and the chair form



Chair form
Most Stable

Half Chair

Twist Boat

Boat form
(Least Stable)

ALKENES

- In dehydration and dehydrohalogenation the preferential order for removal of hydrogen is 3° > 2° > 1° (Saytzeff's rule).
- The lower the ΔH_h (heat of hydrogenation) the more stable the alkene is.
- Alkenes undergo anti-Markonikov addition only with HBr in the presence of peroxides.

ALKYNES

- Alkynes add water molecule in presence of mercuric sulphate and dil. H_2SO_4 and form carbonyl compounds.
- Terminal alkynes have acidic H-atoms, so they form metal alkynides with Na, ammonical cuprous chloride solution and ammoniacal silver nitrate solution.
- Alkynes are acidic because of H-atoms which are attached to sp 'C' atom which has more electronegativity and 's' character than sp^2 and sp^3 'C' atoms.

SAMPLE PAPER - 1

Time : 3 Hrs. **Max. Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.

(ii) Q. no. **1** to **5** are very short answer questions and carry **1** mark each.

(iii) Q. no. **6** to **10** are short answer questions and carry **2** marks each.

(iv) Q. no. **11** to **22** are also short answer questions and carry **3** marks each.

(v) Q. no. **23** is a value based question and carry **4** marks.

(vi) Q. no. **24** to **26** are long answer questions and carry **5** marks each.

(vii) Use log tables if necessary, use of calculators is not allowed.

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1. Express the number 45000 in exponential notation to show four significant figure.

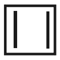
2. What is the effect of temperature on

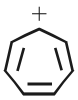
(i) surface tension and (ii) viscosity?

3. Give one difference between isolated system and closed system.

4. Define reversible process.

5. Predict which of the following systems will be aromatic and why?

(i) 

(ii) 

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

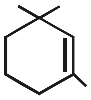
7. State ($n + l$) rule. Illustrate with the help of example. Give the sequence of filling orbitals using ($n + l$) rule.

8. Draw the shapes of the following hybrid orbitals : (a) sp^2 (b) sp^3

OR

Draw the Lewis structures for the following molecules and ions : H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

9. Give the IUPAC names of the following compounds:

(i) 

(ii) $H_2C = HC - C \equiv CH$

10. (i) Why do beryllium and magnesium do not impart colour to the flame in the flame test?

(ii) Mg_3N_2 when reacted with water gives off ammonia but HCl is not obtained when $MgCl_2$ reacts with water at room temperature. Explain.

11. Discuss the anomalous behaviour of Lithium. Give its diagonal relationship with Magnesium.

12. (a) Carbon dioxide is non-polar while water is polar. What conclusion do you draw about their structures from these.

(b) What is dry ice? Why is it so called?

OR

Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?

13. (i) What is the cause of acid rain ? How is it harmful to the environment?

(ii) What do you understand by greenhouse effect ? What are the major greenhouse gases ?

14. For the reaction. $2\,A(g) + B(g) \rightarrow 2\,D(g)$, $\Delta U^\circ = 10.5$ kJ and $\Delta S^\circ = -44.10\ JK^{-1}$

Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously.

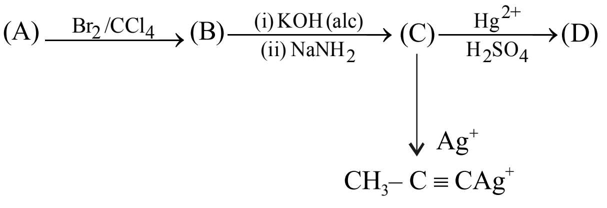
15. Explain the following :

(a) Alkaline earth metals always form divalent cations, both in the solid state as well as in their aqueous solutions even though their second ionization enthalpies are almost double than their first ionization enthalpies.

(b) During preparation of Plaster of Paris, temperature is maintained around 393 K. Assign reason.

16. (a) Write a chemical equation for Friedel-Crafts reaction.

(b) Identify A, B, C and D in the following reaction :



$$\begin{tikzcd}(A) \arrow[r, "Br_2/CCl_4"] & (B) \arrow[r, "(i)\ KOH(alc)", "(ii)\ NaNH_2"'] & (C) \arrow[r, "Hg^{2+}", "H_2SO_4"'] \arrow[d, "Ag^+"] & (D) \\ & & CH_3-C\equiv CAg^+ & \end{tikzcd}$$

(White ppt)

17. Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.

18. At 473 K, the equilibrium constant K_c for decomposition of phosphorus pentachloride is 8.3×10^{-3}, If decomposition is represented by :

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\quad \Delta H_f^\circ = +124.8\ kJ\ mol^{-1}$$

(i) Write expression of K_c for the reaction.

(ii) What would be the effect on K_c if :

(a) more PCl_5 is added

(b) pressure in increased

(c) temperature is increased

(d) catalyst is added.

19. Discuss the chemistry of Lassaigne's test for detection of nitrogen in the organic compound. Why is the extract boiled with HNO_3 before testing for halogens and sulphur?

20. A sample of 0.5 g an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 ml of 0.5 M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

21. (a) Why is hydrated barium peroxide used in the preparation of hydrogen peroxide instead of anhydrous barium peroxide? Explain.

(b) Write chemical reactions to justify that hydrogen peroxide acts an oxidising as well as reducing agent.

22. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. Find out the number of iron atoms (at. wt. of Fe = 56) present in the molecule of haemoglobin. Explain how interaction of carbon monoxide with haemoglobin makes it poisonous ?

23. Saturated aliphatic hydrocarbons are called alkanes. They are mainly used as fuels. Depending upon their physical properties such as boiling points, density and solubility, they have many other uses. Now answer the following questions.

(i) Out of propane and butane why is propane used as a fuel for barbecue gill?

(ii) Which alkane is used as a fuel in cigarette lighters?

(iii) What is vaseline ? Mention some of its uses.

24. (a) Discuss the mechanism of nitration of benzene.

(b) Write the Newman projection formulae for staggered and eclipsed conformation of ethane.Which of the two is more stable and why?

OR

(a) Identify [A] – [D] in the following sequence of reaction :

$$C_6H_5CH = CH_2 \xrightarrow[CCl_4]{Br_2} [A] \xrightarrow[\text{Liq. } NH_3]{NaNH_2\,(3\text{ equiv.})}$$

$$(B) \xrightarrow{CH_3{-}I} [C] \xrightarrow{\text{Dil. } H_2SO_4\ /\ HgSO_4} (D)$$

(b) What is peroxide effect ? Why is the peroxide effect observed only with HBr and not with HCl or HI ? Explain.

25. (a) Balance the following equation in basic medium by ion electron method

$$Cl_2(g) + OH^-\,(aq) \longrightarrow Cl^-\,(aq) + ClO_3^-\,(aq)$$

(b) What happens when :

(i) Cl_2 is passed through a solution of F^- and I^- ions.

(ii) Iron nails are added to $AgNO_3$ solution.

(iii) A dilute solution of $AgNO_3$ is electrolysed using silver electrodes.

OR

(a) 20 ml of a solution of $K_2Cr_2O_7$ is allowed to react with a saturated solution of KI. The iodine thus liberated reacts completely with 16 ml of M/25 $Na_2S_2O_3$ solution. Calculate the concentration of $K_2Cr_2O_7$ solution in gL^{-1}?

(b) Explain the following redox reactions with one example in each case.

(i) Combination reactions (ii) Decomposition reactions.

(c) Copper vessel can be used to store dil. HCI but not dil. HNO_3. Explain why ?

26. (i) Arrange the following in decreasing order of their bond angle : H_2O, NH_3, H_2S

(ii) Sketch the bond moments and resultant dipole moment of the following molecule

H_2O, NH_3, NF_3 and PCl_3

(iii) Draw shape of the following molecules on the basis of VSEPR theory

XeF_4 and SF_4 (At. No. of Xe = 54, At. No of S = 16)

OR

State the hybridization and draw the molecular structure of the following.

(a) PF_5 (b) I_3^- (c) NH_3 (d) XeO_3 (e) CH_4

SAMPLE PAPER - 2

Time : 3 Hrs. **Max. Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. **1** to **5** are very short answer questions and carry **1** mark each.
(iii) Q. no. **6** to **10** are short answer questions and carry **2** marks each.
(iv) Q. no. **11** to **22** are also short answer questions and carry **3** marks each.
(v) Q. no. **23** is a value based question and carry **4** marks.
(vi) Q. no. **24** to **26** are long answer questions and carry **5** marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Given that density of water is 1 g ml^{-1}. What is its density in kg m^{-3} ?

2. Write the electronic configuration of Ni^{2+} (Z for Ni = 28)

3. Why σ bond is stronger than π bond?

4. Hydrogen generally forms covalent compounds. Explain why?

5. Green house effect leads to global warming. Which substances are responsible for greenhouse effect?

6. Assign oxidation number to the underlined elements in each of the following species:

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$

7. CO_2 is inert and harmless gas. yet it is thought to be a serious pollutant. Explain.

8. At a certain altitude, the density of air is 1/10th of the density of the earth's atmosphere and temperature is –10°C. What is the pressure at that altitude? Assume that air behaves like an ideal gas, has uniform composition and is at S.T.P. at the earth's surface.

OR

Chloroform, $CHCl_3$ is a volatile (easily vapourised) liquid solvent. Calculate the density of chloroform vapour at 99ºC and 745 mmHg. Give the answer in gram per litre.

9. A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2.

Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

10. For the reaction at 298 K, $2A + B \longrightarrow C$, $\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

11. (a) The mass of an electron is 9.1×10^{-28} g. If its K.E. is 3.0×10^{-25} J, calculate its wavelength in Angstrom.

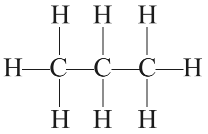
(b) What is photoelectric effect?

12. Calculate the lattice enthalpy of $MgBr_2$. Given that

Enthalpy of formation of $MgBr_2$ = – 524 kJ mol^{-1}
Sublimation energy of Mg = – 148 kJ mol^{-1}
Ionization energy of Mg = 2187 kJ mol^{-1}
Vapourisation energy of $Br_2(l)$ = 31 kJ mol^{-1}
Dissociation energy of $Br_2(g)$ = 193 kJ mol^{-1}
Electron gain enthalpy of Br (g) = 331 kJ mol^{-1}

OR

Propane has the structure



$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & \\ & & H & & H & & H & \end{array}$$

If standard enthalpy change ($\Delta_r H^\circ$) for the reaction

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ is -2.05×10^3 kJ/mol and bond energies of C—C, C—H, C==O and O—H are 347, 414, 741 and 464 respectively. Calculate the energy of oxygen-oxygen bond in O_2 molecule.

13. At 473 K, equilibrium constant, K_c, for the decomposition of phosphorus pentachloride PCl_5 is 8.3×10^{-3}

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\ \Delta_r H^\circ = 124\ kJ\ mol^{-1}$.

(a) Write an expression of K_c for the reaction.

(b) What is the value of K_c for the reverse reaction at the same temperature?

(c) What would be the effect on K_c if the temperature is increased?

14. Give reasons for the following :

(i) Alkali metals impart colour to the flame.

(ii) LiF is almost insoluble in water whereas LiCl is soluble not only in water but also in acetone.

(iii) The reaction $>\!\!C—Cl + MF \rightarrow >\!\!C—F + MCl$

proceeds better with KF than with NaF ?

15. (a) What are Fullerenes ? How are they prepared ?

(b) Classify the following compounds into acidic, basic and amphoteric oxides :

Al_2O_3, Cl_2O_7

16. Describe with the help of chemical equations

(i) Anti-Markovnikov's rule.

(ii) Decarboxylation.

17. How would you justify the presence of 18 elements in the 5th period of the periodic Table.

18. Explain the following :

(a) Alkynes are less reactive than alkenes towards electrophilic addition reaction.

(b) Although benzene is highly unsaturated, it does not undergo addition reactions.

(c) Birch reduction of but-2-yne gives trans-2-butene.

19. (a) Write the structures of all the aromatic compounds having the molecular formula, C_7H_8O. What type of isomerism is shown by them ?

(b) What is the principle of Duma's method for estimation of nitrogen in an organic compound ?

20. 9.9 g of an amide with molecular formula $C_4H_5N_xO_y$ on heating with alkali liberated 1.7 g of ammonia. if the percentage of oxygen is 32.33%, determine the ratio of N and O atoms in the compound.

21. (a) How do you account for the strong reducing power of lithium in aqueous solution ?

(b) Lithium is the only alkali metal which forms nitride directly. Give reason.

22. A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate

(i) the energy of the photon (eV)

(ii) the kinetic energy of the emission and

(iii the velocity of the photoelectron ($1\ eV = 1.6020 \times 10^{-19}$ J).

23. To prevent damage and facilitate easy shipping many fruits such as bananas, mangoes, pineapples, etc. and some vegetables such as tomatoes are often plucked before they are ripe. Before the fruit or the vegetable is brought to the market, it is exposed to some chemical which accelerates the ripening process. If, however, the fruit or the vegetable is allowed to stay on the plant, natural ripening process starts.

Now answer the following questions :

(i) What happens during natural ripening process?

(ii) Name two chemicals which are used to ripen the fruits/vegetable artificially.

(iii) Do the artificially ripen fruits/vegetables safe to use? Do they taste the same as naturally ripen fruits?

24. (a) Explain why :

(i) BCl_3 is a Lewis acid.

(ii) Boric acid is a monobasic acid.

(b) When metal X is treated with sodium hydroxide, a white percipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCI to form compound (C). The compound (A) when heated strongly gives (D), Which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

OR

(a) A certain compound (X) of boron gives the following results.

(i) Its queous solution is alkaline to litmus.

