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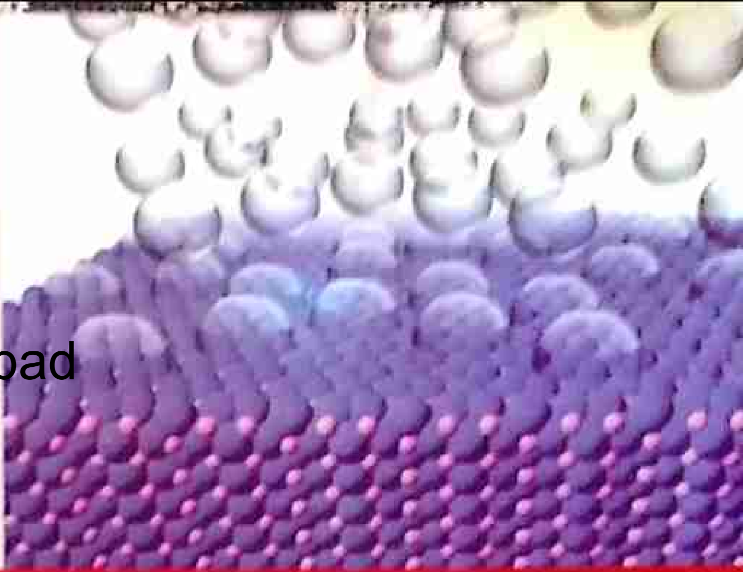

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# Test Your Chemistry

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Haq Nawaz Bhatti

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# TEST
# YOUR
# CHEMISTRY

**(Revised & Enlarged)**

*For*
*All Competitive Examinations in Chemistry and Interviews for Civil Services and Armed Forces Services.*

***(CSS, PCS, Educators, Grades 16 & 17, etc.)***

*By*

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***Dedicated***

***to***

***My Loving Parents***

***Whose Affection will ever Haunt Me***

# PREFACE TO THE SECOND EDITION

Chemistry is the branch of Science which deals with the structure of matter and composition of substances, their transformation, analysis, synthesis and manufacturing. To facilitate the study of Chemistry, it has been divided into various branches viz; Physical, Inorganic, Organic, Analytical etc. The knowledge of the basic concepts is absolutely essential for better understanding of the subject matter. To augment the ability of the students to understand the subject, the present book is written.

The book in your hand is primarily meant for graduate and postgraduate students of Chemistry with the intention that they could show better performance during various competitive examinations and interviews held for Civil and Military Services. At the same time it is equally useful for those who desire to be well informed in various disciplines of chemistry.

The revised edition of this book consists of nine parts — Physical, Organic, Inorganic, Analytical, Environmental Applied/Industrial, Biochemistry, Spectroscopy Techniques and Biotechnology. Simple and lucid language has been used to express the subject matter. The information has been categorized under relevant headings. The questions are so framed that they clarify minute misconceptions. Some useful conversions and important reactions have also been incorporated.

At last but not least at all, my sincere thanks to **Ch. Ahmad Najeeb** for giving open offer to publish this book. To make this endeavor more useful or for its improvement in making this as glaring garland in the subject, the suggestions will be welcomed from all corners.

**Prof. Dr. Haq Nawaz Bhatti**
(hnbhatti2005@yahoo.com)

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# *Part One*
# PHYSICAL CHEMISTRY

## 1.1. Atomic Structure and Quantum Chemistry

**Q. What is Mechanics ?**

**Ans.** The branch of physical science dealing with the behaviour of matter under the action of forces.

**Q. What is the difference between Newtonian Mechanics and Quantum Mechanics?**

**Ans.** Newtonian Mechanics is based on Newton's laws of motion and provides an accurate means of determining the motions of bodies possessing ordinary velocities.

Quantum Mechanics is a method of interpreting physical phenomena occurring on a very small scale (e.g., the motion of electron and nuclei within atoms).

**Q. State Planck's law of radiation.**

**Ans.** The energy of electromagnetic radiation is composed of discrete quanta, the magnitude of which is given by the product of Planck's constant and the frequency of radiation.

**Q. Explain the terms "quantum" and "quantized".**

**Ans.** According to the quantum theory, energy exists in discrete units, only whole numbers of which can exist; each unit is called a quantum (plural 'quanta'). The quantum of electromagnetic radiation is called photon.

A quantity is said to be quantized if, in accordance with quantum mechanics, it can only have certain discrete values. Such a quantity cannot vary continuously, differences in value being separated by `jumps'.

**Q. What is photoelectric effect?**

**Ans.** When a beam of visible or ultraviolet light falls on a clean metal surface in vacuum, the surface emits electrons. This effect is known as photoelectric effect.

**Q. Define Compton effect.**

**Ans.** When light of a short wavelength strikes on an electron, it is scattered and its frequency is shifted towards lower value. This shift of frequency is independent of the frequency of incident radiation. This behaviour is called the Compton effect.

**Q. What is de-Broglie hypothesis?**

**Ans.** Louis de-Broglie suggested that every material particle is associated with a wave. He argued that if light can sometimes behave as particle, then it should be possible for matter to exhibit wave-like behaviour under suitable conditions.

**Q. State Heisenberg Uncertainty Principle.**

**Ans.** It is impossible to measure simultaneously both the position and momentum (or velocity) of a microporticle with certainty.

**Q. What is wave mechanical model of the atom ?**

**Ans.** A model which takes into account the wave and particle nature of the electron. This model was proposed by an Austrian Physicist E. Schrodinger in 1926.

**Q. Briefly discuss the significance of Schrodinger wave equation.**

**Ans.** Schrodinger wave equation describes the wave motion of an electron along three-dimensional axes. This equation is used to calculate energy and wave function of microparticle such as electron.

**Q. What is a wave function ?**

**Ans.** In wave mechanics, electrons are not treated as particles, but as three-dimensional standing wave systems represented by a wave function, $\psi$, the magnitude of which represents the varying amplitudes of the wave system at various points around the nucleus.

**Q. Define eigen function and eigen value.**

**Ans.** When an operator operates on a function and the same function is reproduced with some numerical value or constant, then the function is called eigen function and numerical value is called its eigen value.

**Q. What is a normalized wave function ?**

**Ans.** A function is said to be normalized wave function if it satisfies the following condition

$$\int_{-\infty}^{+\infty} \psi^2 \, d\tau = 1 \qquad \text{..... 1.1}$$

Such a condition is called normalization of the wave function.

**Q. What are orthogonal wave functions ?**

**Ans.** When the integral of the product of two different wave functions is equal to zero, the wave functions are said to be orthogonal.

$$\int_{-\infty}^{+\infty} \psi_p \, \psi_q \, d\tau = 0 \qquad p \neq q \text{ ..... 1.2}$$

**Q. What is tunnel effect ?**

**Ans.** It is a quantum mechanical effect in which a particle can penetrate a region even though it does not have the energy to penetrate classically. For example, emission of alpha particles and flow of current between two electrodes.

**Q. What are quantum numbers ?**

**Ans.** Integral or half integral numbers which specify the state of a system or its components in quantum mechanics. An electron within an atom is specified by four quantum numbers:

*(i)* The principal quantum number, n, defining the energy level in which the electron occurs;

*(ii)* the azimuthal quantum number, *l*, defining the shape and multiplicity of the orbital within that shell,

*(i)* the magnetic quantum number, m, which determines the orientation of orbital with reference to a strong magnetic field; and

*(ii)* the spin quantum number, s, which determines the direction of spin of an electron in a magnetic field.

**Q. Explain Zeeman effect.**

**Ans.** When a substance which emits a line spectrum is placed in a strong magnetic field, the single lines are split up into groups of closely spaced lines. Such a splitting is called Zeeman effect.

**Q. Define Pauli exclusion prin-ciple.**

**Ans.** According to this principle, no two electrons in an atom can have the same values of all the four quantum numbers.

**Q. What is Hund's rule ?**

**Ans.** When several orbitals of same energy are available, electrons would prefer to occupy separate orbitals and remain unpaired rather than to live in the same orbital and leave the other empty.

**Q. Define Aufbau principle.**

**Ans.** The orbitals are filled up in order of increasing energy. As a working rule, a new electron enters the orbital where n + *l* value is minimum.

**Q. Define orbit and orbital.**

**Ans.** Orbit is the path of an electron around the nucleus of an atom, while an orbital is the volume containing all the points within a free atom at which the wave function of an electron has an appreciable magnitude.

## 1.2. The Gaseous State

**Q. What is Boyle's law ?**

**Ans.** At constant temperature, the volume of a given quantity of a gas is inversely proportional to the pressure of the gas.

**Q. State Charles law.**

**Ans.** The volume of certain mass of a gas increases or decreases by 1/273.15 of its volume at 0°C for every 1°C rise or fall in the temperature, provided the pressure remains constant.

or

The volume of certain mass of a gas is directly proportional to the absolute temperature, provided the pressure remains constant.

**Q. Define Avogadro's law.**

**Ans.** Equal volumes of all the gases at the same temperature and pressure contain the same number of molecules.

**Q. What is ideal gas law? Give the value of gas constant in different units.**

**Ans.** An ideal gas law is defined as

$$PV = nRT \qquad ..... 1.3$$

where R is gas constant. Its value in different units is given below

$R = 0.0821$ litre atm $K^{-1}$ $mol^{-1}$

$= 8.314$ Nm $K^{1}$ $mol^{-1}$

$= 8.314$ $JK^{-1}$ $mol^{-1}$

$= 1.987$ cal $K^{-1}$ $mol^{-1}$

**Q. Explain Dalton's law of partial pressure.**

**Ans.** At constant temperature, the total pressure exerted by a mixture of gases in a definite volume is equal to the sum of the partial pressures which each gas would exert if present alone in the same volume.

**Q. State Graham's law of diffusion.**

**Ans.** At constant temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities.

**Q. State some important postulates of kinetic theory of gases.**

**Ans.** *(i)* Every gas consists of a very large number of tiny particles called molecules/atoms.

*(i)* All molecules collide with each other and with the walls of the container. The collisions between the molecules and walls of the container are perfectly elastic.

*(ii)* The volume occupied by the gas molecules themselves is negligible as compared with the total volume of the gas.

*(iii)* There are no forces of attraction or repulsion between the gas molecules.

**Q. Define mean, root mean square and most probable velocity.**

**Ans.** The mean or average velocity of molecules of a gas is defined as the sum of the velocities of all the molecules divided by total number of all molecules. Mathematically,

$$\bar{u} = \frac{u_1 + u_2 + u_3 + ..... + u_n}{n} \qquad ..... 1.4$$

If we put squares of the velocities in Eq. (1.4), we get

$$\overline{u}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + ..... + u_n^2}{n} \qquad ..... 1.5$$

Where $\overline{u}^2$ is the mean square velocity. The square root of the mean square velocity is known as root mean square velocity. The velocity possessed by the maximum number of gas molecules at a given temperature is known as most probable velocity.

**Q. Describe the relation between molecular velocities.**

**Ans.** It has been found that

Most probable velocity, ump $= \sqrt{\frac{2RT}{M}}$ ..... 1.6

Mean velocity, $\overline{u} = \sqrt{\frac{8RT}{\pi M}}$ ..... 1.7

Root mean square velocity, $u_{rms} = \sqrt{\frac{3RT}{M}}$ ..... 1.8

Thus $u_{rms} : \overline{u} : u_{mp} = 1.00 : 0.92 : 0.82$

Average velocity = $0.92 \times u_{rms}$

Most probable velocity = $0.82 \times u_{rms}$

**Q. What is a molecular collision?**

**Ans.** Molecular collision may be defined as a process in which a change in the direction of motion of the approaching molecules takes place.

**Q. What are elastic and inelastic collisions?**

**Ans.** Such collisions between molecules in which there is no net loss or gain of energy are referred as elastic collisions. But when the collisions between the molecules result in the loss or gian of energy, then such collisions are known as inelastic collisions.

**Q. Define mean free path and collision frequency.**

**Ans.** The average distance travelled by a molecule between two successive collisions is called mean free path.

The number of collisions made by a molecule of a gas per unit time per unit volume is known as collision frequency.

**Q. What is degree of freedom?**

**Ans.** The degree of freedom of a particle may be defined as the number of co-ordinates necessary to describe the position of a particle. In general, a molecule having N atoms, has 3N degrees of freedom.

**Q. Explain law of equipartition of energy.**

**Ans.** The law states that the total energy possessed by a molecule is equally distributed amongst its different degrees of freedom.

**Q. Explain specific and molar heat capacity.**

**Ans.** Specific heat capacity of a substance is defined as the quantity of heat required to raise the temperature of 1 g of that substance through 1°C or 1K.

The molar heat capacity is likewise the quantity of heat required to raise the temperature of 1 mole of substance by 1°Cor 1K.

**Q. What is the relation between $C_p$ and $C_v$?**

**Ans.** $C_p - C_v = R$

**Q. What are ideal and non-ideal gases?**

**Ans.** Gases which obey gas laws under all conditions of temperature and pressure are termed as ideal gases.

Gases which show deviations from ideal behaviour are called non-ideal or real gases.

**Q. Why gases show deviations from ideal behaviour?**

**Ans.** In the discussion of kinetic theory, it was assumed that the volume occupied by gas molecules is negligibly small as compared to the total volume of the gas and the molecules do not exert forces of attraction on each other. But in reality both these assumptions are wrong. All gas molecules have a definite volume and exert forces of attraction.

**Q. Define critical temperature and critical pressure.**

**Ans.** It is the temperature above which a gas cannot be liquefied and below which a continuous increase of pressure would result in the liquefaction of a gas.

The pressure required to liquefy the gas at the critical temperature is called critical pressure.

**Q. Explain law of corresponding states.**

**Ans.** This law states that when two or more substances have the same reduced temperature and pressure, they will have the same reduced volume. Substances under these conditions are said to be in the corresponding states.

**Q. How liquefaction of a gas be done?**

**Ans.** A gas can be liquefied by applying high pressure and low temperature. Compression of the gas brings the molecules closer and a decrease in temperature, reduces the kinetic energy of the molecules.

**Q. What principles are involved in the liquefaction process?**

**Ans.** The principles involved in the liquefaction are:

*(i)* A gas must be at or below its critical temperature. Lower the temperature below the critical value, easier would be the liquefaction.

*(ii)* The gas is cooled either by doing external work or by expanding against the internal molecular forces.

**Q. Write down some applications of liquefaction phenomenon.**

**Ans.** Liquefied gases find numerous applications in many fields. For example,

*(i)* It is possible to obtain high vacuum by using liquefied gases.

*(ii)* Liquid chlorine has almost replaced bleaching powder.

*(iii)* Liquid oxygen when mixed with powdered charcoal and detonated, can be employed for preparing explosives.

**Q. Define molar volume.**

**Ans.** The volume occupied by 1 mole of a gas at STP is called its molar volume. It is taken as 22.4 $dm^3$.

**Q. What are van-der Waals forces?**

**Ans.** These are attractive forces existing between atoms or molecules of all substances. These forces arise as a result of electrons in neighbouring atoms or molecules moving in sympathy with one another.

**Q. Define absolute zero.**

**Ans.** It is the lowest temperature theoretically possible; the zero of thermodynamic temperature. 0°K = 273.15°C = 459.67°F.

**Q. What does N.T.P. or S.T.P. signify?**

**Ans.** Normal (standard) temperature and pressure. A pressure of 101325 pascals and a temperature of 0°C; standard conditions under which volumes of gases are compared.

**Q. What are dipole-dipole interactions?**

**Ans.** Two equal point electric charges of opposite sign, separated by a small distance is called a dipole. In polar molecules like $NH_3$, $H_20$ HCl etc. the negative end of one molecule is attracted by a positive end of another molecule. These type of interactions are called dipole-dipole interactions.

**Q. What do you mean by effusion of gases?**

**Ans.** The passage of gases through small apertures under pressure is called effusion of gases. In diffusion, molecules of all gases move freely and tend to distribute themselves equally within the limits of the vessel enclosing the gas.

## 1.3. The Liquid State

**Q. How do liquids resemble with gases?**

**Ans.** The liquids resemble with gases in their lack of rigidity-neither of the two possess permanent resistance to a shearing stress.

**Q. What are additive and constitutive properties?**

**Ans.** The properties which are the sum of the corresponding properties of the individual components of a system are called additive properties. Mass and molecular weight are strictly addictive properties. The properties that depend primarily on the arrangement of atoms in the molecule and to some extent on their nature and number are known as constitutive properties. Surface tension, optical activity and viscosity are examples of constitutive properties.

**Q. Define vapour pressure.**

**Ans.** It is the pressure exerted by the vapours in equilibrium with the liquid at constant temperature.

**Q. What is the difference between boiling and evaporation?**

**Ans.** Boiling occurs at a definite temperature, while evaporation takes place at any temperature.

**Q. What is the effect of temperature on the vapour pressure?**

**Ans.** The vapour pressure of a liquid increases with rise in temperature.

**Q. Define boiling point of a liquid.**

**Ans.** It is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric (or external) pressure. When the external pressure is one atm, the term normal boiling point is used.

**Q. Define surface tension and give its units.**

**Ans.** Surface tension is a measure of contracting tendency of a liquid, and is defined as the force in newtons acting at right angles along the surface of a liquid one metre in length. It is expressed in $Nm^{-1}$ or dynes $cm^{-1}$ and is dented by $\gamma$ (gamma).

**Q. What is surface free energy ?**

**Ans.** It is the amount of work done to increase the surface area of a liquid by unity.

**Q. Why a falling drop of a liquid has spherical shape?**

**Ans.** Surface tension of liquids accounts for the spherical shape of drops of liquid. Due to surface tension, every liquid tend to minimize its surface area. Since a sphere has the smallest surface area for a given volume, hence a small drop of liquid would assume a spherical shape.

**Q. Why water rises in a capillary tube and mercury level falls in a capillary?**

**Ans.** The rise or fall of liquid levels in a container depends on the interactions between the liquid surface and the walls of the container. If the intermolecular forces between liquid molecules are weaker than the forces between the liquid and the solid surface, the liquid will rise and wet the solid surface. If the solid-liquid interactions are weaker than the intermolecular forces in the liquid, its level will fall and the liquid will not wet the solid surface.

**Q. How surface tension of a liquid be determined?**

**Ans.** There are many methods which can be employed for the measurement of surface tension. Two of the commonly used methods are:

(*i*) the capillary rise method, and

(*ii*) the drop weight method.

**Q. Define interfacial tension.**

**Ans.** When two immiscible or partially miscible liquids A and B are in contact, then the force operative at the surface of separation between the two liquids is called the interfacial tension and is denoted by $\gamma_{ab}$

**Q. What is the effect of temperature on surface tension?**

**Ans.** Surface tension decreases with increase of temperature and vanishes at the critical temperature.

**Q. Discuss the significance of parachor.**

**Ans.** Parachor may be defined as the molar volume of a liquid at a temperature where its surface tension is unity. It is an additive and constitutive property and can be used to draw conclusions about the structures of the compound.

$$[P] = \frac{M}{D}\gamma^{1/4} \qquad \text{..... 1.9}$$

**Q. Define viscosity.**

**Ans.** The resistance to flow exhibited by liquids and gases is known as viscosity. Because of this property some liquids flow slowly than others.

**Q. What is coefficient of viscosity? Give its units.**

**Ans.** The coefficient of viscosity, $\eta$ may be defined as the force per unit area required to maintain unit difference of velocity between two layers in the liquid unit distance apart. The unit of viscosity is dynes $cm^{-2}$ s and is known as poise. In SI units, it is expressed in $Nm^{-2}$ s or $kgm^{-1}s^{-1}$ which is equal to 1 pascal second.

$$1 \text{ kg m}^{-1} \text{ s}^{-1} = 1 \text{ Pas}$$

**Q. What is fluidity?**

**Ans.** The reciprocal of the coefficient of viscosity is called the fluidity and is denoted by $\phi$. It is a measure of ease with which a liquid can flow.

**Q. Define kinematic viscosity.**

**Ans.** The ratio of viscosity and density is known as kinematic viscosity.

**Q. How the viscosity of a liquid be measured?**

**Ans.** The viscosity of a liquid is measured with the help of apparatus known as viscometer.

**Q. What is the effect of temperature on the viscosity?**

**Ans.** The viscosity of a liquid decreases with rise in temperature. Due to rise in temperature, the intermolecular forces become weak and viscosity decreases.

**Q. Give some applications of viscosity measurements.**

**Ans.** Measurements of viscosity of solutions have been used in the determination of molar masses of polymers by using he following empirical relationship.

$$[\eta] = KM^a \qquad \text{..... 1.10}$$

here M' is the molar mass, 'K' and '*a*' are constants depending on the solvent, polymer and temperature.

**Q. What is the difference between relative and specific viscosity?**

**Ans.** If $\eta$ and $\eta_o$ are the coefficients of viscosity of the solution and the pure solvent at the same temperature, then the relative viscosity is defined as

$$\eta_r = \frac{\eta}{\eta_o} \qquad \text{..... 1.11}$$

The specific viscosity $\eta_{sp}$, is defined as

$$\eta_{sp} = \eta_r - 1 = \frac{\eta - \eta_o}{\eta_o} \qquad \text{..... 1.12}$$

**Q. Define rheochor. Give its significance.**

**Ans.** Rheochor may be defined as the molar volume of a liquid at a temperature where its viscosity is unity.

$$R = \frac{M}{D}\eta^{1/8} \qquad \text{..... 1.13}$$

Use of rheochor as an additive and constitutive property in elucidating the structure of compounds has met with little success.

**Q. Define dipole moment. Give its units.**

**Ans.** The degree of polarity of a molecule can be expressed in terms of dipole moment. It is the product of magnitude of charge and the distance between them. It is expressed as

$$\mu = q \times r \qquad \text{..... 1.14}$$

The unit of dipole moment is Debye.

$$1\ D = 10^{-18}\ \text{esu.cm}$$

**Q. What is the cause of dipole moment?**

**Ans.** The dipole moment arises due to the difference in electro-negativities of two atoms held together by a chemical bond.

**Q. What is electrical polarization?**

**Ans.** When a molecule is put under the influence of an electric field, the positive nuclei is attracted towards negative plate and electrons towards positive plate. Under these conditions, there will be an electrical distortion of the molecule to form an electric dipole. Such a distortion is called electrical polarization or distortion polarization of the molecule.

**Q. How the dipole moment of a substance be measured?**

**Ans.** Two important methods normally used to determine dipole moment are:

(*i*) The vapour temperature method, and
(*ii*) The refractometric method.

**Q. What are the applications of dipole moment measurements?**

**Ans.** The measurement of dipole moments gives an idea about the extent of polar character of a chemical bond. It also gives us information about the geometry and shapes of molecules.

## 1.4. The Solid State

**Q. Define solid state of matter.**

**Ans.** The physical state of matter in which the constituent molecules, atoms, or ions have no translatory motion although they vibrate about the fixed positions which they occupy in a crystal lattice.

**Q. What are the important characteristics of solids?**

**Ans.** The solids are characterized by their definite shape and volume and also their considerable mechanical strength and rigidity.

**Q. Why are solids rigid?**

**Ans.** The rigidity of solids is due to the absence of translatory motion of structural units (atoms, ions or molecules) of solids.

**Q. What is the difference between crystalline solids and amorphous solids?**

**Ans.** In crystalline solids, the structural units (atoms, ions etc.) are arranged in a definite pattern giving a definite geometrical configuration. They have sharp melting points. Amorphous solids are the substances which have no regular internal structure. They do not possess sharp melting points.

**Q. What are isotropic and anisotropic substances?**

**Ans.** Isotropic substances possess the same value of any property in all directions.

Anisotropic substances possess different value of a property in different directions.

**Q. Define crystal and crystal lattice.**

**Ans.** A crystal is defined as a homogeneous portion of a solid substance in which the atoms or ions are packed closely together in such a way that the total potential energy is at a minimum.

A crystal lattice or space lattice is defined as a highly ordered three dimensional structure formed by atoms, ions or molecules.

**Q. What is a Unit Cell?**

**Ans.** A unit cell is the smallest building unit of the crystal. A unit cell in three-dimensional lattice is characterized by definite lengths and angles between them.

**Q. What is the difference between primitive unit cell and multiple unit cell?**

**Ans.** The simplest unit cell having the lattice points at the corners is called a simple or primitive unit cell. The unit cell, when it contains more than one lattice point is called a non-primitive or multiple unit cell.

**Q. What are Bravais lattices?**

**Ans.** Bravais showed that there are 14 different unit cells to account for the lattice points at the corners of the unit cell as well as those at the centres and some of the faces. These 14 unit cells or space lattices are known as Bravais lattices.

**Q. Write down the names of various crystal systems.**

**Ans.** Cubic, tetragonal, orthorhombic, hexagonal, trigonal, monoclinic and triclinic.

**Q. Define crystallography.**

**Ans.** It is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances.

**Q. State law of constancy of interfacial angles.**

**Ans.** This law states that for a given substance the corresponding faces or planes forming the external surface of a crystal always intersect at a definite angle and that this angle remains constant no matter how the faces develop.

**Q. What is the law of rationality of indices?**

**Ans.** This law states that the ratio between the intercepts on the axes for the different faces of a crystal can always be expressed by rational numbers.

**Q. What is the function of goniometer?**

**Ans.** It is an instrument which is used for measuring interfacial angle.

**Q. Explain the law of symmetry.**

**Ans.** It states that all the crystals of the same substance possess the same elements of symmetry.

**Q. What do you mean by cleavage?**

**Ans.** The manner of breaking of a crystalline substance, so that more or less smooth surfaces are formed.

**Q. Why X-rays are used in the study of crystal structure?**

**Ans.** X-rays are electromagnetic radiations of short wave-length of the order of 0.1nm. This wavelength is comparable with the spacings of the atoms in the crystals.

**Q. What is the significance of Bragg's equation?**

**Ans.** The Bragg's equation is

$$2d \sin\theta = n\lambda \quad \ldots\ldots 1.14$$

This equation forms the basis of X-rays crystallography, and connects wavelength of X-rays, spacings between successive lattice points and the angle of maximum reflection.

**Q. Explain the term allotropy.**

**Ans.** It is the existence of a chemical substance in two or more forms differing in physical properties but giving rise to identical chemical compounds. The various forms are known as allotropic forms or allotropes.

## 1.5. Solutions and Colloids

**Q. What is a true solution?**

**Ans.** A true solution is defined as a homogeneous mixture of two or more substances that form a single phase.

**Q. Explain the terms solute and solvent.**

**Ans.** The constituents of a solution are generally referred to as the solute and the solvent. A solute is frequently a substance that dissolves and a solvent is one in which dissolution takes place. The solvent is generally present in large amount in comparison to the solute.

**Q. What is the difference between saturated and unsaturated solution?**

**Ans.** When a solution contains, at a given temperature as much solute as can be dissolved, the solution is said to be saturated. If the quantity of solute is less than this amount, it is known as unsaturated solution.

**Q. What is the difference between a dilute and concentrated solution?**

**Ans.** A dilute solution is one in which the quantity of solute is very small as compared to that of solvent. A concentrated solution contains relatively higher amount of solute.

**Q. What is a binary solution?**

**Ans.** A solution containing only two components is called a binary solution.

**Q. Define mass percent of a solution.**

**Ans.** The mass percent of component B in a solution is given by

$$\text{Mass percent of B} = \frac{W_B}{W_A + W_B} \times 100$$

Where $W_A$ and $W_B$ are the masses of A and B respectively.

**Q. Explain the terms molarity and formality.**

**Ans.** The molarity of a solution is defined as the no. of moles of solute per $dm^3$ of the solution at a given temperature. It is represented by M.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume in } dm^3 \text{ of the solution}}$$

Sometimes, the term formality is used for solutions of ionic substances. It is the number of formula weights dissolved per $dm^3$ of the solution at a given temperature. It is usually denoted by F.

**Q. What is the difference between normality and molality?**

**Ans.** The normality of a solution is defined as the number of gram equivalents of the solute dissolved per $dm^3$ of the solution at a given temperature. It is denoted by N.

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume in } dm^3 \text{ of the solution}}$$

Molality is defined as the number of moles of solute dissolved in one kg of the solvent. It is usually denoted by m.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in kg}}$$

**Q. What is mole fraction?**

**Ans.** The mole fraction of a component in a solution is given by the ratio of the number of moles of that component to the number of moles of all the components present in the solution.

$$X_A = \frac{n_A}{n_A + n_B} \qquad \text{..... 1.15}$$

**Q. State Henry's law.**

**Ans.** This law states that the solubility of a gas in a given volume of the liquid at constant temperature is directly proportional to the pressure of the gas.

**Q. What is Raoult's law?**

**Ans.** This law states that at a given temperature, the vapour pressure of any volatile component of a solution is equal to the vapour pressure of pure component multiplied by mole fraction of that component in a solution.

**Q. What are ideal and non-ideal solutions?**

**Ans.** Solutions which obey Raoult's law over the whole range of concentrations are called ideal solutions. Moreover, in ideal solutions, there is complete uniformity in cohesive forces. The solutions which do not obey Raoult's law are known as non-ideal or real solutions.

**Q. Why solutions show deviations from ideal behaviour?**

**Ans.** The deviations from ideal behaviour are due to the differences in the molecular structures of the two components which result in the difference in the intermolecular forces.

**Q. Explain the difference between concentration and activity.**

**Ans.** The concentration of a solution is defined as the number of moles of solute dissolved per unit volume of the solution or in a given amount of the solvent. The effective concentration of a solute in a solution is called its activity.

**Q. What are colligative proper-ties?**

**Ans.** Colligative properties are those properties which depend only on the number of particles of the solute in the solution and not any way on the nature of particles. For example, lowering of vapour pressure, evaluation in boiling points, depression in freezing points and osmotic pressure.

**Q. What do you mean by elevation of boiling points?**

**Ans.** The difference between the boiling point of a solution and a pure solvent is known as the elevation of boiling point.

**Q. Define ebullioscopic constant.**

**Ans.** It is defined as the elevation in boiling point of a solution of unit molality. It is also known as molal elevation constant.

**Q. Define freezing point of a liquid.**

**Ans.** It is the temperature at which the solid phase begins to separate out from the liquid. At this temperature, solid and liquid phases are in equilibrium and have equal pressures.

**Q. Define cryoscopic constant.**

**Ans.** It is defined as the depression in freezing point of a solution of unit molality. It is also known as molal depression constant.

**Q. Explain osmosis and osmotic pressure.**

**Ans.** When a solution is separated from a pure solvent by a suitable membrane, there is a spontaneous flow of solvent into the solution. This phenomenon is known as osmosis. By applying a certain pressure to the solution, osmosis can be prevented. The minimum pressure required to prevent osmosis is known as osmotic pressure.

**Q. What is a semi-permeable membrane ?**

**Ans.** A membrane which allows only solvent molecules to pass through it. For example, animal membranes, cellulose membrane etc.

**Q. What is the difference between osmosis and diffusion?**

**Ans.** In osmosis, there is a flow of solvent into the solution through a semi-permeable membrane. On the other hand, diffusion involves a flow of both the solute and solvent and no semi-permeable membrane is required.

**Q. What is the important use of colligative properties measurements?**

**Ans.** The colligative properties are used to determine molecular mass of non-volatile and non-electrolyte solute.

**Q. What is van't Hoff factor?**

**Ans.** It is defined as the ratio of the experimental value of a colligative property to the calculated value of that property.

$$i = \frac{\text{Experimental value of any colligative property}}{\text{Calculated value of that colligative property}}$$

**Q. What is a colloidal solution?**

**Ans.** A colloidal solution is defined as a heterogeneous system consisting of two phases

*(i)* a disperse phase which consists of colloidal particles, and

*(ii)* a dispersion medium in which the dispersion of particles takes place. The dispersion medium usually forms the large fraction of the colloids. Each of the two phases may be solid, liquid or a gas.

**Q. What is the difference between true solutions, colloids and coarse suspensions?**

**Ans.** The essential difference between the solutions, colloids and coarse suspensions lies in their relative particle size. In solutions, the particle size is less than 1nm and in suspensions, it is larger than 100nm. On the other hand, colloids have particle size in the range of 1 – 100 nm.

**Q. What are sols and hydrosols?**

**Ans.** Colloidal solutions are generally known as sols. If the dispersion medium is water, then they are called hydrosols.

**Q. What are lyophobic and lyophilic sols?**

**Ans.** Lyophobic sols are systems which have little attraction between the dispersed phase and dispersion medium. For example, sols of metals, sulphur and silver halides.

Lyophilic sols are systems in which the dispersed phase shows some definite affinity for the dispersion medium, e.g., gums, starch, etc.

**Q. How colloids differ from crystalloids?**

**Ans.** Colloids are the substances which diffuse slowly and pass through the animal membrane very slowly e.g., gelatin, starch. Crystalloids are the substances which diffuse rapidly and pass through the animal membrane easily e.g., NaCl, sugar.

**Q. How sol. of oxides of iron is prepared?**

**Ans.** It is prepared by adding a small quantity of iron chloride into a large volume of boiling water.

$$2FeCl_3 + 6H_2O \longrightarrow Fe_2O_3.3H_2O + 6HCl$$

**Q. How would you prepare $As_2S_3$ sol.?**

**Ans.** Arsenious sulphide sol is obtained by mixing solutions of arsenious oxide and hydrogen sulphide.

$$2As^{3+} + 3S^{2-} \longrightarrow As_2S_3$$

**Q. What is peptization?**

**Ans.** The process of dispersing a precipitate into a colloidal solution by adding small quantity of an electrolyte is called peptization. The electrolyte added is called a peptizing agent.

**Q. Define dialysis and ultra-filtration.**

**Ans.** The process of removing crystalloids or other impurities from a colloid by diffusion through a permeable membrane is known as dialysis.

Ultrafiltration is similar to the filtration of an ordinary precipitate except with the difference that the membrane used here is designed in such a way that it permits the passage of only electrolytes and medium and not of colloidal particles.

**Q. What is Tyndall effect?**

**Ans.** The scattering of light by particles of matter in the path of light, thus making a visible `beam' is known as Tyndall effect.

**Q. What is the nature of colloidal particles?**

**Ans.** Colloidal particles always carry some charge (positive or negative) otherwise the colloidal system would be unstable. This charge is due to the presence of acidic or basic group or due to the dissociation of surface molecules or due to preferential adsorption of ions.

**Q. Define electrophoresis or cataphoresis.**

**Ans.** The migration of colloidal particles under the influence of an electric field is known as electrophoresis or cataphoresis.

**Q. What is electro-osmosis?**

**Ans.** The movement of dispersion medium under the influence of electric field when the dispersed particles are prevented from moving is known as electro-osmosis.

**Q. Define coagulation.**

**Ans.** It is the process of breaking up of a colloidal solution resulting in the precipitation of the particles of the dispersed phase.

**Q. What is precipitation value?**

**Ans.** The minimum concentration of an electrolyte which is able to bring about the coagulation of a sol is called its flocculation or precipitation value. It is generally expressed in millimoles of electrolyte per $dm^3$ of the sol.

**Q. What is an emulsion and emulsifier?**

**Ans.** An emulsion is a dispersed system in which both the dispersed phase and dispersion medium are liquids. Milk is a naturally occurring emulsion. An emulsifier is a substance to reduce the interfacial tension between the two liquids forming the emulsion.

**Q. What are gels?**

**Ans.** Colloidal systems containing a liquid dispersed in a solid are called gels. Jelly is a common name for a gel. Some examples of gels are curd and table jelly.

**Q. What do you known about aerosols?**

**Ans.** An aerosol is a colloidal system composed of fine liquid or solid particles dispersed in air or gaseous phase. The gaseous medium is usually, but not always, air. Smokes and dusts consist of solid particles dispersed in a gaseous medium, whereas in fog, mist and cloud, the dispersed phase is liquid.

**Q. What is an azeotropic mixture?**

**Ans.** A mixture of two or more liquids which distils at a given constant temperature and has a constant composition, at a given pressure.

## 1.6. Chemical Thermodynamics and Thermochemistry

**Q. Define chemical thermodynamics. Give its significance.**

**Ans.** It is the study of general laws governing processes which involve heat changes and the conservation of energy. It can predict whether a given process will occur spontaneously or not under a given set of conditions.

**Q. Explain system and surroundings.**

**Ans.** A system is that part of the universe which is under thermodynamic study and the rest of the universe is called its surroundings. Both are separated by a real or an imaginary surface called boundary.

**Q. Discuss different types of systems.**

**Ans.** A system which can exchange both matter and energy with the surroundings is known as open system. A system which can exchange energy but not matter with the surroundings is called a closed system, while a system which can neither exchange matter nor energy with the surroundings is called an isolated system.

**Q. What are extensive and intensive properties?**

**Ans.** Extensive properties are those properties of a system whose magnitudes depend on the amount of matter present in the system. Mass, volume, internal energy and free energy are examples of extensive properties.