(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X, crystals of an acid Z separate out. Write equations for all the above reactions and identify X, Y and Z

(b) How would you explain the lower atomic radius of Ga as compared to Al ?

(c) Explain why the B-F bond length in BF_3 (130 pm) and BF_4^- (143 pm) differ.

25. (a) In both water and diethyl ether, the central atom viz. O-atom has same hybridisation. Then why have they different bond angles? Which one has greater bond angle ?

(b) why o-nitrophenol is volatile in steam but p-nitrophenol is not ?

(c) What would be the electronic configuration of HeH^- molecular ion ? Calculate its bond order and comment on its stability.

OR

(a) Explain what do you understand by enthalpy driven and entropy driven reactions?

(b) Derive how the free energy change is related to the total entropy change of a system.

26. Complete the following reaction :

(a) Isopropyl bromide $\xrightarrow[\Delta]{\text{alc. KOH}}$ A $\xrightarrow[\text{Peroxide}]{\text{HBr}}$ B

(b) *n*-Propyl alcohol $\xrightarrow[443\text{K}]{\text{Conc.} H_2SO_4}$ C $\xrightarrow[\Delta]{KMnO_4.OH^-}$ D

(c) 1, 1, 2, 2– tetrachloroethane $\xrightarrow[\Delta]{\text{Zn / alcohol}}$ E $\xrightarrow[\text{tube}]{\text{Redhot}}$ F

(d) Acetylene $\xrightarrow{NaNH_2}$ G $\xrightarrow{CH_3CH_2Br}$ H

(e) Propyne $\xrightarrow[\text{Quinoline}]{H_2 / Pd / BaSO_4}$ I $\xrightarrow[\text{(ii) Zn} / H_2O]{\text{(i)} O_3}$ J

OR

(i) Arrange the following compounds according to the increasing order of boiling point: Hexane, Heptane, 3-methyl pentane, 2, 2-dimethyl butane.

(ii) Account for the following :

(a) The boiling points of hydrocarbon decreases with increase in branching.

(b) Hydrocarbons with odd number of carbon atoms have a melting point lower than expected.

(c) Boiling point of *n*-pentane is greater than that of neo-pentane but melting point of neo-pentane is greater than that of *n*-pentane.

SAMPLE PAPER - 3

Time : 3 Hrs. **Max. Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. **1** to **5** are very short answer questions and carry **1** mark each.
(iii) Q. no. **6** to **10** are short answer questions and carry **2** marks each.
(iv) Q. no. **11** to **22** are also short answer questions and carry **3** marks each.
(v) Q. no. **23** is a value based question and carry **4** marks.
(vi) Q. no. **24** to **26** are long answer questions and carry **5** marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Give an example of an intramolecular redox reaction.

2. Ga^+ undergoes disproportionation reaction. Give reason.

3. What is the angular momentum of an electron in $4f$ orbital?

4. What is the value of the gas constant in S.I. units ?

5. Define bond dissociation energy.

6. A cell is prepared by dipping a zinc rod in 1 M $ZnSO_4$ solution and a lead rod in 1 M $Pb(NO_3)_2$ solution. The standard electrode potentials for Pb^{+2}/Pb and Zn^{+2}/Zn electrodes are – 0.126V and – 0.763 V respectively.

(a) How will you represent the cell ?

(b) Write the half cell reactions and the overall cell reaction.

7. An organometallic compound on analysis was found to contain, C = 64.4%, H = 5.5% and Fe = 29.9%. Determine its empirical formula (At mass of Fe = 56 u)

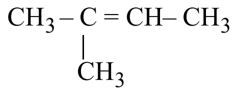
8. Which out of NH_3 and NF_3 has higher dipole moment and why ?

OR

All transition elements are *d*-block elements. but all *d*-block elements are not transition elements. Explain.

9. (a) Arrange the following alkenes in increasing order of stablility along with reasons

$CH_3-CH=CH_2, CH_3-CH=CH-CH_3,$

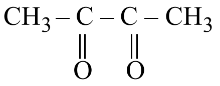


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$

(b) Write IUPAC name of

(i) $CH_3-CH=CH-COOCH_3$

(ii)



$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$

10. How many electrons in sulphur (Z =16) can have $n + l = 3$?

11. What are smogs ? How classical and photochemical smogs different ?

12. Why BBr_3 is a stronger Lewis acid as compared to BF_3 though fluorine is more electronegative than bromine.

OR

What do you understand by the term 'auto-protolysis' of water ? what is its significance?

13. (a) Show the difference of ortho and para hydorgen by a diagram.

(b) Difference in chemical behaviour of compound of hydrogen with elements of atomic number 17 and 20.

14. Give the reasons of the following :

(a) Fluorine has less negative electron gain enthalpy than chlorine.

(b) Noble gases tend to be less reactive.

(c) First ionisation enthalpy of 'Mg' is more than that of 'Na' but second ionisation enthalpy of 'Mg' is less than that of 'Na'.

15. What is Plaster of Paris? how is it prepared? Give its any two important uses.

16. Two buffers (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffer ? ($K_{HA} = 1.0 \times 10^{-5}$)

17. Calculate the entropy change for the rusting of iron according to the reaction :

$4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3\,(s), \Delta H° = -\,1648\ kJ\ mol^{-1}$

Given that standard entropies of Fe, O_2 and Fe_2O_3 are 27.3, 205.0 and 87.4 J K^{-1} mol^{-1} respectively. Will the reaction be spontaneous at room temperature (25°C) ? Justify your answer with appropriate calculations.

18. Calculate the degree of ionization and pH of 0.05 M ammonia solution. The ionization constant of ammonia (K_b) is 1.77×10^{-5}. Also calculate the ionic constant of the conjugate acid of ammonia.

19. Calculate the amount of lime, $Ca(OH)_2$, required to remove hardness of 50,000 litres of well water which has been found to contain 1.62 g of calcium bicarbonate per 10 litre.

20. State as to why

(a) Solution of Na_2CO_3 is alkaline

(b) Alkali metals are prepared by electrolysis of their fused chlorides

(c) Sodium is found to be more useful than potassium.

21. (a) Phosphoric acid is preferred over sulphuric acid for preparing hydorgen peroxide from peroxides. Why?

(b) Calculate the strength of 5 volume H_2O_2 solution.

22. Calculate the enthalpy of formation of benzene, using the following data:

$$C_6H_6\,(l) + \frac{15}{2}\,O_2\,(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l);\ \ \Delta_c H° = -\,3266.0\ kJ$$

$$C(s) + O_2\,(g) \longrightarrow CO_2(g);\ \ \Delta_f H° = -\,393.1\ kJ$$

$$H_2(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O(l);\ \ \Delta_f H° = -\,286.0\ kJ$$

23. Liquefied Petroleum Gas (LPG) used at home is colourless and odourless. Its leakage can cause serious explosion or fire hazard. To detect the leakage, the manufacturing companies mix some suitable compound in the LPG which has a very strong, highly obnoxious odour that can be detected as low as 1 part in a billion parts of air when a leakage occurs.

After reading the above paragraph, answer the following questions:

(a) Which compound is generally mixed in the LPG to detect the leakage?

(b) What steps should be taken if the leakage is detected?

24. (a) Why is the + 2 oxidation state of Mn (25) is quite stable, while the same is not true for iron (26).

(b) What is meant by dual nature of electrons ? Calculate the energy and wavelength of the photon emitted by hydrogen atom when electron makes a transition from $n = 2$ to $n = 1$. Given that the ionization potential is 13.6 eV. (le V = 1.6×10^{-19}J)

OR

(i) Calculate the wavelength of photon which will be emitted when the electron of hydrogen atom jumps from the fourth shell to the first shell. The ionization energy of hydrogen atom is 1.312×10^3 kJ mol^{-1}.

(ii) Which orbital in each of the following pairs is lower in energy in a multi–electron system?

(a) 2*s*,2*p* (b) 3*p*, 3*d* (c) 3*s*, 4*s* (d) 4*d*, 5*f*

25. (a) At 340 K, K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ is 0.8 atm. Calculate the percent dissociation of N_2O_4 at 340 K and a total pressure of 1 atmosphere.

(b) For the reaction $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant $K_c = 62.5$ at 800 K amd $\Delta H = -10.4$ kJ. Calculate K_c at 1000 K.

OR

Carbonic acid, H_2CO_3, is a weak diprotic acid formed by the reaction of carbon dioxide with water, For this acid, $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 5.6 \times 10^{-11}$. What are the equilibrium concentrations of each species in a 0. 10 M solution of carbonic acid?

26. (a) Carry out the following conversions :

(i) Acetylene to propyne.

(ii) *n*- Hexane to benzene

(b) Draw main conformation of n-butane obtained by rotation around C-2 and C-3 also give the names of these conformations. Which of these conformation is most and which is the least stable and why ?

(c) How will you bring about the following conversions :

(i) Ethene to Bromoethane.

(ii) Toluene to Benzene ?

OR

(i) Why is the Wurtz synthesis not a good method for preparing propane?

(ii) What alkanes would be expected from the reaction of sodium with 50 : 50 mixture of 1-chloropropane and 2-chloropropane ?

SOLUTIONS

SAMPLE PAPER 1

1. 4.500×10^4
2. Both decrease with increase of temperature.
3. Isolated system can neither exchange matter nor energy with the surrounding. Whereas closed system can exchange energy but not matter with the surrounding.
4. Reversible process is a process in which products can react to form reactants back.
5. Compound (ii) is aromatic because of planar structure, cyclic cloud of delocalised π electrons above and below the plane and follows Huckel rule i.e. contain $(4n + 2)\pi$ electron where π is an integer, its value may be 0, 1, 2, 3, 4.
6. 1 mol of ^{12}C atoms = 6.022×10^{23} atoms = 12 g
   Thus, 6.022×10^{23} atoms of ^{12}C have mass = 12 g

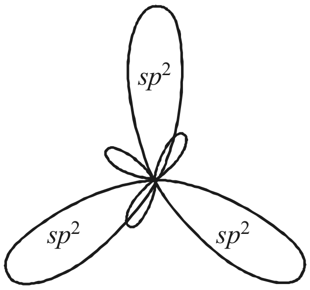
$$\therefore \quad 1 \text{ atom of } ^{12}\text{C will have mass} = \frac{12}{6.022 \times 10^{23}} \text{ g}$$

$$= 1.9927 \times 10^{-23}\text{g}$$

7. (i) $(n + \ell)$ rule : It states that orbitals having lowest value of $(n + \ell)$ will be filled first. If two orbitals have same value of $(n + \ell)$, then the one which has lower value of n will be filled first, e.g., for 4*s* orbital, $n + \ell = 4 + 0 = 4$, for 3*d*, $n + \ell = 3 + 2 = 5 \therefore$ 4*s* orbital is filled before 3*d* orbital

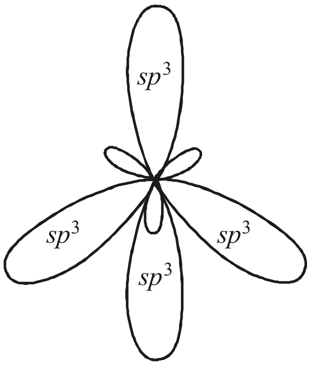
$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$ .....

8· (a) sp^2



Planar bond angle 120°.

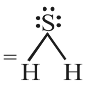
(b) sp^3



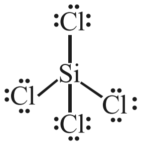
Tetrahedral bond angle 109° 28'.

OR

(i) H_2S =



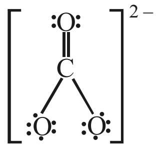
(ii) $SiCl_4$ =



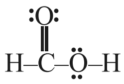
(iii) BeF_2 =

$:\ddot{\underset{..}{F}}-Be-\ddot{\underset{..}{F}}:$

(iv) CO_3^{2-} =



(v) HCOOH =



$H-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}-H$

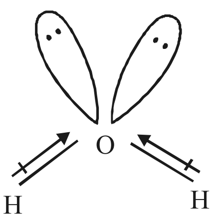
9. (i) 1, 3, 3- Trimethylcyclohex-1 -ene
   (ii) But-1-en-3-yne.
10. (i) Because of the small size, the ionization enthalpies of Be and Mg are much higher than those of other alkaline earth metals. Therefore, they need large amount of energy for excitation of their valence electrons to higher energy levels. Since such a large amount of energy is not available in Bunsen flame, therefore, these metals do not impart any colour to the flame.
    (ii) Mg_3N_2 is a salt of a strong base $Mg(OH)_2$ and a weak acid NH_3. Therefore, it undergoes hydrolysis to give NH_3

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2\,NH_3$$

In contrast, $MgCl_2$ is a salt of a strong base $Mg(OH)_2$ and a strong acid HCI. Therefore, it does not undergo hydrolysis to give HCI

$$MgCl_2 + 2H_2O \not\longrightarrow Mg(OH)_2 + 2HCl$$

11. Li shows anomalous behaviour due to smallest size, highest ionisation energy and highest polarising power.
    Resemblance with Mg :
    (i) Both react with N_2 to form nitrides
    (ii) Both form predominantly covalent compounds.
    (iii) Both form monoxides.
    (iv) Carbonates of both are thermally unstable.
12. (a)  is linear, bond moments are equal and opposite, net dipole moment is zero. Water is bent molecule, it has net dipole moment. Thus due to net dipole moment water is polar.

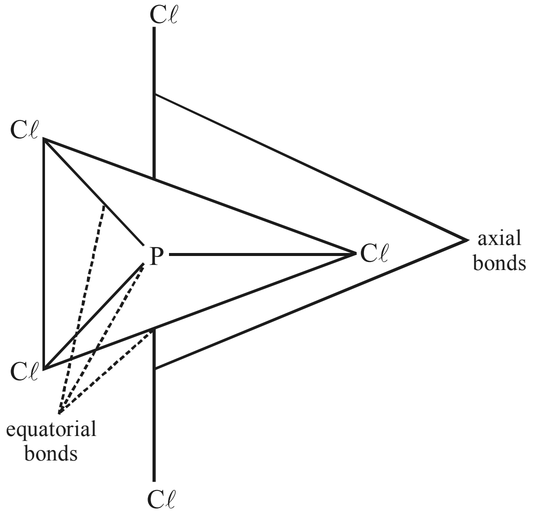


(b) Solid CO_2 is called dry ice because it directly change into vapours.

OR

In $PC\ell_5$ the hybridization is sp^3d, thus it has a trigonal bi–pyramidal structure. This is because one of the 3*s* electron of '*p*' gets promoted to 3*d* orbital giving the electronic configuration $1s^22s^22p^63s^13p_x^{\ 1}3p_y^{\ 1}3p_z^{\ 1}3d^1$, thus it involves sp^3d hybridization.

The equatorial and the axial bond lengths in PCl_5 are different. The axial bond lengths are longer than the equatorial bond length. This is due to minimize bond–pair bond–pair repulsion for the large sized chlorine atoms.



13. (i) When rain falls through polluted air, it comes across chemicals such as gaseous oxides of sulphur, oxides of nitrogen, mists of hydrochloric acid and phosphoric acid etc, pH lowers down from 5.6 to 3.5. Sometimes, it becomes as low as 2.

(a) It is harmful for aquatic animals which cannot survive at pH below 4.

(b) It is harmful for plants. Leaf pigments are decolourised and acid rain affects chlorophyll of plants.

(c) It damages textiles, paper, leather products. Buildings made-up of limestone, marble, dolomite, mortar and slate are damaged by acid rain.

(ii) Greenhouse effect is the phenomenon in which earth's atmosphere traps the heat from the sun and prevents it from escaping into outer space.

14. For the given reaction, $\Delta n_g = 2 - (3) = -1$

$\therefore$ $\Delta H° = \Delta U° + \Delta n_g RT = -10.5\ kJ + (-1)(8.314 \times 10^{-3}\ kJ)(298) = -10.5 - 2.48 = -12.98\ kJ$

$\Delta G° = \Delta H° - T\Delta S° = -12.98\ kJ - 298\ (-44.1 \times 10^{-3}\ kJ) = -12.98\ kJ + 13.14\ kJ = 0.16\ kJ$

As $\Delta G°$ comes out to be +ve, the reaction will not occur spontaneously.

15. (a) The divalent cations of alkaline earth metals acquires stable inert gas configuration.

The divalent cations results in stronger lattices then monovalent cations and hence a lot of energy called lattice energy released during formation of divalent cations than monovalent cation which compensates the high second ionization energy.

The existence of divalent ions in the aqueous solution is due to greater hydration of the divalent ions which counter balance the high value of second ionization energy.

(b) Plaster of Paris is prepared by heating gypsum to 393 K.

$$2\,CaSO_4.\,2\,H_2O \xrightarrow{393K} 2CaSO_4.\,1/2\,2H_2O + H_2O$$

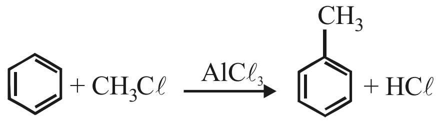
Gypsum Plaster of Paris

If the temperature is raised above 393 K. Plaster of Paris is further dehydrated to form anhydrous calcium sulphate which is also called dead burnt plaster since it loses the properties of setting with water

$$2\,CaSO_4.1/2\,H_2O \xrightarrow{>393\,K} 2CaSO_4 + H_2O$$

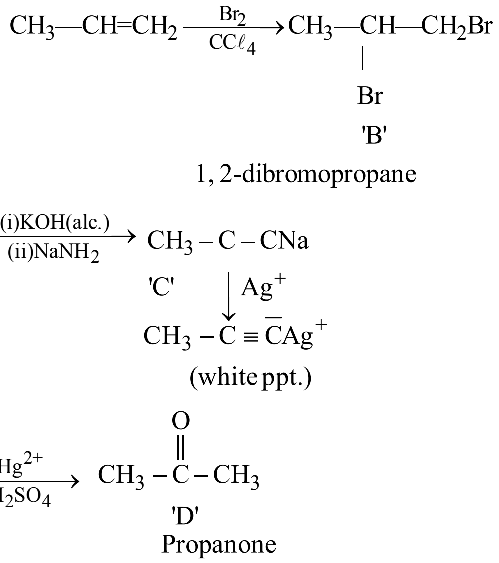
Plaster of Paris Dead burnt plaster

16. (a) Friedel-Crafts Reaction



Benzene Toluene

(b)



$$CH_3—CH{=}CH_2 \xrightarrow[CC\ell_4]{Br_2} \underset{\substack{|\\ Br}}{CH_3—CH—CH_2Br}$$

'B'

1, 2-dibromopropane

$$\xrightarrow[(ii)NaNH_2]{(i)KOH(alc.)} CH_3 - C - CNa$$

'C' $\downarrow Ag^+$

$$CH_3 - C \equiv \bar{C}Ag^+$$

(white ppt.)

$$\xrightarrow[H_2SO_4]{Hg^{2+}} CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$$

'D'

Propanone

17. Suppose molecular masses of A and B are M_A and M_B respectively. Then their number of moles will be

$$nA = \frac{1}{M_A},\ nB = \frac{2}{M_B}$$

$P_A = 2$ bar, $P_A + P_B = 3$ bar. i.e., $P_B = 1$ bar

Applying the relation, $PV = nRT$

$$P_AV = n_A . RT. P_BV = n_B RT$$

$$\therefore \quad \frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{1/M_A}{2/M_B} = \frac{M_B}{2M_A}$$

or $\dfrac{M_B}{M_A} = 2 \times \dfrac{P_A}{P_B} = 2 \times \dfrac{1}{2} = 4$

or $M_B = 4\,M_A$.

18. $PC\ell_5(g) \rightleftharpoons PC\ell_3(g) + C\ell_2(g)\ \Delta_f H^\circ = +124.8\ \text{kJ mol}^{-1}$

(i) $K_c = \dfrac{[PC\ell_3][C\ell_2]}{[PC\ell_5]}$

(ii) (a) K_c will not be affected if more $PC\ell_5$ is added.

(b) K_c does not change with increase in pressure.

(c) K_c will increase, when temperature in increased.

(d) K_c is not affected by catalyst.

19. **Chemistry of the test**. During fusion, carbon and nitrogen of the organic compound combine to form sodium cyanide.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

(From organic compound)

On heating the filtrate with ferrous sulphate, sodium ferrocyanide, i.e., sodium hexacyanoferrate (II) is formed and at the same time some ferrous (Fe^{2+}) ions are oxidised to ferric (Fe^{3+}) ions. These Fe^{3+} ions then react with sodium hexacyanoferrate (II) to produce iron (III) hexacyanoferrate (II) or ferriferrocyanide which is prussion blue in colour.

$$2NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Fe(CN)_2$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Soduim hexacyanoferrate (II)}}{Na_4[Fe(CN)_6}$$

$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \longrightarrow \underset{\substack{\text{Iron (III) hexacyanoferrate (II)} \\ \text{Prussion blue}}}{Fe_4[Fe(CN)_6]_3} + 12\,Na^+$$

The extract is boiled with HNO_3 as the organic compound also contains nitrogen or sulphur. the Lassaigne's extract on boiling with dil. HNO_3 decomposes sodium cyanide or sodium sulphide formed during fusion

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN \uparrow$$

$$Na_2S + 2HNO_3 \longrightarrow 2\,NaNO_3 + H_2S \uparrow$$

If cyanide and sulphide ions are not decomposed, they will react with silver nitrate and hence will interfere with the test.

$$NaCN + AgNO_3 \longrightarrow \underset{\text{Silver cyanide (White ppt.)}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \longrightarrow \underset{\text{Silver sulphide (Black ppt.)}}{Ag_2S} + 2NaNO_3$$

20. Volume of acid taken = 50 ml. of 0.5 M H_2SO_4 = 25 ml of 1 M H_2SO_4

Volume of alkali used for neutralization of excess acid = 60 ml of 0.5 M NaOH = 30 ml of 1 M NaOH.

Now 1 mole of H_2SO_4 neutralizes 2 moles of NaOH

$\therefore$ 30 ml of 1 M NaOH $\equiv$ 15 ml of 1 M H_2SO_4

$\therefore$ Volume of acid used by ammonia = 25 – 15 = 10 mL

Now % of N can be determined by applying the following equation.

$$\%N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol. of the acid used}}{\text{Mass of substance taken}}$$

Substituting the values of all the items in the above equation.

we have, $\%N = \dfrac{1.4 \times 1 \times 2 \times 10}{0.5} = 56.0$

21. (a) If anhydrous barium peroxide is used in the preparation of H_2O_2, the $BaSO_4$ formed during the reaction forms an insoluble protective coating on the surface of solid barium peroxide.

$$BaO_2\,(s) + H_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + H_2O_2\,(aq)$$

This prevents further action of the acid and ultimately the reaction stops. If, however, hydrated barium peroxide (in the form of thin paste) is used, the water of crystallization does not allow $BaSO_4$ to deposit on the surface of BaO_2 and the reaction goes to completion.

(b) H_2O_2 can act as an oxidising as well as a reducing agent both in acidic and basic media as given below :

(i) Oxidising agent in acidic medium

$$2\,Fe^{2+}(aq) + 2\,H^+(aq) + H_2O_2\,(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,H_2O\,(l)$$

(ii) Oxidising agent in basic medium

$$Mn^{2+}(aq) + H_2O_2\,(aq) + 2\,OH^-(aq) \longrightarrow \underset{\text{Manganese dioxide}}{MnO_2\,(s)} + 2\,H_2O\,(l)$$

Reducing agent in acidic medium

(iii) $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

(iv) Reducing agent in basic medium

$$I_2\,(s) + H_2O_2\,(aq) + 2\,OH^- \longrightarrow 2I^-(aq) + 2H_2O\,(l) + O_2(g)$$

22. Total wt. of Fe in haemoglobin $= \dfrac{0.33}{100} \times 67200 = 221.76$

At. wt. of Fe = 56

Total no. of Fe atoms per molecule of haemoglobin

$$= \frac{221.76}{56} = 3.96$$

Total No. of Fe atoms/ molecule of haemoglobin = 4.
Interaction of CO with haemoglobin,
CO combines with haemoglobin irreversibly to form carboxyhaemoglobin

Haemoglobin + CO ⟶ Carboxyhaemoglobin
Thus the highly poisonous nature of CO arises due to its ability to form a complex with haemoglobin.

23. (i) Barbecue is usually done in the open. In cold countries, although both propane and butane can be used but propane is preferred because it works better at low temperatures. The reason being that due to lower boiling point (231 K), propane always remain as a gas in the cylinder in spite of cooling produced by Joule-Thomson effect during its use and thus ensures a constant supply of the gas. In contrast, butane due to its higher boiling point (272.5 K) and cooling produced by Joule-Thomson effect, it becomes liquid in the cylinder an thus the supply of gas becomes slower and slower as the gas is being used.

(ii) Butane is used in cigarette lighters since it can be easily liquefied at room temperature.

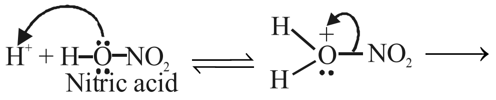
(iii) Vaseline or petrolium jelly, is a mixture of solid alkanes having low melting points. It can prevent moisture loss from chapped lips and soften nail cuticles, It is also used in ointments and cosmetics.

24. (a) **Nitration**. It is carried out by treating benzenes and other arenes with a mixture of conc. HNO_3 + conc. H_2SO_4 commonly called the nitrating mixture. The various steps involved are :

Step 1. Genereation of an electrophile, i.e., NO_2^+ (nitronium ion)

In presence of conc. H_2SO_4, HNO_3 acts as the base and accepts a proton to form protonated nitric acid which then loses a molecule of H_2O to form nitronium ion.

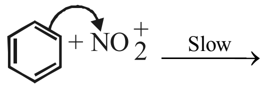
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

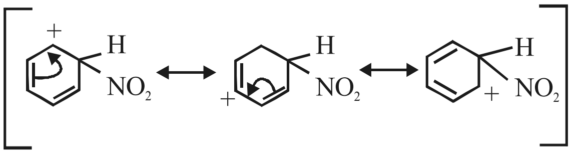


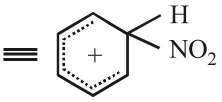
$$H_2O + \overset{+}{N}O_2$$

Nitronium ion

Step 2. Formation of σ-complex or carbocation intermediate. Nitronium ion attacks the benzene ring to form a carbocation which is stabilized by resonance.







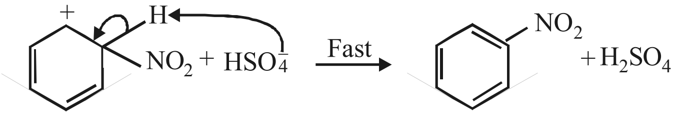
Resonance hybrid

Resonance stabilization of carbocation or the σ-complex

This step is slow and hence is the rate-determining step of the reacion.

Step 3. Loss of a proton from the carbocation intermediate.