The properties whose magnitudes do not depend on the quantity of matter present in the system are called intensive properties. For example, surface tension, refractive index, temperature etc.

**Q. What are state functions?**

**Ans.** The fundamental properties of a system which completely define the state of a system are called state functions or state variables e.g., volume, temperature and pressure.

**Q. Define thermodynamic equilibrium and process.**

**Ans.** A system is said to be in a state of thermodynamic equilibrium if its state variables do not change with time and space.

A thermodynamic process is defined as the path or process by which a system changes from one state to another.

**Q. What is the difference between isothermal and adiabatic process?**

**Ans.** A process which takes place under constant temperature condition is known as isothermal process, while a process in which no heat is exchanged between the system and surroundings is called adiabatic process.

**Q. Define isochoric and isobaric process.**

**Ans.** In isochoric process, the volume of the system remains constant, while in isobaric process, the pressure of the system remains constant.

**Q. State exact and inexact differential.**

**Ans.** An exact differential is one which integrates to a finite difference. An inexact differential, on the other hand, is one which integrates to a total quantity depending upon the path of integration.

**Q. What is the difference between work and heat?**

**Ans.** Energy is transferred in the form of work, when there is no difference of temperature between system and its surroundings.

Energy is transferred in the form of heat, when there is a difference of temperature between system and its surroundings.

**Q. Define internal energy of a system.**

**Ans.** It is the energy possessed by a system due to translational, vibrational and rotational motions of the molecules along with the electronic energy.

**Q. What is the difference between reversible and irreversible process?**

**Ans.** A process is said to be reversible when the properties of the system at any instant remain uniform during the process. A process which does not satisfy the conditions of reversibility, it is called an irreversible process.

**Q. State first law of thermodynamics.**

**Ans.** It states that the total energy of a system and its surroundings remains constant.

**Q. What is enthalpy?**

**Ans.** The total heat content of a system is called its enthalpy.

**Q. What are sign conventions for $\Delta H$ ?**

**Ans.** $\Delta H$ is positive for endothermic reactions and negative for exothermic reactions.

**Q. Define heat capacity.**

**Ans.** The heat capacity of a system is defined as the amount of heat required to raise the temperature of the system by one degree.

**Q. What is thermochemistry?**

**Ans.** It is the branch of physical chemistry that deals with the heat changes accompanying various physical and chemical transformations.

**Q. Define heat of reaction.**

**Ans.** It is the amount of heat evolved or absorbed when molar quantities of the reactants shown by the balanced equation react completely at a given temperature.

**Q. What is the heat of formation?**

**Ans.** It is the enthalpy change ($\Delta H$) involved in the formation of 1 mole of a compound from its elements. If the elements are in their standard states, the heat of formation is called standard heat of formation or standard enthalpy of formation.

**Q. Define heat of combustion. Give its significance.**

**Ans.** Heat of combustion of a compound or element is the enthalpy change involved in the complete combustion of 1 mole of the substance. Heats of combustion are important from the industrial standpoint of view for calculating the calorific value of gaseous and liquid hydrocarbons. Moreover, heats of combustion of fats, proteins and carbohydrates are of great significance in nutritional studies.

**Q. Explain heat of neutralization.**

**Ans.** It is defined as the change in enthalpy when one gram equivalent of an acid is neutralized by one gram equivalent of a base. It has been observed that the heat of neutralization of any strong acid by a strong base is practically the same i.e., 57.32 kJ mol$^{-1}$. Because every neutralization reaction involves the combination of $H^+$ and $OH^-$ ions to form unionized water.

**Q. State Hess's law.**

**Ans.** This law states that the total enthalpy change for a reaction is the same whether the reaction takes place in a single step or in several steps.

**Q. What is a bomb calorimeter?**

**Ans.** The heat evolved or absorbed during a chemical reaction is measured with the help of an apparatus known as calorimeter. The bomb calorimeter is used for determining the heats of combustion of organic compounds.

**Q. Define bond dissociation energy and bond energy.**

**Ans.** The amount of energy required to break 1 mole of a particular bond in a given compound and separate the resulting gaseous atoms is known as the bond dissociation energy.

The average value of the bond dissociation energy of a molecule is known as the bond energy.

**Q. What is a spontaneous process?**

**Ans.** A process which takes place of its own without the external intervention of any kind is known as spontaneous process. For example, water flows from a higher level to the lower level.

**Q. State second law of thermodynamics.**

**Ans.** It is impossible for self acting machine to convey heat from a body at lower temperature to another at higher temperature without the expenditure of energy.

or

The entropy of the universe remains constant in a reversible process but it increases in an irreversible process.

**Q. What is thermodynamic temperature?**

**Ans.** The thermodynamic temperature is a basic physical quantity, which depends on the concept of temperature as a measure of thermal energy of random motion of the particles of a system in thermal equilibrium. Originally, thermodynamic temperature was defined in terms of the ice point and steam point of water using a gas thermometer. However, in 1954, this was replaced by a definition using only one fixed point, the triple point of water which was fixed as 273.16 Kelvins exactly. The magnitude of the unit of thermodynamic temperature, the Kelvin, is the same as the degree on the International practical Scale of Temperature.

**Q. Define entropy of a system.**

**Ans.** Entropy is a measure of disorder or randomness in a system. Mathematically,

$$dS = \frac{\delta q}{T} \qquad \text{..... 1.16}$$

**Q. Explain Helmholtz free energy and Gibbs free energy.**

**Ans.** Helmholtz free energy or work function is a measure of maximum work that can be obtained from the process. The maximum work includes both mechanical and non-mechanical work. Mathematically,

$$A = E - T\,S \qquad \text{..... 1.17}$$

Gibbs free energy is a measure of useful work that can be obtained from a reversible process taking place at constant pressure and temperature. Mathematically,

$$G = H - T\,S \qquad \text{..... 1.18}$$

**Q. Briefly discuss the significance of free energy.**

**Ans.** If $\Delta G^\circ$ is negative, the reaction is spontaneous. If $\Delta G^\circ$ is positive, the reaction is non-spontaneous and a zero value of $\Delta G^\circ$ indicates the reaction at equilibrium.

**Q. State third law of thermodynamics**

**Ans.** It states that entropy of all pure crystalline substances (solids) may be taken as zero at absolute zero of temperature.

## 1.7. Chemical Equilibrium and Phase Rule

**Q. What do you mean by chemical equilibrium?**

**Ans.** Chemical equilibrium represents a state of a system at which there is no apparent change in the observable properties (pressure, concentration, colour, density etc.) of a system under a given set of conditions.

**Q. What are reversible reactions?**

**Ans.** Reactions which proceed in both directions are known as reversible reactions.

**Q. What is the difference between homogeneous and heterogeneous equilibria?**

**Ans.** In homogeneous equilibria all the components occur in only one phase, while in heterogeneous equilibria, more than one phases exist.

**Q. Define law of mass action.**

**Ans.** This law states that at constant temperature, the rate of a chemical reaction is proportional to the active masses of the reacting substances.

**Q. What is an active mass?**

**Ans.** The effective concentration of a reactant is called its active mass or activity.

**Q. Define equilibrium constant.**

**Ans.** It is defined as the ratio of the product of the molar concentration of the products to that of the reactants. Let us consider the following reversible reaction

$$A + B \rightleftharpoons C + D$$

The equilibrium constant of the above reaction can be written as

$$K_c = \frac{[C]\,[D]}{[A]\,[B]} \qquad \text{..... 1.19}$$

**Q. Briefly describe the significance of equilibrium constant.**

**Ans.**

(*i*) It enables one to tell roughly, at a glance, the extent to which a reaction will proceed, before equilibrium is reached.

(*ii*) It enables one to calculate equilibrium concentration if the starting concentrations are known.

**Q. What is Le-Chatelier's Principle?**

**Ans.** According to this principle, "if a system at equilibrium is disturbed by changing the variables such as temperature, pressure or concentration, then the system will tend to adjust itself so as to minimize the effect of that change as far as possible."

**Q. State Phase Rule. Explain the various terms involved.**

**Ans.** The phase rule is an important generalization, dealing with heterogeneous equilibria. It predicts qualitatively the effect of temperature, pressure and concentration on poly-phase equilibria. This rule states that the number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) present in the system at equilibrium by the equation.

$$F = C - P + 2 \qquad \text{..... 1.20}$$

**Phase.** A phase is defined as a homogeneous, physically distinct and mechanically separable part of the system.

**Components.** The number of components of a system is the smallest number of independently variable constituents by means of which the composition of each phase can be expressed.

**Degrees of freedom.** The degree of freedom or variance of a system is defined as the smallest number of independent variables such as pressure, temperature and concentration that must be specified in order to define the system completely.

**Q. Define the terms univariant, bivariant and invariant.**

**Ans.** A system having one degree of freedom is called univariant. A bivariant system has two degrees of freedom and an invariant system is that which has no degree of freedom.

**Q. Calculate the number of phases, the number of components and the number of degrees of freedom of water system at its boiling point.**

**Ans.** $P = 2$ (liquid water, vapour), $C = 1$, $F = 1$

$(\therefore\ F = C - P + 2)$

**Q. What are phase diagrams?**

**Ans.** Phase diagrams are the graphs showing interdependence of variables. With the help of these diagrams, the coexistence of different phases in a multiphase system can be studied.

**Q. What is the maximum value of degree of freedom for a one component system?**

**Ans.** $F = C - P + 2 = 1 - P + 2 = 3 - P = 3 - 1 = 2$

**Q. Define triple point.**

**Ans.** Triple point is defined as a point in the phase diagram where three phases coexist in equilibrium.

**Q. Define eutectic mixture and eutectic point.**

**Ans.** A solid solution of two or more substances, having the lowest freezing point of all the possible mixtures of the components is known as eutectic mixture. The minimum freezing point attainable, corresponding to the eutectic mixture, is termed the eutectic point.

**Q. What are congruent and incongruent melting compounds?**

**Ans.** The compounds which completely melt at the constant temperature and the liquids so formed has the same composition as the melting compounds are called congruent melting compounds. While the compounds in which the composition of both, melt and new solid forms, differ from that of the original solid compounds are called incongruent melting compounds.

**Q. State Nerst Distribution Law.**

**Ans.** According to this law, a dissolved substance distributes itself between two immiscible solvents in contact with each other in such a way that at equilibrium, the ratio of the concentrations of the substance in two layers is constant at any given temperature.

$$K_D = \frac{C_A}{C_B} \qquad \text{.....}\ 1.21$$

Where KD is the distribution constant or partition coefficient and CA and CB are the concentrations of the substance in two media.

**Q. What conditions are necessary for the validity of distribution law?**

**Ans.** *(i)* The molecular state of the solute should be same in both the solvents.

*(ii)* The solution should be dilute.

*(iii)* The two solvents should be immiscible or slightly miscible with each other.

(iv) Temperature of the system should remain constant.

**Q. Give some applications of distribution law.**

**Ans.** *(i)* From the knowledge of partition coefficient, the solubility of a solute can be determined.

*(ii)* We can study complex formation of various substances. e.g.,
$I^- + I_2 \longrightarrow I_3^-$

*(iii)* This law also finds applications in solvent extraction.

*(iv)* The molecular state of a solute in various solvents can be ascertained.

## 1.8. Chemical Kinetics and Photochemistry

**Q. Define chemical kinetics.**

**Ans.** Chemical kinetics deals with the study of rates of chemical reactions and the mechanisms by which they occur.

**Q. What do you mean by rate of a reaction?**

**Ans.** Rate of a chemical reaction is defined as the change in the concentration of reactants per unit time.

**Q. Define rate law.**

**Ans.** It states that rate of a chemical reaction is proportional to the concentration of the reactants taking part in a chemical reaction.

**Q. What factors affect the rate of a reaction?**

**Ans.** Temperature, catalyst, pressure, concentration, light, pH etc.

**Q. Explain rate constant or velocity constant.**

**Ans.** The rate constant may be defined as the rate of reaction when molar concentrations of reactants are unity. Its value is specific for a particular reaction at a given temperature.

**Q. Define order and molecularity of a reaction.**

**Ans.** The order of a reaction may be defined as the number of atoms, ions or molecules whose concentration change during a chemical reaction.

The molecularity of a reaction is defined as the number of atoms, ions or molecules participating in the reaction as given by the stoichiometric equation.

**Q. What is zero order reaction ?**

**Ans.** A reaction is said to be zero order if the rate of reaction is independent of reactant concentrations.

**Q. Define first order and second order reaction.**

**Ans.** In a first order reaction, the rate of a reaction is proportional to the concentration of only one reactant and is independent of others, if present. When the rate of a reaction is directly proportional to the product of the concentrations raised to the power unity, of two different reactants, the reaction is said to be second order.

**Q. What are opposing and consecutive reactions?**

**Ans.** Reactions exhibiting the tendency to reverse themselves are called opposing or reversible reactions e.g.

$$2HI \rightleftharpoons H_2 + I_2$$

Reactions which take place in more than one stages are called successive step or consecutive reactions.

**Q. What is the significance of half-life period in kinetic studies?**

**Ans.** Half-life period is the time in which the concentration of a reactant is reduced to one half of its initial value. The half-life period for first order reaction is independent of initial concentration. For a second order reaction, it is inversely proportional to the first power of the initial concentrations. In general.

$$t_{1/2} \propto \frac{1}{a^{n-1}} \qquad \text{..... 1.22}$$

Where n is the order of a reaction.

**Q. Define activated complex and activation energy.**

**Ans.** An activated complex is an unstable arrangement of atoms which is very short lived. Activation energy is defined as the minimum energy which the molecules must absorb before the reaction can take place.

**Q. Define photochemistry.**

**Ans.** It is a branch of physical chemistry which is concerned with the characteristics of chemical reactions resulting from the exposure of a system to radiation (uv-visible radiation).

**Q. How do photochemical reactions differ from chemical reactions?**

**Ans.** Chemical reactions which are initiated by exposure to light are called photochemical reactions. They are independent of temperature, while ordinary reactions depend on the temperature.

**Q. What is Grotthus-Draper law?**

**Ans.** This law states that only those radiations which are absorbed by the reacting systems are effective in producing chemical change.

**Q. State Einstein Law of photochemical equivalence.**

**Ans.** This law states that any molecule or atom activated by light absorbs only one quantum of light causing the reaction.

**Q. What is quantum yield or efficiency?**

**Ans.** It is defined as the number of molecules of reactants consumed or product formed per quantum of light absorbed, i.e.,

$$\phi = \frac{\text{Number of molecules formed or decomposed in a given time}}{\text{Number of quanta absorbed in the same time}}$$

**Q. What is chemiluminescence?**

**Ans.** It is defined as the emission of light by a system at ordinary temperature as a result of chemical reactions. In a sense it may be regarded as the reverse of a photochemical reaction.

**Q. How do fluorescence differ from phosphorescence?**

**Ans.** An excited atom or molecule formed in the primary process may emit the radiation of either the same or of different frequency. The emission is either fluorescence or phosphorescence. In fluorescence the emitted radiation ceases immediately when the exciting source is removed, but in phospho-rescence it may persist for longer periods.

**Q. What is a phosphor?**

**Ans.** A substance which is capable of luminescence, i.e., storing energy and later releasing it in the form of light.

## 1.9. Electrochemistry

**Q. What is the subject of electrochemistry?**

**Ans.** Electrochemistry is the branch of physical chemistry which deals with the study of all physical and chemical changes which are brought about by electrical energy and the changes which proceed with the generation of electrical energy.

**Q. What are conductors and insulators?**

**Ans.** The substances which allow the passage of electric current through them are called conductors, e.g. metals and molten salts. Those substances which do not conduct electric current are known as insulators, e.g. wood, rubber etc.

**Q. What is the difference between metallic conductors and electrolytic conductors?**

**Ans.** In metallic conductors, the conduction of electric current is due to the movement of free electrons without producing chemical changes. While in electrolytic conductors, the flow of current is due to the migration of charged particles called ions.

**Q. Define electrolysis.**

**Ans.** Electrolysis is a phenomenon in which chemical changes take place at the electrodes due to the passage of electric current.

**Q. What is the difference between cathode and anode?**

**Ans.** The electrode connected to the positive terminal of the battery is called anode, while the electrode connected to the negative terminal of the battery is known as cathode.

**Q. State Faraday's laws of electrolysis.**

**Ans.** The first law states that the amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

The second law states that if the same quantity of electricity is passed through different electrolytes, the amounts of different substances deposited or dissolved are proportional to their chemical equivalent masses.

**Q. Define electrochemical equivalent of a substance.**

**Ans.** It is the mass of a substance deposited by the passage of one ampere current for 1 second.

**Q. State Ohm's law.**

**Ans.** According to Ohm's law, the strength of an electric current flowing through a conductor is directly proportional to the potential difference applied across the conductor and is inversely proportional to the resistance. Mathematically.

$$I = \frac{V}{R} \qquad \text{..... 1.23}$$

**Q. What are the units of current, potential difference, resistance and charge?**

**Ans.** The unit of current is ampere. It is defined as the invariable current of such strength that on passing through an aqueous solution of silver nitrate will deposit 0.001118 g of silver in 1 second.

The unit of resistance is ohm. It is the resistance at 0°C of a column of mercury of uniform cross section, 106.3 cm long, and containing 14.4521 g of mercury.

The unit of potential difference is volt. It is defined as the potential difference required to send a current of one ampere through a resistance of 1 ohm.

The unit of charge or quantity of electricity is coulomb. It is the quantity of electricity passing through a conductor, when a current of one ampere flows in one second.

**Q. Define joule and watt.**

**Ans.** Joule is the electrical unit of energy, and is defined as the amount of work performed by a current of 1 ampere flowing for 1 second under a potential drop of 1 volt.

Watt is the unit of electrical power and is equal to the work done at the rate of 1 joule per second.

**Q. Define specific conductance. Give its units.**

**Ans.** Specific conductance is defined as the conductance of a metre cube of the solution. The units of specific conductance are ohm$^{-1}$ m$^{-1}$ or Sm$^{-1}$.

**Q. What is the difference between molar and equivalent conductance?**

**Ans.** The molar conductance is defined as the conductance of a volume of solution containing one mole of the solute, when placed between parallel electrodes 1 m apart, and large enough to contain between them all of the solution.

The equivalent conductance of an electrolyte is defined as the conductance of a volume of solution containing one gram equivalent of dissolved substance, when placed between two parallel electrodes 1 m apart and large enough to contain between them all of the solution.

**Q. Define cell constant. How is it determined?**

**Ans.** Cell constant is defined as the ratio of the specific conductance to the observed conductance. It is determined by using a solution of potassium chloride having known concentration.

**Q. State Kohlrausch's law.**

**Ans.** This law states that at infinite dilution, where ionization of all electrolytes is complete, each ion migrates independently of its co-ion, and contributes a definite share to the total equivalent conductance of an electrolyte.

**Q. Define degree of ionization. How is it determined?**

**Ans.** The degree of ionization or dissociation of an electrolyte is defined as the fraction of the total number of molecules of solute present in the solution as ions. It is usually determined by measuring the equivalent conductance of the solution of an electrolyte at any given dilution.

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \qquad \text{..... 1.24}$$

Where $\Lambda_0$ is the equivalent conductance at infinite dilution.

**Q. What is an ionic mobility?**

**Ans.** The velocity of an ion under a potential gradient of 1 volt per metre is known as the ionic mobility.

**Q. What is the difference between strong and weak electrolytes?**

**Ans.** Substances whose aqueous solutions are good conductors of electricity are known as strong electrolytes e.g. solutions of acids, bases and salts. On the other hand, there are many substances whose aqueous solutions are poor conductors of electricity. These are called weak electrolytes. These include many organic acids and bases.

**Q. State Ostwald's dilution law.**

**Ans.** Ostwald's dilution law is defined as

$$K_a = \frac{\alpha_2}{(1-\alpha)V} \qquad \text{..... 1.25}$$

It represents the variation of degree of dissociation of weak electrolyte with dilution. It states that the degree of dissociation for weak electrolytes is directly proportional to the square root of dilution.

**Q. Define transport number of an ion.**

**Ans.** The transport number or transference number of an ion represents the fraction of the total current carried by that ion. The sum of the transport numbers of cation and anion is unity.

**Q. What is an electrochemical cell?**

**Ans.** It is a device for the conversion of electrical energy into chemical energy and vice virsa. It consists of two electrodes dipping into an ionic solution and connected by an external metallic conductor.

**Q. Explain the difference between a galvanic cell and an electrolytic cell.**

**Ans.** A galvanic cell is a device where the chemical energy is converted into electrical energy, such as a dry cell or lead storage battery. In an electrolytic cell, the electrical energy from an external source is used to bring about a physical or a chemical change. Charging of a lead storage battery or electrolytic purification of metals are examples where electrical energy brings about chemical changes.

**Q. Define electrode potential.**

**Ans.** The potential difference that exists across the metal-solution interface is known as electrode potential. If the ions in the solution are at unit activity, the electrode potential is termed as the standard electrode potential.

**Q. What is EMF?**

**Ans.** It is an abbreviation for electromotive force, and is defined as the difference of potential between the electrodes which causes the current to flow from one electrode to the other.

**Q. What is the relationship between free energy and EMF of a cell?**

**Ans.** $-\Delta G = nFE$ ..... 1.26

**Q. What is the physical significance of pH value?**

**Ans.** pH value is defined as

$$pH = -\log [H^+] \qquad \text{..... 1.27}$$

It is a series of numbers which expresses the degree of acidity or alkalinity of a solution, as contrasted with the total quantity of acid or base in some material.

**Q. Write the names of various methods used for measuring pH value.**

**Ans.** *(i)* Taste *(ii)* Litmus paper *(iii)* Hydrion paper
*(iv)* Indicators *(v)* pH meter

Potentiometric method (pH meter) is the most accurate method.

**Q. What is the relation between pH and pOH values?**

**Ans.** pH + pOH = 14

**Q. What is the importance of pH measurements?**

**Ans.** It has got a great importance in biochemical reactions such as digestion of food, working of enzymes etc. Large number of qualitative and quantitative analysis are carried out at definite pH values. pH has got a great importance in agriculture. Soil is often tested to determine whether acidic or basic fertilizers are required for a particular crop. Moreover, food preservation also needs definite pH values.

**Q. What is a buffer solution?**

**Ans.** A buffer solution is an aqueous system that tends to resist changes in its pH value. It consists of a weak acid and its conjugate base or a weak base and its conjugate acid. For example, acetic acid and sodium acetate, ammonium hydroxide and ammonium chloride etc.

**Q. Define buffer capacity.**

**Ans.** $$\text{Buffer capacity} = \frac{\text{No. of equivalents of acid/base added per dm}^3}{\text{Unit change in pH value}}$$

**Q. What are three main buffer systems in living materials?**

**Ans.** The three main buffer systems in living materials are protein, bicarbonate and phosphate.

## 1.10. Nuclear Chemistry

**Q. What is nuclear chemistry?**

**Ans.** Nuclear chemistry is that branch of chemistry which deals with the structure, composition and properties of a nucleus.

**Q. Explain the term nuclide.**

**Ans.** Any species of atoms with a definite number of protons and neutrons is called a nuclide e.g. $^4_2He$, $^{14}_7N$ etc.

**Q. What is the difference between isotopes, isobars and isotones.**

**Ans.** Nuclides with the same number of protons are called isotopes.

For example, $^1_1H$, $^2_1H$ and $^3_1H$ are isotopes of hydrogen. Nuclides with the same mass number are called isobars.

For example, Isobar of A = 3 $^3_1H$, $^3_2He$.

While nuclides with the same number of neutrons are called isotones. For example, $^3_1H$ and $^4_2He$.

**Q. What are nuclear isomers ?**

**Ans.** Nuclides having the same atomic number and mass number but differing in their energy contents or radioactive properties are called nuclear isomers.

**Q. Define mass defect and discuss the significance of nuclear binding energy.**

**Ans.** Mass defect is the difference between the mass of an atom and the sum of the masses of its protons, neutrons and electrons. Nuclear binding energy is the energy released when a nucleus is formed from its constituent protons and neutrons. The binding energy reflects the stability of a nucleus. The larger the binding energy, the more stable is the nucleus.

**Q. How are the binding energies usually expressed?**

**Ans.** Binding energies are usually expressed in units of electron volts (eV) or million electron volts (MeV).

**Q. What are magic numbers?**

**Ans.** It has been observed that a nuclide is more stable if its neutron and proton numbers are 2, 8 20, 28, 50, 82 or 126. These numbers are called magic numbers.

**Q. Define radioactivity, and radioactive substance.**

**Ans.** Radioactivity is defined as the spontaneous emission of radiation by an element. The element which exhibits radioactivity is said to be radioactive.

**Q. Who discovered the phenomenon of radioactivity.**

**Ans.** The phenomenon of radioactivity was discovered by H. Becquerel in 1895.

**Q. What do you know about Marie Curie?**

**Ans.** Marie Curie was a polish pupil of H. Becquerel. She proposed the name of radioactivity. She became an illustrious scientist and got two Nobel Prizes.

**Q. What are alpha, beta and gamma rays?**

**Ans.** Alpha rays are positively charged particles, each carries two units of positive charge. Beta rays are negatively charged particles. These are actually fast moving electrons. Gamma rays are not charged particles. These are electromagnetic radiations analogous to X-rays.

**Q. Which rays have higher penetrating power?**

**Ans.** Gamma rays have very high penetrating power due to very short wavelength. It is about 10 to 100 times more than beta-rays.

**Q. What are the units of radioactivity?**

**Ans.** The standard unit of radioactivity is Curie, which is defined as the amount of any radioactive material which gives $3.70 \times 10^{10}$ disintegrations per second. One gram of radium — 226 undergoes $3.70 \times 10^{10}$ disintegrations per second and is also equal to one Curie.

The SI unit of radioactivity is Becquerel, which is defined as the activity due to one disintegration per second.

$$1 \text{ Ci} = 3.70 \times 10^{10} \text{ Bq}$$

**Q. State radioactive law.**

**Ans.** This law states that the rate of decay at any instant of time is proportional to the number of radioactive atoms present. Mathematically,

$$-\frac{dN}{dt} = \lambda N \qquad \text{..... 1.28}$$

Where $\lambda$ is decay constant.

**Q. Briefly discuss the significance of half-life.**

**Ans.** Half-life of a radioactive element is defined as the time in which the radioactive atoms are reduced to half of their initial atoms. Mathematically,

$$t_{1/2} = \frac{0.693}{\lambda} \qquad \text{..... 1.29}$$

Half-life period is a useful property for the identification of various radioactive species.

**Q. Define average life. Give its relation with half-life.**

**Ans.** The average life of a radioactive element is equal to the sum of all possible life times divided by the total number of atoms. The reciprocal of the decay constant gives the average life of a radioactive element.

$$\text{Average life} = 1.44\, t_{1/2} \qquad \text{..... 1.30}$$

**Q. State Group Displacement law.**

**Ans.** This law states that whenever a parent nucleus emits an alpha particle, its atomic number is decreased by two units and the new element is shifted two positions to the left in the periodic table. On the other hand, when the parent nucleus emits a beta particle, the atomic number is increased by one unit and hence the product is shifted one place to the right in the periodic table.

**Q. Give some examples of radioactive elements.**

**Ans.** $^{215}_{84}\text{Po}$, $^{211}_{82}\text{Pb}$, $^{211}_{83}\text{Bi}$, $^{211}_{84}\text{Po}$, $^{215}_{92}\text{U}$, $^{235}_{92}\text{U}$

**Q. What do you mean by Transmutation of an element?**

**Ans.** The conversion of one element into another is called Transmutation of an element. For example,

$$^{30}_{15}P \longrightarrow ^{30}_{14}Si + \beta+$$

**Q. Define a nuclear reaction.**

**Ans.** A nuclear reaction is a process in which some change in the character of a nucleus takes place either spontaneously or as a result of bombardment by a particle. For example,

$$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{8}_{4}Be + \gamma$$

**Q. Explain nuclear fission and nuclear fusion.**

**Ans.** Nuclear fission is a process in which a heavy nucleus is broken into two intermediate nuclei with the release of energy. For example,

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3^{1}_{0}n + \text{energy}$$

Nuclear fusion may be considered as the reverse of fission. It may be defined as the process of combining two lighter nuclei to form a heavier nucleus with the release of energy. For example

$$^{2}_{1}H + ^{3}_{2}He \longrightarrow ^{4}_{2}He + ^{1}_{1}H + 18.4\text{ MeV}$$

**Q. Give some medical uses of radioisotopes.**

Ans. *(i)* Sodium-24 is used to locate obstructions in the circulatory system.

*(i)* Iodine-131 concentrates in the thyroid gland, the liver and certain parts of brain, and is used to monitor goiter and other thyroid problems.

*(ii)* Thallium-201 tends to concentrate in the healthy heart muscles, while technetium-99 concentrates in the abnormal heart tissue.

**Q. What is a nuclear reactor?**

**Ans.** Nuclear reactor is a device to obtain the nuclear energy in a controlled way to be used for peaceful purposes. It is also known as atomic pile.

**Q. What are the components of a nuclear reactor?**

**Ans.** A typical nuclear reactor consists of the following major compounds.

*(i)* Fuel rods
*(ii)* Moderator
*(iii)* Coolant
*(iv)* Control reds
*(v)* Shielding

**Q. What is nuclear energy?**

**Ans.** It is the energy released during a nuclear reaction as a result of the conversion of mass into energy. Nuclear energy is released in nuclear reactors and nuclear weapons. It is also known s atomic energy.

**Q. What is a nuclear fuel?**

**Ans.** A substance which undergoes nuclear fission or nuclear fusion in a nuclear reactor, a nuclear weapon, or a star, e.g., U – 235 and Pu – 239.

**Q. What are nuclear weapons?**

**Ans.** Weapons in which the explosive power is derived from nuclear fission or a combination of nuclear fission and nuclear fusion, e.g., atomic bomb and hydrogen bomb.

**Q. What do you know about atomic bomb?**

**Ans.** The atomic bomb or fission bomb is a nuclear weapon which works on the principle of nuclear fission. It consists essentially of two or more masses of a suitable fissile material (e.g. U – 235 and Pu – 239) each of which is less than the critical mass. When the bomb is detonated, the subcritical masses are brought rapidly together to form a super critical assembly, so that a single fission at the point of contact sets off an uncontrolled chain reaction. The resulting release of energy produces a devastating explosion the effect of which is comparable to the explosions of tens of kilotons of T.N.T.

**Q. Briefly describe the working of H-bomb.**

**Ans.** The fusion bomb, thermonuclear bomb or H-bomb consists of a fission bomb surrounded by a layer of hydrogenous material (lithium deuteride). At the temperature resulting from explosion of the fission bomb, fusion of hydrogen nuclei to form helium nuclei takes place with the evolution of even greater quantities of energy. The explosive effect of fusion bomb is comparable to the explosion of tens of megatons of T.N.T.

**Q. What is carbon dating?**

**Ans.** It is a scientific method of dating and based on the fact that a known amount of carbon is present in all living creatures, in particular C – 14 (a radioactive isotope of carbon). When a creature dies, the C – 14 in its body decays at a fixed rate. This makes it possible to calculate the age of human skeleton or a piece of wood, from the amount of carbon left in it.

# *Part Two*

# ORGANIC CHEMISTRY

## 2.1. Introduction to Organic Chemistry

**Q. What do you know about the origin of the term "organic"?**

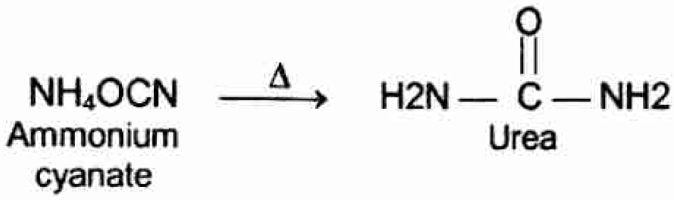
**Ans.** Around 1800, chemical substances were divided into two groups. The substances derived from plants and animals (organic or living sources), were called *organic substances*. Amongst these were table sugar from sugarcane and urea from urine of mammals. The substances obtained from nonliving sources such as rocks and minerals were grouped as *inorganic substances*. Sulphur, salt (NaCl) and marble (CaCO3) belonged to this type.

**Q. What is vital force theory?**

**Ans.** According to this theory it was widely believed that plants and animals contain a mysterious life principle or vital force. It was under the influence of this vital force that organic substances were formed. Thus it was considered impossible to prepare them by ordinary laboratory methods.

**Q. What do you know about Friedrich Wohler?**

**Ans.** Friedrich Wohler was a German chemist who discarded the vital force theory. He accomplished the preparation of urea by simply heating ammonium cyanate, a purely inorganic salt, in the laboratory.



$$NH_4OCN \xrightarrow{\Delta} H2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH2$$

**Q. Define organic chemistry.**

**Ans.** Organic chemistry is the branch of chemistry devoted to the study of compounds of carbons.

However, the oxides of carbon (CO, $CO_2$), carbonates ($CO_3^{2-}$), bicarbonates (HCO3–) and cyanides (CN–) etc. are exceptions to this general definition. These carbon containing compounds do not contain a functional group in their molecules. These are studied under inorganic chemistry.

Hydrocarbons are organic compounds in which carbon atoms are joined to H-atoms by covalent bonds. All other compounds could be regarded as derivatives of hydrocarbons. Thus another definition of organic chemistry could be:

*a study of hydrocarbons and their derivatives*

This appears to be a more appropriate definition as the study of oxides of carbon, carbonates or bicarbonates is kept out of its preview.

**Q. What is the importance of organic chemistry?**

**Ans.** A large number of organic materials, both natural and synthetic, are essential to our well being and living standard. The food we take, the clothes we wear, the paper in our books, the medicines we use when we are sick, are all organic in nature. The modern synthetic organic products are: gasoline, plastics, surface coatings, vitamins, medicinal drugs, dyes, artificial flavourings, refrigerants, insecticides, preservatives and artificial sweetners. The human body itself is made of a variety of "organics" and the very life process is supported by numerous enzymes-catalyzed reactions that occur in our body.

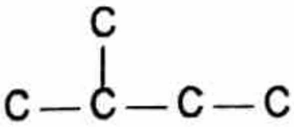
**Q. Why carbon forms a large number of compounds?**

**Ans.** The number of organic compounds known today is about four million. Thousands of new ones are being synthesized and described daily. The existence of such a large number of compounds of carbon is made possible by the unique bonding characteristics of the element. The three exceptional properties of carbon atom are:

**1. Strong carbon-carbon bonds.**

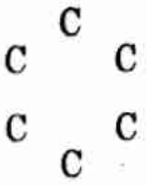
C — C — C — C

Open chain



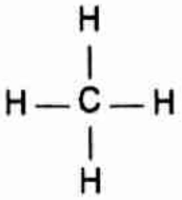
$C-\overset{\overset{C}{|}}{C}-C-C$

Open chain with branch

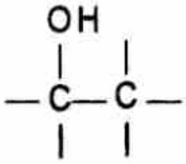


Ring

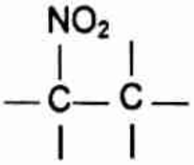
**2. Covalent bonds with other elements.**



$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$

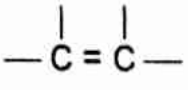


$-\overset{\overset{OH}{|}}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$



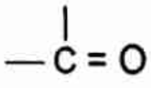
$-\overset{\overset{NO_2}{|}}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$

**3. Multiple bonds**



$-\overset{|}{C}=\overset{|}{C}-$

$-C\equiv C-$



$-\overset{|}{C}=O$

$-C\equiv N$

It is evident from the above discussion that countless molecular structures containing carbon atoms are possible. This accounts for the vast number and variety of the organic molecules that exist.

**Q. Write down some marked differences between organic and inorganic compounds.**

**Ans.** There are some distinct differences between the composition, molecular structure and properties of organic and inorganic compounds.

| | Organic Compounds | Inorganic Compounds |
|---|---|---|
| 1. | Made of carbon and a few other elements, chiefly H, O, N and halogens. | Made of two or more elements of the periodic table. |
| 2. | Carbon atoms join with each other and some other atoms by covalent bonds to form complex structures. | Form simple ionic molecules. |
| 3. | Show isomerism whereby the same molecular formula represents two or more different compounds. | Do not show isomerism. |
| 4. | Gases, liquids or solids. | Generally solids. |
| 5. | Insoluble in water, soluble in organic solvents. | Soluble in water, insoluble in organic solvents. |
| 6. | Low melting points. | High melting points. |
| 7. | Reactions are slow and do not proceed to completion. | Reactions are fast and proceed to equilibrium. |

**Q. Define atomic weight, molecular weight and formula weight.**

**Ans. Atomic Weight**

The mass of the atom of an element relative to that of carbon as 12, is called the relative atomic mass or atomic weight. On the atomic mass scale, H = 1, C = 12, O = 16 and so on.