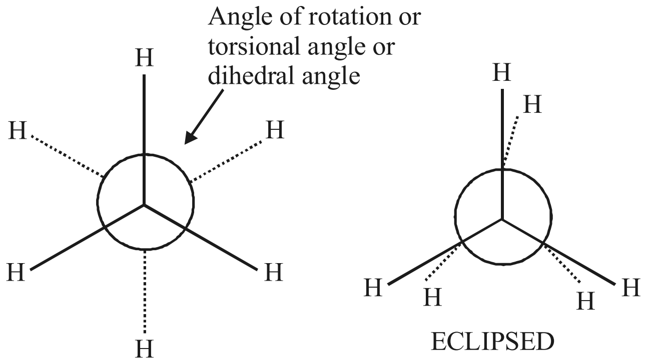
Finally, the carbocation loses a proton to the base (HSO_4^-) to form nitrobenzene.



Nitrobenzene

This step is fast and does note affect the rate of the reaction.

(b) The Newman projections for staggered and eclipsed conformations of ethane are shown in Fig.



STAGGERED ECLIPSED

In staggered conformation, each of the hydrogen atoms on the front carbon lies exactly in between each of the hydrogen atoms on the back carbon. In other words, in this conformation, any two hydrogen atoms on adjacent carbon atoms (nonbonded hydrogens) are as far apart as possible (internuclear H to H distance = 3·1 Å or 310 pm). As a result, the repulsions between the electron clouds of σ-bonds of two non-bonded hydrogen atoms is minimum. On the other hand, in eclipsed conformation, each of the hydrogen atoms on the back carbon lies exactly behind each of the hydrogen atoms on the front carbon In other words, the non-bonded hydrogen atoms are quite close (2·29 Å or 229 pm). As a result, the electron clouds of the σ -bonds of two non-bonded hydrogen atoms repel each other. This raises the energy of the eclipsed conformation relative to staggered conformation. This repulsive interaction between the electron clouds which affects the stability of a conformation is called **torsional strain.** The magnitude of the torsional strain, however, depends upon the angle of rotation about C-C bond. This angle is also called dihedral angle or torsional angle. Thus due to minimum energy staggered conformation is more stable.

OR

(a) $A = C_6H_5CHBr-CH_2Br$; $B = C_6H_5C \equiv C^-Na^+$;
$C = C_6H_5C \equiv CCH_3$; $D = C_6H_5 - COCH_2CH_3$

$$C_6H_5CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} C_6H_5CHBr-CH_2Br$$

$$\xrightarrow[\text{Liq. } NH_3]{NaNH_2 \text{(3 equiv.)}} C_6H_5C \equiv C^-Na^+ \xrightarrow{CH_3-I}$$

$$C_6H_5C \equiv CCH_3 \xrightarrow{\text{Dil. } H_2SO_4 \text{ / } HgSO_4} C_6H_5 - COCH_2CH_3$$

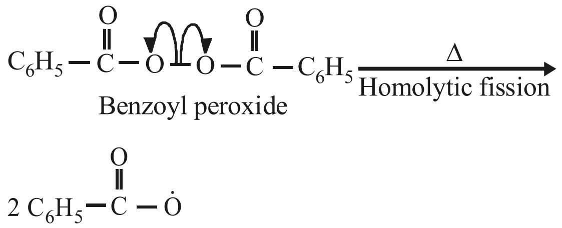
(b) **Peroxide effect.** It states that when HBr is added to unsymmetrical alkene or alkyne in presence of peroxide, negative part of molecule is added to least substituted carbon. Thus,

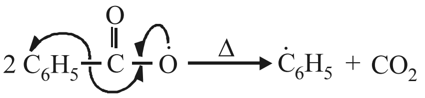
$$CH_3CH{=}CH_2 + HBr \xrightarrow[\text{Anti-Mark.addn.}]{(C_6H_5COO)_2\Delta} CH_3CH_2{-}CH_2Br$$

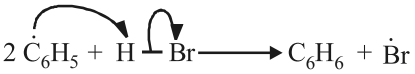
Propene (Propylene) 1-Bromopropane (n-Propyl bromide)

Mechanism. The addition of HBr to alkenes in presence of peroxides occurs by a free radical mechanism. It consists of the following three steps.

(a) **Initiation.**

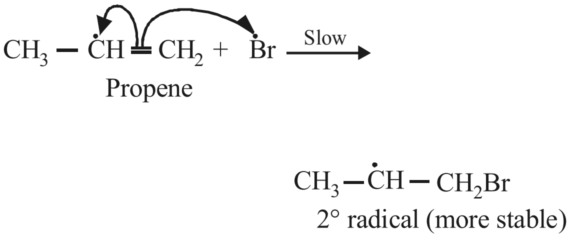
(i)


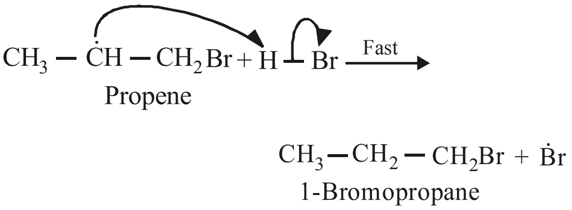
(ii)


(iii)


(b) **Propagation.** It consists of two steps.

During the first step a Br. adds to the double bond in such a way so as to give the more stable free radical. In the second step the free radical thus produced abstracts a H• from HBr to complete the addition.

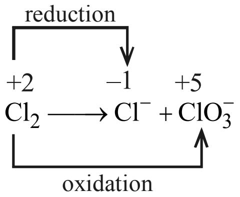
(i)


(ii)


HCl and HI do not show peroxide effect. Radical chain reactions are successful when propagation steps are exothermic. An endothermic propagation step is reversible and would break the chain. With HI, the first propagation step is endothermic, because H-I bond is weak. Moreover, HI is oxidized by peroxide to I_2 under reaction conditions. With HCl, the second propagation step is endothermic, because the H-Cl bond is strong.

With HBr, both the propagation steps are exothermic and HBr adds to the double bond by free- radical mechanism.

25. (a)



Oxidation half-reaction:

$$Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10e^- + 6H_2O$$

Reduction half-reaction:

$\{Cl_2 + 2e^- \rightarrow 2Cl^-\} \times 5$

Net balanced redox reaction:

$$6Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10Cl^- + 6H_2O$$

OR

$$3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- 3H_2O$$

(b) (i) Cl_2 ($E°_{Cl_2/Cl^-} = +1.36$ V) being a stronger oxidising agent than I_2 ($E°_{I_2/I^-} = 0.54$ V) oxidises I^- ions to I_2. Conversely, Cl_2 being a weaker oxidising agent than F_2 ($E°_{F_2/F^-} = +2.87$ V) cannot oxidise F^- ions to F_2. therefore, only I_2 is liberated.

(ii) Iron ($E°_{Fe^{2+}/Fe} = -0.44$ V) being a stronger oxidising agent than silver ($E°_{Ag^+/Ag} = +0.80$ V) reduces Ag^+ ions to Ag metal. As a result, Ag gets deposited on the iron nails.

(iii) Thus, when an aqueous solution of $AgNO_3$ is electrolysed Ag from anode dissolves while Ag^+ (aq) ions present in the solution get reduced and get deposited at the cathode.

At Cathode : $Ag^+ + e^- \rightarrow Ag$

At Anode : $Ag \rightarrow Ag^+ + e^-$

OR

(a) Applying molarity equation on the balanced redox reaction between $Cr_2O_7^{2-}$ and $S_2O_3^{2-}$,

$$Cr_2O_7^{2-}+6S_2O_3^{2-}+14H^+\rightarrow 2Cr^{3+}+3S_4O_6^{2-}+7H_2O$$

We have, $\frac{M_1\times 20}{1}(Cr_2O_7^{2-})=\frac{16\times 1}{6\times 25}(S_2O_3^{2-})$

$\therefore\quad M_1(Cr_2O_7^{2-})=\frac{16}{6\times 25\times 20}\,molL^{-1}$

$\therefore$ Conc. of $K_2Cr_2O_7$ in g L^{-1} $\frac{16\times 294}{6\times 25\times 20}=1.568$ g

($\because$ Mol mass of $K_2Cr_2O_7=294$ g mol^{-1})

(b) **(i) Combination reactions.** A reaction in which two atoms or molecules combine together to form a third molecule is called a combination reaction, For example, $A+B\rightarrow C$

For this reaction to be a redox reaction, either one or both A and B must be in the elemental form. example

(i) $\overset{0}{3Mg}(s)+\overset{0}{N_2}(g)\rightarrow \overset{+2}{Mg_3}\,\overset{-3}{N_2}(s)$

(ii) $\overset{0}{Fe}(s)+\overset{0}{S}(s)\rightarrow \overset{+2}{Fe}\,\overset{-2}{S}(s)$

(ii) Decomposition reactions. A reaction in which a molecule breaks down to form two or more components is called a decomposition reaction. It is essential that one of the products of decomposition must be in the elemental state. For example,

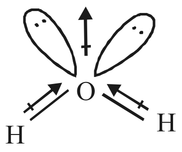
(i) $2\overset{+1}{Na}\overset{-1}{H}(s)\xrightarrow{\Delta}2\overset{0}{Na}(s)+\overset{0}{H_2}(g)$

(ii) $2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3}(s)\xrightarrow{\Delta}2\overset{+1}{K}\,\overset{-1}{Cl}(s)+3\overset{0}{O_2}(g)$

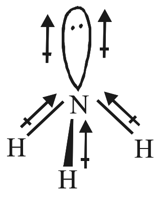
(c) Since E° of Cu^{2+}/Cu electrode(+0.34 V) is higher than that of H^+/H_2 electrode (0.0 V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and hence Cu does not dissolve in dil. HCl. In contrast the electrode potential of NO_3^- ion i.e. NO_3^-/NO electrode (+ 0.97 V) is higher than that of copper electrode and hence it can oxidise Cu to Cu^{2+} ions and hence Cu dissolves in dil. HNO_3. This is reason, that copper vessels are used to store dil. HCl but not dil HNO_3.

26. (i) $NH_3>H_2O>H_2S$.

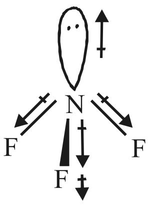
(ii)



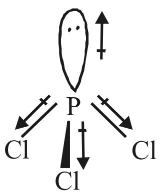
H_2O



NH_3

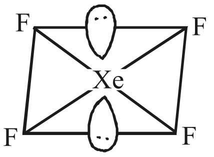


NF_3



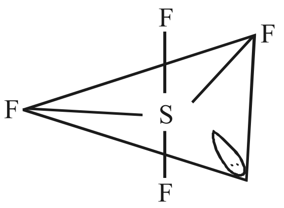
PCl_3

(iii)



Square planar

XeF_4

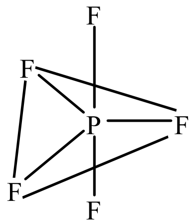


See-saw shape

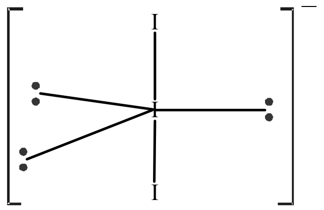
SF_4

OR

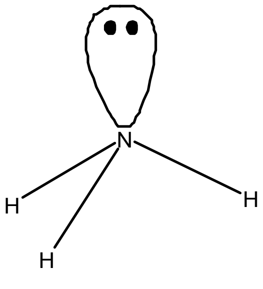
(a) PF_5 hybridization sp^3d, molecular shape – Trigonal bipyramidal



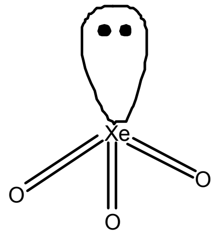
(b) I_3^{-1} – hybridization sp^3d, molecular shape – Linear



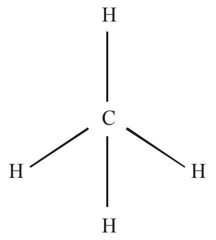
(c) NH_3 – hybridization sp^3, molecular shape – Trigonal pyramidal



(d) XeO_3 – hybridization sp^3, molecular shape– Pyramidal



(e) CH_4 – hybridization sp^3, molecular shape – Tetrahedral



SAMPLE PAPER 2

1. $1\text{ g ml}^{-1} = 1\text{ cm}^{-3} = \dfrac{1\text{g}}{1\text{cm}^3}$

$$= 1\text{ g} \times \frac{1\text{kg}}{1000\text{g}} \times \frac{1}{\text{cm}^3} \times \frac{100\text{cm}}{1\text{m}} \times \frac{100\text{cm}}{1\text{m}} \times \frac{100\text{cm}}{1\text{m}}$$

$= 1000\text{ kg m}^{-3}$

2. Ni^{2+} (28) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^8$.

3. σ bond is formed by end to end or head on overlapping and therefore extent of overlapping is more.

π bond is formed by side wise overlapping, extent of overlapping is less. Thus σ bond is stronger.

4. The ionization enthalpy of H is very high (1312 kJ mol^{-1}) and its electron gain enthalpy is slightly negative (–73 kJ mol^{-1}), As a result, it does not have high tendency to form ionic bonds but rather prefers to form only covalent bonds.

5. Trapping of heat by geenhouse gases namely carbon dioxide, methane, nitrous oxide (N_2O), ozone and chlorofluorocarbons (CFC's) is responsible for greenhouse effect.

6. (a) $NaH_2\underline{P}O_4$

$+1 + 2 + x - 8 = 0$

$\boxed{x = +5}$

(b) $NaH\underline{S}O_4$

$+1 + 1 + x - 8 = 0$

$\boxed{x = 6}$

7. CO_2 absorbs infrared radiations from atmosphere which leads to global warming. If CO_2 level increases beyond 0.03% the natural greenhouse balance may get disturbed. CO_2 is major contributor to global warming therefore it is considered as serious pollutant.

8. $d = \dfrac{MP}{RT}$ or $P = \dfrac{dRT}{M}$.

Hence $\dfrac{P_2}{p_1} = \dfrac{d_2T_2}{d_1T_1}$ or

$$P_2 = \frac{P_1T_2}{T_1}\left(\frac{d_2}{d_1}\right) = \frac{760 \times 263}{273}\left(\frac{1}{10}\right) = 73.2\text{ mm.}$$

OR

$M = 119.5\text{ g mol}^{-1}$

$T = 99 + 273 = 372\text{ K}$

$P = \dfrac{745}{760} = 0.98\text{ atm}$

$d = \dfrac{PM}{RT}$

$$= \frac{0.98\text{ atm} \times 119.5\text{g mol}^{-1}}{0.0821\text{ L atm mol}^{-1}\text{ K}^{-1} \times 372\text{K}}$$

$d = 3.83\text{ g L}^{-1}$.

9. The reaction is : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\dfrac{8.13}{20}\text{mol L}^{-1}\right)^2}{\left(\dfrac{1.57}{20}\text{mol L}^{-1}\right)\left(\dfrac{1.92}{20}\text{mol L}^{-1}\right)^3} = 2.38 \times 10^3$$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.

As $Q_c > K_c$, the net reaction will be in the backward direction.

10. Let us first calculate the temperature at which the reaction will be in equilibrium, i.e., $\Delta G = 0$.

Now, $\Delta G = \Delta H - T\Delta S \therefore 0 = \Delta H - T\Delta S$ or $T = \dfrac{\Delta H}{\Delta S}$

$$= \frac{400\text{kJ mol}^{-1}}{0.2\text{kJ K}^{-1}\text{mol}^{-1}} = 2000\text{ K}$$

For reaction to be spontaneous, i.e., for ΔG to be – ve, T should be greater than 2000 K.

11. (a) $m = 9.1 \times 10^{-28}\text{ g} = 9.1 \times 10^{-31}\text{ kg}$

K. E. $= 3.0 \times 10^{-25}$ J

$\dfrac{1}{2}mV^2 = 3.0 \times 10^{-25}$ J

$$\lambda = \frac{h}{\sqrt{2m \times K.E.}} = \frac{6.6\times10^{-34}\,\text{Js}}{\sqrt{2\times3\times10^{-25}\times9.1\times10^{-31}}}$$

$$\lambda = \frac{6.6\times10^{-34}}{\sqrt{54.6\times10^{-56}}} = \frac{6.6\times10^{-34}}{7.39\times10^{-28}} = 9\times10^{-7}\text{ m}$$

$\lambda = 9 \times 10^{-7} \times 10^{10}$ Å $= 9 \times 10^{3}$ Å $= 9000$ Å.

(b) When a beam of light having frequency more than threshold frequency is made to fall on metals like alkali metals, electrons are ejected. These electrons are called photo electrons and this phenomenon is called photo electric effect.

12. $\Delta H_f = \Delta H_{sub} + \Delta H_{ion} + \Delta H_{EA} + \Delta H_D + \Delta H_{Lattice} + \Delta H_{vap}$

$-524 = 148 + 2187 - 331 + 193 + 31 + \Delta H_{Lattice}$

$\Delta H_{Lattice} = -524 - 2228 = -2752 \text{ kJ mol}^{-1}$.

OR

$\Delta_r H° = \sum \text{BE(reactants)} - \sum \text{BE (products)}$

$\Delta_r H° = [8\,\text{BE(C—H)} + 2\,\text{BE(C—C)} + 5\,\text{BE(O=O)}] - [6\,\text{BE(C=O)} + 8\,\text{BE(O—H)}]$

$-2.05 \times 10^3 = [8 \times 414 + 2 \times 347 + 5\,\text{BE(O = O)}] - [6 \times 741 + 8 \times 464]$

$-2050 = 4006 + 5\,\text{BE (O=O)} - 8158$

$5\text{BE (O=O)} = 2102$

$\text{BE(O=O)} = 420.4 \text{ kJ mol}^{-1}$

13. (a) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(b) $K_c = \dfrac{1}{8.3\times10^{-3}} = \dfrac{1000}{8.3} = 120.48$

(c) K_c will increase with increase in temperature because the process in endothermic.

14. (i) Alkali metals have low ionization enthalpies. Their valence electrons easily absorb energy from the flame and are excited to higher energy levels. When these excited electrons return to the ground state the absorbed energy is emitted in the form of light.

(ii) Difference in lattice enthalpy and hydration enthalpy of LiCl is higher i.e., – 42 kJ mol^{-1} [– 887 – (– 845] than that of LiF i.e., – 16 kJ mol^{-1} [–1021– (–1005)] and hence LiF is sparingly soluble in water while LiCl is soluble. Therefore, we can say that LiF is almost insoluble in water because of much higher lattice energy (–0005 kJ mol^{-1}) than that of LiCl (–845 kJ mol^{-1}). Furthermore, Li$^+$ ion can polarize bigger Cl$^-$ ion more easily than the smaller F$^-$ ion. As a result, according to Fajan rules. LiCl has more covalent character than LiF and hence is soluble in organic solvents like acetone.

(iii) The standard enthalpies of formation of alkali metal chlorides become more and more negative as we move down the group i.e., $\Delta_f H°$ of KCl is more negative (–428 kJ mol^{-1}) than that of NaCl (–400 kJ mol^{-1}). Therefore, with KF the reaction is more exothermic than with NaF.

15. (a) Fullerenes are allotropes of carbon having structure similar to soccer ball. They are made by heating graphite in electric arc in presence of inert gases such as helium or argon.

(b) Al_2O_3 is amphoteric whereas Cl_2O_7 is acidic oxide.

16. (i) **Anti-Markovnikov's rule :** It states when HBr is added to unsymmetrical alkene or alkyne in presence of peroxide negative part of molecule is added to least substituted carbon.

$$CH_3 - CH = CH_2 + HBr \xrightarrow[\textit{peroxide}]{\textit{Benzoyl}} CH_3CH_2CH_2Br$$

(ii) **Decarboxylation :** When sodium salt of acid is heated with soda lime hydrocarbon is obtained.

$$CH_3COONa + NaOH(CaO) \xrightarrow{\textit{heat}} CH_4 + Na_2CO_3$$

17. In the modern periodic table. each period starts with the filling of a principal energy level. Thus, the 5th period begins with filling of principal quantum number $n = 5$. When $n = 5$, $l = 0, 1, 2, 3$. But according to Aufbau principle, the electrons are added to different orbitals in order of their increasing energies. Now the energies of 5*d*- and 5*f*- subshells are higher than that of 6*s*-subshell but the energy of 4*d*-subshell is lower than that of 5*p*-subshells. Therefore in 5th period, electrons can be filled only in 5*s*, 4*d* and 5*p* subshells. whose energies increase in the order : 5 *s* < 4 *d* < 5 *p*. Now *s*-subshell has two, *p*-subshell has three and *d*-subshell has five-orbitals. Hence, in all there are 9 (1 + 3 + 5) orbitals that can be filled in this period. Since according to Pauli's exclusion principle, each orbital at the maximum can have 2 electrons, therefore, 9 orbitals, at the maximum, can have 18 electrons and hence 5th period has 18 elements.

18. (a) The lower reactivity of alkynes as compared to alkenes towards electrophilic addition reactions is due to following two reasons :

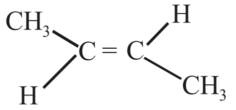
(i) The electronegativity of *sp*- hybridized carbon atoms of a triple bond is greater than sp^2- hybridized carbon atoms of double bond. The π electrons of alkynes are more tightly held than π electrons of alkenes and hence are less easily available for reaction with electrophiles. As a result, alkynes are less reactive than alkenes towards electrophilic addition reactions.

(ii) Due to cylindrical nature of the π electron cloud of alkynes, the π electrons of a triple bond are more delocalized.

(b) The π electrons in benzene are delocalised which provide stability to benzene ring. Due to addition reactions the stability and aromaticity of benzene is disturbed. Thus does not undergo addition reaction.

(c) Chemical reduction i.e., **Birch reduction** of non-terminal alkynes with Na or Li in liquid NH_3 at 196-200 K gives trans-alkenes.

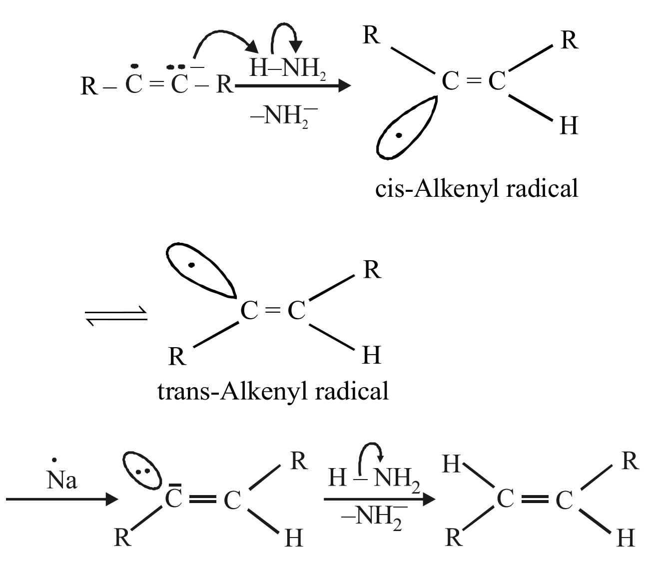
$$\underset{\text{But–2–yne}}{CH_3–C \equiv C–CH_3} \xrightarrow[\text{(ii) Ethanol}]{\text{(i) Na/Liq.}NH_3\text{,196–200 K}}$$



trans-But-2-ene

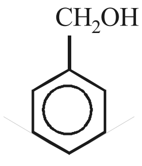
Chemical reduction is believed to occur through two electron transfers and two proton transfers as shown below :

$$\underset{\text{Alkyne}}{R-C\equiv C-R} + \cdot Na \longrightarrow$$

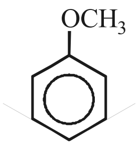


The formation of trans-product is due to the rapid equilibrium between the cis-and trans alkenyl radicals, in which the trans-radical being more stable is readily formed.

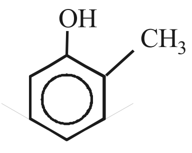
19. (a) Structure of all aromatic are compound having the molecular formula C_7H_8O are



Benzyl alcohol (I)

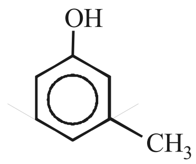


Anisole (II)

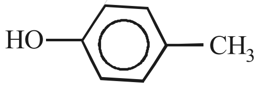


o-Cresol (III)

or



m-Cresol (IV)



p-Cresol (V)

Structure I, II, IV and I, II, V represent functional isomers.

Isomers (III, IV and V) may also be regarded as position Isomers.

(b) Dumas method is applicable to all organic compounds containing nitrogen.

If the organic compound having nitrogen is assumed to have $C_xH_yN_z$ as the molecular formula then the complete combustion equation may be written as

$$C_xH_yN_z + (2x + y/2)\,CuO \xrightarrow{\Delta} xCO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)\,Cu$$

Let mass of organic compound = Wg

Volume of nitrogen collected = V_1 mL

Room temp = T_1 K

$$\text{Volume of } N_2 \text{ at STP} = \frac{P_1V_1 \times 273}{760 \times T_1} \text{ (Let it be V mL)}$$

P_1 = Atm. pressure - Aqueous tension

22400 mL N_2 at STP weighs 28 g.

$$\text{VmL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400}\text{ g}$$

$$\%\text{ of } N_2 = \frac{28 \times V \times 100}{22400 \times W}$$

20.

$$\underset{\text{1 mole}}{C_4H_5N_xO_y} \xrightarrow{\text{Alkali}, \Delta} \underset{x\text{ moles}=x\times 17g}{x\,NH_3}$$

Now 1.7 g of NH_3 is produced from amide = 9.9 g

∴ 17x g of NH_3 will be produced from 1 mole of amide

$$= \frac{9.9}{1.7} \times 17x = 99x\text{ g}$$

∴ Mol. wt. of amide = 99 x

$$\therefore \quad \%\,N = \frac{14x}{99x} \times 100 = \frac{1400}{99}$$

∴ No. of N atoms (x) in one molecule of amide

$$= \frac{1400}{99 \times 14} = 1.01$$

∴ % of N = 32.33 (given)

∴ No. of O atoms (y) in 1 molecule of amide

$$= \frac{32.33}{16} = 2.02$$

Ratio of N and O atoms, i.e., $x : y = 1.01 : 2.02 = 1 : 2$

21. (a) Li due to its smallest size, has high hydration energy among the alkali metals. All other factors like ionization enthalpy etc are compensated due to its high hydration energy. Thus Li is strong reducing agent due to high hydration energy.

(b) Due to small size Li^+ has high polarising power and hence it strongly attracts the large negatively charged nitride ion (N_3^-) towards itself. As a result, lattice energy of Li_3N is high and due to this high lattice energy Li_3N is easily formed.