**Molecular Weight**

The mass of the molecule of a compound relative to the mass of carbon atom as 12, is called its relative molecular mass or molecular weight.

The terms atomic weight and molecular weight are still widely used although technically relative atomic mass and relative molecular mass are the correct ones and are now recommended by SI.

**Formula Weight**

The term formula weight is interchangeably used with molecular weight. The sum of the atomic weights of the atoms in a chemical formula, is referred to as the formula weight. Thus the formula weight of methane is 16.

**Q. How are the molecular weights of organic compounds determined?**

**Ans.** There are a number of physical and chemical methods available for the determination of molecular weights of organic compounds. The commonly used methods are:

*(i)* Victor Meyer's method.

*(ii)* The gas syringe method.

(*iii*) Silver salt method for acids.

(*iv*) Platinichloride method for bases.

**Q. What is the most common modern method for determination of molecular masses?**

**Ans.** The mass spectrographic method is the most common method for determination of molecular masses.

**Q. Define empirical formula, molecular formula and structural formula.**

**Ans. Empirical Formula**

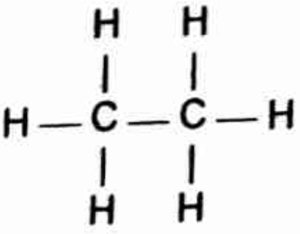
The empirical formula of a compound is its simplest formula that represents the smallest ratio between the atoms of different elements present in the molecule. For example, the smallest ratio between the atoms of carbon, hydrogen and oxygen in glucose, $C_6H_{12}O_6$ is 1 : 2 : 1. Thus the empirical formula of glucose is $CH_2O$.

**Molecular Formula**

The molecular formula of a compound is a multiple of the empirical formula showing the actual number of atoms present in the compound. For example, the molecular formula of benzene, $C_6H_5$, is six times its empirical formula, CH.

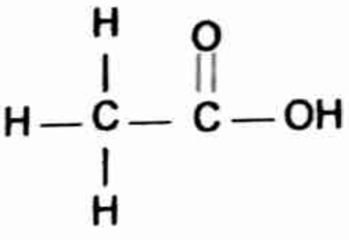
**Structural Formula**

The structural formula of a compound shows the exact picture as to how the various atoms are bonded to each other in the molecule. For example, the structural formulas of ethane and acetic acid are:



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$$

Ethane



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$$

Acetic acid

**Q. What is the relation between molecular formula and empirical formula?**

**Ans.** We know that the molecular formula is a multiple (n) of the empirical formula:

$$\text{Molecular formula} = n \times \text{Empirical formula}$$

It also follows that:

$$\text{Molecular weight} = n \times \text{Emp. formula weight}$$

$$\text{or} \quad n = \frac{\text{Molecular wieght}}{\text{Emp. formula weight}}$$

Knowing the molecular weight and empirical formula weight (calculated from atomic weights), the value of n can be found.

**Q. How the structural formula of an organic compound can be determined?**

**Ans. 1. Traditional Analytical Method**

It consists of three steps:

*(a)* **Identification of Functional Groups.** The various functional groups such as — OH, — CHO, — COOH, — $NH_2$ etc., are first identified by their specific chemical tests.

*(b)* **Degradation into Simpler Molecules.** Large organic molecules are broken down to simpler ones by oxidation, reduction, hydrolysis etc. Each fragment is identified by the usual chemical tests. The probable molecular model is then constructed by working back through the various stages of degradation.

*(c)* **Confirmation by Synthesis.** The compound under investigation is now synthesized from simple molecules of know structure. If the synthetic compound has the same melting point as the original sample, the structure of the latter stand confirmed.

**2. Spectroscopic Methods**

In recent years, the spectroscopic methods have almost superseded the traditional methods. The chief advantages of these newer methods are their remarkable precision and sensitivity, and the extremely small quantity of the material required. The three important methods that are commonly used in modern practice are:

*(i)* Infrared spectroscopy

*(ii)* Ultraviolet and visible spectroscopy.

*(iii)* Nuclear magnetic resonance (NMR) spectroscopy.

**Q. What are subatomic particles?**

**Ans.** An atom is composed of electrons, protons and neutrons. These particles are known as sub-atomic particles. They are defined by their relative mass and charge.

| | **Relative mass** | **Charge** |
|---|---|---|
| Proton (P) | 1 | + 1 |
| Electron ( $\bar{e}$ ) | negligible | – 1 |
| Neutron (n) | 1 | 0 |

**Q. What is nucleus?**

**Ans.** A nucleus is the central part of an atom surrounded by electrons. It bears a positive charge which is balanced by electrons around it. It contains protons and neutrons. Each of these particles has unit mass, therefore, mass of the nucleus is equal to the total number of protons and neutrons.

**Q. Define atomic number.**

**Ans.** Atomic number is defined as the number of protons in the atomic nucleus of an element. Atom being electrically neutral, the atomic number gives the number of electrons surrounding the nucleus.

**Q. What is the significance of valence shell?**

**Ans.** The outermost incomplete shell of various atoms is called valence shell. It plays an important role in chemical bonding as it determines the valance or the bonding capacity of an element. The electrons in the valence shell are called *valence electrons.*

**Q. What is Octet Rule?**

**Ans.** It was stated by G.N. Lewis that all the noble gases (except helium) have a stable outer shell of eight electrons. Therefore, in general, atoms of other elements tend to acquire a stable 8-electron outer shell (octet) by transfer or sharing of valence electrons so as to form chemical bonds.

**Q. Define chemical bond. Discuss its various types.**

**Ans.** A chemical bond is defined as the attractive force that holds two or more atoms together in a molecule or an ion. It has three types.

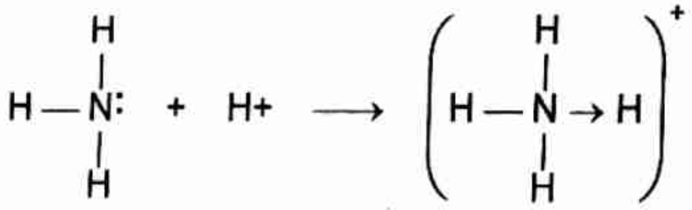
*(a)* **Ionic Bond.** This type of bond is formed by transfer of one or more electrons from one atom to another atom.

$$\overset{\times}{Na} + \cdot\ddot{\underset{..}{Cl}}: \longrightarrow Na^+ Cl^-$$

*(b)* **Covalent Bond.** A covalent bond is formed between two atoms by sharing of electrons.

$$H\bullet + {}_\times H \longrightarrow H-H$$

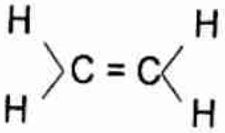
*(c)* **Coordinate Bond.** It is covalent bond in which both the shared electrons come from the same atom.



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{N}}}}: + H^+ \longrightarrow \left(H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{N}}}}\rightarrow H\right)^+$$

**Q. What are multiple bonds?**

**Ans.** Multiple covalent bonds or multiple bonds are formed by sharing two or more electron pairs between two atoms.



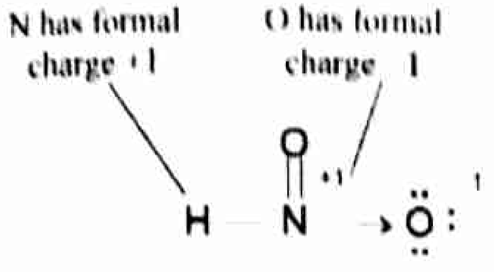
Double bond

$$H-C\equiv C-H$$

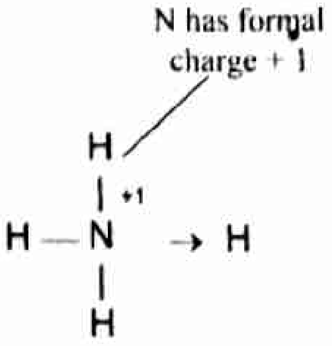
Triple bond

**Q.** **What is a formal charge?**

**Ans.** Some atoms in a coordinate molecule carry a positive or negative charge called a *formal charge*. The donor atom of the coordinate bond has a formal charge +1 and the acceptor atom has a formal charge −1. Since both charges are within the same molecule, the molecule as a whole is neutral. If however, the opposite charges do not cancel, the structure represents an ion, e.g., $NH_4^+$



Nitrous acid



Ammonium ion

**Q.** **How the formal charge on a particular atom can be calculated?**

**Ans.** The formal charge on a particular atom can be calculated by the equation

Formal charge

$$= \begin{pmatrix}\text{no. of valence } \bar{e} \\ \text{in neutral atom}\end{pmatrix} - \tfrac{1}{2}\begin{pmatrix}\text{no. of} \\ \text{shared } \bar{e}\end{pmatrix} - \begin{pmatrix}\text{no. of} \\ \text{unshared } \bar{e}\end{pmatrix}$$

For illustration, in nitrous acid structure:

Formal charge on $N = 5 - \frac{1}{2} \times 8 - 0 = +1$

Formal charge on $O = 6 - \frac{1}{2} \times 2 - 6 = -1$

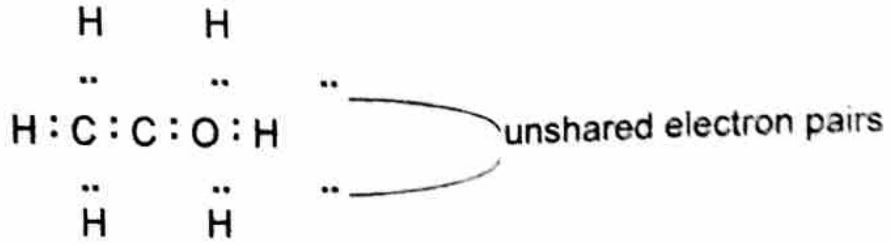
The formal charge on N of ammonium ion is

$$= 5 - \frac{1}{2} \times 8 - 0 = +1$$

**Q.** **How the structural formula of a given compound be represented?**

**Ans.** The structural formula of a given compound may be represented with paper and pencil in different ways. Each method may be used when necessary.

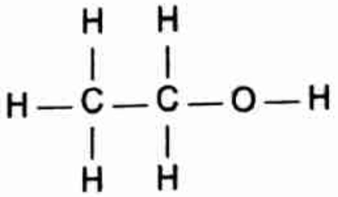
*(a)* **Electron-dot-formula.** Here, all valence electrons are shown by dots. For example,



$$H:\underset{H}{\overset{H}{C}}:\underset{H}{\overset{H}{C}}:\underset{..}{\overset{..}{O}}:H$$

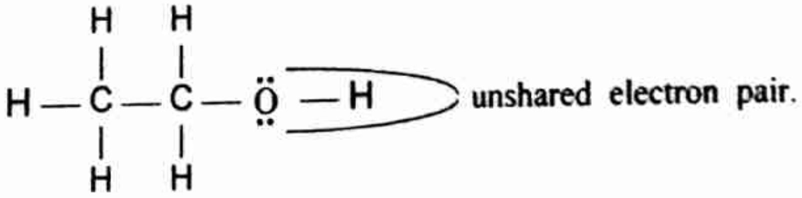
It is cumbersome to write the electron-dot-formula everytime. However, it displays all valence electrons and makes it possible to calculate the formal charge within functional groups.

*(b)* **Dash Formula.** This formula is written by using a dash (–) for a covalent bond. Unshared electrons may be shown if desired. For example, ethyl alcohol may be represented as



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$$

or



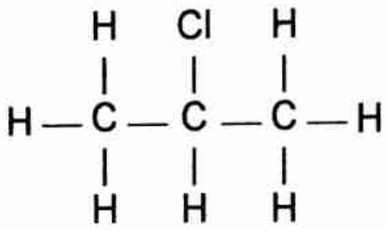
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{..}{\overset{..}{O}}-H$$

Advantages of a dash formula are:

*(i)* it displays all covalent bonds clearly; and

*(ii)* functional groups are easily identified.

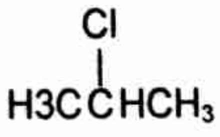
*(c)* **Condensed Formula.** Here each carbon atom and its attached atoms are condensed to a single line.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-H$$

Dash formula

H3CCHClCH3 or

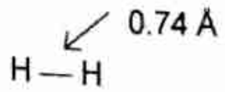


$$H3C\overset{Cl}{C}HCH_3$$

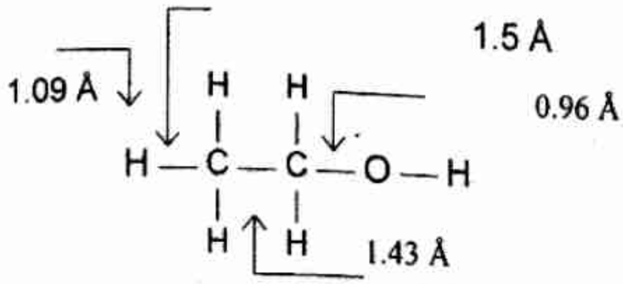
Condensed formula

**Q. Define bond Length. What factors affect the bond length?**

**Ans.** The distance between the nuclei of covalently bonded atoms is called *bond distance* or *bond length*. For example, the distance between the two nuclei of H atoms in hydrogen molecule is 0.74 Å. This is referred to as H — H bond length.

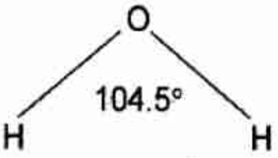


The bond length depends on the nature of atoms bonded together and other environmental factors. The various bond lengths in ethyl alcohol molecule are shown below:



## Q. What is bond angle?

**Ans.** The angle between any two bonds at a carbon or hetero atom (0, N, S), is called a *bond angle*. For example, the bond angle in a water molecule, H — O — H, is 104.5°.



The bond angles vary from 60° to 180°, depending on the nature of bonded atoms.

## Q. What do you know about bond energy?

**Ans.** The heat energy applied to break a bond or released to form a bond, is called the *bond energy*.

Bond energy is expressed in kcal/mole. For example, the bond energy of a H — H bond is 103 kcal per mole of hydrogen molecule.

$$H:H \longrightarrow H^{\bullet} + {}^{\bullet}H$$

103 kcal/mole applied

$$2H^{\bullet} \longrightarrow H:H$$

103 kcal/mole applied

## Q. Explain the term electro-negativity.

**Ans.** When two atoms join together by a covalent bond, the nucleus of each atom attracts the shared electron pair towards itself. This ability of an atom to attract the shared electron pair in covalent bond is termed as its *electronegativity.*

All the elements in a periodic table have their characteristic electro-negativity values. The student should remember the electronegativities of selected elements.

$$F > O > N \geq Cl > C > H$$

**Q. What are polar and non-polar covalent bonds?**

**Ans.** A covalent bond formed by the atoms having same or nearly equal electronegativities is called *non-polar covalent bond*. For example, bonds as H — H and C — H are non-polar covalent bonds.

On the other hand, a covalent bond formed by the atoms have different electronegativities is called a *polar covalent bond*. For example, a bond as H — Cl is called a polar covalent bond.

$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \quad \text{or} \quad \overset{+\longrightarrow}{H-Cl}$$

**Q. What is the significance of polar-covalent bonds in organic molecules?**

**Ans.** The presence of polar bonds in organic molecules exerts special effects on their physical and chemical properties.

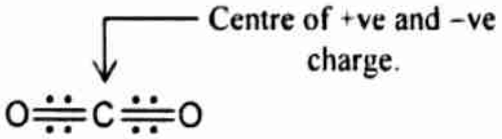
**Q. What are polar and non-polar molecules?**

**Ans.** A molecule containing one or more polar covalent bonds and in which the centres of positive and negative charges are separated, is said to be a *polar molecule*. For example, H — I and water (H — O — H) are polar molecules.

A molecule containing one or more non-polar covalent bonds only is said to be a *non-polar molecule*. The centres of positive and negative charges in such a molecule coincide. Examples of non-polar molecules are $H_2$, $CH_4$, $C_2H_2$, etc.

**Q. Molecules such as $CO_2$ and $CCl_4$ are non-polar, comment.**

**Ans.** Polyatomic molecule such as CO2 and CCl4 are non-polar, because the centres of positive and negative charges in such molecules coincide.



**Q. What are dipoles?**

**Ans.** Molecules containing polar bonds have positive and negative ends and are called *dipoles*. For example, $CH_3Cl$ and $CH_3I$.

**Q. Define dipole moment. Give its significance.**

**Ans.** Dipole moment of a polar molecule is the vectorial sum of the individual bond moments. It is equal to the product of magnitude of the partial charges and the distance between the centre of opposite charges.

$$\mu = q \times d$$

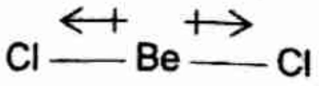
It is measured in Debye (D) unit. The dipole moment of a molecule measures the concentration of positive and negative charges.

**Q. Can a molecule without polar bonds has dipole moment?**

**Ans.** No.

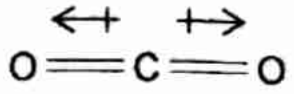
**Q. Write down the name of polar molecules which have no dipole moment.**

**Ans.** If the polar bonds are arranged symmetrically so that the effect of any one bond is canceled out by the other, then the net effect will be zero and molecule will have no dipole moment.



$$\mathrm{Cl}\overset{\leftarrow\!+}{\text{——}}\mathrm{Be}\overset{+\!\rightarrow}{\text{——}}\mathrm{Cl}$$

$\mu = 0$



$$\mathrm{O}\overset{\leftarrow\!+}{=\!=}\mathrm{C}\overset{+\!\rightarrow}{=\!=}\mathrm{O}$$

$\mu = 0$

**Q. $CO_2$ possesses no dipole moment but $SO_2$ has net dipole moment. Explain.**

**Ans.** Carbon in $CO_2$ is sp hybridized and the molecule is linear. The individual bond moments oppose each other and cancel one another out. While the $SO_2$ molecule has bent structure ($sp^2$ hybridized). The individual bond moments are oriented in such a way so as to provide overall electrical dissymmetry. Thus $SO_2$ has net dipole moment.

**Q. What kind of bond would you expect between carbon and alkali-metal and carbon and alkaline earth metal.**

**Ans.** The bond between carbon and alkali metal is totally ionic, while the bond between carbon and alkaline earth metal is highly polar.

$$CH_3\bar{C}\,H2\overset{+}{K}\,,\quad \overset{\delta-}{CH3} - \overset{\delta+}{Mg} - \overset{\delta-}{CH3}$$

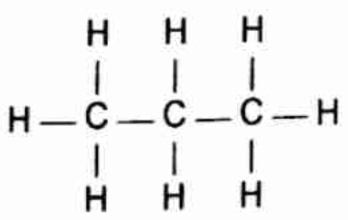
**Q. Define electron affinity.**

**Ans.** Electron affinity is the energy released when an electron is added to a neutral gaseous atom to form a negative ion.

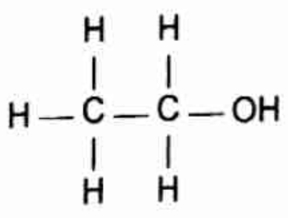
Only halogens release energy when they acquire electrons to become negatively charged ions. All other elements, however, absorb energy in the formation of an anion.

**Q. Explain the difference between aliphatic and aromatic compounds.**

**Ans. Aliphatic Compounds.** These compounds are made of open-chains of carbon atoms. These are often referred to as *open-chain compounds.* For example,



Propane



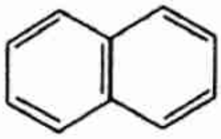
Ethyl alcohol

Aliphatic compounds containing single carbon-carbon bonds are called *saturated compounds*. Those containing double and triple carbon-carbon bond are called *unsaturated compounds*.

**Aromatic Compounds**

The hydrocarbon benzene ($C_6H_6$) contains a six-carbon ring with three double bonds in alternate positions. The compounds made of one or more structural units of benzene are called aromatic compounds.

Benzene



Naphthalene

**Q. What is a functional group? Write formulae of some important functional groups.**

**Ans.** An atom or group of atoms that gives a particular set of physical and chemical properties to a compound is called a *functional group*.

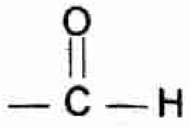
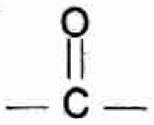
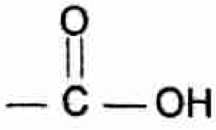
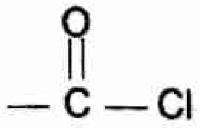
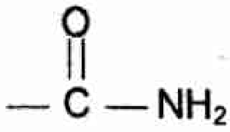
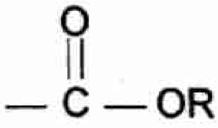
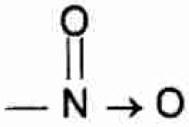
Simple organic molecules are made of a hydrocarbon part bonded to another reactive atom or group of atoms.

The molecule owes its characteristic physical and chemical properties to the presence of reactive group X.

A series of compounds having a same functional group is called a *class* or *family*. The compounds belonging to a class will have similar physical and chemical properties.

**Table. Common Functional Groups and Classes**

| Functional group | | Name of class |
|---|---|---|
| **Structure** | **Name** | |
| $>C=C<$ | Carbon-carbon double bond | Alkenes |
| $—C \equiv C—$ | Carbon-carbon triple bond | Alkynes |
| —X (F, Br, Cl, I) | Halo | Alkyl halides |
| —OH | Hydroxyl | Alcohols |
| $—\overset{\vert}{\underset{\vert}{C}}—O—\overset{\vert}{\underset{\vert}{C}}—$ | Ether | Ethers |

| | | |
|---|---|---|
|  $-\overset{O}{\overset{\|}{C}}-H$ | Aldehyde | Aldehydes |
|  $-\overset{O}{\overset{\|}{C}}-$ | Ketone | Ketones |
|  $-\overset{O}{\overset{\|}{C}}-OH$ | Carboxyl | Carboxylic acids |
|  $-\overset{O}{\overset{\|}{C}}-Cl$ | Acid chloride | Acid chlorides |
|  $-\overset{O}{\overset{\|}{C}}-NH_2$ | Amide | Amides |
|  $-\overset{O}{\overset{\|}{C}}-OR$ | Esters | Esters |
| $-NH_2$ | Amino | Amines |
| $-C\equiv N$ | Cyano | Nitriles |
|  $-\overset{O}{\overset{\|}{N}}\rightarrow O$ | Nitro | Nitroalkanes |

**Q. Define homologous series**

**Ans.** A series of chemical compounds of uniform chemical type, showing a regular gradation in physical properties, and capable of being represented by a general molecular formula. Members of the same homologous series are called *homologues;* e.g., methane and ethane.

**Q. What is Trivial or Common name?**

**Ans.** An ordinary name assigned to a compound without reference to its structure. Thus, formic acid, HCOOH, was so named as it was obtained by distillation of red ants (Latin formica = ants).

**Q. What is IUPAC System of Nomenclature?**

**Ans.** In 1957, the International Union of Pure and Applied Chemistry (IUPAC) evolved a scheme for assigning systematic names to organic compounds on the basis of structure. This is known as *IUPAC system.* This system has set rules for naming organic molecules from the structural formula.

**Q. What is the significance of IUPAC name?**

**Ans.** An IUPAC name is unambiguous i.e., one compound has one name only. It is superior to a trivial name because it gives an insight into the structure of a molecule. Knowing the IUPAC name of a compound, we can at once write its structural formula.

## 2.2. Covalent Bonding

**Q. How covalent bonds are formed?**

**Ans.** Covalent bonds are formed by the sharing of electrons between two atoms.

**Q. What is the nature of electron according to modern approach?**

**Ans.** According to modern theory, electron is believed to have wave-properties (e.g., wavelength, frequency), as well as the properties of a particle such as mass, energy and momentum.

**Q. Define orbital.**

**Ans.** An orbital is a region around the nucleus where the probability of finding the electron is maximum.

**Q. How an electron in an atom is described?**

**Ans.** An electron in an atom is described by the Schrodinger wave equation which relates the energy of a system to the wave motion.

**Q. What are the shapes of s and p orbitals?**

**Ans.** An s orbital is spherical with the atomic nucleus at the centre. Being symmetrical it has no direction. A p orbital has a dumbbell-like shape. The atomic nucleus is between the two lobes of the orbital. p-orbital is directional in character.

**Q. What are the rules of filling the atomic orbitals?**

**Ans.** The filling of the atomic orbitals is done according to the following rules:

*(i)* An atomic orbital cannot contain more than two electrons.

*(ii)* Orbitals of lower energy are filled first.

*(iii)* No orbital is filled with two electrons until all the orbitals of equal energy have at least one electron.

**Q. How is a molecular orbital formed?**

**Ans.** A molecular orbital is formed by the overlap of half-filled atomic orbitals. The degree of overlapping of atomic orbitals determines the strength of a covalent bond. The greater the strength of overlap, the stronger is the bond formed.

**Q.** **Explain the difference between sigma and pi bonds.**

| | Sigma bond | pi bond |
|---|---|---|
| *(i)* | It is formed by the linear overlap of s and/or p orbitals. | It is formed by the lateral overlap of two p-orbitals. |
| *(ii)* | It is symmetrical around the nuclear axis. | It is not symmetrical around the nuclear axis. |
| *(iii)* | It is a strong bond. | It is a weak bond. |
| *(iv)* | It has one region of electron density. | It has two regions of electron density. |
| *(v)* | Rotation about a sigma bond occurs more frequently. | Rotation about a pi bond is not possible. |

**Q.** **Define orbital hybridization.**

**Ans.** It is a hypothetical process of transforming a number of dissimilar atomic orbitals into a new set of 'mixed' or hybrid orbitals. Carbon forms hybrid orbitals from s and p atomic orbitals in three different ways, $sp^3$ - $sp^2$ and sp.

**Q.** **What is the significance of hybridization?**

**Ans.** Hybridization explains the covalency of atoms. It explains the geometry of molecules which could not be explained on valence bond theory.

**Q.** **Why a bond formed by sp hybrid orbitals is stronger than either s or p orbitals?**

**Ans.** sp hybrid orbitals extend out in space towards the other atoms more than the s or p orbitals and so permit greater overlap.

**Q.** **Why the bond angles between $sp^2$ and $sp^3$ hybrid orbitals are 120° and 109.5°?**

**Ans.** This arrangement of angles of hybrid orbitals permits the electron to get as far away from each other as possible.

**Q.** **Account for the observed bond angle of 105° in $H_2O$ molecule.**

**Ans.** In water molecule, oxygen undergoes $sp^3$ hybridization. Two of them are half-filled and are used for bonding with hydrogen atoms. The other two contain unshared electron pairs. The unshared electron pair occupy more space and the bond angle is reduced to 105°.

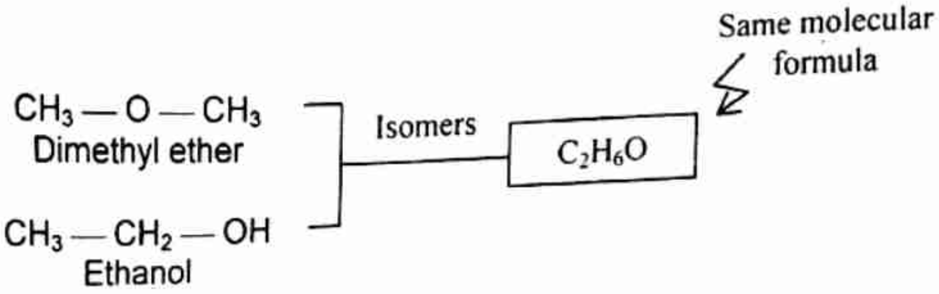
**Q.** **Why does carbon not form more than four bonds?**

**Ans.** Hybridization of carbon's one 2s and three 2p atomic orbitals gives rise four sp3 hybrid orbitals. Each hybrid orbital can form only one sigma bond.

## 2.3. Stereoisomerism

**Q.** **What is isomerism?**

**Ans.** Two or more compounds which have the same molecular formula but different structures are known as isomers and this phenomenon is known as isomerism. For example, dimethyl ether and ethanol, both have the molecular formula $C_2H_6O$. They are isomers of each other.



**Q. What are two main types of isomerism?**

**Ans.** There are two main types of isomerism shown by organic compounds:

**1. Stereoisomerism**

In this phenomenon, the isomers have the same molecular formula but differ in their molecular geometry in space. The individual isomers of this type are called *stereoisomers.*

**2. Structural Isomerism**

In this phenomenon, two or more compounds have the same molecular formula but different structural formulas. The individual isomers are called *structural* or *constitutional isomers.*

**Q. Discuss two types of Stereoisomerism.**

**Ans.** The two types of Stereoisomerism are:

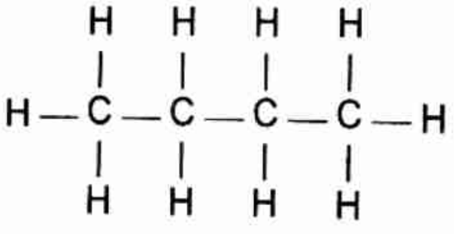
*(i)* **Geometric Isomerism.** It is due to different spatial arrangement of groups about a double bond.

*(ii)* **Optical Isomerism.** It is due to different spatial arrangement of groups about an asymmetric or chiral carbon atom.

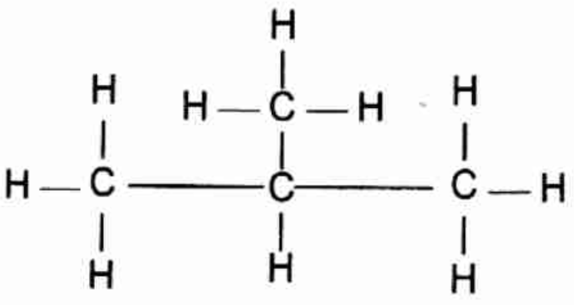
**Q. What are different types of structural isomerism?**

**Ans.** Organic compounds display four types of structural isomerism:

*(i)* **Chain Isomerism.** When two or more compounds have the same molecular formula but differ in respect of the carbon skeleton, they are called *chain isomers.*



n-butane

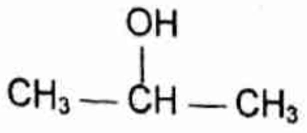


2-methyl propane

*(ii)* **Position Isomerism.** When two or more compounds have the same molecular formula and the same skeletal carbon chain, but differ in the

position of a functional group on the chain, they are called *position isomers*. The phenomenon is called position isomerism.

$CH_3-CH_2-CH_2-OH$



$$CH_3-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3$$

Propyl alcohol Isopropyl elchohol

(iii) **Functional Group Isomerism.** When two or more compounds have the same molecular formula, but contain different functional groups. They are called *functional group isomers*. The phenomenon is called functional group isomerism.

$CH_3-CH_2-OH$
Ethyl alcohol

$CH_3-O-CH_3$
Dimethyl ether

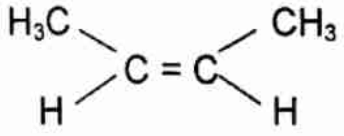
(iv) **Metamerism.** Isomers in which different alkyl groups are attached to a particular functional group atom, are called *metamers*. This type of isomerism which exists in compounds of same class, is called *metamerism*.

$CH_3CH_2-O-CH_2CH_3$
Diethyl ether

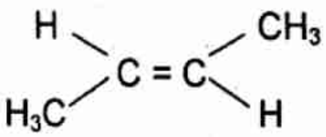
$CH_3-O-CH_2CH_2CH_3$
Methyl n-propyl ether

**Q. Give some examples of geometric isomers.**

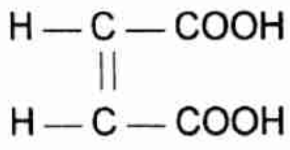
**Ans.**



cis-2-butene

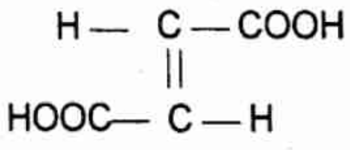


trans-2-butene



$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix}$$

Maleic acid (cis isomer)



$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix}$$

Fumaric acid (trans-isomer)

**Q. What conditions are necessary for geometric isomerism?**

**Ans.** A compound can exist as a pair of geometric isomers if the following two conditions are satisfied.

(i) The molecule must have restricted rotation. This is caused not only by the presence of a $C=C$ bond, but also by a ring structure.

(ii) Geometric isomerism is possible only if both the carbon atoms of the double bond bear two different groups.

**Q. Explain the difference between configuration and conformation.**

**Ans.** Configuration relates to those arrangements in space of atoms in a molecule that can be changed only by making and breaking of bonds.

Conformation relates to an infinite number of arrangements of atoms in space that can arise from rotation about a C — C bond. The energy barrier to this rotation is so small that the different conformations equilibrate with each other rapidly and cannot be isolated.

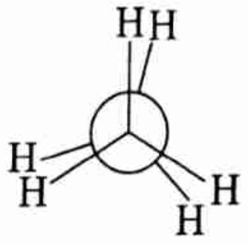
**Q. Write different conformations of ethane.**

**Ans.** In case of ethane, the following conformations are observed.

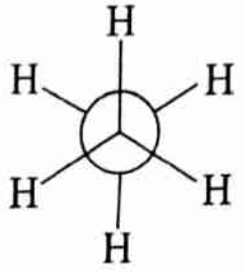
*(i)* **The Eclipsed form** in which the rear methyl group is completely eclipsed and the only one nearer to the eye is visible.

*(ii)* **The Staggered form** in which the rear methyl group has been rotated upside down and all the six H-atoms of the two methyl groups are staggered symmetrically.

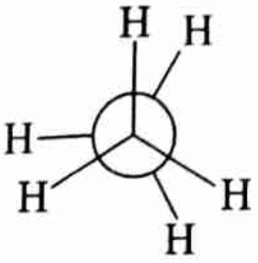
*(iii)* **The Skew forms.** Obviously, there will be many more arrangements or forms possible in between the two extreme forms. These are called skew forms.



Eclipsed



Staggered



Skew

**Q. Define conformational analysis.**

**Ans.** The study of the energy changes accompanying the rotation of the groups about single bonds is known as *conformational analysis.*

**Q. Define plane-polarized light. How is it produced?**

**Ans.** A light radiation vibrating in one plane is called *plane-polarized* light. It is produced by passing ordinary light through a Nicol prism.

**Q. What is optical activity?**

**Ans.** Many naturally occuring organic compounds have the power to rotate the plane of polarized light. These compounds are said to be *optically active.* This property of a compound is called *optical activity.*

**Q. Define plane of symmetry.**

**Ans.** A plane which divides an object into two symmetrical halves is said to be *plane of symmetry.*

**Q. What is the criterion of optical activity?**

**Ans.** The molecule should not contain a plane of symmetry.

**Q. Explain the term 'chiral' and 'achiral'.**

**Ans.** When an object or molecule lacks a plane of symmetry and cannot be superimposed over its mirror image, it is said to be *chiral.* Thus a hand is chiral.

A ball is symmetric and can be superimposed over its mirror image. It is therefore, referred to as *achiral.*

**Q. What is asymmetric carbon atom?**

**Ans.** A carbon atom which is bonded to four different atoms or groups is called an *asymmetric carbon atom.*

The term asymmetric carbon atom is rather misleading. It only means that a carbon atom is bonded to four different groups and a molecule of the type lacks a plane of symmetry. Such a molecule is called *asymmetric,* that is without symmetry. Presently, the term *disymmetric* or *chiral molecules* is frequently used for asymmetric molecules.

**Q. What are enantiomers?**

**Ans.** Isomers whose mirror-image are nonsuperimposable on each other are called *enantiomers.* They represent the two optical isomers *dextro* and *levo.*

**Q. What is racemic mixture?**

**Ans.** When optical isomers are mixed together in equal proportions, the optical rotation of one isomer is exactly cancelled by that of the other. Such a mixture is called *racemate* or *racemic mixture.* As expected, it is optically inactive.

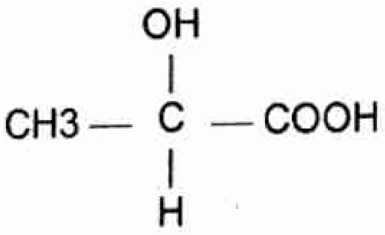
**Q. What conditions are necessary for optical isomerism?**

**Ans.** 1. The compound must contain an asymmetric carbon atom.

2. Its three-dimensional structure should not have a plane of symmetry.
3. The two possible formulas should be non-superimposable mirror-images.