The other alkali metals do not form their corresponding nitrides because their lattice energies are not only low but also decrease further as their sizes increase from Na to Cs.

$$6\,Li\,(s) + N\,(g) \xrightarrow{\Delta} 2\,Li_3N\,(s)$$

22. (i) Energy of the photon (E) $= h\nu = \dfrac{hc}{\lambda}$

$$= \frac{(6.626\times10^{-34}\,Js)\times(3\times10^{8}\,ms^{-1})}{4\times10^{-7}\,m}$$

$$= 4.97\times10^{-19}\,J = \frac{4.97\times10^{-19}}{1.602\times10^{-19}}\,eV = 3.10eV$$

(ii) Kinetic energy of emission $\left(\dfrac{1}{2}mv^2\right)$

$$= h\nu - h\nu_0 = 3.10 - 2.13 = 0.97\,eV$$

(iii) $\dfrac{1}{2}mv^2 = 0.97eV = 0.97\times1.602\times10^{-19}\,J$

i.e. $\dfrac{1}{2}\times(9.11\times10^{-31}\,kg)\times v^2 = 0.97\times1.602\times10^{-19}\,J$

or $v^2 = 0.341\times10^{12} = 34.\,1\times10^{10}$

or $v = 5.84\times10^{5}\,m\,s^{-1}$

23. (i) Plant emits ethylene hormone which promotes the ripening process.

(ii) The two chemicals used are: Ethylene and calcium carbide. Fruits, vegetables are exposed to ethylene gas. Alternatively, they are placed on the floor and calcium carbide is placed in between them. They are then covered with a tarpaulin and water is sprinkled on it. Calcium carbide reacts with water to give acetylene gas which like ethylene accelerates the ripening process.

$$\underset{\text{Calcium carbide}}{CaC_2} + 2\,H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{HC\equiv CH}$$

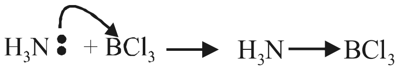
(iii) Commercial calcium carbide has impurities of calcium arsenide and calcium phosphide. These also react with water producing arsine (AsH_3) and phosphine (PH_3) respectively.

$$Ca_3As_2 + 6\,H_2O \longrightarrow 3Ca(OH)_2 + 2\,AsH_3$$

$$Ca_3P_2 + 6\,H_2O \longrightarrow 3Ca(OH)_2 + 2\,PH_3$$

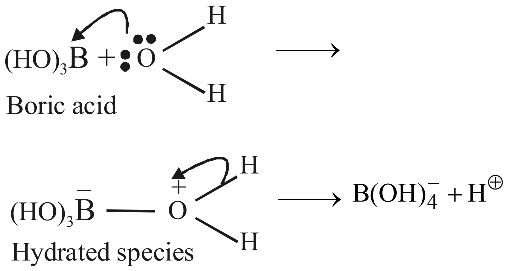
Both arsine and phoshine are poisonous gases. therefore, it is not always safe to use artificially ripen fruits. Since the process of artificial ripening cannot be banned, therefore, fruits/vegetables must be properly washed before using. Further, it is a common observation that artifically ripen fruits/vegetables do not taste the same as naturally ripen fruits/vegetables.

24. (a) (i) The central atom in BCl_3 is electron-deficient atom to complete its octet, boron, accept a pair of electron and hence acts as a Lewis acid.



$$H_3N\!: + BCl_3 \longrightarrow H_3N \rightarrow BCl_3$$

(ii) Because of the small size of boron and presence of six electrons in its valence shell. $B(OH)_3$ accepts a lone pair of elecrons from the oxygen atom of the H_2O molecule to form a hydrated species.



The +ve charge on the O-atom, in turn, pulls the σ-electrons of the O–H bond towards itself thereby facilitating the release of a proton. As a result $B(OH)_3$ acts as a weak monobasic lewis acid.

(b) Since metal X reacts with NaOH to first give a white ppt. (A) which dissolves in excess of NaOH to give a soluble complex (B), therefore, metal (X) must be Al; ppt (A) must bAl $(OH)_3$ and complex (B) must be sodium tetrahydroxoaluminate (III)

$$\underset{(X)}{2\,Al} + 3\,NaOH \longrightarrow \underset{\text{Aluminium hydroxide (ppt.)}}{Al\,(OH)_3\downarrow}\ NaOH + 3Na^+$$

$$\underset{(A)}{Al(OH)_3} + NaOH \longrightarrow \underset{(B)}{Na^+[Al(OH)_4]^-}$$

Sod. tetrahydroxaluminate (III)

Since (A), i.e., $Al(OH)_3$ reacts with dil. HCl to give compound (C), therefore, (C) must be $AlCl_3$.

$$\underset{(A)}{Al(OH)_3} + 3\,HCl \longrightarrow \underset{(C)}{AlCl_3} + 3\,H_2O$$

Since (A) on heating gives (D) which is used to extract metal (i.e., electrolysis of Al_2O_3 gives Al metal), therefore, (D) must be alumina (Al_2O_3)

$$\underset{(A)}{2\,Al\,(OH)_3} \xrightarrow{\Delta} \underset{(D)}{Al_2O_3} + 3\,H_2O$$

OR

(a)

(i) Since the aqueous solution of salt (X) is alkaline to litmus, it must be the salt of a strong base and a weak acid.

(ii) As salt (X) swells up to a glassy material (Y) on strong heating, therefore, (X) must be borax and (Y) must be a mixture of sodium metaborate and boric anhydride.

(iii) When conc. H_2SO_4 is added to a hot solution of X, i.e., borax, white crystals of an acid (Z) separate out, therefore, (Z) must be orthoboric acid. The equations for the reactions involved in the question are :

(i) $$\underset{\text{Borax (X)}}{Na_2B_4O_7 . 10\,H_2O} \xrightarrow{\text{Water}} \underset{\text{(Strong alkali)}}{2\,NaOH} + \underset{\text{(Weak acid)}}{H_2B_4O_7} + 8\,H_2O$$

(ii) $$\underset{\text{(X)}}{Na_2B_4O_7 . 10H_2O} \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10\,H_2O\ :$$

$$Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{2\,NaBO_2 + B_2O_3}_{\text{Glassy material (Y)}}$$

(iii) $$Na_2B_4O_7 . 10H_2O + H_2SO_4 \longrightarrow$$

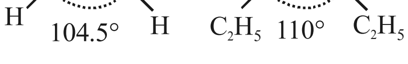
$$\underset{\text{Boric acid (Z)}}{4\,H_3BO_3} + Na_2SO_4 + 5\,H_2O$$

(b) The effective nuclear charge of Ga is greater in magnitude than of Al due to poor shielding of the valence electrons of Ga by the inner 3*d*-electrons. Due to this the electrons in gallium experience greater force of attraction by the nucleus than in Al and hence atomic size of Ga (135 pm) is slightly less than that of Al (143 pm.).

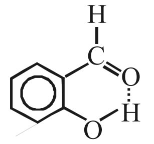
(c) BF_3 is a planar in which B is *sp*^{2}- hybridized. It has an empty 2*p*-orbital and thus accepts lone pair. $p\pi$ - $p\pi$ back bonding occurs and a lone pair of electrons is transferred from F to B.

Due to back bonding B-F bond acquires some double bond character. In contrast, in $[BF_4]^-$ ion, B is *sp*^{3}-hybridized and does not have an empty *p*-orbital available to accept the electrons donated by the F atom. B–F is a purely single bond. As double bonds are shorter than single bonds, threfore, the B–F bond length in BF_3 is shorter (130 pm) than B–F bond length (143 pm) in $[BF_4]^-$.

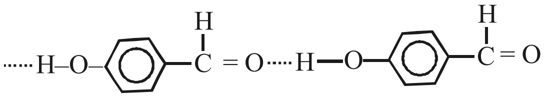
25. (a) The central atom in each case is *sp*^{3} hybridized. The greater repulsion between two ethyl groups, in diethyl ether than between the two H-atoms in H_2O result in greater bond angle (110°) in diethyl ether than in H_2O (104.5°).



(b) Due to Intramolecular hydrogen bonding association of the molecules does not occur in o-hydroxybenzaldehyde whereas in *p*-hydroxy benzaldehyde, there is Intermolecular hydrogen bonding and hence, there is association among the molecules.



o-hydroxybenzaldehyde
(Intramolecular H-bonding)



p-hydroxybenzaldehyde
(Intermolecular H-bonding)

As a result, *o*-hydroxybenzaldehyde is a liquid whereas *p*-hyroxybenzaldehyde is a solid.

(c) Total number of electrons in $HeH^- = 2 + 1 + 1 = 4$

∴ Its electronic configuration will be $\sigma^2_{Is}\ \sigma^{*2}_{Is}$

Bond order $= \frac{1}{2}\ (2 - 2) = 0$. Hence, this ion does not exist.

OR

(a) For Endothermic Reactions, ΔH is always positive, i.e., this factor opposes the process. If TΔS is negative, this factor will also oppose the process and process will be non-spontaneous. However, if TΔS is (so that it favours the process), then the process can occur if magnitude of the factor TΔS is greater than the magnitude of ΔH. The reaction is then said to be entropy driven.

(b) For Exothermic Reactions, ΔH is always negative, i.e., this factor always favours the process. Thus, if TΔS is positive, this factor will also favour the process and the process will be spontaneous. However, if TΔS is negative (so that it opposes the process) then the process can occur only if the magnitude of ΔH is very large so that ΔG is negative. The reaction is then said to be enthalpy driven.

(b) According to Gibbs energy equation.

$\Delta G = \Delta H - T\Delta S$

Depending upon the signs of ΔH and TΔS and their relative magnitudes, the following different possibilities arise.

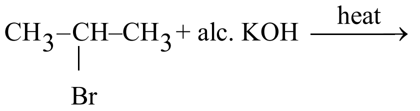
I. When both ΔH *and* TΔS are negative, it.

- (i) If $\Delta H > T\Delta S$ the process is spontaneous and ΔG is negative.
- (ii) If $\Delta H < T\Delta S$, the process is non-spontaneous and ΔG is positive.
- (iii) If $\Delta H = T\Delta S$, the process is in equilibrium and ΔG is zero.

II. When both ΔH and TΔS are positive,
   (i) If ΔH > TΔS, the process is non-spontaneous and ΔG is positive.
   (ii) If ΔH < TΔS, the process is spontaneous and ΔG is negative.
   (iii) If ΔH = TΔS, the process is in equilibrium and ΔG is zero.

III. When ΔH is negative but TΔS is positive. The process will be highly spontaneous and ΔG will be highly negative.

IV. When ΔH is positive but TΔS is negative. The process will be highly non-spontaneous and ΔG will be highly positive.

26. (a) 

$$\underset{\text{Br}}{\underset{|}{CH_3-CH-CH_3}} + \text{alc. KOH} \xrightarrow{\text{heat}}$$

2 – Bromopropane
(Isopropy bromide)

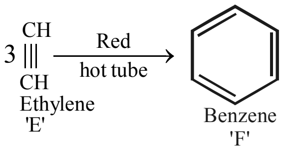
$$\underset{\text{Propene 'A'}}{CH_3-CH=CH_2} - \xrightarrow[\text{peroxide}]{\text{HBr}} \underset{\text{I-Bromopropane 'B'}}{CH_3CH_2CH_2Br}$$

(b) $$\underset{\text{Propane-l-ol}}{CH_3CH_2CH_2OH} \xrightarrow[\text{443 K}]{\text{Conc } H_2SO_4}$$

$$\underset{\text{Propene 'C'}}{CH_3-CH=CH_2} \xrightarrow[\text{heat}]{KMnO_4/OH^-}$$

$$\underset{\text{Ethanoic acid 'D'}}{CH_3COOH} + CO_2 + H_2O$$

(c) $$\underset{\text{1,1,2,2- Tetrachloroethane}}{3Cl_2CH-CHCl_2} \xrightarrow[\text{heat}]{\text{Zn alcohol}}$$



Ethylene
'E'

Benzene
'F'

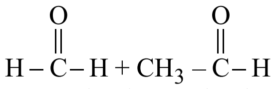
(d) $$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow{NaNH_2} \underset{\text{'G'}}{HC\equiv CNa} + \xrightarrow[\text{Bromoethane}]{CH_3CH_2Br}$$

$$HC\equiv C-CH_2-CH_3 + NaBr$$

(H) But-l-yne

(e) $$\underset{\text{Propyne}}{HC\equiv C-CH_3} + H_2 \xrightarrow[\text{quinoline}]{Pd-BaSO_4}$$

$$\underset{\text{Propene 'I'}}{CH_2=CH-CH_3} \xrightarrow[\text{(ii) Zn / } H_2O]{\text{(i)} O_3}$$



$$H-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{\overset{O}{\|}}{C}-H$$

Methanal Ethanal
'J'

OR

(i) The increasing order of boiling points is 2, 2- dimethyl butane < 3- methyl pentane < hexane < heptane.

Hexane, 3-methyl pentane and 2, 2-dimethyl butane are isomers. As we know that increase in branching reduces the extent of contact between the neighbouring molecules. The van der Waals forces decreases, boiling point also decreases. Heptane has the highest boiling point due to its high molecular mass.

(ii) (a) Branched chain alkanes have lower boiling points than their straight chain isomers, and as branching increases, the boiling point decreases the increased branching gives molecule a more spherical shape and reduces the extent of contact between neighbouring molecules. Consequently, the attractive forces are reduced and the boiling point decreases.

(b) Hydrocarbon with odd number of carbon atoms have lesser melting point than expected. The reason is, in the crystalline state the molecule adopt a highly ordered arrangement in which the carbon chains form a zig-zig pattern. For the even members, different chains peak closer together than for the odd numbered members, so that the attractive forces are larger for the even membered hydrocarbon than for odd membered hydrocarbons of similar size. Therefore, relatively more energy must be applied to separate the molecules with even numbers of carbon atoms and enable them to adopt the more random arrangement of the liquid state than to separate the molecules with odd numbers of carbon atoms.

(c) As compared to neo-pentane due to large surface area. In *n*-pentane, the extent of contact between neighbouring molecules is more. Hence, the attractive forces are more and the boiling point is greater. But the melting point of neo-pentane is greater than that of n-pentane because neo-pentane has a highly symmetrical structure and reduced surface area. Therefore, it is packed in the crystal systems more closely than *n*-pentane. So more energy is required to break the neo-pentane lattice than the *n*-pentane. Hence, neo-pentane has a higher melting point *n*-pentane.

SAMPLE PAPER 3

1. Intramolecular redox reaction can occur if the cation is oxidised and the anion is reduced. For example,

$$\overset{-3}{(NH_4)_2}\overset{+6}{Cr_2O_7} \xrightarrow{\text{Heat}} \overset{0}{N_2} + \overset{+3}{Cr_2O_3} + 4H_2O$$

2. Due to inert pair effect, gallium shows both + 1 and + 3 oxidation states. The reaction is as follows:

$$3\,Ga^+(aq) \rightarrow 2Ga\,(s) + Ga^{3+}(aq)$$

3. Angular momentum of electron $= \sqrt{l(l+1)}\,\dfrac{1}{2\pi}$

For $4f$ orbital, $l = 3$,

$\therefore$ angular momentum $= \sqrt{3(3+1)}\,\dfrac{h}{2\pi} = 2\sqrt{3}\,\dfrac{h}{2\pi}$

$= \sqrt{3}\,\dfrac{h}{\pi}$

4. $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1.}$

5. Bond dissociation energy is defined as average amount of energy required to break one mole of bonds so as to separate them into gaseous atom.

6. (a) $Zn(s)\,|\,Zn^{2+}(1M)\,||\,Pb^{2+}(1M)\,|\,Pb(s)$

(b) At anode : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (Oxidation)

At cathode : $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ (Reduction)

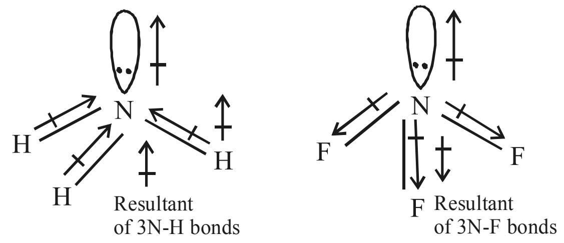
Net cell reaction $\overline{\underline{Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)}}$

7.

Element	%	Atomic	Relative no of atoms	Divide by least	Simplest ratio
C	64.4	12	$\frac{64.4}{12} = 5.36$	$\frac{5.36}{0.53} = 10.1$	10
H	5.50	1	$\frac{5.50}{1} = 5.50$	$\frac{5.50}{0.53} = 10.4$	10
Fe	29.9	56	$\frac{29.9}{56} = 0.53$	$\frac{0.53}{0.53} = 1$	1

Empirical formulae $= C_{10}H_{10}Fe$

8. F is more electronegative than N-therefore direction of bond is from N to F whereas N is more electronegative than H, the direction of bond is from H to N. The resultant dipole moment of N-H bonds add upto the bond moment of lone pair, that of 3N-F bonds partly cancels the resultant moment of lone pair. Hence the dipole moment of NF_3 is less than that of NH_3.

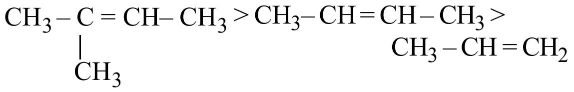


$NH_3\ \mu = 1.47$ D $\quad NF_3\ \mu = 0.24$ D

OR

Elements whose last electron enters in d-orbital are called d-block elements but Zn, Cd and Hg are not regarded as d-block element as their last electron enters in s-orbital. But properties of these elements resemble with d-block elements. Thus due to resemblance in properties all transition elements are d-block elements but according to electronic configuration, all d-block elements are not transition elements.

9. (a)



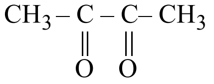
$\underset{\displaystyle CH_3}{CH_3 - \overset{}{C} = CH - CH_3} > CH_3 - CH = CH - CH_3 > CH_3 - CH = CH_2$

Greater the number of alkyl groups, more will be hyperconjugation, more will be stability.

(b) (i) $\overset{4}{CH_3} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{COOCH_3}$

Methylbut-2-enoate

(ii)



$CH_3 - \underset{\displaystyle O}{\underset{\|}{C}} - \underset{\displaystyle O}{\underset{\|}{C}} - CH_3$

Butane-2,3-dione

10. Electronic configuration of $16S = 1s^2\,2s^2\,2p^6\,3s^2\,3p^4$

For $1s^2$, $n + l = 1 + 0 = 1$.

For $2s^2$, $n + l = 2 + 0 = 2$.

For $2p^6$, $n + l = 2 + 1 = 3$

For $3s^2$, $n + l = 3 + 0 = 3$

For $3p^4$, $n + l = 3 + 1 = 4$

Thus, $n + l = 3$ for $2p^6$ and $3s^2$ electrons, *i.e.*, for 8 electrons.

11. The word "smog" is a combination of "smoke" and "fog". The name was so given because for the first time it was found to be formed due to condensation of some kind of fog on the carbon particles present in the smoke produced due to combustion of domestic and industrial fuels like coal and petroleum. However, now it is given a name depending upon the composition or the method of its formation or the place familiar for its formation. It is mainly of two different types as

(1) London smog or Classical smog

(2) Photochemical smog or Los Angeles smog.

Difference between classical smog (London smog) and Photochemical smog (Los Angeles smog).

	Classical smog (London smog)	**Photochemical smog (Los Angeles smog)**
1.	It is formed due to presence of SO_2 and humidity in the air which combine to form H_2SO_4 fog which deposits on the particulates.	It is formed due to photochemical reaction taking place when air contains NO_2 and hydrocarbons.
2.	It involves smoke and fog.	It does not involve any Smoke or fog. The word smog is a misnomer here.
3.	It is formed in the months of winter particularly in the morning hours when the temperature is low.	It is formed in the months of summer during afternoon when there is bright sunlight so that photochemical reactions can take place.
4.	It is reducing in nature.	It is oxidizing in nature.

12. The valence shell of B atom in BF_3 or BBr_3 has only six electrons and hence can accept a pair of electrons to complete its octet. Therefore, both BF_3 and BBr_3 act as Lewis acids. But in BF_3, the size of empty 2*p*-orbital of B and the 2*p*-orbital of F containing the lone pair of electrons are almost identical and hence effective $p\pi–p\pi$ bonding occurs. As a result, the lone pair of F is donated to B atom and hence the electron-deficiency of boron decreases. In comparision to this, in BBr_3, the size of 4*p*-orbital of Br containing the lone pair of electrons is much bigger than the empty 2*p*-orbital of B and hence donation of lone pair of electrons of Br to B does not occur to any significant extent. As a result, the electron- deficiency of B is much higher in BBr_3 than that in BF_3, and hence BBr_3 is a stronger Lewis acid than BF_3.

OR

Self ionization of water is termed as Auto-protolysis

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O + (aq) + OH^-(aq)$$

$\text{Acid}_1 \quad \text{Base}_2 \quad \text{Acid}_2 \quad \text{Base}_1$

Due to auto-protolysis, water is amphoteric in nature, *i.e.*, it reacts with both acids and bases. It acts as a base towards acids stronger than itself and as an acid towards bases stronger than itself. For example:

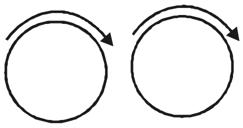
$$H_2O(l) + NH_3(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

$\text{Acid}_1 \quad \text{Base}_2 \quad \text{Acid}_2 \quad \text{Base}_1$

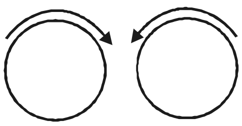
$$H_2O(l) + H_2S(aq) \longrightarrow H_3O^+(aq) + HS^-(aq)$$

$\text{Base}_1 \quad \text{Acid}_2 \quad \text{Acid}_1 \quad \text{Base}_2$

13. (a)



Ortho-hydrogen
(Parallel nuclear spin)



Para-hydrogen
(Anti parallel nuclear spin)

(b) $H_2 + Cl_2 \longrightarrow 2HCl$

Cl_2 is oxidising agent, H_2 is reducing agent.

$Ca + H_2 \longrightarrow CaH_2$

Ca is reducing agent, H_2 is oxidising agent.

14. (a) It is due to more inter electronic repulsion in fluorine atom due to smaller atomic size than chlorine.

(b) It is because they have stable electronic configuration, *i.e.*, their octet is complete except He.

(c) First ionisation energy of Mg is more than that of Na because it has smaller atomic size but 2nd ionisation energy of Mg is less because after losing one electron sodium acquires nearest noble gas configuration.

15. Plaster of Paris is $CaSO_4.\frac{1}{2}H_2O$. It is prepared by heating gypsum at 373 K.

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow[373K]{\text{heat}} \underset{\text{Plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} + \frac{3}{2}H_2O$$

Uses (i) It is used in manufacture of statues.

(ii) It is used for filling gaps before white washing.

16. For buffer X, $pH = pK_a + \log\frac{[Salt]}{[Acid]}$,

$$i.e., 4 = 5 + \log\frac{[Salt]}{0.5} \text{ or } \log\frac{[Salt]}{0.5} = -1$$

$$\text{or } \frac{[Salt]}{0.5} = 10^{-1} \text{ or } [Salt] = 0.05\text{ M}$$

For buffer Y, $pH = pK_a + \log\frac{[Salt]}{[Acid]}$,

$$i.e., 6 = 5 + \log\frac{[Salt]}{0.5} \text{ or } \log\frac{[Salt]}{0.5} = 1$$

$$\text{or } \frac{[Salt]}{0.5} = 10 \text{ or } [Salt] = 5\text{ M}$$

When equal volumes of both the buffers are mixed,

$$[Acid] = 0.5, [Salt] = \frac{5 + 0.05}{2} = 2.5025$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} = 5 + \log\frac{2.5025}{0.5}$$

$$= 5 + \log 5.05 = 5.7$$

17. $\Delta_r S° = \sum S°\text{ (Products)} - \sum S°\text{ (Reactants)}$

$= 2\ S°(Fe_2O_3) - [4\ S°(Fe) + 3\ S°(O_2)]$

$= 2 \times 87.4 - [4 \times 27.3 + 3 \times 205.0]\ J\ K^{-1}\ mol^{-1}$

$= -549.4\ J\ K^{-1}\ mol^{-1}$

This is the entropy change of the reaction,

i.e., system (ΔS_{system})

Now, $\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$= -1648000\ J\ mol^{-1} - 298\ K \times (-549.4\ J\ K^{-1}\ mol^{-1})$

$= -1648000 + 163721\ J\ K^{-1}\ mol^{-1}$

$= -1484279\ J\ K^{-1}\ mol^{-1}$

As $\Delta G°$ is –ve, the reaction is spontaneous.

18. (i) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Initial conc. 0.05 M

Eqm. conc. $0.05(1-\alpha)$ $\quad 0.05\,\alpha \quad 0.05\,\alpha$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\therefore \quad 1.77 \times 10^{-5} = \frac{(0.5\alpha)^2}{0.05(1-\alpha)} \simeq 0.05\alpha^2$$

$$\text{or} \quad \alpha^2 = \frac{1.77 \times 10^{-5}}{0.05} = 3.54 \times 10^{-4}$$

$$\text{or} \quad \alpha = 1.88 \times 10^{-2}$$

Alternatively, apply directly the formula: $\alpha = \sqrt{K_b / C}$

(ii) $[OH^-] = 0.05\,\alpha = 0.05 \times 1.88 \times 10^{-2}$

$= 9.4 \times 10^{-4}$ M

$pOH = -\log(9.04 \times 10^{-4}) = 4 - 0.9562 = 3.04$

$\therefore \quad pH = 14 - 30.4 = 10.96$

(iii) For conjugate acid base pair, $K_a = \dfrac{K_w}{K_b}$

$$= \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.64 \times 10^{-10}$$

19. Given

10 litre of water contain $Ca(HCO_3)_2 = 1.62$ g

$\therefore$ 50,000 litre of water will contain $Ca(HCO_3)_2$

$$= \frac{1.62}{10} \times 50000 \text{ g} = 8100 \text{ g}$$

The balanced equation for the reaction involved is :

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3 + 2\,H_2O$

1 mole $\quad$ 1 mole

$40 + (1 + 12 + 48) \times 2 = 162$ g

$40 + (16 + 1) \times 2 = 74$ g

162 g $Ca(HCO_3)_2$ require lime = 74 g

$\therefore$ 8100 g $Ca(HCO_3)_2$ will require lime

$$= \frac{74}{162} \times 8100 \text{ g}$$

3700 g = 3.7 kg

20. (a) Na_2CO_3 is a salt of strong base NaOH and weak acid H_2CO_3 therefore, when it is dissolved in water concentration of OH^- dominates over H^+ ions that is why solution is alkaline in nature.

(b) It is because alkali metals are highly reactive due to high electropositive character and are strong reducing agents due to low ionisation energy.

(c) Potassium is more reactive than sodium and found in nature to less extent than Na, therefore potassium is less useful than sodium.

21. (a) H_2SO_4 acts as a catalyst for decomposition of H_2O_2. Therefore, some weaker acids such as H_3PO_4 is preferred over H_2SO_4 for preparing H_2O_2 from peroxides.

$$3\,BaO_2 + 2\,H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3\,H_2O_2.$$

Further, this method has the advantage over BaO_2-H_2SO_4 method since almost all the heavy metal (*e.g.*, Pb, etc.) impurities present in BaO_2 and which catalyse the decomposition of H_2O_2 are removed as insoluble phosphates. As a result, the resulting solution of H_2O_2 has good keeping properties.

(b) By definiton, 5 volume H_2O_2 solution means that 1 l of 5 volume H_2O_2 solution on decomposition produces 5 l of O_2 at NTP.