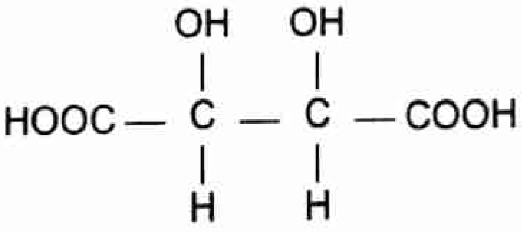
**Q. Give two examples of optical isomers.**

**Ans.**



$$\begin{array}{ccccc} & & \text{OH} & & \\ & & | & & \\ \text{CH3} & - & \text{C} & - & \text{COOH} \\ & & | & & \\ & & \text{H} & & \end{array}$$

Lactic acid



$$\begin{array}{ccccccc} & & \text{OH} & & \text{OH} & & \\ & & | & & | & & \\ \text{HOOC} & - & \text{C} & - & \text{C} & - & \text{COOH} \\ & & | & & | & & \\ & & \text{H} & & \text{H} & & \end{array}$$

Tartaric acid

**Q. What are different forms of lactic acid?**

**Ans.** Lactic acid exists in three different forms, d-lactic acid, *l*-lactic acid and a dl-mixture.

**Q. Why enantiomers sometimes called optical isomers?**

**Ans.** Enantiomers rotate the plane of polarized light through some angle. Due to this property, they are also referred to as optical isomers.

**Q. What is meso variety?**

**Ans.** The optically inactive form which is due to internal compensation is known as the *meso variety.*

**Q. Define racemization.**

**Ans.** Racemization is the process by which 50% of an optically active compound (dextro or levo) may be converted to its enantiomers.

**Q. What do you mean by resolution of racemic mixture? How is it achieved?**

**Ans.** Separation of a racemic mixture (dl-mixture) into the optically pure isomers is known as resolution of racemic mixture. It is achieved by the following methods.

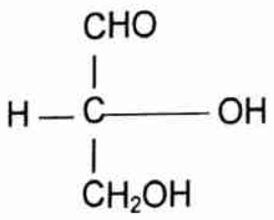
(*i*) **Mechanical Method.** It consists mechanically picking one kind of the crystal from the other kind from the mixture of both.

(*ii*) **Biological Method.** It makes use of special type of bacteria, which attacks one of the two isomeric varieties, consumes it, leaving the other unaffected.

(*iii*) **Chemical Method.** In this method a racemic mixture is treated with a pure optically active substance when two diastereoisomers are obtained which are physically separable.

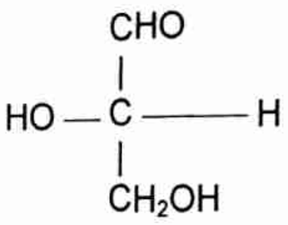
**Q. Define absolute configuration.**

**Ans.** Absolute configuration is the special arrangement of the substituents attached to a chiral centre. For example,



$$\mathrm{H-\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{C}}-OH}$$

D-Glyceraldehyde



$$\mathrm{HO-\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{C}}-H}$$

L-Glyceraldehyde

## 2.4. Reaction Mechanism

**Q. What is reaction mechanism?**

**Ans.** The mechanism of a reaction is simply the path the molecules follow in going from reactants to products.

**Q. How chemical reactions are represented?**

**Ans.** Chemical reactions are represented by writing the formulas of the reactants and products with an arrow (→) in between. The conditions used for the reaction (temperature, pressure, catalyst etc.) are mentioned above or below the arrow.

$$\underbrace{A + B}_{\text{Reactants}} \xrightarrow{\text{Conditions}} \underbrace{C + D}_{\text{Products}}$$

**Q. Write various methods commonly used for elucidating reaction mechanisms.**

**Ans.** In general, there is no one method that is satisfactory for the determination of mechanism of reactions, but the application of a number of methods may help us in justifying the theoretical data with experimental results. Some commonly used methods are:

*(i)* **Kinetics.** Kinetic studies are concerned with rates of reactions under different conditions and make the most general method for determining reaction mechanism.

*(ii)* **Detection and Identification.** The detection or if possible, the isolation of intermediates and identification of all the products.

*(iii)* **Stereochemical Evidence.** Such studies are useful while dealing with optically active compounds.

*(iv)* **The Use of Isotopes.** This method is particularly applied for tracing the part played by a particular atom in a reaction.

**Q. What is isotopic labelling?**

**Ans.** It is a phenomenon in which isotopes are used as tracers, i.e., the starting material is labelled at some particular position and after reaction the labelled atom is then located in the product. In recent years, the use of isotopes has been extremely helpful in the study of reaction mechanisms and rearrangements and in turn the elucidation of structures.

**Q. What is the difference between substrate and reagent?**

**Ans.** Of the two reactants (A and B), one is referred to as the substrate and the other reagent.

The reactant which has a relatively large organic molecule undergoing a change, is called the *substrate.*

The other reactant which is an inorganic or a simple organic molecule producing that change, is called the *reagent.* For example,

$$\underset{\text{Substrate}}{C_2H_5Br} + \underset{\text{Reagent}}{NaOH} \longrightarrow \underbrace{C_2H_5OH + NaBr}_{\text{Products}}$$

**Q. Explain the terms electrophiles and nucleophiles.**

**Ans.** An electrophile is defined as an electron poor positive ion or molecule which can accept an electron pair to form a covalent bond. For example, $H^+$, $NO_2^+$, $CH_3CH_2^+$, $SO_3$, $BF_3$, etc.

A nucleophile is defined as an electron rich negative ion or molecule which can donate an electron pair to form a covalent bond. For example, $OH^-$, $Br^-$, $CN^-$, $H_2O$, $R-OH$ etc.

**Q. Explain Lewis concept of acids and bases.**

**Ans.** According to the Lewis concept, an *acid* is a substance which can accept a pair of electrons and a *base* is one which can donate a pair of electrons.

Thus boron trifluoride ($BF_3$) with six valence electrons on the boron atom is a *Lewis acid.* Ammonia (NH3) with an unshared electron pair on the nitrogen atom is a *Lewis base.*

**Some more examples:**

(*i*) **Lewis Acids:** $BCl_3$, $AlCl_3$, $FeCl_3$, $ZnCl_2$, $SO_3$

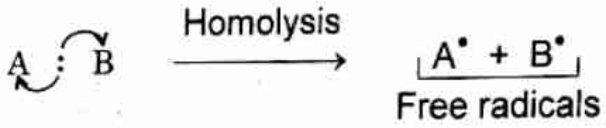
(*ii*) **Lewis Bases:** $OH^-$, $Cl^-$, HOH, $C_2H_5OH — OH$, $RNH_2$

It is noteworthy that in organic reactions, a Lewis acid plays the role of an electrophile and Lewis base that of nucleophile.

**Q. Explain Homolytic and Heterolytic fission.**

**Ans.** An organic reaction occurs by breaking and making of covalent bonds. A covalent bond consists of a pair of electrons. It can undergo breaking or fission in two ways.

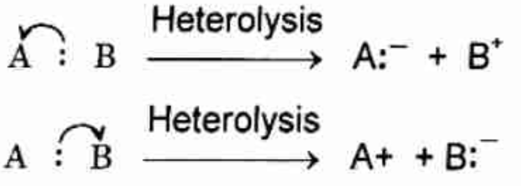
(*i*) **Homolytic Fission or Homolysis.** In this kind of bond fission, one bonding electron goes to each atom. The resulting atoms with an odd electron are known as *free radicals.*



$$A : B \xrightarrow{\text{Homolysis}} \underbrace{A^{\bullet} + B^{\bullet}}_{\text{Free radicals}}$$

Since this type of breaking yields two identical fragments, it is called homolytic fission.

(*ii*) **Heterolytic Fission or Heterolysis.** In this kind of bond fission both the bonding electrons go to one of the two atoms. It is the atom A or B whichever is more electronegative

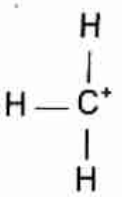


$$A : B \xrightarrow{\text{Heterolysis}} A:^- + B^+ \quad \text{(A more electronegative)}$$

$$A : B \xrightarrow{\text{Heterolysis}} A+ + B:^- \quad \text{(B more electronegative)}$$

**Q. What is the difference between carbonium ion and carbanion?**

**Ans.** A *carbocation* or *carbonium ion* (old name) is an ion in which the carbon atom has only six electrons and bears a positive charge.



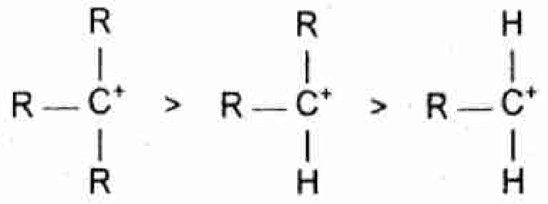
$H—C^+H_2$ (Carbocation)

*Carbanion* is an ion in which a carbon has an unshared electron pair and bears a negative charge.

**Q. Discuss the stability of carbonium ions?**

**Ans.** In the carbonium ion, the carbon atom bears a positive charge and is highly unstable and reactive. When an electron-donating group as alkyl group

(R) is bonded to the positive carbon, the former pumps electrons through the bond. This reduces the positive charge on the carbon and makes the carbonium ion stable. Thus a tertiary carbonium ion is more stable than a secondary carbonium ion, and a secondary carbonium ion is more stable than a primary carbonium ion.

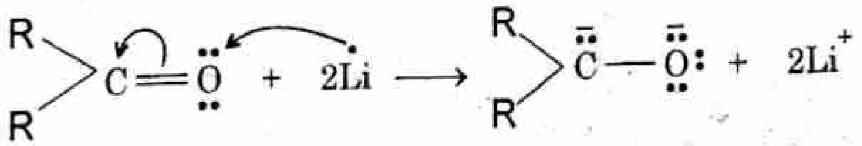


For the same reason, electron attracting groups like —$NO_2$ and —Br will make a carbonium ion less stable.

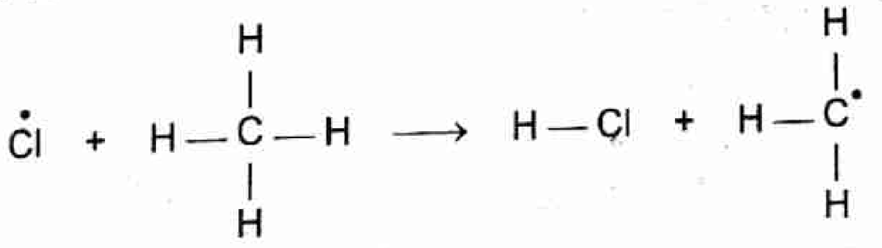
**Q. Discuss various types of reaction mechanisms.**

**Ans.** The reaction mechanisms could be classified into three types:

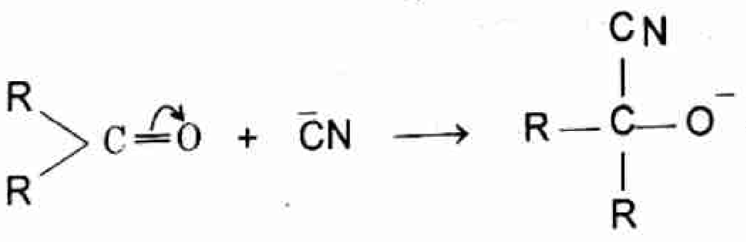
*(i)* **Electron-transfer Mechanism.** Such a mechanism involves a total transfer of electrons from one reagent to the other. For example, lithium metal transfers two electrons to a ketone to yield a doubly negative ion.



*(ii)* **Free radical mechanism.** Here one of the reagents or products is a free radical. There is no transfer of electrons as such. For example,



*(iii)* **Ionic Mechanism.** This type of mechanism involves ions either as reagents or products or both. For example,



**Q. What is a prerequisite for a reaction to occur?**

**Ans.** The existence of positive and negative sites in the substrate molecule is a prerequisite for a reaction to occur.

**Q. What are electronic effects?**

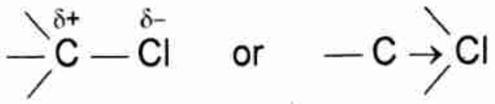
**Ans.** A molecule is neutral as the positive charge of the nucleus of each atom is evenly balanced by the negative charge of outer electrons. The movement of the electrons from one part of the molecule to another will result in the separations of positive and negative charges. The substrate molecule is thus activated for interaction with an electrophilic or nucleophile. Such an effect produced by the movement of electrons is called *electronic effect*. The two important electronic effects involved in the mechanism of organic reactions are:

(*i*) Inductive effect

(*ii*) Resonance or mesomeric effect.

**Q. Write a short note on inductive effect.**

**Ans.** The displacement of an electron pair in a covalent bond due to electronegativity difference of the two joined atoms and consequent polarization of the bond is called inductive effect. For example, inductive effect in alkyl halide may be depicted as follows:

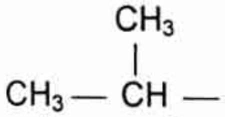


The inductive effect is represented by the symbol I. An arrow-head placed along the bond indicates the direction of the displacement of the electron pair.

(*i*) **Positive Inductive Effect.** When the group bonded to a carbon atom is less electronegative than carbon, the inductive effect involves the displacement of electron pair towards the carbon atom. This is called *positive inductive effect* or *+I effect*. The group causing +I effect by releasing electrons to the carbon atom is called electron releasing group. For example,

$CH_3—$ Methyl

$CH_3CH_2—$ Ethyl



$CH_3—CH(CH_3)—$

Isopropyl

(*ii*) **Negative Inductive Effect.** When the group bonded to a carbon atom is more electronegative, the inductive effect involves the displacement of the electron pair away from the carbon atom. This is called *negative inductive effect* or *–I effect*. The group causing –I effect by withdrawing electrons from the carbon atom is called electron withdrawing group. For example,

| $—NO_2$ | $—NH_2$ | $—X(Cl, Br, I)$ | $—OH$ |
|---|---|---|---|
| Nitro | Amine | Halo | Hydroxy |

**Q. What is the effect of distance on inductive effect?**

**Ans.** The inductive effect diminishes as the distance from the polarizing group increases. The effect is usually negligible after the second carbon atom.

**Q. Write some characteristics of inductive effect.**

**Ans.** (*i*) It is a permanent effect and is always present in a molecule even in the ground state.

*(ii)* It involves the displacement of sigma electrons only.

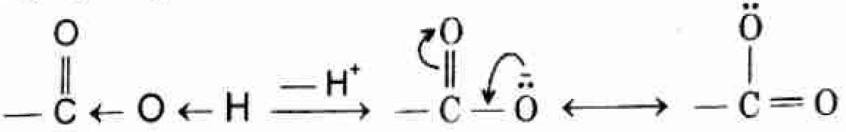
*(iii)* The electron pair never leaves its original atomic orbital. It is displaced only towards more electronegative atom.

*(iv)* It is transmitted over to only short distances.

**Q. How does inductive effect change the strength of an organic acid or a base?**

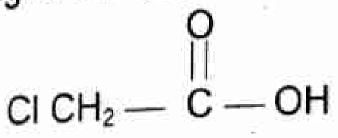
**Ans. 1. Acid strength**

An acid can be defined as a compound which releases $H^+$. Acid strength, therefore, depends upon the ease with which proton is released. Removal of $H^+$ from carboxylic group is due to the electronegative nature of two oxygen atoms present in it. This causes the pulling of O — H bond electrons towards the oxygen releasing hydrogen atom as $H^+$.



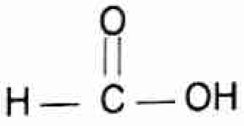
$$-\overset{\overset{O}{\|}}{C}\leftarrow O\leftarrow H \xrightarrow{-H^+} -\overset{\overset{O}{\|}}{C}-\ddot{O}^- \longleftrightarrow -\overset{\overset{\ddot{O}^-}{|}}{C}=O$$

If any group or atom, exerting a – I effect, is attached to the carbon of carboxylic group, it will help in pulling O — H bond electron. This makes the release of $H^+$ easy, thus increasing the acid strength. On the other hand, a substitutent attached to the carboxylic carbon exerts + I effect would oppose the oxygen atom in pulling the O — H bond electrons. This would result in the delaying of the release of $H^+$. Thus, the acid strength decreases.



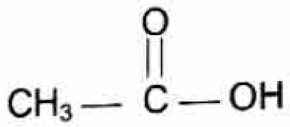
$ClCH_2-\overset{\overset{O}{\|}}{C}-OH$

Chloroacetic acid



$H-\overset{\overset{O}{\|}}{C}-OH$

Formic acid



$CH_3-\overset{\overset{O}{\|}}{C}-OH$

Acetic acid

| | Chloroacetic acid | Formic acid | Acetic acid |
|---|---|---|---|
| pKa | 2.85 | 3.75 | 4.76 |

**2. Base Strength**

A base can be defined as a compound which accepts $H^+$. Base strength, therefore, depends upon the ease with which $H^+$ is accepted, which will depend upon the electron density present on any atom of the base. The higher is the electron density present, the more easily $H^+$ ion is excepted, thus more is the base strength.

Ammonia is basic in nature due to the presence of lone pair of electrons on N-atom. However, when the H-atoms of ammonia are substituted by alkyl groups one by one the strength should go up as the electron density on nitrogen atom increases due to +I effect of alkyl groups. This is not always, true since another factor, steric hindrance, also comes in operation. Thus the decreasing order of basic strength in amines is

$$R_2\ddot{N}H > R\ddot{N}H2 > R3\ddot{N} > \ddot{N}H_3$$

On the other hand, the base strength decreases when the hydrogen atoms of ammonia are substituted by phenyl groups. It is due to the delocalization of lone pair of electrons present on nitrogen to benzene ring due to resonance.

**Q. What is resonance or mesomeric effect?**

**Ans.** Inductive effect is produced by the displacement of electrons in a single bond. A similar electronic effect is caused by the displacement of electrons in a double bond. This is referred to as *resonance* or *mesomeric effect.* Thus resonance effect may be defined as a permanent effect which involves the delocalization of π electrons from a multiple bond to an atom or from a multiple bond to a single bond or from an atom with lone pair of electrons to a single covalent bond.

Mesomeric effect is denoted by M. Like inductive effect, it is also –M, when the delocalization of electrons is towards an atom or group and +M, when the electrons are delocalized away from an atom or group.

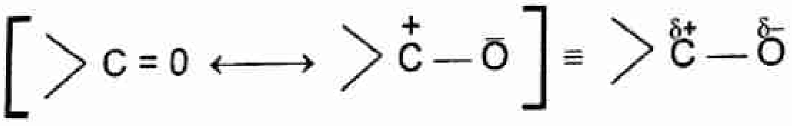
– M effect

+ M effect

**Q. Explain the phenomenon of resonance.**

**Ans.** There are certain compounds which cannot be represented by a single structure. Such compounds are represented by a set of hypothetical structures. None of these structures can explain all the characteristics of compound separately. The real structure of such compounds is said to be an intermediate of all such structures or in other words, the true structure is a *resonance hybrid* of all these structures which cannot be written on a paper. Ingold called this phenomenon *mesomerism* (between the parts), while Heisenberg named it *resonance.*

The various structures which differ only in the disposition of electrons are called *resonating* or *canonical forms.* For example,



Canonical forms Resonance hybrid

**Q. Write some characteristics of mesomeric effect.**

**Ans.**

*(i)* It is a permanent effect and is always present in the molecule even in the ground state (similarly to I effect).

*(ii)* It involves the delocalization of π electrons.

*(iii)* Electrons completely leave their atomic orbitals.

*(iv)* It is transmitted over to any distance.

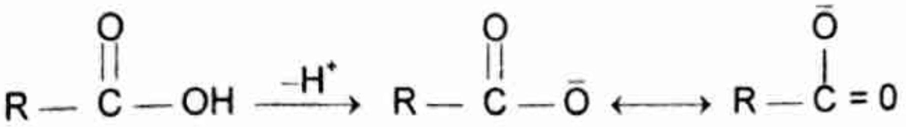
(v) It also influences the properties of compounds.

**Q. How does mesomeric effect influence the properties of compounds.**

**Ans.** Mesomeric effect, being the permanent effect also influences the properties of the compounds. For example;

### Acid Strength

Resonance explains why carboxylic acids are strongly acidic, while alcohols are neutrals. When a carboxylic acid releases $H^+$, a carboxylate ion is formed, which in turn is stabilized by resonance and hence removal of $H^+$ is possible.

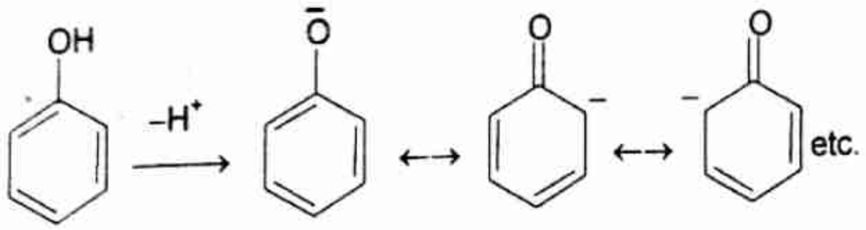


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{-H^+} R-\overset{O}{\overset{\|}{C}}-\bar{O} \longleftrightarrow R-\overset{\bar{O}}{\overset{|}{C}}=0$$

On the other hand, the alkoxide ion does not show resonance and is therefore, unstable and hence is not formed.

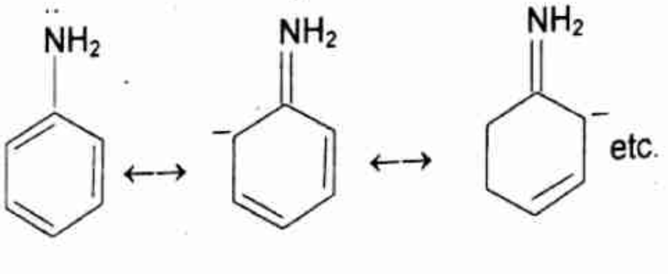
$$R-OH \xrightarrow{-H^+} R-\bar{O}$$

Similarly the acidic nature of phenol can be explain on this phenomenon.



### Base Strength

We have observed earlier that when hydrogen atom of ammonia is replaced by an alkyl group, the base strength increases (I effect). But if the same hydrogen of the ammonia is replaced by an aryl group i.e., benzene ring, an aromatic primary amine is formed which is less basic than ammonia. The decrease in basic strength is due to the delocalization of lone pair of electrons present on the nitrogen to the benzene ring through resonance.



### Bond Length

Resonance is responsible for the shortening or lengthening of bond lengths in the molecules showing resonance.

The usual carbon-carbon bond lengths when they are attached through a single bond and double bond are 1.54 Å and 1.33 Å. However all the carbon-carbon bond lengths in benzene are 1.39 Å.

**Q. Define resonance energy. How is it calculated?**

**Ans.** Resonance energy is defined as the difference between the energy of a resonance hybrid (observed value) and the energy of most stable canonical structure (calculated). The greater the resonance energy, the more stable is the compound.

The resonance energy of a molecule is obtained from heat of formation of a compound or from heat of combustion or from heat of hydrogenation.

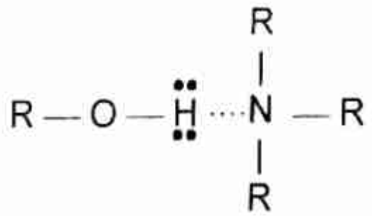
**Q. What is hyperconjugation? Discuss its significance.**

**Ans.** It is a system of conjugation in which the sigma electrons are in conjugation with $\pi$ electrons of the unsaturated system. It was suggested by Baker and Nathan that when the H — C bond is attached to an unsaturated carbon atom, the sigma electrons of H — C bond become less localized by entering into partial conjugation with attached unsaturated system i.e., with $\pi$ electrons leading to $\sigma, \pi$ conjugation.

Like inductive and resonance effects, it is also a permanent effect. The observed bond lengths which are shorter than the normal bond lengths are explained on this phenomenon. Since hyperconjugation leads to the separation of charges, it develops dipole moment in the molecule. It also stabilises a molecule or ion by forming a number of resonating structures (the greater the number of resonating structures, the more stable is a molecule or an ion).

**Q. Define hydrogen bond. Discuss its various types.**

**Ans.** It is the bond which is formed between a hydrogen atom and an atom containing an unshared electron pair like N, O etc. Hydrogen bonds are usually represented by broken or dotted lines. For example, the hydrogen bond complex formed between an alcohol and an amine is represented in the following manner.



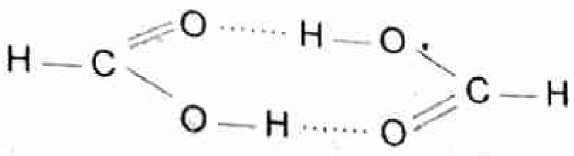
$$R-O-\overset{\bullet\bullet}{\underset{\bullet\bullet}{H}}\cdots\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{N}}-R$$

Hydrogen bond is much stronger than vander Waals forces but much weaker than normal covalent bond.

Generally speaking there are two types of H-bonds.

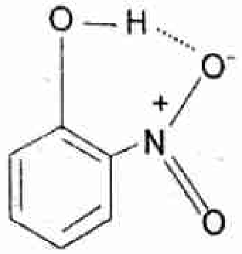
**1. Intermolecular**

In this type of hydrogen bonding, two or more than two molecules combine together to form a dimmer or a polymer respectively. For example,



## 2. Intramolecular

This type of H-bonding occurs between the two atoms of the same molecule. This gives rise to ring formation in he molecule and is a type of *chelation*, for example,



**Q. Enlist some of the physical properties which are affected by hydrogen-bonding.**

**Ans.** Essentially, all physical properties are affected by H-bonding but the following are prominently altered.

*(i)* Transition temperature

*(ii)* Water solubility

*(iii)* Thermal stability

*(iv)* Viscosity

*(v)* Refractive index etc.

**Q. Discuss various types of reactions recognized in organic chemistry.**

**Ans.** There are four basic types of reactions recognized in organic chemistry.

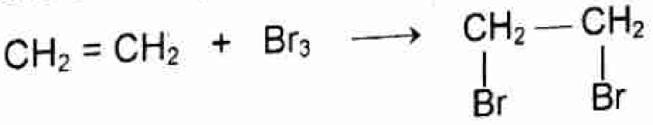
## 1. Substitution Reactions

In a substitution reaction, one atom or group belonging to the substrate is replaced by another from the reagent. For example,

$$CH_4 + Cl_2 \xrightarrow{\text{uv light}} CH_3Cl + HCl$$

## 2. Addition Reactions

In these reactions, the reagent simply adds itself across a double or triple bond of the substrate. For example.



$$CH_2 = CH_2 + Br_3 \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}$$

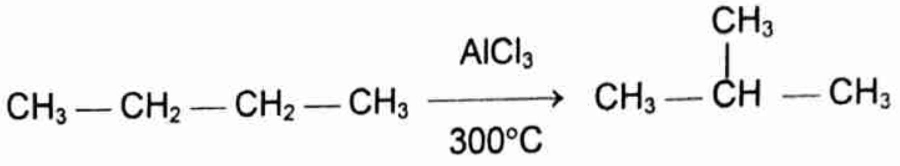
## 3. Elimination Reactions

An elimination reaction involves the removal of a pair of atoms or groups from adjacent carbon atoms. The resulting molecule is an *alkene*. For example,

$$CH_3-CH_2Br + NaOH \longrightarrow CH_2=CH_2 + NaBr + H_2O$$

### 4. Rearrangement Reactions

In a rearrangement reaction, an atom or group is transferred from one part of the substrate to another. The product is an isomer of the substrate. For example,



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[300°C]{AlCl_3} CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

Butane 2-methyl propane

**Q. Briefly discuss various types of reaction intermediates.**

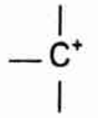
**Ans.** The various types of reaction intermediates are:

### 1. Free Radical Intermediates

A free radical may be defined as an atom or group of atoms having odd unpaired electron(s), e.g., methyl radical $\dot{C}H_3$, triphenyl methyl radical $(C_6H_5)3\dot{C}$ etc. The majority of the free radicals are electrically neutral. All possess addition properties and are extremely reactive, stability of a free radical is believed to be due to resonance.

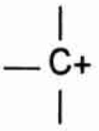
### 2. Carbonium Ion Intermediates

A carbanium ion is one in which a carbon has only three pairs of electrons in its outer most orbit and thus has a positive charge.

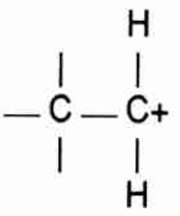


$$-\underset{|}{\overset{|}{C^+}}$$

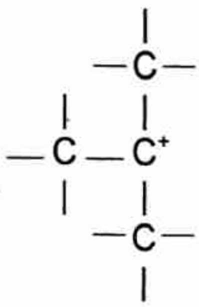
Thus a carbonium ion may be classified as *(i) primary carbonium ion, (ii) secondary carbonium ion,* and *(iii) tertiary carbonium ion.*



*(i)*



*(ii)*



*(iii)*

### 3. Carbanion Intermediates

A carbonion is one in which the carbon has eight electrons in the outermost orbit, six of which belong to three covalent bonds and two lone electrons, hence it has a negative charge. For example, $(C_6H_5)_3C^-$, triphenylmethyl carbanion, is formed as

$$(C_6H_5)_3CH + \ddot{B} \rightleftharpoons (C6H5)3C^{-} + BH$$

## 4. Carbene Intermediates

Carbenes or methylenes are divalent species containing two unpaired electrons. Though carbon in carbene has only six electrons, yet it does not possess any charge. It is a biradical and highly reactive.

$$CH_2N_2 \xrightarrow{hv} :CH_2 + N_2$$

Carbene

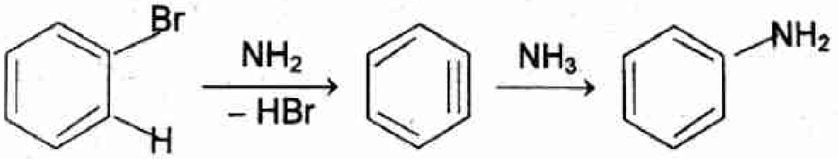
## 5. Nitrenes

They may be considered as the nitrogen analogue of carbenes. The parent nitrene $:\ddot{N}H$ also known as *azene, imene* or *imidogen* is formed by the photolysis of hydrazoic acid in aromatic solvents.

$$HN_3 \xrightarrow{hv} \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H + N2$$

## 6. Benzynes

Benzynes are also referred to as *arynes* or *1,2, dehydrobenzenes,* and are formed as reaction intermediates by the action of strong base, e.g., sodamide, NaNH2 an aryl halides. The reaction involved successive *elimination-addition reactions* via the formation of benzynes to form aromatic amines.



Benzyne Aniline

**Q. What are main characteristics of free radical reactions?**

**Ans.** The main characteristics of free radical reactions are their rapidity, their initiation by radicals themselves or by substances known to produce radicals *(initiators)* and their inhibition or termination.

**Q. How free radicals are detected?**

**Ans.** The most useful method is the electron spin resonance (E.S.R). It depends upon the fact that a free radical in a strong magnetic field orients its odd electron spin in more stable direction but with the absorption of light energy the spin can turn over to the unstable orientation

**Q. What is a biradical?**

**Ans.** It is a substance with two unpaired electrons per molecule. The most family example is the oxygen molecule, a paramagnetic species with an unpaired electron on each atom. Perhaps the simplest biradical in organic chemistry is the *carbene* or *methylene*.

**Q. What are metal ketyls?**

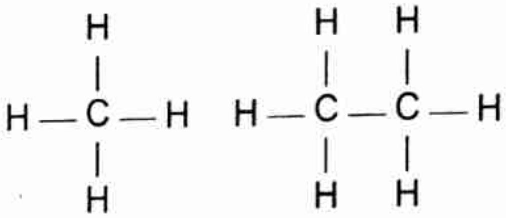
**Ans.** Metallic salts of the free radical are known as *metal ketyls*. Most of the aromatic ketones and a few aliphatic ketones with branched alkyl groups form the metal ketyls. For example,

$$\underset{\text{Benzophenone}}{Ph_2C=O} + \dot{N}a \longrightarrow \underset{\text{Benzophenone sodium ketyl}}{Ph2\dot{C}-ONa}$$

## 2.5. Miscellaneous Questions

**Q. What are alkanes?**

**Ans.** Alkanes are hydrocrbons in which all the four valencies of a carbon atom are used as single covalent bonds. The first two members of the series are:



$$\begin{array}{ccccc} & H & & \\ & | & & \\ H- & C & -H \\ & | & & \\ & H & & \end{array} \qquad \begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$

Methane Ethane

Alkanes are frequently referred to as paraffins (meaning, little affinity) as they are relatively chemically inert. The general formula of alkane is $C_nH_{2n+2}$.

**Q. Why straight chain alkane has the highest boiling point among the isomeric alkanes?**

**Ans.** As branching increases, the molecule becomes more compact (ball-like). With the decreasing surface area, the intermolecular forces of attraction are diminished, requiring less energy to pass from the liquid to the gaseous state.

**Q. Explain pyrolysis.**

**Ans.** The splitting of long-chain alkanes into two or more simpler hydrocarbons by the application of heat is called thermal *cracking* or *pyrolysis* (Greek pyros = fire, lysis = loosening).

$$CH_3-CH_2-CH_3 \xrightarrow{800^\circ} CH3-CH=CH2 + H2$$

**Q. What is marsh gas?**

**Ans.** It is methane and is produced by the microbial decomposition of dead vegetable matter.

**Q. What is lamp black?**

**Ans.** When methane is heated in the absence of oxygen, it is decomposed to give free carbon *(soot)*. The soot so formed is called *lamp black*.

$$\mathrm{CH4} \xrightarrow{1300^{\circ}} + \underset{\text{soot}}{\mathrm{C}} + \mathrm{2H2}$$

**Q. Give some uses of methane.**

**Ans.** Methane is used:

*(i)* as fuel gas in domestic stoves,

*(ii)* for the production of lamp black used in printing inks, shoe polishes, gramophone records and rubber tyres, and

*(iii)* for preparing industrial hydrogen used in synthetic production of methanol and ammonia.

**Q. What is catalytic isomerization?**

**Ans.** Molecular rearrangement of one or more than one isomer is called *isomerization*. Catalytic isomerization changes straight chain alkanes into branched chain ones.

**Q. Write a short note on petroleum.**

**Ans.** Vast deposits of liquid hydrocarbons, mainly alkanes, occur in mines. The oily liquid trapped under rocky strota can be drilled out. This crude oily mixture of hydrocarbons obtained from the mine is called *crude oil* or *petroleum* (petra = rock, oleum = oil).

According to the accepted modern theory, natural petroleum is produced from plant and animal life in ocean. When alive, these absorb solar energy and synthesize organic compounds. The dead organisms settle down at the bottom. These are then decomposed by anaerobic bacteria in the absence of oxygen to form simpler molecules. The organic matter is covered by sand and with the passage of time a layer of rock is formed. A high temperature and pressure develops beneath the rocks. A series of chemical reactions (cracking, polymerization, cyclization et) occur. The product is petroleum.

**Q. What is the compositon of natural gas and petroleum?**

**Ans.** Natural gas is obtained from petroleum mines. It is composed primarily of methane (80%), ethane (13%), propane (3%), butane (1%) and nitrogen.

Petroleum is chiefly a mixtur of alkanes, cycloalkanes and aromatic hydrocarbons. The ratio of various components much depends on the origin of oil.

**Q. What is refining of crude oil?**

**Ans.** The crude oil from mine is a dark brown liquid having offensive odour. It consists of alkanes boiling between a wide range of temperatures. The oil is separated into useful fractions by distillation in a fractonating column. This process of dividing crude oil into a series of fractions with definite boiling ranges is called *refining.*

**Q. What is catalytic reforming?**

**Ans.** It is a process that converts alkanes and cycloalkanes into aromatic hydrocarbons.

**Q. What is knocking?**

**Ans.** In a motor car engine, a mixture of vaporized gasoline is ignited by a spark from the sparking plug. A high quality petrol burns uniformly and gives smooth performance of the engine. A poor quality petrol, on the other hand, explodes intermittently and causes knocking of the engine. This knocking is due to ignition of a portion of the gasoline in the cylinder head due to spontaneous oxidtion reactons rather than to the spark. It causes serious power loss, especially in high compression engines.

**Q. What is octane number? How is it determined?**

**Ans.** Experiments with pure compounds have shown that hydrocarbons of differing structures differ widely in knocking tendency. The relative antiknock tendency of a fuel is generally indicated by its ***octane number***. An arbitrary scale has been set up, with n-heptane, which knocks very badly, being given an octane numebr of zero, and 2,2,4-trimethylpentane (isooctane) being given the octane number of 100. Thus, a rating of 80 for a given fuel indicates that its degree of knocking in a standard test engine is that of a mixture of 80 parts iso-octane and 20 parts n-heptane.

Octane numbers as high as 115 have been obtained by addition of tetraethyl lead to iso-octane.

**Q. How octane number of petrol is boosted?**

**Ans.** The octane number of commercial petrol can be boosted by the following methods:

*(i)* By increasing the concentration of branched chain alkanes and aromatic hydrocarbons.

*(ii)* The octane number of petrol is also improved by the addition of tetraethyl lead which acts as antiknocking agent.

**Q. What is leaded gasoline?**

**Ans.** Gasoline containing tetraethyl lead.

**Q. How does tetraethyl lead work?**

**Ans.** Tetraethyl lead probably works by producing tiny particles of lead oxides, on whose surface certain rection chains are broken.

**Q. What are petrochemicals?**

**Ans.** Petrochemicals are organic compounds for which petroleum or natural gas is the ultimate raw materil. Thus natural gasoline (naphtha), natural gas and gas oil, provide the major starting materials for petrochemicals, e.g., paints, dyes, drugs, cosmetics, rubber, fertilizers, pesticides etc.

**Q.** **What is petroleum jelly?**

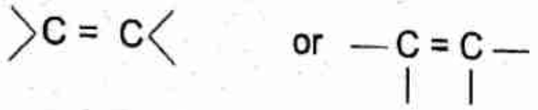
**Ans.** Petroleum jelly (vaseline) is a semisolid or liquid mixture of hydrocarbons derived by distillation of paraffin-base petroleum fractions. Its cheif uses are in mild ointments, cosmetics, as softner in rubber mixtures, and in food processing, protecting coating and defoaming agent.

**Q.** **What is asphalt?**

**Ans.** A dark-brown to black cementitious material which occurs as such or is obtained as residue in petroleum refining. It is used in roofing and road building.

**Q.** **What are alkenes?**

**Ans.** Alkenes are hydrocarbons that contain a carbon-carbon double bond. The characteristic functional group of alkene is



$$>C=C< \quad \text{or} \quad -\underset{|}{C}=\underset{|}{C}-$$

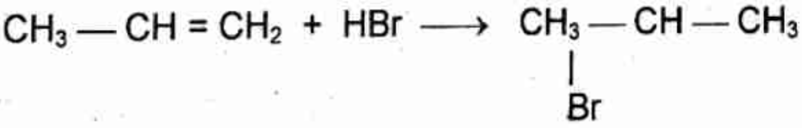
Their old name is *olefines* (meaning, oil producing) as ethylene formed an oily product with chlorine. Their general formula is $C_nH_{2n}$.

**Q.** **Why alkenes are far more reactive than alkanes?**

**Ans.** This is due to the presence of a carbon-carbon double bond. According to orbital model, a double bond is made of one sigma bond and one $\pi$ bond. In ethene $\pi$ bond is about 14.5 kcal $mol^{-1}$ weaker than a sigma bond. It therefore reguires less energy to break a $\pi$ bond than a sigma bond.

**Q.** **State Markovnikov's rule.**

**Ans.** In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the positive hydrogen goes to the double bond carbon attached to greater number of H-atoms.



$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

**Q.** **What is peroxide effect?**

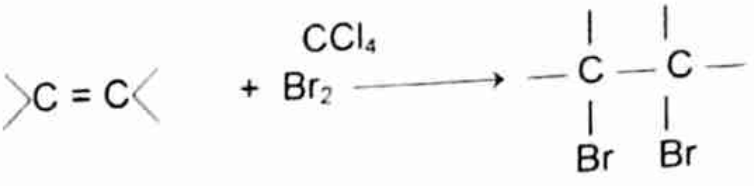
**Ans.** In the presence of peroxides, hydrogen bromide adds contrary to that product predicted by Markovnikov's rule. Thus propene yeilds:

$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2Br$$

Ordinarily propene gives isopropyl bromide. This anti-Markovnikov's addition caused by the presence of peroxides is called the *peroxide effect*.

**Q. How would you detect unsaturation in organic compounds?**

**Ans. 1. Bromine test.** Add to the substance a solution of bromine in CCl4. If it is an alkene (or alkyne) the dark red colour of the bromine solution will be at once discharged.

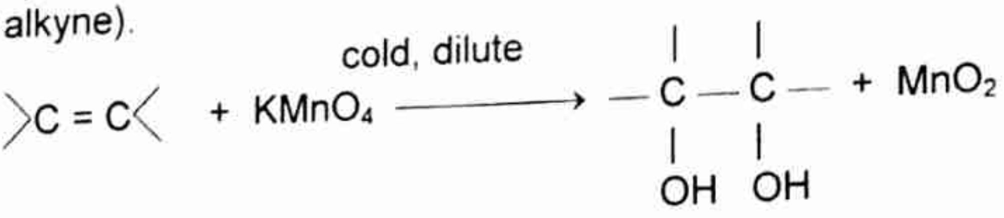


$$>C=C< + Br_2 \xrightarrow{CCl_4} -\underset{\underset{Br}{|}}{\overset{|}{C}}-\underset{\underset{Br}{|}}{\overset{|}{C}}-$$

(dark red) (colourless)

**2. Baeyer test**

Add a dilute alkaline solution of potassium permanganate to the substance. If the purple colour of the permanganate solution disappears and a brown precipitate of manganese dioxide, $MnO_2$, is obtained, the substance is an alkene (or alkyne).



$$>C=C< + KMnO_4 \xrightarrow{\text{cold, dilute}} -\underset{\underset{OH}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}- + MnO_2$$

(purple) (brown ppt)

**Q. What is Ziegler-Natta catalyst?**

**Ans.** It is a mixture of triethyl aluminium ($(C_2H_5)_3Al$) and titanium tetrachloride ($TiCl_4$). Under the influence of this catalyst, ethylene polymerizes to produce polyethylene of exceptional physical properties.

**Q. What are alkynes?**

**Ans.** Alkynes are unsaturated hydrocarbons that contain a carbon-carbon triple bond ($C \equiv C$). The general formula for alkynes is $C_nH_{2n-2}$.

**Q. How acetylene is prepared in the laboratory?**

**Ans.** In the laboratory, acetylene is prepared by adding water to calcium carbide.

$$CaC_2 + H_2O \longrightarrow CH \equiv CH + Ca(OH)_2$$

**Q. How would you distinguish between acetylene and ethylene?**

**Ans.** When acetylene is passed into a ammonical solution of silver nitrate or cuprous chloride, we get insoluble acetylides of silver or copper. Ethylene does not give these tests. So this reaction is used as a visual test to distinguish between acetylene and ethylene.

$$HC \equiv CH + 2Ag^{+} \xrightarrow{2NH_3} Ag-C \equiv C-Ag + 2NH_4^{+}$$

(white ppt)

$$HC \equiv CH + 2Cu^+ \xrightarrow{2NH_3} \underset{\text{(red ppt.)}}{Cu - C \equiv C - Cu} + 2NH_4^+$$

**Q. Give some uses of acetylene.**

**Ans.** Acetylene is used:

*(i)* for illumination in lamps

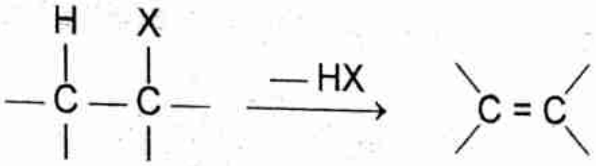
*(ii)* for producing oxy-acetylene flame

*(iii)* for artificial ripening of fruit and vegatables

*(iv)* for manufacture of ehtylene, acetaldehyde, vinyl chloride etc.

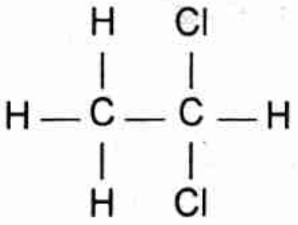
**Q. Define dehydrohalogenation reaction.**

**Ans.** It is a reaction in which a H-atom and a X(Cl, Br, I) atom is removed or eliminated from adjacent carbons. The product is an alkene.



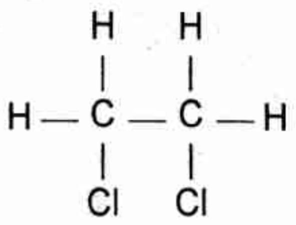
**Q. Explain the difference between gem-dihalides and vic-dihalides.**

**Ans.** The compounds in which two halogens are attached to the same carbon atom, are known as *gem-dihalides*. The compounds in which the two halogens are attached to adjacent carbon atoms are known as *vic-dihalides*.



$$\begin{array}{c} H \quad Cl \\ | \quad\; | \\ H - C - C - H \\ | \quad\; | \\ H \quad Cl \end{array}$$

(a gem dihalide)



$$\begin{array}{c} H \quad H \\ | \quad\; | \\ H - C - C - H \\ | \quad\; | \\ Cl \quad Cl \end{array}$$

(a vic. dihalide)

**Q. Why chloroform is not used as anaesthetic now-a-days?**

**Ans.** Once it was widely used as anaesthetic. Due to its toxic effects on heart and lever, it has been now replaced by other safer anaesthetics.

**Q. Why chloroform is stored in dark coloured bottles?**

**Ans.** Chloroform is stored in dark-coloured bottles filled up to the stopper to prevent the formation of $COCl_2$ (phosgene) which is highly poisonous. In the presence of air and light, it is oxidized to carbonyl chloride.

$$CHCl_3 + \frac{1}{2} O_2 \xrightarrow[\text{air}]{\text{light}} COCl_2 + HCl$$

**Q. What are Grignard Reagents? Mention their synthetic uses.**

**Ans.** Grignard reagents are the compounds that contain an alkyl group attached to a magnesium atom which is joined to a halogen atom.

$$R - Mg - X \qquad (X = Cl, Br, I)$$

They are named as *alkylmagnesium halides*. Alkylmagnesium halides are commonly called *Grignard reagents*. They were discovered by French Chemsit Victor Grignard (Nobel Prize 1912). These reagents are amongst the most useful synthetic reagents in organic chemistry. They react with a number of other reagents to form alkanes, alkenes, alkynes, alcohols, aldehydes, ketones and carboxylic acids. For example.

$CH_3 — Mg — I$ $\qquad$ $CH_3 — CH_2 — Mg — I$

**Q. How would you distinguish between 1°, 2° and 3° alcohols?**

**Ans.** The following tests are used for distinguishing between primary (1°), secondary (2°) and tertiary (3°) alcohol.

**1. Lucas Test**

The unknown alcohol is added to concentrated HCl containing anhy. $ZnCl_2$. The insoluble alkyl chloride appears as a cloud in the reaction mixture.

$$R — OH + HCl \xrightarrow[\text{room temp.}]{ZnCl_2} \underset{\text{cloud}}{R — Cl} + H_2O$$

The time taken for the cloud to appear depends on the type of alcohol.

A tertiary alcohol produces chloudiness immediately.

A secondary alcohol produces cloudiness after 5 minutes.

A primary alcohol produces cloudiness upon heating.

**2. Dichromate Test**

The alcohol is treated with sodium dichromate and sulphuric acid at room temperature. Since a 1° alcohol is oxidized to carboxylic acid and a 2° alcohol to ketone, they change the colour of the reaction mixture from orange ($Cr_2O_7^{2-}$) to green ($Cr^{3+}$). Tertiary alcohol is not oxidized and the colour remains unchanged.

**Q. What is wood alcohol? Give its uses.**

**Ans.** At one time, methyl alcohol was prepared from wood. Therefore it is also called wood alcohol. It is used:

*(i)* as a solvent,

*(ii)* for denaturing ethyl alcohol,

*(iii)* for the manufacture of methyl chloride, methylamine, formaldehyde etc., and

*(iv)* as antifreeze for automobile radiators.

**Q. What is absolute alcohol? How it is obtained?**

**Ans.** Absolute alcohol is 100% ethyl alcohol. The commerical alcohol (methylated spirit) is 95% ethyl alcohol and 5% water. This mixture boils at 71.1°C while pure ethyl alcohol boils at 78.5°C.

Quicklime is added to commercial alcohol which is refluxed for eight hours. It is then distilled to get absolute alcohol.

$$(CH_3CH_2OH + H_2O) + CaO \xrightarrow{\Delta} CH_3CH_2OH + Ca(OH)_2 \downarrow$$

**Q. What is denatured alcohol?**

**Ans.** Heavy excise duty is levied by the government on the sale of alcoholic beverages. But for industrial purposes, alcohol is sold duty free. Therefore to render the commercial alcohol unfit for drinking, it is *'denatured'*. This is done by the addition of poisonous substances such as methyl alcohol and pyridine. Thus denatured alcohol is rectified spirit containing methyl alcohol or pyridine and a blue colour.

**Q. Give some uses of ethyl clcohol.**

**Ans.** Ethyl alcohol is used:

*(i)* as a petrol additive to improve octane number,

*(ii)* as antiseptic to sterilize wounds as it kills germs,

*(iii)* as a solvent for drugs, oils and fats, cosmetics, varnishes, etc;

*(iv)* as a constituent of wines, beer and other alcoholic beverages,

*(v)* for preparation of acetaldehyde, ethyl chloride, ehtyl acetate and acetic acid.

**Q. What is formalin?**

**Ans.** Formalin is 40% aqueous solution of formaldehyde. It is used as disinfectant to sterilize surgical instruments, gloves etc and as preservative for anatomical specimens.

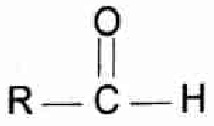
**Q. What is the difference between stereoselective and stereospecific reaction.**

**Ans.** A stereoselective reaction is a reaction that yields predominantly one enantiomer of a possible pair or one diastereomer of several possible diastereomers.

A stereospecific reaction is one in which stereochemically different molecules react differently.

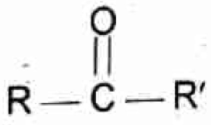
**Q. Compare aldehydes with ketones.**

**Ans.** Both aldehydes and ketones bear a marked structural similarity.



$R-\overset{\overset{O}{\parallel}}{C}-H$

an aldehyde



$R-\overset{\overset{O}{\parallel}}{C}-R'$

a ketone

They have R — CO — in common and thus the reactions due to this part of the molecule are common to both classes of the compounds. The difference in behaviour is obviously due to the fact that the very reactive H-atom in aldehydes has been replced by a relatively inert alkyl group, R′, in ketones. Thus the reducing properties of aldehydes are missing in ketones.

| | **Aldehydes** | **Ketones** |
|---|---|---|
| 1. | Upon oxidation yield a carboxylic acid with same number of C-atoms. | Upon drastic oxidation yield carboxylic acid with less number of C-atoms. |
| 2. | Reduce ammonical silver nitrate, Fehling's solution and Benedict's solution. | Do not reduce these reagents. |
| 3. | React with alcohols to form hemiacetals and acetals. | No reactoion. |
| 4. | Polymerize. | Do not polymerize. |

**Q. What is visual test for aldehydes and ketones?**

**Ans. 2,4-DNPH Test.** Both aldehydes and ketones form coloured precipitates when treated with 2,4-dinitro-phenylhydrazine (2,4-DNPH). This is used as a test for distinguishing them from other classes of compounds.

**Q. How would you distinguish between 1°, 2° and 3° amines?**

**Ans.** Primary (1°), secondary (2°) and tertiary (3°) amines may be distinguished from each other by the following visual tests.

### 1. Hinsberg Test

Take a small amount of the amine and benzenesulphonyl chloride ($C_6H_5SO_2Cl$) in a test tube. Add excess of NaOH solution and shake.

*(i)* ***A clear solution*** indicates a 1° amine. Add dil. HCl. If ppt. is formed, 1° amine is confirmed.

*(ii)* ***A precipitate*** insoluble in dil. HCl indicates a 2° amine.

*(iii)* ***No visible change*** confirms 3° amine.

### 2. Nitrous Acid Test

Dissolve a little amine in dil. HCl in a test tube. Cool it by immersing in ice-bath. Add to it cold sodium nitrite solution gradually with shaking.

*(i)* If $N_2$ gas is evolved (bubbles seen arising in solution), it is a 1° amine.

*(ii)* If a yellow oily layer separates in solution, it is a 2° amine.

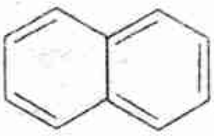
*(iii)* If there is no visible change and the unchanged amine dissolves to give a clear solution, it is a 3° amine.

## Q. Explain aromaticity and Huckel rule.

**Ans.** Benzene is highly unsaturated as it contains three alternate doube bonds in a six-carbon ring. However, unlike alkenes, it readily undergoes substitution reactions instead of addition reactions. This peculiar behaviour of benzene and structurally related compounds is referred to as *aromatic charcter* or *aromticity*. The aromatic character of benzene is attributed to its stability due to the complete delocalization of six π electrons over the entire ring.

The *Huckel rule* may be stated as: A cyclic conjugated system that consists of $(4n + 2)\pi$ electrons will show aromatic character provided n is a whole number integer 1, 2, 3, etc.

aromatic



aromatic

nonaromatic

## Q. Discuss the directive effect of substituents.

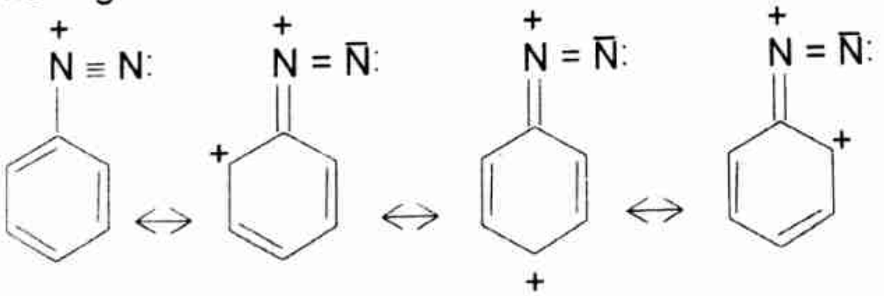
**Ans.** In aromatic disubstitution, the substituent already present on the benzene ring determines the position of the second entering group. This is regardless of the nature of the entering group. The effect by which substitutent directs the orientation of the incoming group on the ring, is referred to as the *Directive effect*. The directing substituents can be divided into two types:

(*i*) **Ortho-Para Directors.** — OH, — OR, — $NH_2$, — NHR, — $NR_2$, — X, — R, etc.

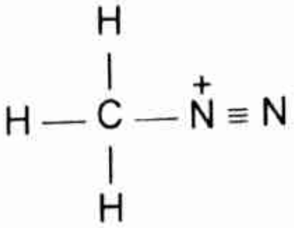
(*ii*) **Meta Directors.** — $NO_2$, — $SO_3H$, — COOH, — CHO, — COR, — CN, etc.

## Q. Why aromatic diazonium salts are stable?

**Ans.** Aromatic diazonium salts are stable, while the aliphatic ones are highly unstable. The stability of the former is attributed to resonance involving the benzene ring.



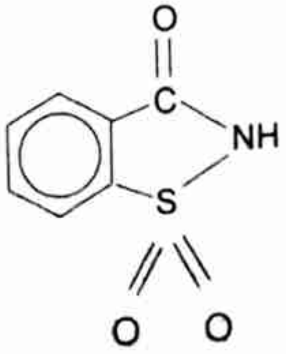
The aliphatic diazonium salts are unstable, because the alkyl group ($CH_3$ —) is incapable of participating in resonance.



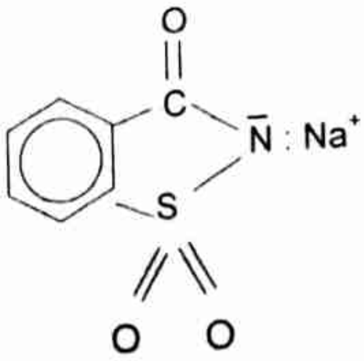
$$H-\underset{H}{\overset{H}{C}}-\overset{+}{N}\equiv N$$

**Q. What is saccharin?**

**Ans.** Saccharin is the imide of o-sulphobenzoic acid. It is 500 times sweeter than table sugar and is placed in the market as soluble sodium salt.



Saccharin

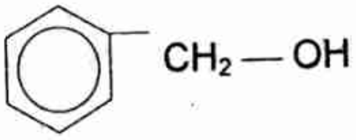


Sodium saccharin

**Q. What are phenols?**

**Ans.** They are derivatives of aromatic hydrocarbons in which a ring hydrogen has been replaced by — OH group. An aromatic hydroxy compound having the — OH on the side chain, and not on the ring, behaves like aliphatic alcohol. It is called an *aromatic alcohol.*

Phenol

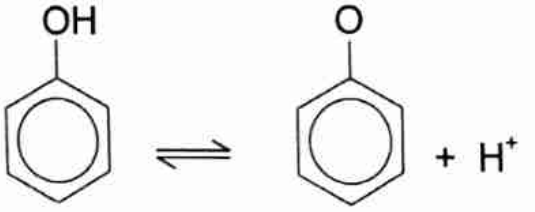


Benzyl alcohol

**Q. Discuss the acidity of phenols.**

**Ans.** The characteristic property which differentiates phenols from aliphatic alcohols is acidity. Phenols are weakly acidic and turn blue litmus paper red. Alcohols, on the other hand, are less **acidic** than water.

$$R—OH \rightleftharpoons R—\bar{O} + H+ \qquad Ka = \sim 10–18$$



$K_a = 1.28 \times 10^{-10}$

Phenol is acidic because it ionizes to form a stable *phenoxide ion* $C_6H_5\bar{O}$, which is stabilized by resonance. In alkoxide ion, no resonance is possible. This makes the alkoxide ion unstable which suppresses the acidity of alcohols.

**Q. Compare phenol with alcohol.**

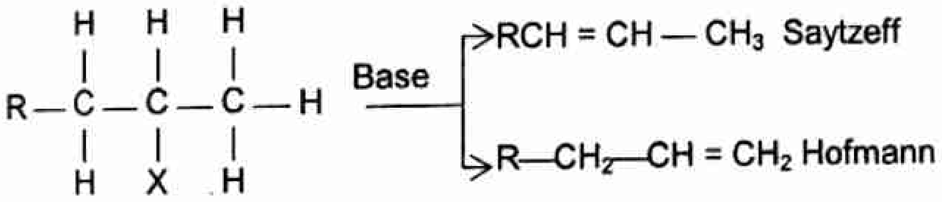
**Ans.** In general, phenols give the same reactions as alcohols at the — OH group. Thus these undergoe alkylation and acylation like alcohols. The differences in the behaviour of the two classes of the compounds are due to the presence of benzene ring in phenol instead of alkyl group in alcohols.

| | **Phenol** | **Alcohol** |
|---|---|---|
| 1. | Acidic to litmus. | Neutral to litmus. |
| 2. | Farms salts with aq. NaOH. | Forms salt with Na-metal. |
| 3. | Produces violet colour with neutral $FeCl_3$ solution. | No reaction. |
| 4. | Does not react with HBr. | Forms ethyl bromide. |
| 5. | Readily undergoes ring substitution reactions. | Does not undergo substitution in the alkyl group. |
| 6. | Forms azo dyes with diazonium salts. | No such reaction. |

**Q. Explain the Hofmann and Saytzeff Rules.**

**Ans.** In many substrates, there are available more than one β-carbon atoms and, therefore, more than one olefins are possible to form. The question arises which olefin will be formed under a given set of conditions. The direction of elimination is governed by two rules.

According to *Saytzeff rule* H is removed from that carbon which has fewer hydrogen atoms bonded to it. On the other hand *Hofmann rule* is said to operate when H is removed from the β-carbon which is richer in hydrogens.



The Saytzeff product dominates when

(*i*) R = an aryl group or RCO —

(*ii*) X in the substrate is halogen and

(*iii*) the base is small sized.

The Hofmann elimination will dominate when the size of the base is large and/or X in the substrate is large sized.

**Q. What are alkaloids?**

**Ans.** The alkaloids may be defined as basic compounds of vegetable origin in which at least one nitrogen atom form a part of a cyclic system. Examples are nicotine, quinine, caffeine, morphine etc.

**Q.** **What are terpenes?**

**Ans.** Terpenes are open chain acyclic or cyclic hydrocarbons whose molecular formulae are sum multiple of $C_5H_8$. Terpenes embrace a vast family of chemical compounds which are isolated chiefly from essential oils and resins of plants. The name terpenes was given for the compounds present in essential oils since an important member of the compounds was found in terpentine oil.

**Q.** **What are essential oils?**

**Ans.** Natural oils obtained by steam distillation of the flowers, fruits, leaves and stems of plants of some families. Such oils have characteristic fragrant odour and hence are called essential oils.

**Q.** **What are steroids?**

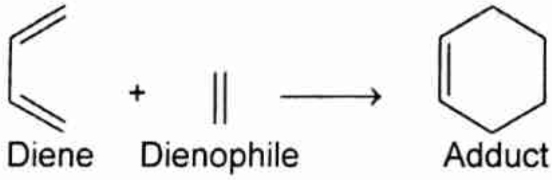
**Ans.** Steroids are a group of polycyclic compounds closely related biochemically to terpenes. They include cholesterol numerous hormones, precursors of certain vitamins, bile acids, alcohols (sterols) and certain natural drugs and poisons.

**Q.** **What is cholesterol?**

**Ans.** Cholesterol is a kind of alcohol called *sterol.* It is a notorious substance deposited on the walls of arteries and as chief constituent of gallstones.

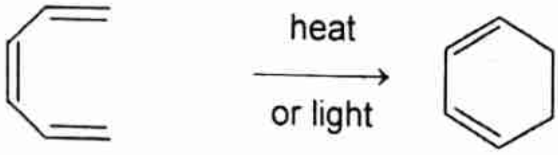
**Q.** **What are cycloaddition reactions?**

**Ans.** A cycloaddition reaction is a reaction in which two unsaturated molecules combine to form a cyclic compound, with $\pi$ electrons being used to form two new $\sigma$ bonds. The Diels-Alder reaction is a [4 + 2] cycloaddition.



**Q.** **Explain electrocyclic reactions.**

**Ans.** In electrocyclic reactions, a conjugated polyene can undergo isomerization to form a cyclic compound with a single bond between the terminal carbons of the original conjugated system, one double bond disappears, and the remaining double bonds shift their positions.



The reverse process can also take place, a single bond is broken and a cyclic compound yields an open chain polyene.

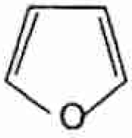
Such interconversions are known as *Electrocyclic reactions*.

**Q. Explain the term antiaromatic.**

**Ans.** Planer conjugated carbocyclic polyenes that are especially less stable than their open chain analogue are called antiaromatic.

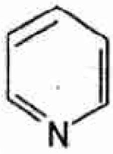
**Q. What are heterocyclic compounds?**

**Ans.** Heterocyclic compounds are cyclic compounds that contain two or more different elements as ring members, the commonest being nitrogen, oxygen, and sulphur. They are compounds containing five or six membered heterocyclic ring systems of stable nature with conjugated double bonds.



Furan

Thiophene



Pyridine

**Q. Benzene gives a negative test with $KMnO_4$ although it has got three double bonds. Why?**

**Ans.** The three double bonds of benzene are made by sharing of p-orbitals. These bonds are delocalized in such a manner that no actual double bond exists in benzene ring, thereby giving a negative test with $KMnO_4$.

**Q. Define diazotization.**

**Ans.** Diazotizatin is a reaction which involves the formation of a diazonium compound by the action of $HNO_2$ on primary aromatic amine.

**Q. Phenols and carboxylic acids, both are acidic towards litmus solution. How can they be distinguished?**

**Ans.** Both carboxylic acids and phenols change blue litmus to red, but phenol is a weak acid as compared to carboxylic acid. When $NaHCO_3$ solution is added to phenol, it does not evolve $CO_2$ while carboxylic acids evolve $CO_2$ with effervescence.

**Q. What is meant by derivative? Why it is prepared?**

**Ans.** A derivative is usually a solid material which can readily be prepared from the unknown and can easily be isolated and purified. This is prepared for the confirmation of a given compound.

**Q. What is the difference between a dye and an indicator?**

**Ans.** A dye is a coloured substance which can be made to adhere to fabrics such as cotton, silk or linen. An indicator is a substance which is used to indicate by its colour change the physicochemical condition of a reaction.

**Q. What are azo colours?**

**Ans.** These are a class of dyes which contain $—N=N—$ group linked to two aromatic nuclei.

**Q. What are hygroscopic substances?**

**Ans.** These are the substances which attract moisture from the atmosphere.

**Q. What is Lassaigne test?**

**Ans.** In Lassaigne test the organic compound is fused with sodium metal to convert nitrogen, sulphur, and halogens (if present) into sodium cyanide, sulphide or halides respectively. These ionic compounds are water soluble and give *individual tests* for ions.

## 2.6. Important Conversions in Organic Chemistry

**1. Ethylene to ethane**

$$CH_2=CH_2 + H_2 \xrightarrow[250°]{Ni} CH_3—CH_3$$

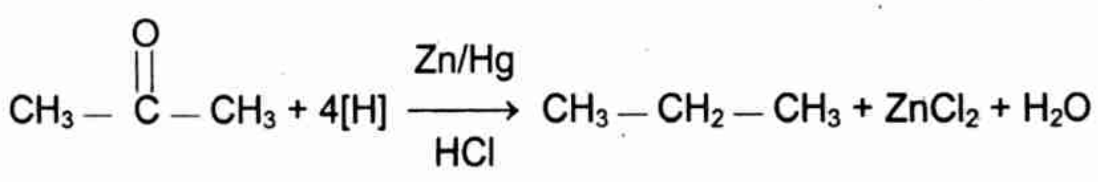
**2. Methyl iodide to methane**

$$CH_3—I + 2[H] \xrightarrow[\text{or Zn/Cu}]{LiAlH_4} CH_4 + HI$$

**3. Methyl iodide to ethane**

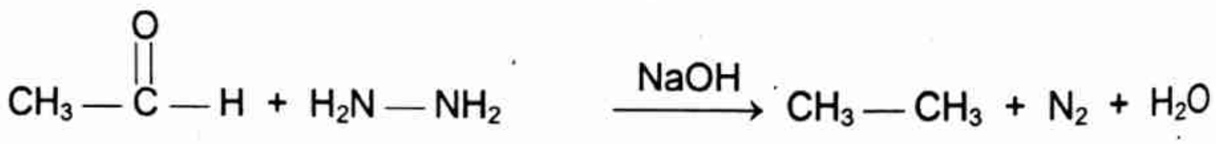
$$2CH_3—I + 2Na \xrightarrow{\text{Ether}} CH_3—CH_3 + 2NaI$$

**4. Acetone into propane**



$$CH_3—\overset{\overset{\displaystyle O}{||}}{C}—CH_3 + 4[H] \xrightarrow[HCl]{Zn/Hg} CH_3—CH_2—CH_3 + ZnCl_2 + H_2O$$

**5. Acetaldehyde into ethane**



$$CH_3—\overset{\overset{\displaystyle O}{||}}{C}—H + H_2N—NH_2 \xrightarrow{NaOH} CH_3—CH_3 + N_2 + H_2O$$

### 6. Ethyl alcohol into ethylene

$$CH_3\,CH_2\,OH \xrightarrow[170^\circ]{H_2SO_4} CH_2=CH_2 + H_2O$$

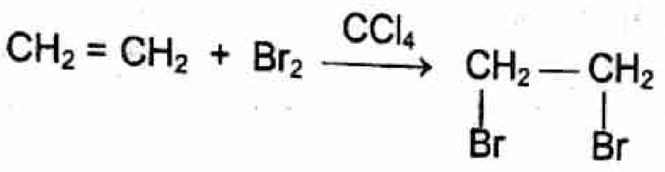
### 7. Propyl bromide to propene

$$CH_3\,CH_2\,CH_2\,Br + KOH \xrightarrow{\text{Alcohol}} CH_3-CH=CH_2 + KBr + H_2O$$

### 8. Propane into propene

$$CH_3\,CH_2\,CH_3 \xrightarrow[500^\circ]{Al_2O_3} CH_3-CH=CH_2 + H_2$$

### 9. Ethylene into 1,2-dibromoethane (Vicinal dihalide)



$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

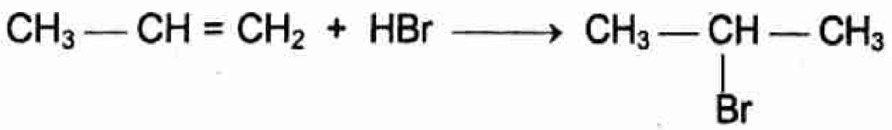
### 10. Ethylene to ethyl bromide

$$CH_2=CH_2 + HBr \xrightarrow{CCl_4} CH_3-CH_2-Br$$

### 11. Propene to 1-bromopropane

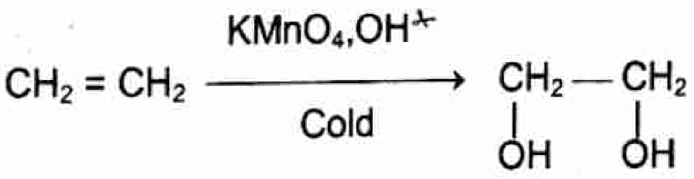
$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2\,Br$$

### 12. Propene to 2-bromopropane



$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH_3$$

### 13. Ethylene into glycol

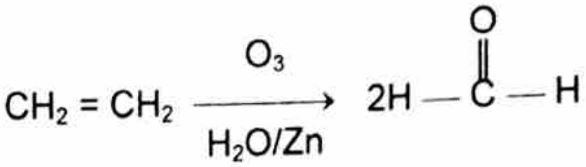


$$CH_2=CH_2 \xrightarrow[\text{Cold}]{KMnO_4,OH^-} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

### 14. Ethylene to ethanol

$$CH_2=CH_2 + H_2O \xrightarrow[240^\circ]{H^+} CH_3\,CH_2\,OH$$

**15. Ethylene to formaldehyde**

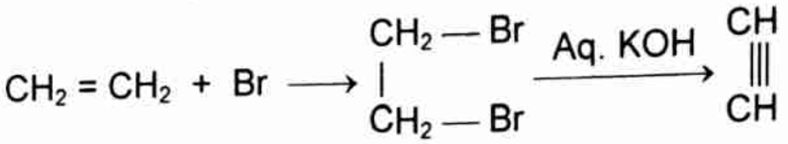


$$CH_2 = CH_2 \xrightarrow[H_2O/Zn]{O_3} 2H-\overset{\overset{O}{\|}}{C}-H$$

**16. Methane into acetylene**

$$2CH_4 \xrightarrow{2700^\circ} HC \equiv CH + 3H_2$$

**17. Ethylene to acetylene**

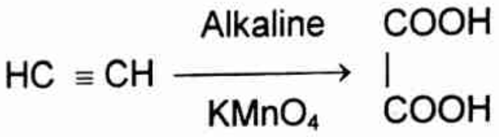


$$CH_2 = CH_2 + Br \longrightarrow \begin{array}{l} CH_2-Br \\ | \\ CH_2-Br \end{array} \xrightarrow{Aq.\ KOH} \begin{array}{c} CH \\ ||| \\ CH \end{array}$$

**18. Acetylene to acetic acid**

$$HC \equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3\,CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

**19. Acetylene to oxalic acid**



$$HC \equiv CH \xrightarrow[KMnO_4]{Alkaline} \begin{array}{l} COOH \\ | \\ COOH \end{array}$$

**20. Acetylene to ethane**

$$HC \equiv CH + H_2 \xrightarrow{Pt} CH_3-CH_3$$

**21. Acetylene to benzene**

$$3HC \equiv CH \xrightarrow[tube]{Red\ hot} C_6H_6$$

**22. Ethane to ethyl chloride**

$$CH_3-CH_3 + Cl_2 \xrightarrow{400^\circ} CH_3\,CH_2\,Cl + HCl$$

**23. Ethyl alcohol to ethyl chloride/bromide**

$$CH_3\,CH_2\,OH + HCl \xrightarrow{ZnCl_2} CH_3\,CH_2\,Cl + H_2O$$

$$CH_3\,CH_2\,OH + HBr \longrightarrow CH_3\,CH_2\,Br + H_2O$$

**24. Ethyl bromide to ethyl alcohol**

$$CH_3\,CH_2\,Br + NaOH \xrightarrow[boil]{H_2O} CH_3\,CH_2\,OH + NaBr$$

**25. Ethyl bromide to diethyl ether**

$$CH_3\,CH_2\,Br + C_2H_5\overset{-}{O}\overset{+}{Na} \xrightarrow{Boil} CH_3\,CH_2 - O - CH_2\,CH_3 + NaBr$$