Consider the decomposition reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$2 \times 34 \text{ g} \longrightarrow 22.7 \text{ l at NTP}$$

Now 22.7 l O_2 at NTP will be obtained from $H_2O_2 = 68$ g.

$\therefore$ 5 l of O_2 at NTP will be obtained from H_2O_2

$$= \frac{68 \times 5}{22.7} \text{ g} = 14.98 \text{ g} = 15 \text{ g}$$

But 5 l of O_2 at NTP is produced from 1 l of 5 volume H_2O_2

$\therefore$ Strength of H_2O_2 solution = 15 g l^{-1}

or Percentage strength of H_2O_2 solution

$$= \frac{15}{1000} \times 100 = 1.5\%.$$

22. $C_6H_6\,(l) + \dfrac{15}{2}\,O_2\,(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$

$$\Delta_c H^\circ = 6\Delta_f H^\circ CO_2 + 3\Delta_f H^\circ H_2O(l) - \Delta H_f^\circ C_6H_6 - \frac{15}{2}\Delta H_f^\circ O_2$$

$-3266 \text{ kJ} = 6 \times -393.1 + 3 \times -286 - \Delta H_f^\circ C_6H_6 - 0$

$\Delta H_f^\circ C_6H_6 = -2358.6 \text{ kJ} - 858 \text{ kJ} + 3266 \text{ kJ}$

$= +49.4 \text{ kJ mol}^{-1}$.

23. (a) A small quantity of a gaseous organic sulphur compound, methyl mercaptan, CH_3SH, is added to LPG by the oil companies.

(b) (i) The supply of gas from gas cylinder should be immediately closed.

(ii) All doors and windows should be opened.

(iii) Don't light match stick or gas lighter.

24. (a) Mn^{2+} (25) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Mn^{2+} is more stable due to half filled *d*-orbital.

Fe^{2+} (26) : $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^0\, 3d^6$.

Fe^{2+} is not stable because it does not have half filled *d*-orbital.

(b) Dual nature of electrons means electron is associated with both particle as well as wave like nature.

$$\Delta E = -13.6\,\text{eV}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= -13.6\,\text{eV}\left(\frac{1}{2^2}-\frac{1}{1^2}\right) = -13.6\left(\frac{3}{4}\right) = 10.2\,\text{eV}$$

$$\Delta E = 10.2 \times 1.6 \times 10^{-19}\,\text{J} = 16.32 \times 10^{-19}\,\text{J}$$

$$\Delta E = \frac{hc}{\lambda};\ \lambda = \frac{hc}{\Delta E} = \frac{6.26\times10^{-34}\times3\times10^{8}}{16.32\times10^{-19}}$$

$$= 1.22 \times 10^{-7}\,\text{m} = 122\,\text{nm}$$

OR

(i) For H atom, $E_n = -1.312 \times 10^3\,\text{kJmol}^{-1}$

$$= -1.312 \times 10^6\,\text{Jmol}^{-1}$$

$$= -\frac{1.312\times10^{6}}{6.023\times10^{23}}\,\text{J atom}^{-1}$$

$$= -2.18 \times 10^{-18}\,\text{J atom}^{-1}$$

Here, $n_{\text{final}} = 1$; $n_{\text{initial}} = 4$

$$E_{\text{initial}} = -\frac{2.18\times10^{-18}}{(4)^2}$$

$$= -0.136\times10^{-18}\,\text{J atom}^{-1}$$

$$E_{\text{final}} = -\frac{2.18\times10^{-18}}{(1)^2} = -2.18\times10^{-18}\,\text{J atom}^{-1}$$

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$= -2.18 \times 10^{-18}\,(-0.316 \times 10^{-18})$$

$$= -1.864 \times 10^{-18}\,\text{J}$$

Also, $\Delta E = hc/\lambda$

$$\lambda = hc/\Delta E = \frac{6.626\times10^{-34}\times3\times10^{8}}{1.864\times10^{-18}}$$

$$= 10.66 \times 10^{-8}\,\text{m}$$

(ii) (a) $2s < 2p$ (b) $3p < 3d$

(c) $3s < 4s$ (d) $4d < 5f$

25. (a)

$$\begin{array}{lcc} & N_2O_4\,(g) & \rightleftharpoons 2NO_2\,(g) \\ \text{Initial} & 1 & 0 \\ \text{Final} & 1-\alpha & 2\alpha \end{array}$$

where 'α' is degree of dissociation.

Total number moles $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$P_{NO_2} = \frac{2\alpha}{1+\alpha} \times P$$

$$P_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{\frac{(2\alpha)^2}{(1+\alpha)^2}\times P^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} = \frac{4\alpha^2}{1-\alpha^2} \times P$$

$$0.8 = \frac{4\alpha^2}{1-\alpha^2} \times 1$$

$$0.8 - 0.8\alpha^2 = 4\alpha^2$$

$$4.8\,\alpha^2 = 0.8$$

$$\alpha^2 = \frac{0.8}{4.8} = \frac{1}{6} = 0.166 = 16.6 \times 10^{-2}$$

$$= 4.08 \times 10^{-1} = 4.08 \times 10^{-1} \times 100 = 40.8\%$$

(b) $$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\log\frac{K_2}{62.5} = \frac{-10.4\times1000}{2.303\times8.314}\left(\frac{1}{800}-\frac{1}{1000}\right)$$

$$\log\frac{K_2}{62.5} = -\frac{10400}{19.147} \times \frac{200}{800\times1000}$$

$$\log\frac{K_2}{62.5} = \frac{-104.0}{765.88} = \frac{-104.0}{766}$$

$$= -0.135 = -0.135 + 1 - 1 = \bar{1}.865$$

$$\frac{K_2}{62.5} = \bar{1}.865\ \text{Antilog} = 0.7328$$

$$K_2 = 62.5 \times 0.7328 = 48.7$$

OR

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$K_{a_1} = [H^+][HCO_3^-]/[H_2CO_3] = 4.3 \times 10^{-7}$$

And $$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$K_{a_2} = [H^+][CO_3^{2-}]/[HCO_3^-] = 5.6 \times 10^{-11}$$

As K_{a_1} is much larger than K_{a_2}, we can safely assume that nearly all the hydrogen ion in the solution is derived from the first step of the dissociation. In addition, only very little amount of the HCO_3^- ion formed in the first step will undergo further dissociation. On the basis of this we can calculate the equilibrium concentrations of H^+ and HCO_3^- by using the expression for K_{a_1} alone.

$$K_{a_1} = [H^+][HCO_3^-]/[H_2CO_3]$$

If we consider x be the number of moles per litre of H_2CO_3 that dissociate, we obtain, from the stoichiometry of the first step, x mol/L of H^+ and x mol/L of HCO_3^-. At equilibrium, there will be (0. 10 – x) mol/L of H_2CO_3 remaining.

	Initial Molar Concentrations	Change	Equilibrium Molar Concentrations
H^+	0.0	+x	x
HCO_3^-	0.0	+x	x
H_2CO_3	0.10	–x	$0.10 - x \approx 0.10$

As x is very small, we may assume that x will be negligible in comparison to 0. 10 and thus equilibrium concentration of $[H_2CO_3] = 0.10 - x = 0.10$ M

substituting these equilibrium concentration values into the expression for K_{a_1} we have

$(x)(x)/0.10 = 4.3 \times 10^{-7}$

$x^2 = 4.3 \times 10^{-8}$ or $x = 2.07 \times 10^{-4}$

therefore, the equilibrium concentrations from first dissociation are

$[H^+] = 2.07 \times 10^{-4}$M ; $[HCO_3^-] = 2.07 \times 10^{-4}$M ;

$[H_2CO_3] = 0.10$ M

By employing K_{a_2} , we can now calculate the equilibrium concentration of CO_3^{2-}

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Consider y be the number of moles per litre of HCO_3^- that dissociates. Thus, the total hydrogen ion concentration from both the first and second dissociations will be $(2.07 \times 10^{-4} + y)$, and y mol /L of CO_3^{2-} . At equilibrium, there will be $(2.07 \times 10^{-4} - y)$ mol / L of HCO_3^-

	Initial Concentrations	Change	Equilibrium Concentrations
H^+	2.07×10^{-4}	+ y	$2.07 \times 10^{-4} + y$
CO_3^{2-}	0.0	+ y	y
HCO_3^-	2.07×10^{-4}	–y	$2.07 \times 10^{-4} - y$

Make the assumption that y will be negligible as compared to 2.07×10^{-4}. Our equilibrium concentrations then become

$[H^+] = 2.07 \times 10^{-4} + y \approx 2.07 \times 10^{-4}$ M

$[CO_3^{2-}] = y$

$[HCO_3^-] = 2.07 \times 10^{-4} - y \approx 2.07 \times 10^{-4}$ M

Note that the value of y is very much smaller than the value of x obtained for the first step in the dissociation.

By substituting these equilibrium concentration values in K_{a_2}, we obtain

$$K_{a_2} = \frac{(2.1 \times 10^{-4})(y)}{(2.1 \times 10^{-4})} = 5.6 \times 10^{-11}$$

$y = 5.6 \times 10^{-11}$

Therefore equilibrium concentrations of all species,

$[H^+] = 2.07 \times 10^{-4}$ M ;$[HCO_3^-] = 2.07 \times 10^{-4}$M; $[CO_3^{2-}] = 5.6 \times 10^{-11}$ M; $[H_2CO_3] = 0.10$M

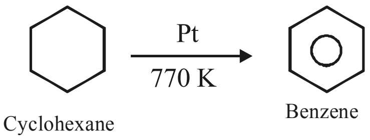
26. (a) (i) Acetylene to propyne

$$\underset{\text{Acetylene}}{HC \equiv CH} + NaNH_2 \longrightarrow HC \equiv CNa + NH_3$$

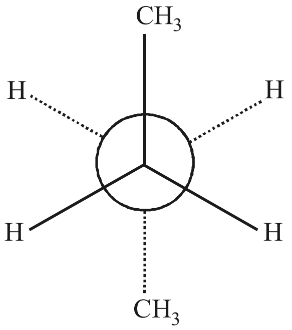
$$HC \equiv CNa + CH_3Cl \longrightarrow \underset{\text{propyne}}{HC \equiv C{-}CH_3} + NaCl.$$

(ii) n- Hexane to benzene

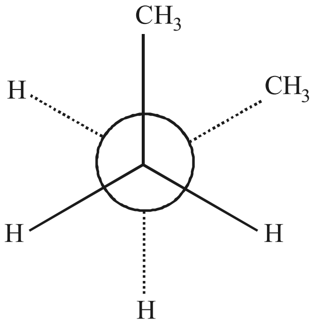
$$\underset{\text{n- Hexane}}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3} \xrightarrow[\text{heat 770 K}]{\text{Pt}}$$



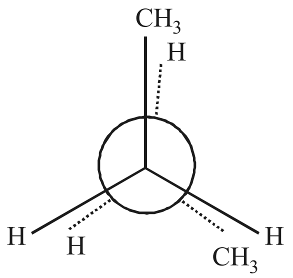
(b)



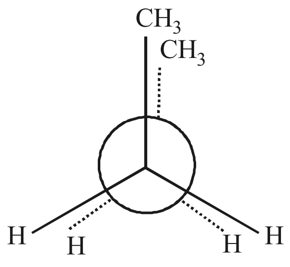
Anti
(or Staggered)
I



Gauch
(or Skew)
II



Partially
Eclipsed
III

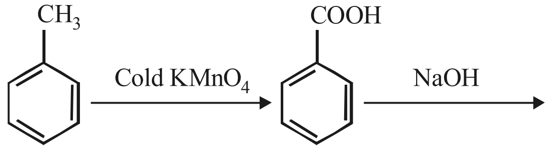


Fully
Eclipsed
IV

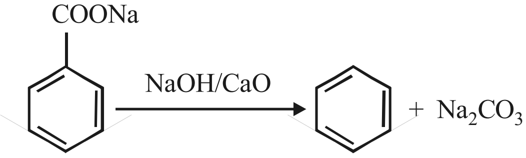
Anti conformation of butane is most stable because there is least repulsion whereas fully eclipsed conformation is least stable because of maximum repulsion.

(c) (i) $\underset{\text{Ethene}}{CH_2 = CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br}$

(ii)



Toluene

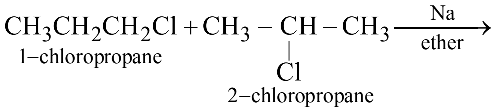


Benzene

OR

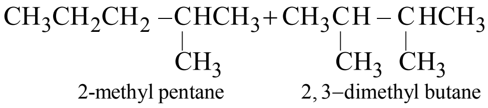
(i) Two different alkyl halides must be used; ethyl and methyl chloride. When reacted in the presence of sodium, three reactions occur; giving a mixture of three product. Methyl couples with methyl to give ethane; methyl with ethyl to give propane; and ethyl with ethyl to give butane. Due to which Wurtz synthesis is not good method for preparing propane.

(ii) Three alkanes are obtained from the reaction of sodium with equimolar mixture of 1-chloropropane and 2-chloropropane.



$$\underset{\text{1–chloropropane}}{CH_3CH_2CH_2Cl} + \underset{\text{2–chloropropane}}{CH_3 - \underset{\substack{|\\ Cl}}{CH} - CH_3} \xrightarrow[\text{ether}]{\text{Na}}$$

$$\underset{\text{hexane}}{CH_3CH_2CH_2 - CH_2CH_2CH_3}$$



$$\underset{\text{2-methyl pentane}}{CH_3CH_2CH_2 - \underset{\substack{|\\ CH_3}}{C}HCH_3} + \underset{\text{2, 3–dimethyl butane}}{CH_3\underset{\substack{|\\ CH_3}}{C}H - \underset{\substack{|\\ CH_3}}{C}HCH_3}$$