**26. Alkyl halide to amines**

$$R - X + NH_3 \xrightarrow{heat} R - NH_2 + HX$$

$$R - X + R - NH_2 \longrightarrow R_2NH + HX$$

$$R - X + R_2NH \longrightarrow R_3N + HX$$

**27. Alkyl halide to Grignard reagents**

$$R - X + Mg \xrightarrow{dry\ ether} R - MgX$$

**28. Ethyl bromide to ehtylbenzene**

$$C_6H_6 + CH_3CH_2Br \xrightarrow{AlCl_3} C_6H_5 - CH_2\,CH_3 + HBr$$

**29. Methylmagnesium iodide to acetic acid**

$$CH_3 - MgI + CO_2 \xrightarrow{H_2O} CH_3COOH$$

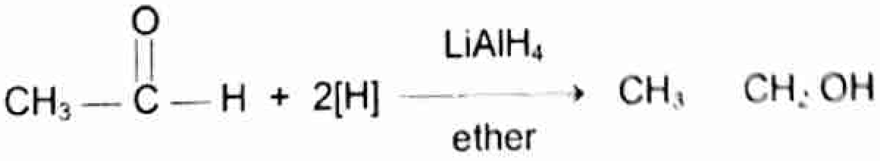
**30. Methylmagnesium iodide to methane**

$$CH_3 - MgI + H_2O \longrightarrow CH_4$$

**31. Methylmagnesium iodide to ethanol**

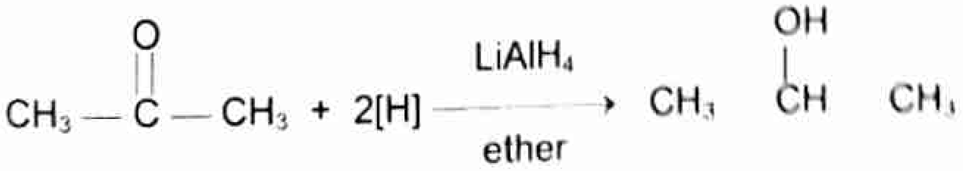
$$CH_3 - MgI + H_2C = O \xrightarrow{H_2O} CH_3\,CH_2\,OH$$

**32. Aldehyde into primary alcohol**



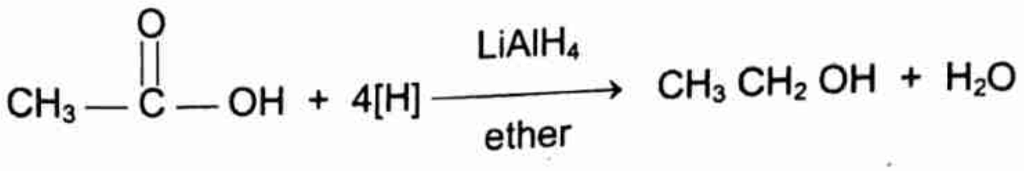
$$CH_3 - \overset{\overset{O}{\|}}{C} - H + 2[H] \xrightarrow[ether]{LiAlH_4} CH_3 \quad CH_2\,OH$$

**33. Ketone into secondary alcohol**



$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 2[H] \xrightarrow[ether]{LiAlH_4} CH_3 \quad \overset{\overset{OH}{|}}{CH} \quad CH_3$$

**34. Acetic acid into ethyl alcohol**



$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 4[H] \xrightarrow[ether]{LiAlH_4} CH_3\,CH_2\,OH + H_2O}$$

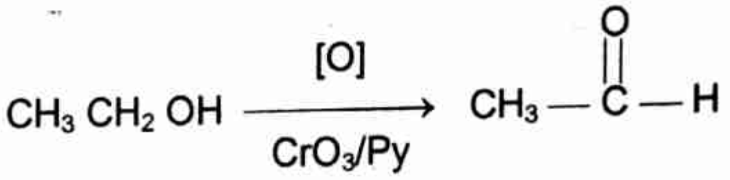
**35. Ethyl alcohol into ethyl acetate**

$$\mathrm{C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O}$$

**36. Ethyl alcohol to acetic acid**

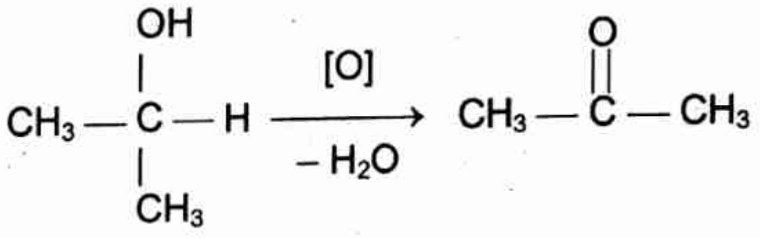
$$\mathrm{CH_3\,CH_2\,OH \xrightarrow[Na_2Cr_2O_7/H_2SO_4]{[O]} CH_3COOH}$$

**37. Ethyl alcohol to acetaldehyde**



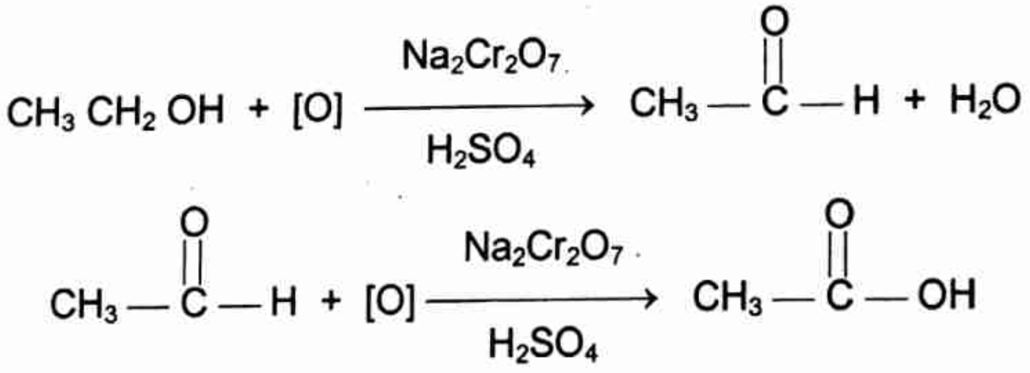
$$\mathrm{CH_3\,CH_2\,OH \xrightarrow[CrO_3/Py]{[O]} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

**38. Isopropyl alcohol to acetone**



$$\mathrm{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H \xrightarrow[-H_2O]{[O]} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

**39. Ethyl alcohol to acetic acid**



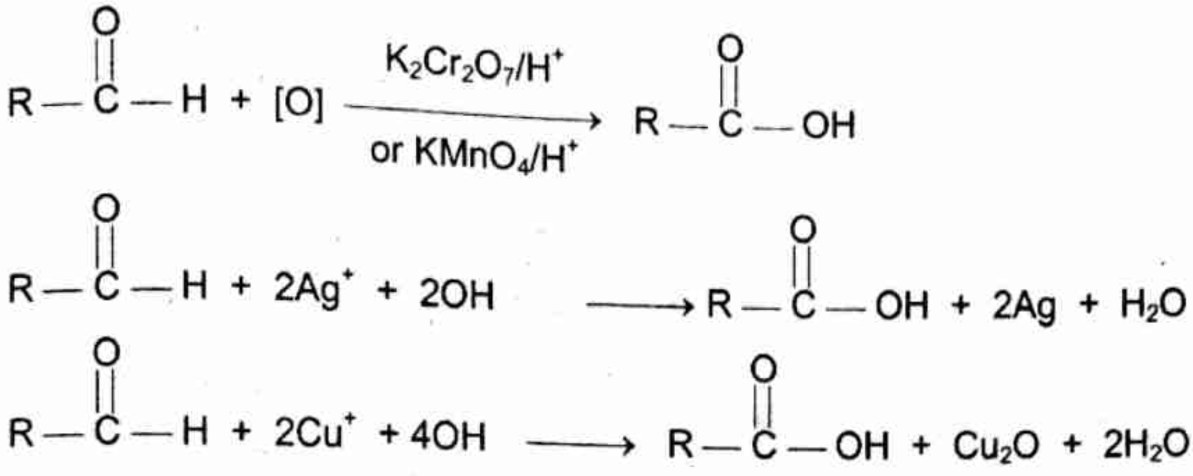
$$\mathrm{CH_3\,CH_2\,OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O}$$

$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

**40. Ethyl alcohol to ether**

$$\mathrm{2C_2H_5OH \xrightarrow[140^\circ]{H_2SO_4} C_2H_5-O-C_2H_5 + H_2O}$$

### 41. Aldehyde into carboxylic acid

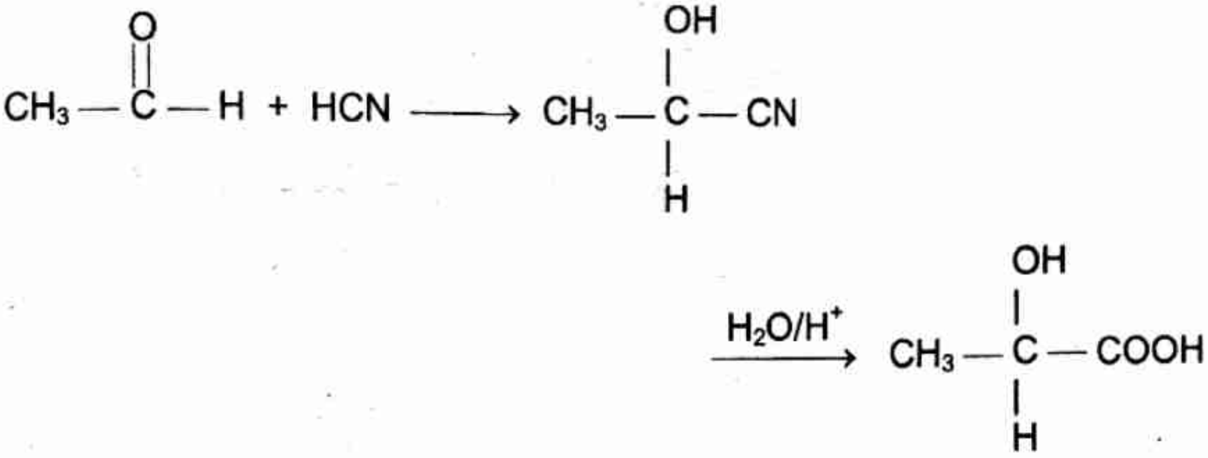


$$R-\overset{\overset{O}{\|}}{C}-H + [O] \xrightarrow[\text{or } KMnO_4/H^+]{K_2Cr_2O_7/H^+} R-\overset{\overset{O}{\|}}{C}-OH$$

$$R-\overset{\overset{O}{\|}}{C}-H + 2Ag^+ + 2OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + 2Ag + H_2O$$

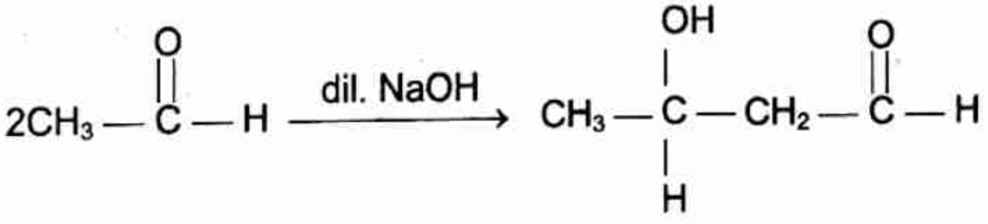
$$R-\overset{\overset{O}{\|}}{C}-H + 2Cu^+ + 4OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + Cu_2O + 2H_2O$$

### 42. Acetaldehyde into lactic acid



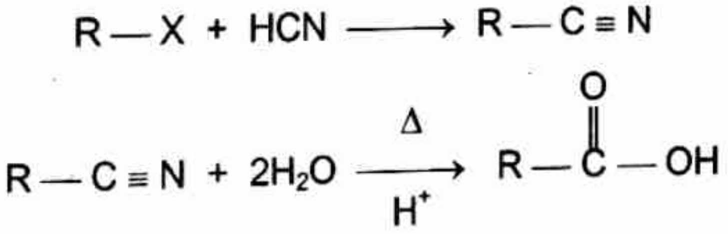
$$CH_3-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CN \xrightarrow{H_2O/H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-COOH$$

### 43. Aldehyde into aldol



$$2CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{dil. NaOH}} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

### 44. Alkyl halide into carboxylic acid



$$R-X + HCN \longrightarrow R-C\equiv N$$

$$R-C\equiv N + 2H_2O \xrightarrow[H^+]{\Delta} R-\overset{\overset{O}{\|}}{C}-OH$$

### 45. Ester into carboxylic acid

$$CH_3COOC_2H_5 + NaOH \xrightarrow{\Delta} CH_3COO^-Na^+ + C_2H_5OH$$

$$CH_3COO^-Na^+ + HCl \longrightarrow CH_3COOH + NaCl$$

**46. Alkene to carboxylic acid**

$$CH_3-C\equiv C-CH_3 + 4[O] \xrightarrow[\Delta]{KMnO_4,\ OH^-} 2CH_3COOH$$

**47. Acetic acid into sodium acetate**

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

**48. Acetic acid into acetyl chloride**

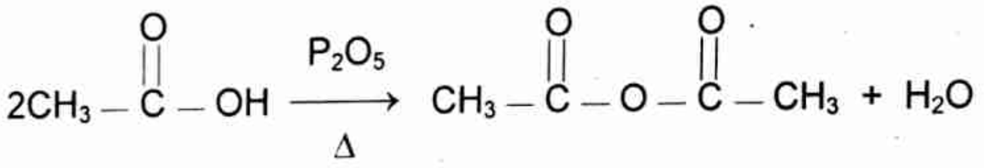
$$CH_3COOH + SOCl_2 \xrightarrow{\Delta} CH_3COCl + SO_2 + H_2O$$

$$CH_3COOH + PCl_5 \xrightarrow{\Delta} CH_3COCl + POCl_3 + HCl$$

**49. Acetic acid into ethyl acetate**

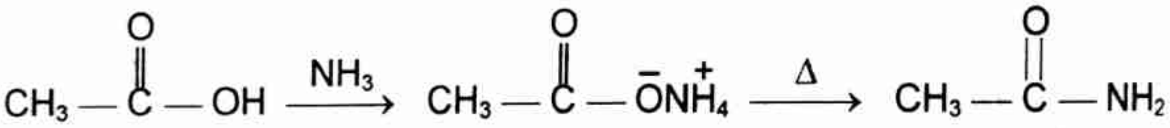
$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

**50. Acetic acid into acetic anhydride**



$$2CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\Delta]{P_2O_5} CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

**51. Acetic acid into acetamide**



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{NH_3} CH_3-\overset{\overset{O}{\|}}{C}-\bar{O}\overset{+}{N}H_4 \xrightarrow{\Delta} CH_3-\overset{\overset{O}{\|}}{C}-NH_2$$

**52. Acetic acid to methane and ethane**

$$CH_3COOH \xrightarrow{NaOH} CH_3COO^-Na^+ \xrightarrow[\Delta]{NaOH} CH_4 + Na_2CO_3$$

$$2CH_3COO^- \xrightarrow{\text{at anode}} CH_3-CH_3 + 2CO_2 + 2e^-$$

**53. Acetic acid to trichloroacetic acid**

$$CH_3COOH + Cl_2 \xrightarrow{\text{red P}} Cl_3C\ COOH + HCl$$

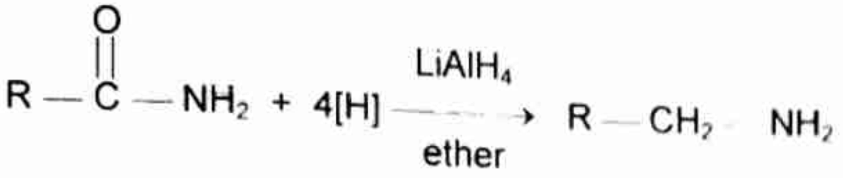
**54. Nitroethane to ethyl amine**

$$CH_3\ CH_2\ NO_2 + 3H_2 \xrightarrow{Pt} CH_3\ CH_2\ NH_2 + 2H_2O$$

### 55. Nitrile to amine

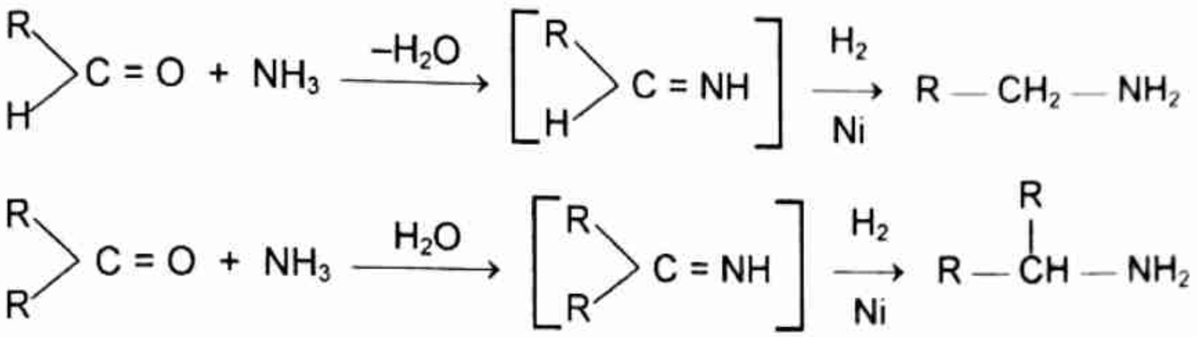
$$R-C\equiv N + 4[H] \xrightarrow[\text{ether}]{LiAlH_4} R-CH_2-NH_2$$

### 56. Amide to amine



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + 4[H] \xrightarrow[\text{ether}]{LiAlH_4} R-CH_2-NH_2$$

### 57. Aldehyde and ketone to amine



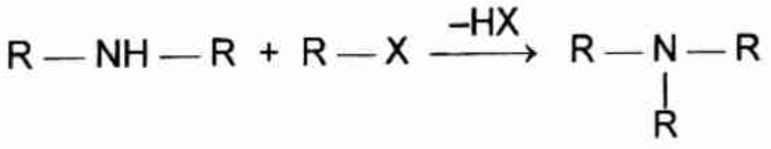
$$R(H)C=O + NH_3 \xrightarrow{-H_2O} \left[R(H)C=NH\right] \xrightarrow[Ni]{H_2} R-CH_2-NH_2$$

$$R_2C=O + NH_3 \xrightarrow{H_2O} \left[R_2C=NH\right] \xrightarrow[Ni]{H_2} R-\underset{}{\overset{R}{\overset{|}{C}}}H-NH_2$$

### 58. Primary amine to secondary amine

$$RNH_2 + R-X \xrightarrow{-HX} R-NH-R$$

### 59. Secondary amine to tertiary amine

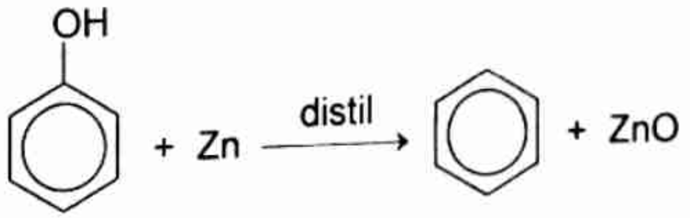


$$R-NH-R + R-X \xrightarrow{-HX} R-\underset{\underset{\displaystyle R}{|}}{N}-R$$

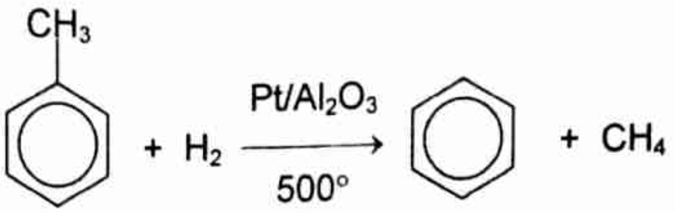
### 60. Amine into alcohol

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2/HCl} R-OH + N_2 + H_2O$$

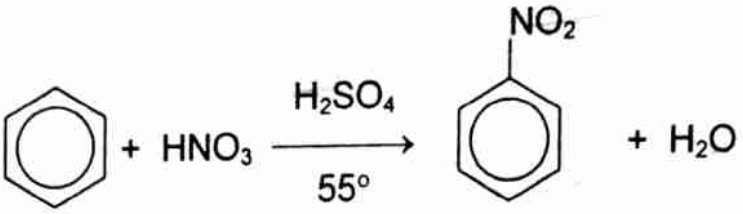
### 61. Phenol to benzene



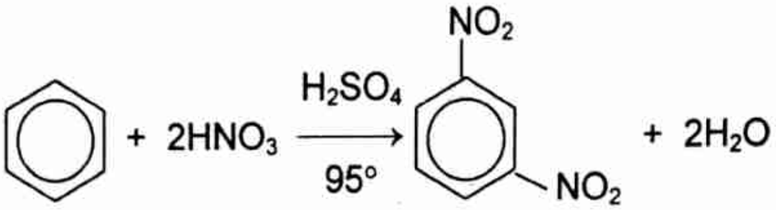
### 62. Toluene to benzene



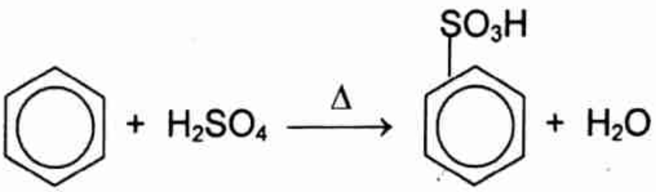
### 63. Benzene to nitrobenzene



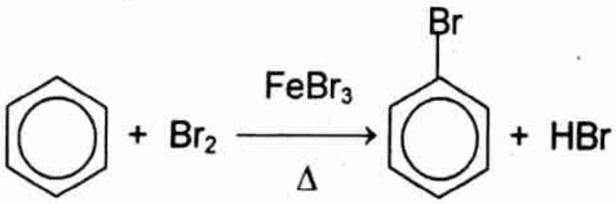
### 64. Benzene to m-dinitrobenzene



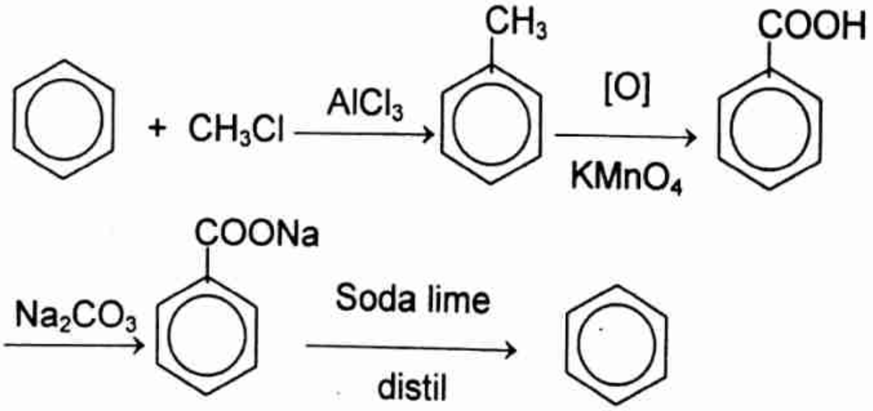
### 65. Benzene to benzene sulphonic acid



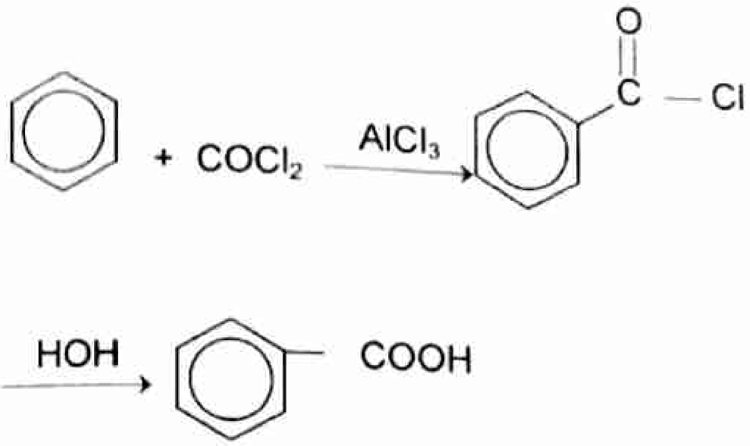
### 66. Benzene to bromobenzene



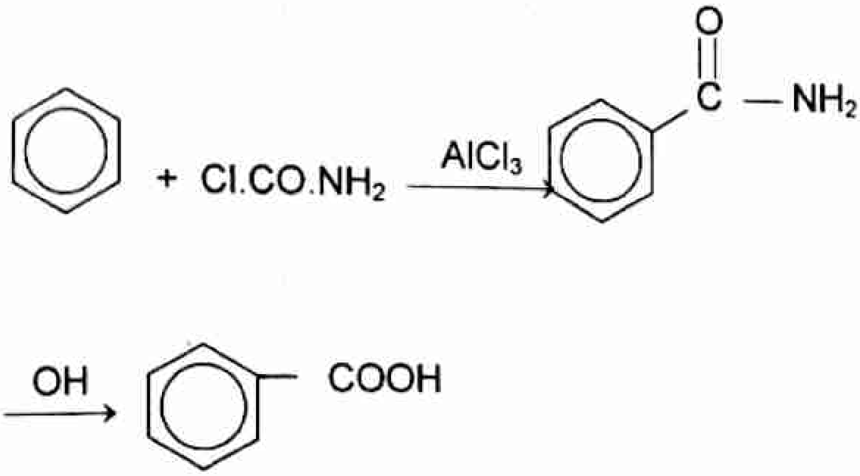
### 67. Benzene to toluene and vice versa



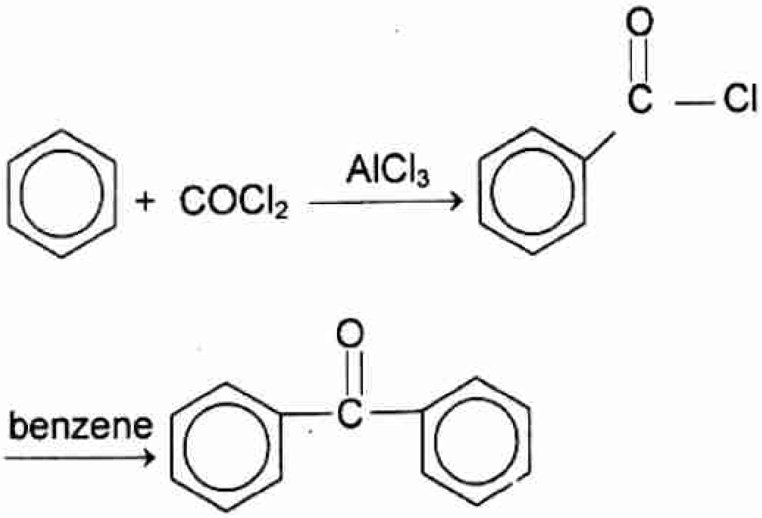
### 68. Benzene to benzoyl chloride and benzoic acid



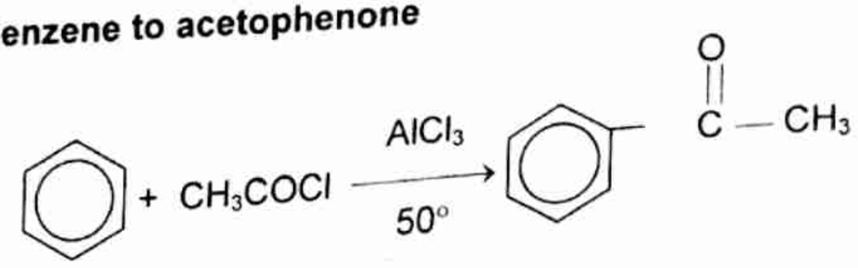
### 69. Benzene to benzamide and benzoic acid



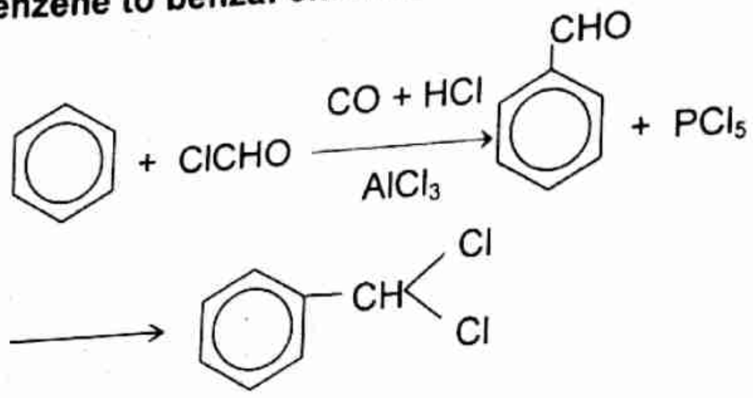
### 70. Benzene to benzophenone



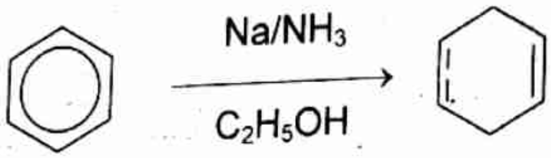
### 71. Benzene to acetophenone



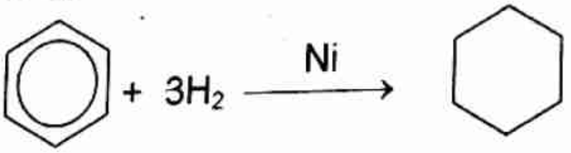
### 72. Benzene to benzal chloride



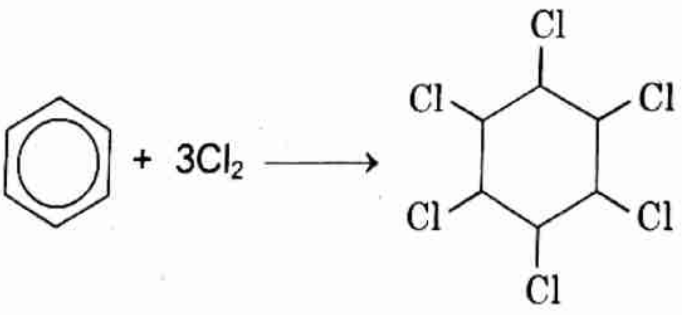
### 73. Benzene to 1,4-dihydrobenzene



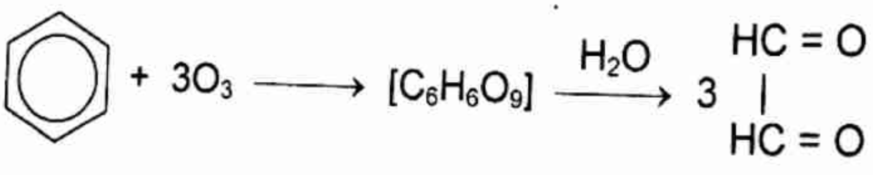
### 74. Benzene to cyclohexane



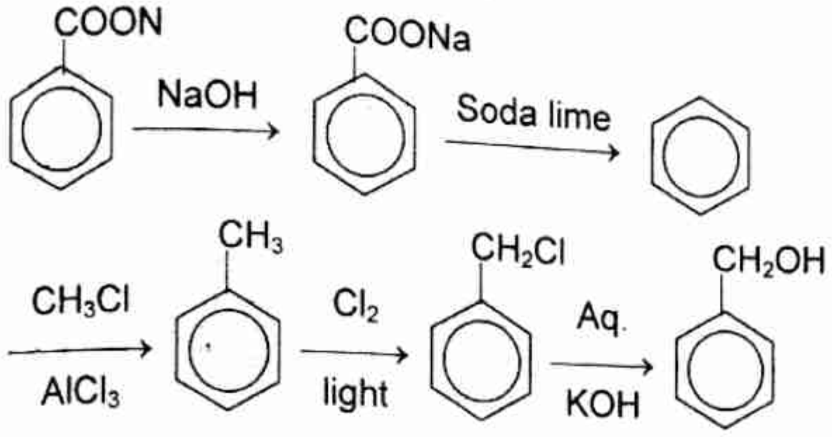
### 75. Benzene to benzene hexachloride



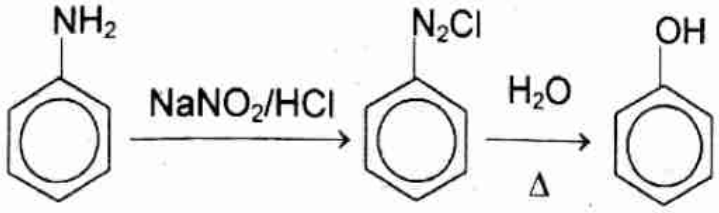
### 76. Benzene to glyoxal



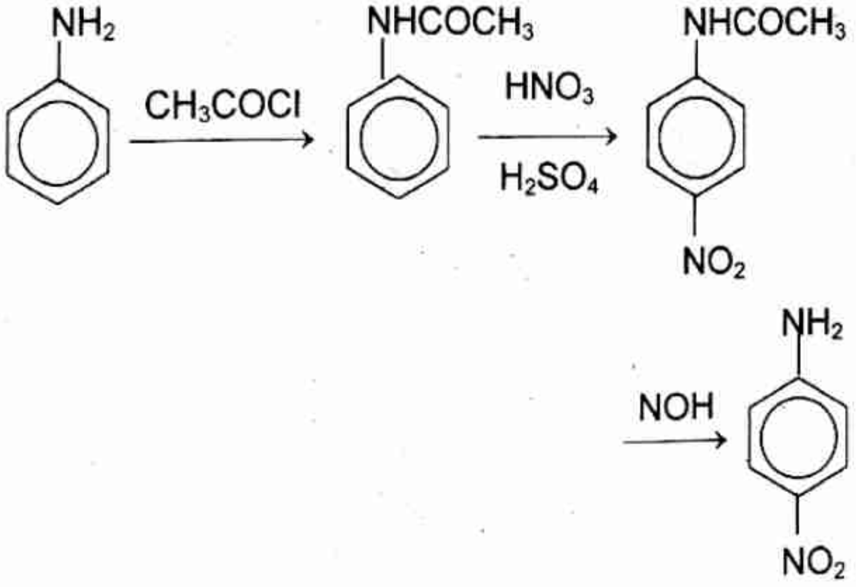
### 77. Benzoic acid to benzyl alcohol



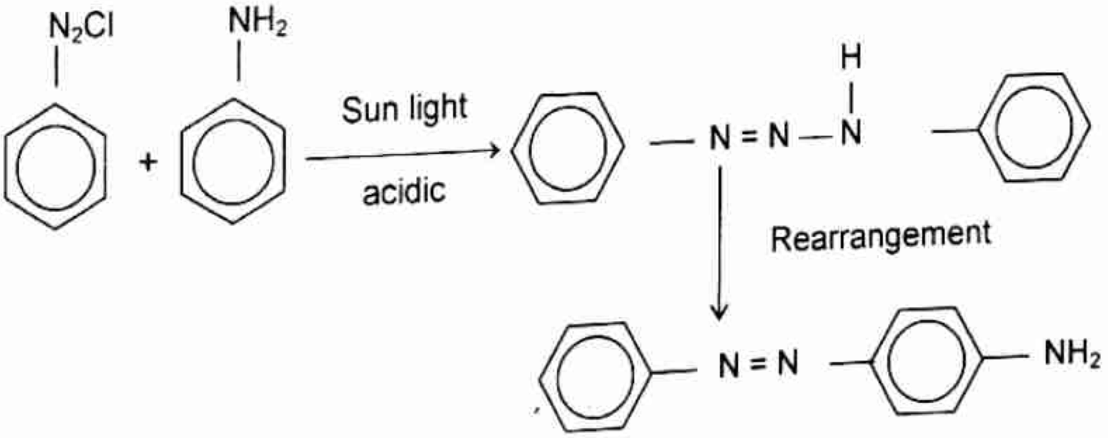
### 78. Aniline to phenol



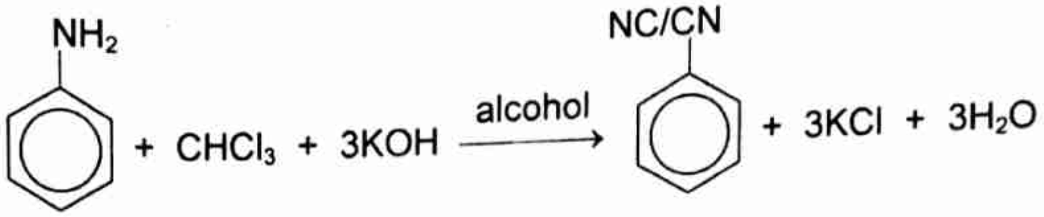
### 79. Aniline to p-nitroaniline



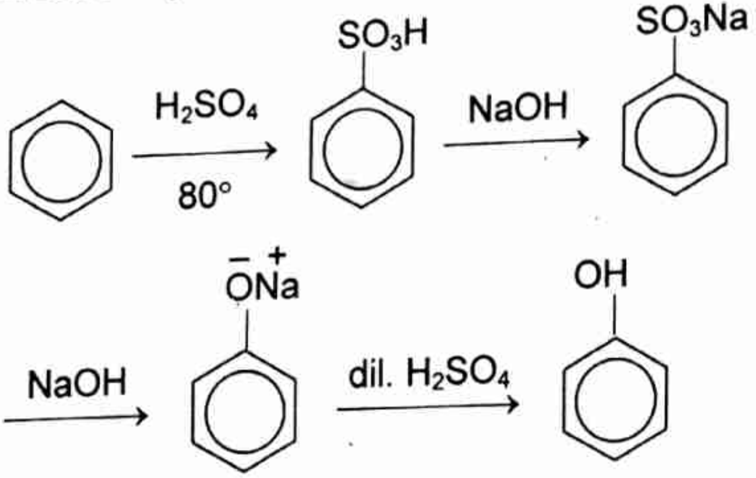
### 80. Aniline to p-aminoazobenzene



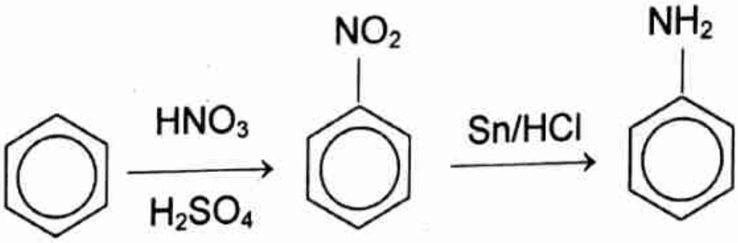
### 81. Aniline to phenyl isocyanide



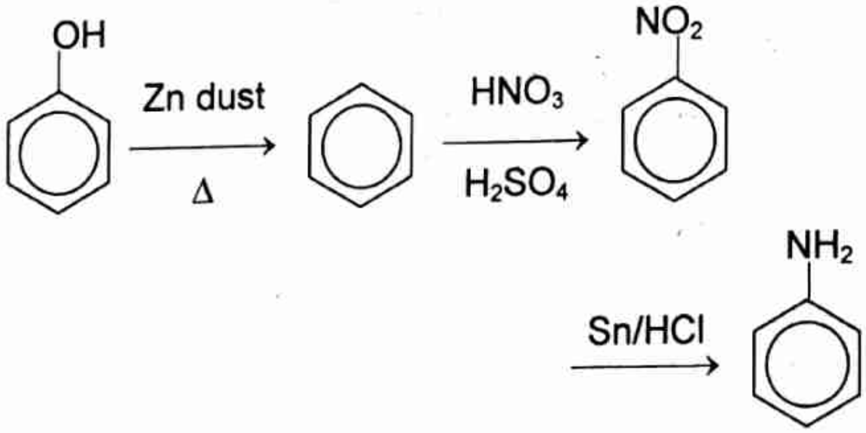
### 82. Benzene to phenol



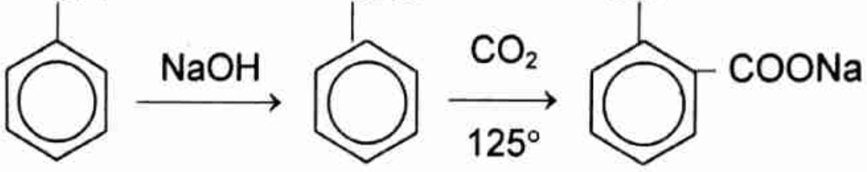
### 83. Benzene to aniline

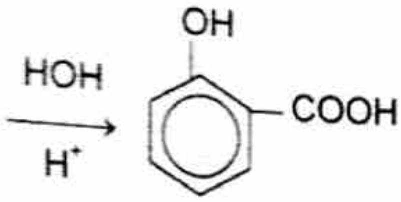


### 84. Phenol to aniline

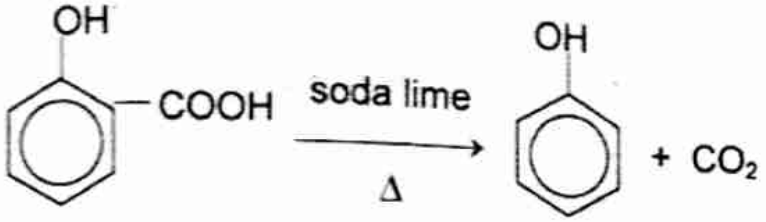


### 85. Phenol to salicylic acid

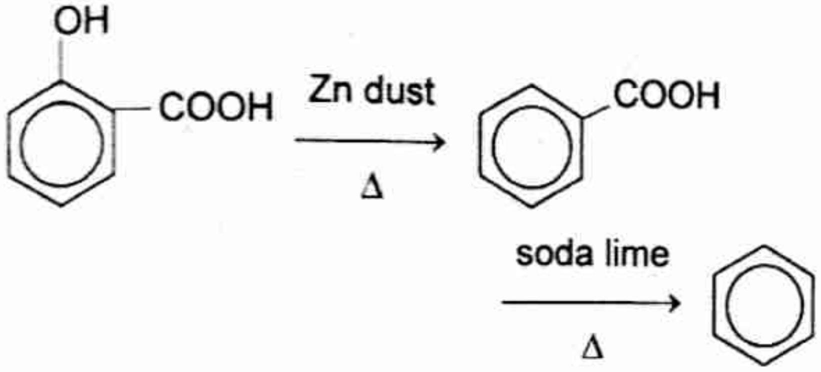




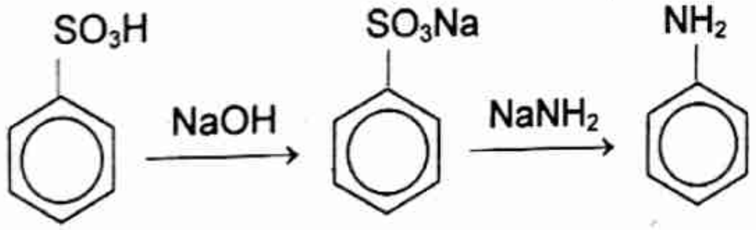
### 86. Salicylic acid to phenol



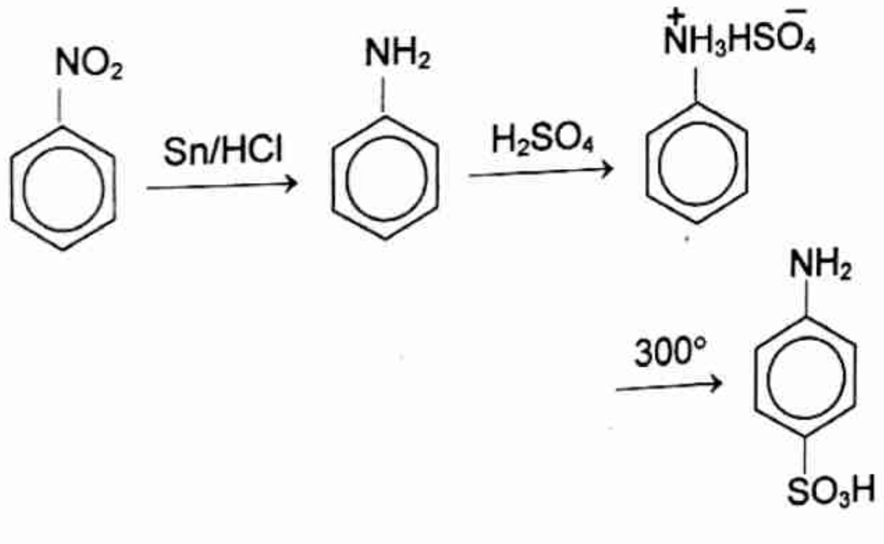
### 87. Salicylic acid to benzene



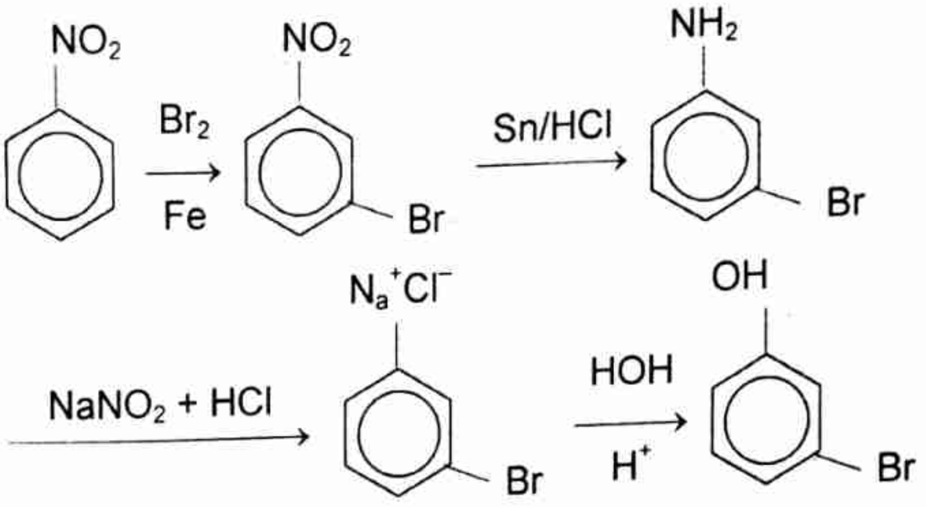
### 88. Benzene sulphonic acid to aniline



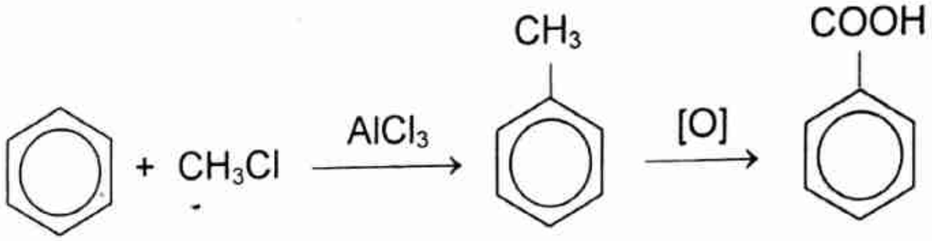
### 89. Nitrobenzene to sulphanilic acid



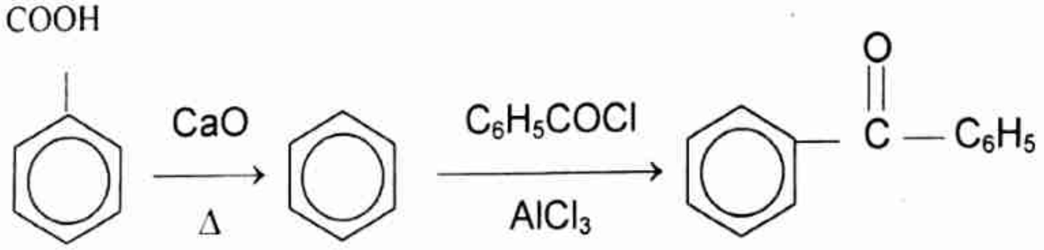
**90. Nitrobenzene to m-bromophenol**



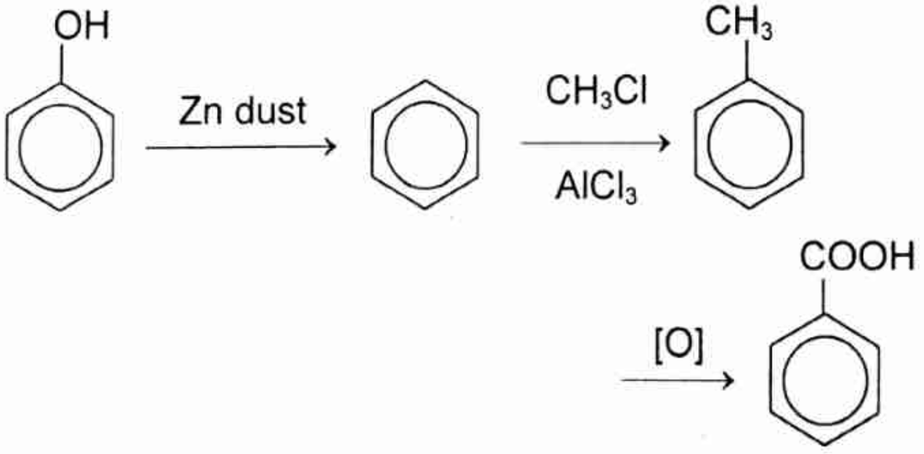
**91. Benzene to benzoic acid**



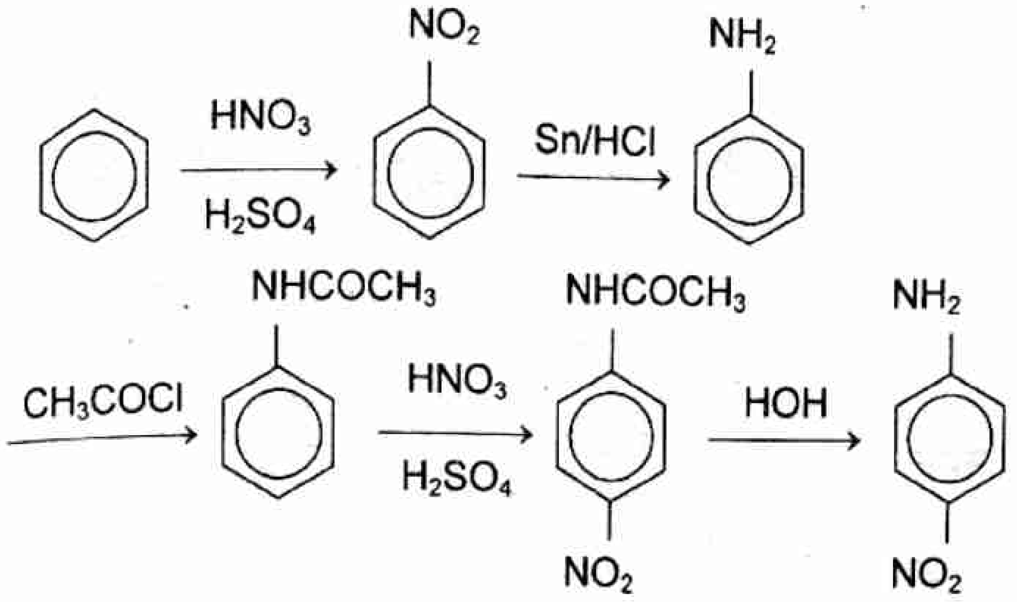
**92. Benzoic acid to benzophenone**



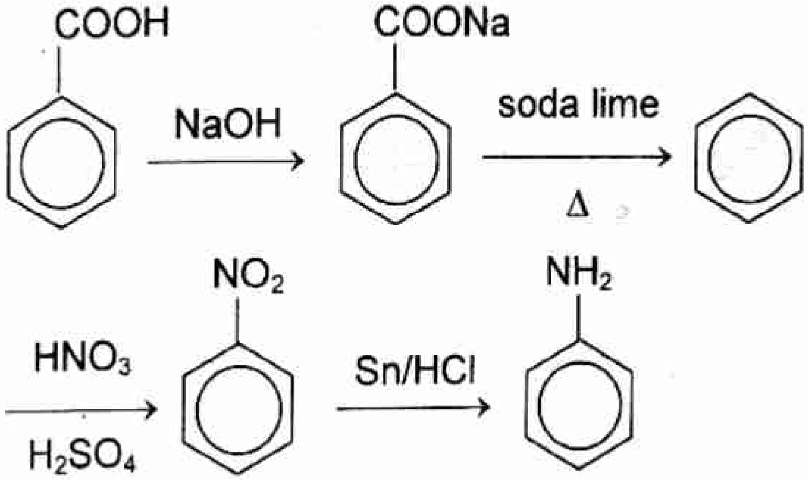
**93. Phenol to benzoic acid**



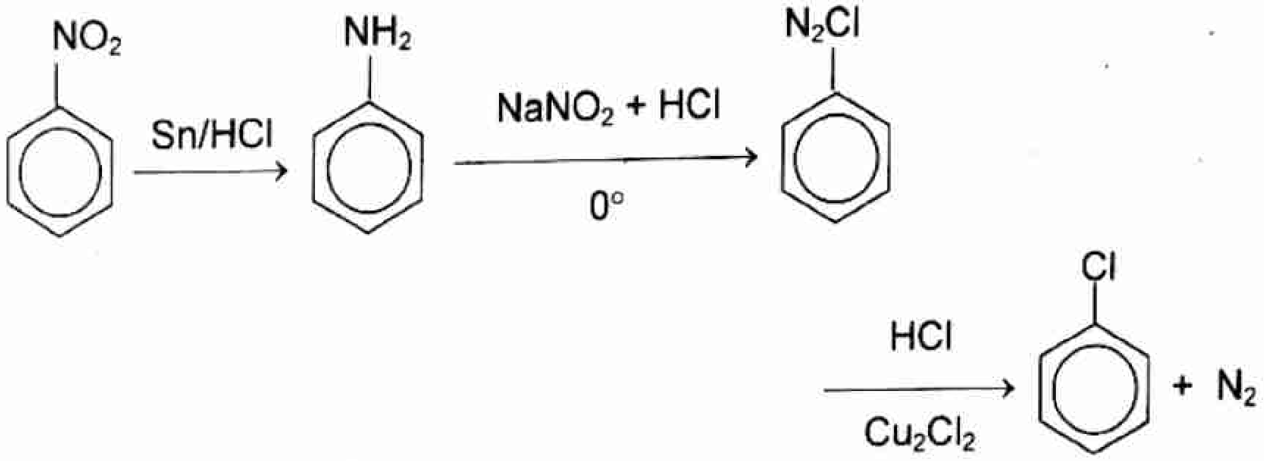
### 93. Benzene to p-nitroaniline



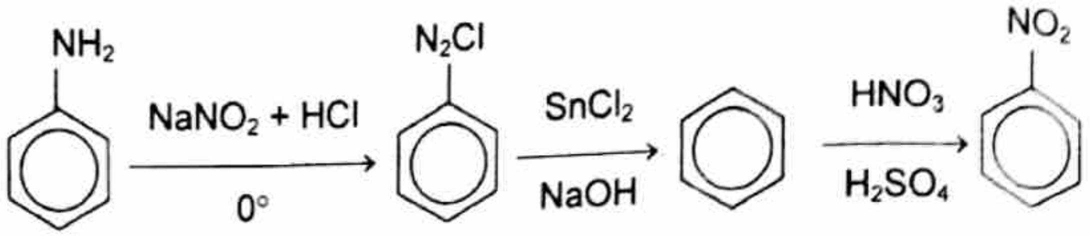
### 94. Benzoic acid to aniline



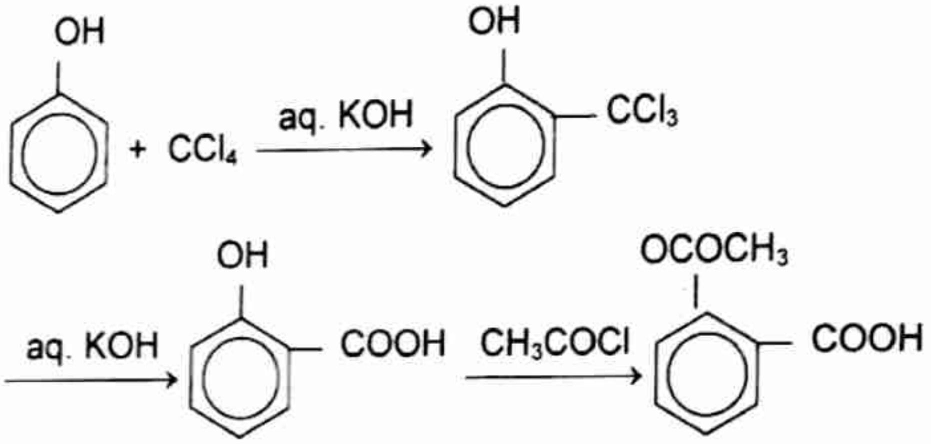
### 95. Nitrobenzene to chlorobenzene



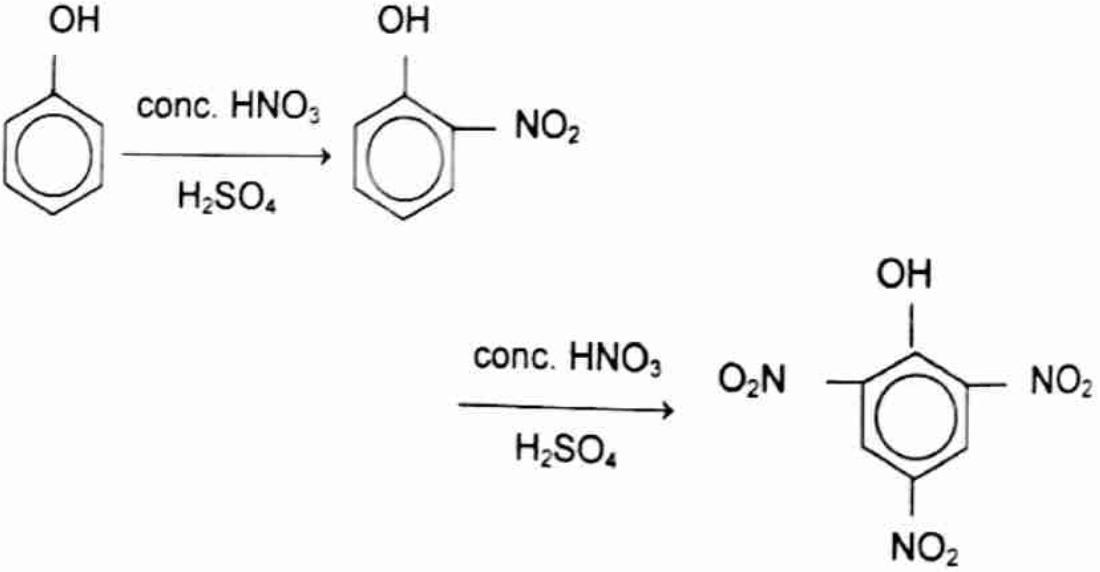
**96. Aniline to nitrobenzene**



**97. Phenol to aspirin**



**98. Phenol to picric acid**



# 2.7. Some Important Name Reactions

## 1. Aldol Condensation

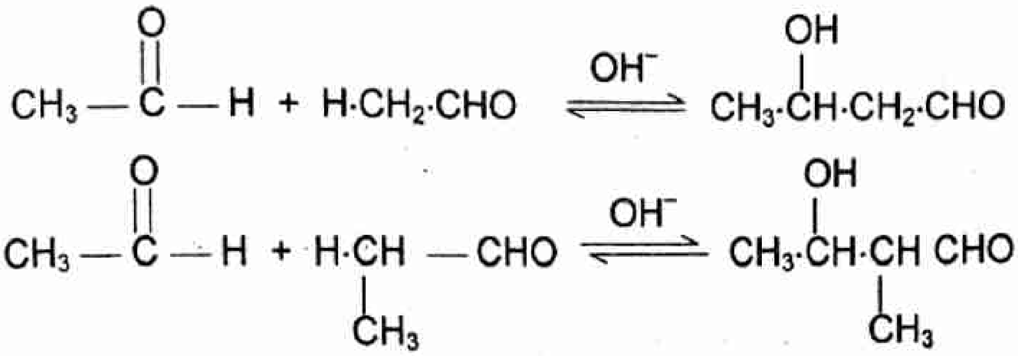
Carbonyl compounds containing at least one α-hydrogen, when warmed with dilute alkali, undergo self-addition reaction known as *aldol condensation.* The aldol condensation can occur

(*i*) between two aldehydes (identical or different);

(*ii*) between two ketones (identical or different); and

(*iii*) between an aldehyde and a ketone.

Whatever be the nature of carbonyl compound, it is only he α-H atoms which are involved in the aldol conversation.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + H\cdot CH_2\cdot CHO \overset{OH^-}{\rightleftharpoons} CH_3\cdot\overset{\overset{OH}{|}}{C}H\cdot CH_2\cdot CHO$$

$$CH_3-\overset{\overset{O}{\|}}{C}-H + H\cdot\underset{\underset{CH_3}{|}}{C}H-CHO \overset{OH^-}{\rightleftharpoons} CH_3\cdot\overset{\overset{OH}{|}}{C}H\cdot\underset{\underset{CH_3}{|}}{C}H\ CHO$$

## 2. Bouveault-Blanc Reduction

Louis Bouveault and Gustav Blanc (1903) presented a method for the preparation of alcohols. The method is known as *Bouveault-Blanc reduction.* This technique consists in the reduction of esters, aldehydes and ketones into alcohols, by refluxing with excess of sodium and ethanol, e.g.,

1. Esters

$$R\cdot COOCH_3 \xrightarrow{[H]} R\cdot CH_2\cdot OH$$

2. Aldehydes

$$R\cdot CHO \xrightarrow{[H]} R\cdot CH_2\cdot OH$$

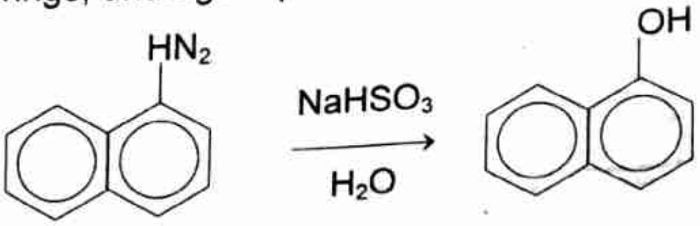
3. Ketones

$$R\cdot CO\cdot R \xrightarrow{[H]} R\cdot CHOH\cdot R$$

## 3. Bucherer Reaction

The replacement of an amino group by a hydroxyl group in the presence of aqueous sulphite or bisulphite is known as *Bucherer reaction.*

This reaction is practically confined to only naphthalene derivatives and resorcinol. Dihydroxyl or diamino naphthalenes in which two groups are present in different rings, undergo replacement of only one group.



### 4. Cannizzaro Reaction

Aldehydes containing no α-H, when treated with aqueous or ethanolic alkali undergo disproportionation to a salt of corresponding acid and alcohol. This simultaneous oxidation and reduction of aldehydes is known as *Cannizzaro reaction.*

$$2HCHO + NaOH \xrightarrow[\text{room temp.}]{} CH_3OH + HCOO^-Na^+$$

$$2C_6H_5CHO + NaOH \xrightarrow[\text{room temp.}]{} C_6H_5CH_2OH + C_6H_5COO^-Na^+$$

### 5. Claisen Condensation

The Claisen condensation consists of the reaction of an ester having hydrogen on the α-carbon atom with an active methylene compound (such as esters, aldehydes, ketones, nitriles) in the presence of certain bases (e.g., sodium ethoxide).

The preparation of ethyl acetoacetate by the self condensation of ethyl acetate in the presence of sodium ethoxide forms a classical example of Claisen condensation.

$$CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-Na^+} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

### 6. Claisen-Schmidt Reaction (Claisen Reaction)

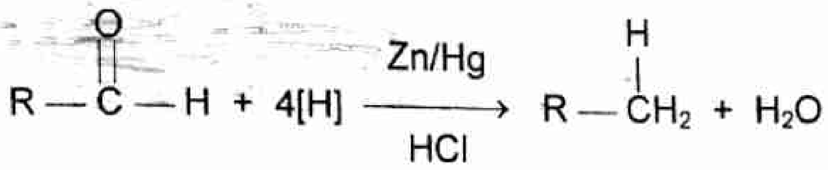
The Claisen-Schmidt reaction consists of the condensation between an aromatic aldehyde or ketone having no active hydrogen and aliphatic aldehyde, ketone or ester having an active H-atom in the α-position in the presence of dilute alkali (say 10% NaOH) to form an α, β-unsaturated compound.

$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{cinnamaldehyde}}{C_6H_5CH = CH{\cdot}CHO} + H_2O$$

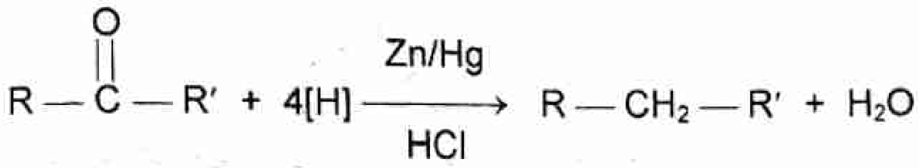
$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{NaOH} \underset{\text{Benzalacetone}}{C_6H_5CH = CHCOCH_3}$$

## 7. Clemmensen Reduction

This reaction provides a method for replacing oxygen atom of the carbonyl group in an aldehyde or ketone by two hydrogen atoms with the help of amalgamated zinc and concentrated hydrochloric acid.



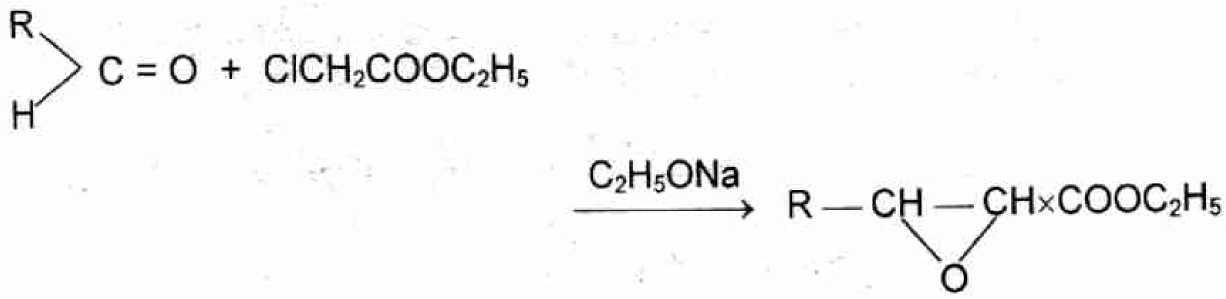
$$R-\overset{\overset{O}{\|}}{C}-H + 4[H] \xrightarrow[HCl]{Zn/Hg} R-\overset{\overset{H}{|}}{C}H_2 + H_2O$$

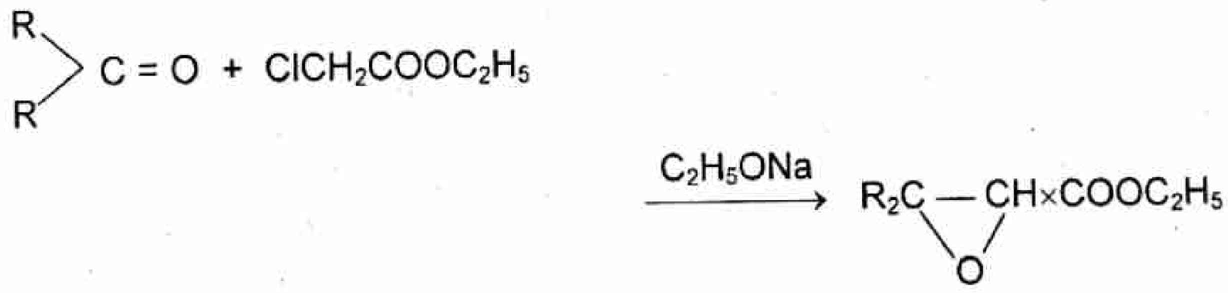


$$R-\overset{\overset{O}{\|}}{C}-R' + 4[H] \xrightarrow[HCl]{Zn/Hg} R-CH_2-R' + H_2O$$

## 8. Darzen Condensation

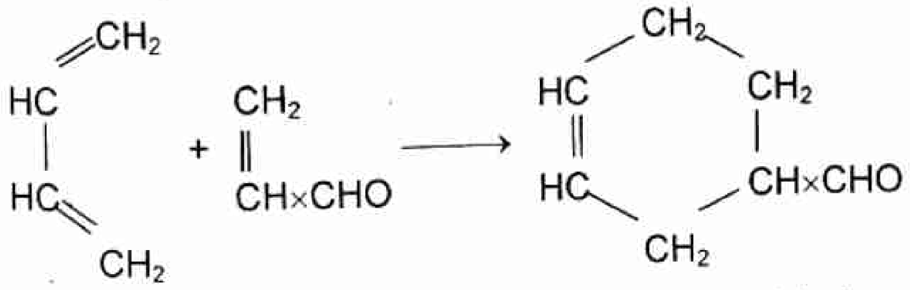
This reaction is a condensation of an α-haloester and an aldehyde or ketone in presence of sodium ethoxide or sodamide to give an α, β-epoxy-ester, i.e., glycidic ester.





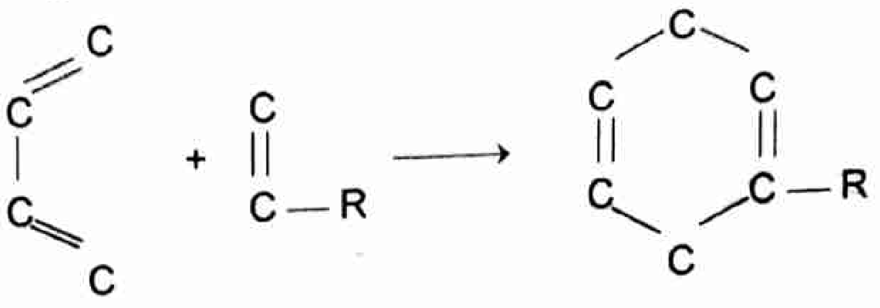
## 9. Diels-Alder Reaction

Diels-Adler reaction consists in the 1,4-addition of conjugated diene to second unsaturated molecule, called a *dienophile*, to form a six membered ring. A simple example of Diels-Alder reaction is the addition of a conjugated diene to an ethylenic compound in which the double bond is adjacent to a carbonyl group.

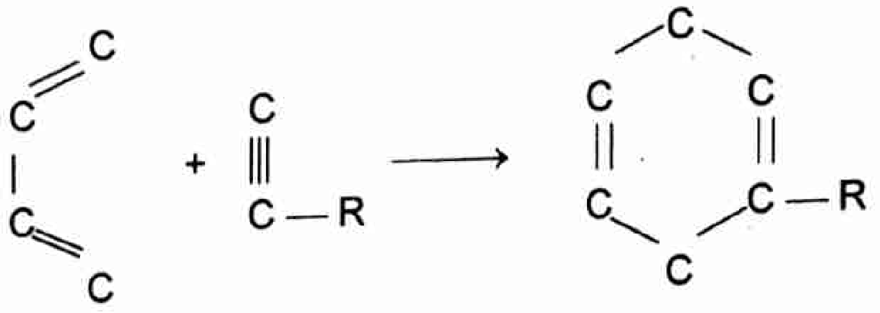


Tetrahydrobenzaldehyde

In general, the diene synthesis is the following type of condensation:



and



## 10. Wurtz Reaction

Wurtz reaction is a method of synthesizing alkanes by the action of sodium on an etheral solution of an alkyl halide.

$$2C_2H_5Br + 2Na \xrightarrow{\text{Ether}} C_2H_5—C_2H_5 + 2NaBr$$

$$C_2H_5Br + CH_3Br + 2Na \xrightarrow{\text{Ether}} C_2H_5—CH_3 + 2NaBr$$

## 11. Fittig Reaction

This is a modification of *Wurtz reaction* which is a method of synthesizing alkanes by the action of sodium on alkyl halides. The modification is the use of aryl halides in place of alkyl halides as the starting materials. *Fittig reaction*, therefore, provides a method to synthesize unfused polynuclear aromatic hydrocarbons, e.g.,

$$\underset{\text{Iodobenzene}}{2C_6H_5I} + 2Na \longrightarrow \underset{\text{Diphenyl}}{C_6H_5 \cdot C_6H_5} + 2NaI$$

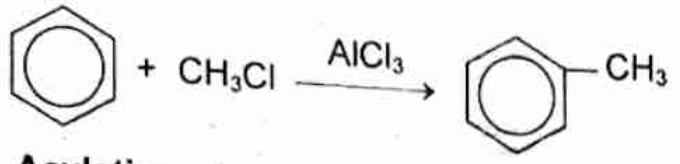
However, when a mixture of an aryl halide and alkyl halide is used as the starting material, the reaction is known as *Wurtz-Fittig reaction.*

$$C_6H_5I + CH_3I + 2Na \longrightarrow C_6H_5—CH_3 + 2NaI$$

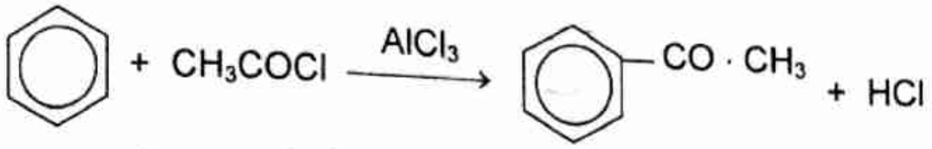
## 12. Friedel-Craft's Reaction

This reaction is used for introduction of alkyl, substituted alkyl or acyl groups in the benzene ring. Anhydrous aluminium chloride is used as a catalyst in this reaction.

1. **Friedel Craft's Alkylation.** Benzene reacts with alkyl halides in the presence of anhydrous $AlCl_3$ to form alkyl benzenes. The reaction is very vigorous at room temperature.



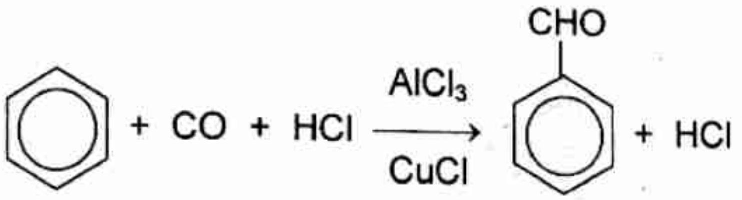
2. **Friedel Craft's Acylation.** Introduction of an acyl group in benzene ring is affected by acid chlorides.



It is an electrophilic substitution reaction.

### 13. Gattermann-Koch Reaction

Gattermann-Koch reaction is used for obtaining aromatic aldehydes. The method includes the passing of a mixture of gaseous CO and HCl in the presence of $AlCl_3$ along with a small amount of CuCl in benzene.



### 14. Knoevengel Reaction

Knoevengel reaction consists in the condensation of aldehydes, both aliphatic and aromatic with malonic acid and other compounds having a methylene group activated by carbonyl, nitrile, or nitro group under basic catalyst to form α,β-unsaturated acid.

$$RCHO + CH_2(COOH)_2 \xrightarrow{\text{base}} R\cdot CH = C(COOH)_2$$

$$\xrightarrow{-CO_2} R\cdot CH = CH\text{–}COOH$$

### 15. Meerwein-Ponndorf-Verley Reduction

This unique method of reducing carbonyl compounds to corresponding alcohols was arrived at independently by Verley (1925), Meerwein and Schmidt (1925), and Ponndorf (1925) and hence is known as *Meerwein-Ponndort-Verley reduction.*

Thus, the selective reduction of a carbonyl compound to an alcohol in the presence of aluminium alkoxides is commonly referred to as Meerwein-Ponndorf-Verley reduction.

By selective, it means that this reducing agent (aluminium isopropoxide) is specific for carbonyl group, and so may be used for reducing aldehydes and ketones containing some other functional group that is reducible, e.g., a nitro group.

$$RCHO + CH_3CH_2OH \xrightleftharpoons{Al(OC_2H_5)_3} RCH_2OH + CH_3CHO$$

$$C_6H_5COC_6H_5 \xrightleftharpoons[(CH_3)2CHOH]{Al(OC_3H_7)_3} C_6H_5CHOHC_6H_5$$

## 16. Oppenauer Oxidation

The reversible of the Meerwein-Ponndorf-Verley reduction led R.V. Oppenauer to discover this oxidation in 1937. The method consists in the oxidation f secondary alcohols to ketones by treatment with aluminium tert. butoxide (or isopropoxide) in combination with acetone. The reaction can be expressed by the general equation.

$$RR'CHOH + (CH_3)_2CO \xrightleftharpoons{Al(OC_3H_7)_3} RR'CO + (CH_3)_2CHOH$$

## 17. Ullmann Reaction

This reaction consists in the refluxing of acetanilide, potassium carbonate, bromobenzene and a little copper powder in nitrobenzene for the synthesis of diphenylamines.

$$C_6H_5NHCOCH_3 + C_6H_5Br + K_2CO_3 \xrightarrow{Cu}$$

$$(C_6H_5)_2NH + CO_2 + KBr + CH_3COOK$$

Similarly phenyl ether may be prepared by refluxing a mixture of bromobenzene, phenol, potassium hydroxide with a small amount of copper as catalyst.

$$C_6H_5Br + C_6H_5OH + KOH \xrightarrow{Cu} (C_6H_5)_2O + KBr + H_2O$$

## 18. Wolff-Kishner Reduction

The conversion of the carbonyl group of aldehydes and ketones to methylene group by heating the semicarbazone, the hydrazone or the azine (of the carbonyl compound) in the a presence of an alkaline catalyst such as sodium ethoxide or hydroxide is known as *Wolff-Kishner reduction*.

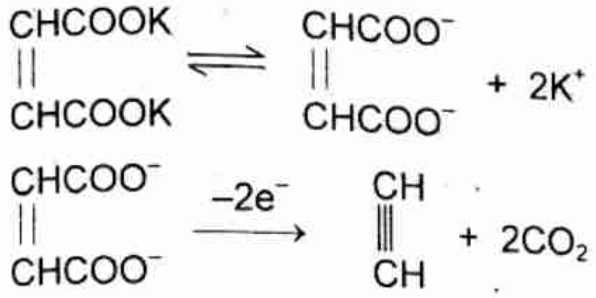
$$>C=O \xrightarrow{N_2H_4} >C=N-NH_2 \xrightarrow{NaOH} >CH_2 + N_2$$

## 19. Kolbe's Electrolytic Reaction

This reaction is employed for the preparation of saturated and unsaturated hydrocarbons. These are prepared by the electrolysis of sodium salt of monocarboxylic acids and salts of dicarboxylic unsaturated acids.

$$2CH_3COONa \rightleftharpoons 2CH_3COO^- + 2Na^+$$

$$2CH_3COO^- \xrightarrow{-2e^-} \underset{\text{unstable}}{2CH_3COO} \longrightarrow CH_3-CH_3 + 2CO_2$$

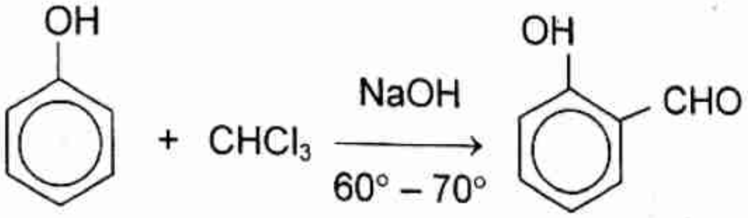


$$\begin{array}{c}\text{CHCOOK}\\ \| \\ \text{CHCOOK}\end{array} \rightleftharpoons \begin{array}{c}\text{CHCOO}^-\\ \| \\ \text{CHCOO}^-\end{array} + 2K^+$$

$$\begin{array}{c}\text{CHCOO}^-\\ \| \\ \text{CHCOO}^-\end{array} \xrightarrow{-2e^-} \begin{array}{c}\text{CH}\\ ||| \\ \text{CH}\end{array} + 2CO_2$$

## 20. Reimer-Tiemann Reaction

This reaction consists in the treatment of phenol with $CHCl_3$ and aqueous alkali at 60° – 70°C to get salicylaldehyde.



## 21. Sandmeyer Reaction

The diazonium group can be replaced by —Cl, —Br or —CN by mixing diazonium salt solution with cuprous chloride in HCl, cuprous bromide in HBr or cuprous cyanide in HCN at room temperature.

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2 + HCl$$

$$C_6H_5N_2^+Cl^- \xrightarrow{CuBr/HBr} C_6H_5Br + N_2 + HCl$$

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCN/HCN} C_6H_5CN + N_2 + HCl$$

## 22. Hofmann's Reaction

When alkaline solution of an amide is treated with bromine, it gives an amine having one carbon atom less than the starting amide.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + H_2O$$

## 23. Rosenmund's Reaction

Aldehydes are obtained by the catalytic hydrogenation of acid chlorides. It is carried out by passing hydrogen gas through a hot solution of acid chloride in xylene. Palladium deposited on $BaSO_4$ is used as catalyst.

$$R{\cdot}COCl + H_2 \xrightarrow{Pd-BaSO_4} RCHO + HCl$$

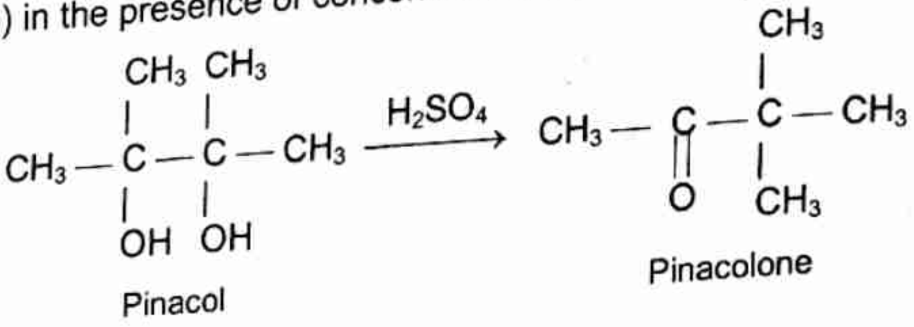
### 24. Williamson's Synthesis

It is used to get simple as well as mixed ethers Alkyl halides are treated with sodium alkoxides to get the product.

$$R—X + R'ONa \longrightarrow R'—O—R + NaX$$

### 25. Pinacol-Pinacolone Rearrangement

The transformation of a 1,2-glycol to an aldehyde or ketone via the migration of an alkyl or aryl group, in the presence of strong acid, is known as *Pinacol-Pinacolone rearrangement.* The classical example of this rearrangement is the conversion of tetramethyl glycol (pinacol) to methyl tert. butyl ketone (pinacolone) in the presence of concentrated sulphuric acid.



$$CH_3—\underset{OH}{\overset{CH_3}{C}}—\underset{OH}{\overset{CH_3}{C}}—CH_3 \xrightarrow{H_2SO_4} CH_3—\underset{O}{\overset{\|}{C}}—\underset{CH_3}{\overset{CH_3}{C}}—CH_3$$

Pinacol

Pinacolone

## 2.8. Practical Organic Chemistry

**Q. Define distillation.**

**Ans.** It is a technique which is used to separate a mixture of two or more materials (usually liquids) that differ in their ease of vaporization.

**Q. What is distillate?**

**Ans.** The pure liquid obtained after distillation is known as distillate.

**Q. Define boiling point. Give its significance.**

**Ans.** It is the temperature of a liquid at which the vapour pressure of a liquid becomes equal to the pressure upon it. It is used to check the purity of a compound.

**Q. How different impurities affect the boiling point?**

**Ans.** A liquid will boil at a higher temperature in the presence of impurities.

**Q. What is bumping? How can it be controlled?**

**Ans.** Ordinarily, bubbles of vapour should form in the liquid at the boiling point emperature. These bubbles rise to the surface and cause *ebullition.* If the liquid is perfectly clear, bubbles of vapour may fail to form immediately and the liquid may be heated above its boiling point. When bubbles do form in super heated liquid, they are produced so suddenly and expand so rapidly that the liquid *bumps* and some of it may be thrown over into the condenser. This phenomenon is known as *bumping* or *irregular boiling* and is due to local super heating of the liquid.

To avoid the hazards associated with bumping a dependable source of bubbles should always be introduced into the flask, before its contents are heated to boiling. For example, a few fragments of unglazed porous porcelain often termed as boiling chips, or a few pieces of glass beads can be used to avoid bumping. This type of material contains innumerable capillaries filled with air. When the temperature is raised, expansion of air causes the escape of small bubbles of air which serve as the nuclei for the vaporisation of liquid.

**Q. Is bubble formation necessary for the phenomenon of boiling?**

Yes, it is necessary to observe the phenomenon. Liquids heated in containers that have been degassed do not boil although they vaporise explosively if heated to sufficient high temperature.

**Q. What is the purpose of wire gauze?**

Its main purpose is to avoid superheating and decomposition of the liquid or vapour that might result from heating the sides and the upper portion of the flask.

**Q. What is normal boiling point?**

It is the boiling point of a liquid at one atmospheric pressure.

**Q. What is stem correction?**

When a thermometer with a long scale is used, the pure boiling point (or melting point) is not registered because the mercury column is not entirely at the temperature of the mercury in the bulb of the thermometer. The portion of the mercury column that extends above the stopper of the distillation adapter is cooled by the surrounding atmosphere and the registered temperature is below the true temperature of the vapour in the flask. For temperature below 100°C, this cooling effect does not cause any definite error, but for high temperature, the observed temperature may be several degrees below the true temperature. This error can be corrected by adding a stem correction calculated by the formula.

$$\text{Stem correction (deg)} = 0.000154\,(t_1 - t_2)N$$

0.000154 = Coefficient of expansion of mercury in glass

$N$ = Number of degrees on the stem of the thermometer from the lower exposed surface to the temperature read.

$t_1$ = Temperature read.

$t_2$ = Average temperature of the exposed mercury column.

**Q. What is the purpose of fractional distillation?**

**Ans.** It used to separate a mixture of two or more liquids which are miscible with each other and having appreciable differences in their boiling points.

**Q. What is the use of fractionating column?**

**Ans.** Its main use is to increase the cooling surface and to provide obstruction to the ascending vapours or the descending liquid.

**Q. Define the terms, capacity and efficiency of a column.**

**Ans.** The capacity of a column is a measure of the quantity of a vapour and liquid which can be passed counter-current to each other in a column without causing it to flood. The efficiency of a column is the separating power of a definite length of the column.

**Q. What is the practical advantage of steam distillation?**

**Ans.** Its practical advantage is that the mixture distils at a temperature below the boiling point of the low boiling component.

**Q. What types of compounds are separated by steam distillation?**

**Ans.** This technique is usually applied for those liquids which are steam volatile (soluble), water insoluble having high vapour pressure.

**Q. What is the principle of steam distillation?**

**Ans.** This technique is based on a simple law: the total vapour pressure equals the sum of the vapour pressures of each component.

**Q. What types of compounds are separated by distillation under reduced pressure?**

**Ans.** The compounds which are expected to undergo partial or complete decomposition under normal pressure before reaching their boiling points, are usually separated by this technique.

**Q. How are solids purified?**

**Ans.** The common technique used for the purification of the solids is recrystallisation.

**Q. What is the principle of recrystallisation?**

**Ans.** This technique is based on the differences in the solubility in a given solvent or a mixture of solvents.

**Q. What types of solvents are used for recrystallisation?**

**Ans.** *(a)* The selected solvents have a high solvating power for the substance at high temperature and low solvating power at room temperature.

*(b)* They yield well formed crystals.

*(c)* They are chemically inert and have low boiling points.

**Q. What is meant by solvent extraction?**

**Ans.** Solvent extraction is a method that makes use of differences in partition of various substance between two immiscible liquids.

$$D = \frac{C_A}{C_B}$$

This technique is used for the isolation of dissolved substances from solution, or from solid mixture or for the removal of undesired soluble impurities.

**Q. Define filtration.**

**Ans.** It is process of separating solids or suspended particles from liquids by passing through a porous material.

**Q. What is sublimation?**

**Ans.** Certain solids on heating do not pass into the liquid but go directly into the vapour state, and on cooling return to the solid state without being converted into liquid state. This phenomenon is known as *sublimation* e.g., camphor, naphthalene etc.

**Q. What is the necessary condition for sublimation?**

**Ans.** For the sublimation to occur, a solid should have a relatively high vapour pressure at a temperature below its melting point.

**Q. Define melting point. Give its significance.**

**Ans.** The melting point of a crystalline solid is the temperature at which the solid begins to change into a liquid under a pressure of one atmosphere. A pure crystalline substance usually possesses a sharp melting point (within 0°C to 1°C), hence the temperature is valuable for purposes of identification. More over, the melting point, is considerably influenced by the presence of other substances and therefore it is an important criterion of purity.

**Q. What is the difference between the melting point and the freezing point of a substance?**

**Ans.** If the melted substance is cooled, solidification will occur at the same temperature, and for a pure substance the melting point and the freezing point are identical. The freezing point is usually defined as the temperature at which both the liquids and solids can exist in contact with each other under a total pressure of one atmosphere. Melting point is usually concerned with solids and freezing point with liquids.

**Q. Freezing points are more difficult to determine. Comment.**

**Ans.** Since super cooling of a liquid below its equilibrium freezing point is common phenomenon, hence freezing points, are more difficult to determine. Super heating of solids is not observed, so melting points are usually determined.

**Q. What is the effect of impurity on melting point?**

**Ans.** It is general observation that an impurity usually lowers the melting point of a pure substance. This is due to lowering of partial vapour pressure of the pure substance in the melt.

**Q. Define mixed melting point.**

**Ans.** The identified organic compound is mixed with the same known compound taken from the laboratory and its melting point is determined. This melting point which is called mixed melting point should be exactly same and sharp as that of identified compound.

**Q. What are super cooled substances?**

**Ans.** Those substances which can be cooled below their freezing points, are called super cooled or sub-cooled substances e.g., water and acetic acid.

**Q. Define deliquescence.**

**Ans.** A substance is said to be deliquescent (to become liquid) when it forms a solution or a liquid phase upon standing in the air. The essential condition is that the vapour pressure of the saturated solution of the highest hydrate at room temperature should be less than the partial pressure of the aqueous vapours. KOH and NaOH are deliquescent while $CuSO_4.5H_2O$ is not deliquescent.

**Q. Define efflorescence.**

**Ans.** A salt hydrate is said to efflorence (to blossom) when it losses water and falls to powder upon exposure to the atmosphere. Efflorescence will occur only when the vapour pressure of the salt hydrate is greater than that of water vapour in the atmosphere e.g., washing soda ($Na_2CO_3.10H_2O$) which gives off water with the production of monohydrate ($Na_2CO_3.H_2O$).

**Q. Explain the term hygroscopic.**

**Ans.** A substance is said to be hygroscopic when it attracts moisture from the atmosphere. All deliquescent compounds are consequently hygroscopic, but there are many hygroscopic substances which absorb water vapour without deliquescing. Substances which are commonly regarded as hygroscopic include quick lime, cupric oxide, conc. sulphuric acid etc.

**Q. Define actual yield and theoretical yield.**

**Ans.** The actual yield is the amount of pure product actually obtained in the experiment. The theoretical yield (sometimes called the calculated yield) is the amount that could be obtained under ideal condition; that is the main reaction is assumed to proceed to completion without side reactions or mechanical losses.

**Q. What is percentage yield? Give its significance.**

**Ans.** The percentage yield is obtained by comparing the actual yield with the theoretical yield, in the following manner.

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

The percentage yield is the measure of over all efficiency of the preparation, since many factors, such as incomplete reactions, side reactions and mechanical losses affect the actual yield

**Q.** **How is an organic substance usually dried?**

**Ans.** An organic solid is usually dried by heating it in thin layers in a drying oven at a temperature below the melting point or by placing in a desiccator.

**Q.** **Write down the names of some drying agents.**

**Ans.** Anhydrous calcium chloride, solid sodium hydroxide, phosphorus pentoxide etc.

**Q.** **Give the name of the most widely used antipyretic and analgesic drug.**

**Ans.** The most widely used antipyretic (fever reducing) and analgesic (pain relieving) drug is acetylsalicylic acid, (aspirin).

**Q.** **What are azo colours?**

**Ans.** These are a class of dyes which contain the $-N=N-$ group linked to two aromatic nuclei.

**Q.** **What is the difference between a dye and an indictor?**

**Ans.** A dye is a coloured substance which can be made to adhere to fabrics such as cotton, silk or linen. An indicator is a substance which is used to indicate by its colour change the physicochemical condition of a chemical reaction.

**Q.** **Are all coloured compounds dyes?**

**Ans.** Though all dyes are coloured compounds, all coloured compounds are not dyes e.g., azobenzene is a coloured compound, but it is not a dye.

**Q.** **What is the effect of $-OH$ and $-NH_2$ groups on the benzene ring?**

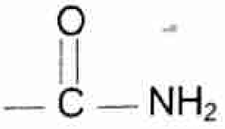
**Ans.** Both these groups activates the benzene ring.

**Q.** **The qualitative detection of N, S and X in organic compounds is more difficult than in inorganic compounds. Why?**

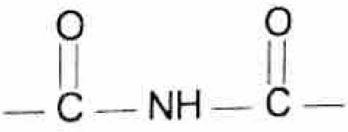
**Ans.** Because most organic compounds are not appreciably ionized in solution.

**Q.** **Write the formulas of functional groups of amide, imide and anilide.**

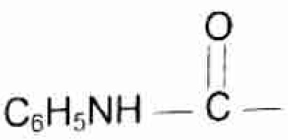
**Ans.** Amide


$-\overset{\overset{O}{\|}}{C}-NH_2$

Imide


$-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-$

Anilide


$C_6H_5NH-\overset{\overset{O}{\|}}{C}-$

**Q.** **Why diaotization is performed at 0°—5°C?**

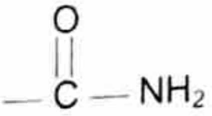
**Ans.** Diazonium ion is stable only at low temperature.

**Q. 45.** **How is unsaturated detected by modern methods?**

**Ans.** By UV-visible spectroscopy.

**Q. 46.** **How are functional groups detected by modern methods?**

**Ans.** IR-spectroscopy plays an important role in the detection of various functional groups present in the molecule of an organic compound e.g.

| | |
|---|---|
| $—OH$ | absorbs at 3650 – 3580 $cm^{-1}$ |
|  $—\overset{\overset{O}{\|\|}}{C}—NH_2$ | absorbs at 1650 $cm^{-1}$ |
| $—COOH$ | absorbs at 1752 – 1700 $cm^{-1}$ |
| $—NH_2$ | absorbs at near 3400 $cm^{-1}$ |

**Q.** **Name some oxidizing reducing and dehydrating agents.**

**Ans.** Oxidizing agents : $KMnO_4$, $K_2Cr_2O_7$, $HNO_3$, $H_2O_2$; reducing agents: Sn/HCl, $SnCl_2$ sodium amalgam and dilute $H_2SO_4$; dehydrating agents: Conc. $H_2SO_4$, $CaCl_2$, $P_2O_5$.

**Q.** **What is Bi-uret test?**

**Ans.** When amides are heated, they evolve ammonia gas, producing a compound called Bi-uret. When dissolved in NaOH solution and a drop of dil. $CuSO_4$ a violet coloration is produced.

**Q.** **What is the function of Bromine water in organic analysis?**

**Ans.** It acts as bromination or mild oxidizing agent.

**Q.** **Generally aliphatic compounds burn without soot but aromatic substances burn with soot. Why?**

**Ans.** Soot is a black deposit of carbon particles obtained when certain substances are burnt. Aromatic compounds contain higher percentage of carbon. During burning some carbon remains unburned and is deposited as soot.

**Q.** **Which aliphatic compounds burn with soot?**

**Ans.** $CHCl_3$ and $CH_2Cl_2$ burn with smoky flame, since they contain more %age of carbon.

**Q.** **Being acidic, phenol does not liberate $CO_2$ with $NaHCO_3$. Why?**

It is weakly acidic.

**Q. What is the difference between aqueous and alcoholic $FeCl_3$ solutions ?**

**Ans.** Aqueous $FeCl_3$ solution undergoes hydrolysis and becomes acidic acquiring pH less than 7, while alcoholic $FeCl_3$ solution is almost neutral with pH equal to 7.

**Q. Name the organic substances which yield picrate derivatives.**

**Ans.** Aromatic hydrocarbons, phenols, secondary and tertiary amines, halogenated aromatic hydrocarbons.

**Q. Why some of the organic compounds are coloured in nature?**

**Ans.** The appearance of colour is due to the presence of chromophoric groups, i.e., colour bearing groups. Chromophores are unsaturated groups like nitro; azo, quinonoid, conjugated double and tripe bonds. Their compounds absorb some part of visible light and transmit the other which appears as colour.

**Q. What is Lassaigne test? For which purpose it is used?**

**Ans.** In Lassaigne test organic compound is fused with sodium metal to convert nitrogen, sulphur and halogens (if present) into sodium cyanide, sulphide or halides, respectively. These ionic compounds formed are soluble in water and give individual tests for ions. This test is used to detect the presence of nitrogen, sulphur and halogens in an organic compound.

**Q. Why the fusion tube is kept dry during the Lassaigne test?**

**Ans.** Sodium reacts explosively with water. Therefore, water if present in the tube will react with sodium metal and make it inactive.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$$

**Q. Can other elements like potassium, calcium or magnesium be used in place of sodium in Lassaigne test?**

**Ans.** Yes, but potassium is too reactive to handle, whereas calcium and magnesium are much less reactive.

**Q. During the detection of nitrogen in an organic compound, freshly prepared ferrous sulphate solution is used, why?**

**Ans.** Ferrous ions are subjected to ready autoxidation and hydrolysis to ferric ions in the presence of moist atmospheric oxygen. Therefore old solution of ferrous sulphate is not required for usual test of nitrogen.

$$4FeSO_4 + O_2 + 2H_2O \longrightarrow 4Fe(OH)SO_4$$

Basic ferric sulphate

**Q.** **Why freshly prepared solution of sodium nitroprusside is used for detecting sulphur?**

**Ans.** Sodium nitroprusside is unstable in aqueous medium, therefore its fresh solution is used.

**Q.** **How the presence of oxygen is determined in an organic compound?**

**Ans.** "Ferrix" paper is used to detect the presence of oxygen in an organic compound. A strong solution of ferric thiocyanate in pure methyl alcohol is made. Filter paper is dipped into the solution of compound in dry benzene. The colour of filter paper change to pink, indicating the presence of oxygen.

**Q.** **Sodium fusion extract is acidified before testing for halogens, why?**

**Ans.** Acidification of sodium fusion extract is necessary before adding silver nitrate solution to prevent precipitation of silver hydroxide or oxide.

**Q.** **How halogens are detected in an organic compound in the presence of nitrogen and sulphur?**

**Ans.** Sodium extract is first boiled with conc. $HNO_3$ before adding $AgNO_3$ solution for detection of halogens. Boiling with $HNO_3$ will destroy the CN and S which if present will give white and black ppt., respectively.

**Q.** **Polyhalogens and polynitro compounds are not subjected to Lassaigne test, why?**

**Ans.** Certain classes of organic compounds like trichloro methane, tetrachloro methane, trinitro toluene and trinitro benzene explode violently when heated with sodium or potassium. Therefore, they generally are not fused with Na for the preparation of Lassaigne solution.

**Q.** **Why must HCN and $H_2S$ be expelled before a test is made for halide ion?**

**Ans.** Because CN and S will form white and black ppt. of AgCN and $Ag_2S$, respectively with $AgNO_3$ and presence of halide ions cannot be detected.

**Q.** **What is the layer test for halogens? Why is it performed?**

**Ans.** Sodium extract (1 $cm^3$) + chloroform along with chlorine water and shake. A formation of brown or violet layer will show the presence of bromine and iodine, respectively. This test is performed to distinguish between bromine and iodine.

**Q.** **Why the addition of chlorine water is necessary in layer test?**

**Ans.** Due to more electronegative nature of chlorine than bromine and iodine, it displaces them from their salts liberating them free.

**Q. State the function of $CHCl_3$ or $CCl_4$ in layer test.**

**Ans.** The bromine or iodine which is liberated from its compound by the addition of chlorine water is absorbed by $CHCl_3$ or $CCl_4$ and the layer of solvent becomes coloured.

**Q. Why the aromatic compounds give a smoky flame on ignition?**

**Ans.** Large percentage of carbon is present in aromatic compounds. Therefore on ignition their flame still consists of unburned carbon particles i.e., smoky flame. Compounds containing C, H ratio of 1:1 or 1:2 give smoky flame. For example, $CH_2Cl_2$, $CHCl_3$ also give smoky flame.

**Q. Name the compounds in addition to carboxylic acids which give brisk effervescence when treated with aqueous $NaHCO_3$ solution.**

**Ans.** Sulphonic acids and nitrophenols are also acidic in nature and give brisk effervescence of $CO_2$ on treating with aqueous solution of $NaHCO_3$.

**Q. How will you differentiate between cyclohexane and benzene?**

**Ans.** On applying ignition test, benzene gives smoky flame due to its aromatic character, whereas cyclohexane gives a non-smoky flame being non-aromatic.

**Q. How will you distinguish between aldehydes and ketones?**

**Ans.** They can be distinguished by their smell i.e. the smell of aldehyde is unpleasant while that of ketone is sweet. Aldehydes give positive test with Fehling solution and ammonical $AgNO_3$ soln., whereas ketone gives the negative test with these reagents.

**Q. What is Fehling solution (A and B)?**

**Ans.** Fehling solution is a mixture of copper sulphate solution, sodium hydroxide and sodium potassium tartarate solution. It is obtained in solution form by mixing equal volumes of 7% copper sulphate solution having 2-3 drops of conc. $H_2SO_4$ (Fehling A) with sodium hydroxide and salt of sodium potassium tartarate (Fehling B).

**Q. What is the function of Rochelle salt in Fehling solution?**

**Ans.** Rochelle salt avoids precipitation of $Cu(OH)_2$ due to the formation of complex salt with cupric ions.

**Q. What is Tollen reagent?**

**Ans.** It is ammonical silver nitrate solution. It is obtained by adding $NH_4OH$ dropwise to $AgNO_3$ solution until the ppt. of silver hydroxide first formed is almost redissolved.

**Q. What is meant by Schiff reagent?**

**Ans.** Schiff reagent consists of an aqueous solution of fuschine (p-rosaniline hydrochloride) decolorized by passing $SO_2$ gas.

**Q. A compound gives a positive test with 2,4-dinitrophenyl hydrazine but it does not reduce Tollen reagent. What is the nature of the compound?**

**Ans.** The compound is ketonic in nature.

**Q. Which are the organic compounds giving silver mirror test with Tollen reagent?**

**Ans.** The compounds which are easily oxidizable and are of reducing nature give silver mirror test. Such compounds are aldehydes, reducing sugars as glucose, fructose, formic acid and hydroquinones.

**Q. Why are aldehydes more reactive than ketones?**

**Ans.** Aldehydes are easily oxidizable to carboxylic acids whereas ketones can not be oxidized by mild oxidizing agents like Tollen, Schiff, Benedict reagents etc.

**Q. Why is fluorine not detected in sodium extract with $AgNO_3$ solution? Suggest a method for its detection.**

**Ans.** Fluorine is not detected, since silver fluoride formed with $AgNO_3$ solution, is soluble in water. A drop of sodium fusion extract acidified with acetic acid if gives yellow coloured spot on zirconium-alzarin test paper (red in colour) indicates the presence of fluoride.

**Q. How will you distinguish between a halogen present in the side chain and that in the aromatic nucleus?**

**Ans.** Silver nitrate test is performed with the halogen compound. The formation of the ppt. shows the presence of halogen in side chain. A negative test indicates its presence in the nucleus.

**Q. O-Nitrophenol does not give $FeCl_3$ test of phenolic group. Why?**

**Ans.** O-Nitrophenol does not have free phenolic group due to the formation of intramolecular hydrogen bonding between phenolic group (– OH) and nitro group (– $NO_2$).

**Q. What is baeyer reagent. For what purpose it is used?**

**Ans.** It is 1% alkaline $KMnO_4$ solution and is used to detect unsaturation in an organic compound.

**Q. Give a test which is common to both alcohol and phenol?**

**Ans.** Ceric ammonium nitrate test is commonly used for both alcohols and phenols. Alcohols produce red colour while phenols give greenish brown colour or precipitate.

**Q. Name any liquid carbohydrate.**

**Ans.** There is no carbohydrate which is liquid as all the carbohydrates are solid.

**Q. What is meant by derivative? For what purpose it is prepared?**

**Ans.** A derivative is usually a solid material which can readily be prepared form the unknown and can easily be isolated and purified. This is used for the confirmation of a given compound.

**Q. Recrystallization of the derivative is essential. Why?**

**Ans.** Only purified substances give sharp m.p. Hence, in order to obtain a sharp m.p. a derivative is recrystallized to get it in purified form.

**Q. What are the common derivatives made for hydrocarbons?**

**Ans.** Nitro and picrate derivatives are commonly used.

**Q. What test is performed to know the aliphatic or aromatic nature of an organic compound?**

**Ans.** Ignition test of the organic compound is performed to see the aliphatic or aromatic nature. Aliphatic compounds burn with a nonsmoky flame, while aromatic burn with a smoky flame.

**Q. Name the group common in aldehydes and ketones.**

**Ans.** Carbonyl. (> C = O) group.

**Q. Define carbolic acid and carbonic acid.**

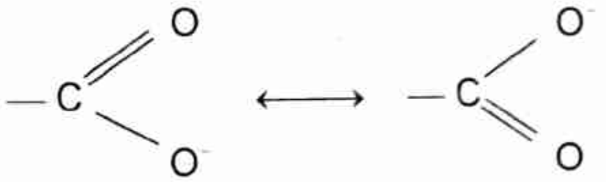
**Ans.** Simple phenol ($C_6H_5OH$) is termed as carbolic acid, whereas carbonic acid is obtained by sufficient bubbling of $CO_2$ through water.

**Q. Phenols and carboxylic acids both are acidic towards litmus solution. How can they be distinguished?**

**Ans.** Both carboxylic acids and phenols change blue litmus to red, but phenol is a weak acid as compared to carboxylic acid. When $NaHCO_3$ solution is added to the phenol it does not evolve $CO_2$ while carboxylic acid evolves $CO_2$ with brisk effervescence which turns lime water milky.

**Q. The carboxylic group has carbonyl group but it does not show the reaction of ketonic group. Why?**

**Ans.** The carboxylate ion is a resonance hybrid. Therefore, a single formula cannot be written for it. The negative charge in the hybrid is equally distributed to both the oxygen.



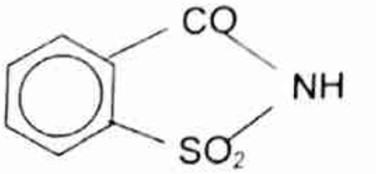
Due to this reason the double bond character is lessened and the carboxylic acid does not behave like the carbonyl group of ketone.

**Q. What is meant by invert sugar?**

**Ans.** Ordinary sugar or sucrose is dextro-rotatory but after hydrolysis it changes into a mixture of glucose and fructose in equimolar quantities and become levo-rotatory. This is called inversion and mixture of sugar is called invert sugar.

**Q. Name any compound which is many times sweeter as compared to sugars.**

**Ans.** Saccharin is a compound which is 500 times sweeter than sugar. It is marketed as sodium salt, as saccharin itself is sparingly soluble in water. The structure of saccharin is



**Q. Name substances which are used for storing reactive metals like Na and K?**

**Ans.** These elements are very reactive in open atmosphere. Therefore in order to avoid explosion these are stored in inactive compounds. For this purpose most commonly used are naphtha, xylene and kerosene oil.

**Q. Monocarboxylic acids are called fatty acids. Why?**

**Ans.** The name fatty acid is coined, since they are found in fats and oils as triglycerides. They are the long chain aliphatic mono carboxylic acids.

**Q. What is the chemical nature of an oil or fat?**

**Ans.** All naturally occurring fats or oils of either plant or animal origin are the esters of glycerol with long chain mono carboxylic acids. These esters are termed as trighlycerides or simply glycerides.

**Q. What is the advantage to use alkaline $KMnO_4$ in unsaturation test?**

**Ans.** Alkaline $KMnO_4$ with unsaturated compound yields oxidation products like $MnO_2$ which are coloured and easy to identify. On the other hand with acidified $KMnO_4$ the oxidation products $K_2SO_4$ and $MnSO_4$ are colourless and also somewhat soluble, and are thus not easily detectable and may lead to wrong conclusions.

**Q. What is the reason of calling pure acetic acid as "glacial acetic acid"?**

**Ans.** Pure acetic acid solidifies at low temperature and looks like ice. It is common phenomenon especially in cold countries. Therefore, it is termed as glacial, i.e. ice like.

**Q.** **Give a test which can distinguish between amides and ammonium salts.**

**Ans.** Nitrogen containing compounds such as amines, amides, ammonium salt etc. liberate ammonia on treating with NaOH. In case of ammonium salts $NH_3$ is liberated in cold state on addition of NaOH, while amides liberate $NH_3$ on heating.

**Q.** **Certain organic compounds yield whitish precipitates on addition of bromine water to them. Why?**

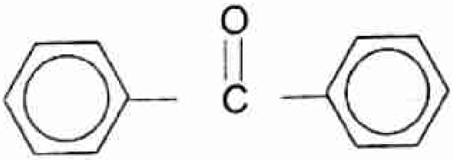
**Ans.** Aromatic compounds yield bromo derivatives on addition of bromine-water to them which are white in colour. Therefore when an aromatic compound is treated with bromine-water, bromine atom is substituted in the benzene ring giving a bromo derivative.

**Q.** **Addition of NaOH to Lassaigne filtrate is necessary or not.**

**Ans.** Sodium extract is already alkaline in nature due to the conversion of excess Na into NaOH and $H_2$ in the presence of water. However, if the filtrate is not alkaline it is made so by the addition of few drops of NaOH.

**Q.** **Why benzophenone does not give most of the reactions of a carbonyl group?**

**Ans.** The carbonyl group of benzophenone is surrounded by two bulky benzene rings on both the sides.



They offer steric hindrance and the reactant is pulled away form carbonyl group by them. Hence, benzophenone although a ketone does not give most of the reactions of carbonyl group.

**Q.** **Benzene gives a negative test with $KMnO_4$ for unsaturation although it has got three double bonds. Why?**

**Ans.** The three double bonds of benzene are made by sharing of p-orbitals. These bonds are delocalized in such a manner that no actual double bond exists in benzene ring, thereby giving a negative unsaturation test with $KMnO_4$.

**Q.** **Define crystalline melting point.**

**Ans.** The temperature at which the crystals of a solid are abruptly changed into liquid phase is termed as crystalline melting point.

**Q.** **Can you name physical constants other than m.p., b.p. which are helpful in establishing the purity of organic compounds?**

**Ans.** Yes, specific gravity, viscosity and surface tension are the other physical constants.

**Q.** **Name the compound which gives no flame.**

**Ans.** $CCl_4$.

**Q.** **2, 4 Dinitrophentle hydrazine is preferred over phenyl hydrazine. Why?**

**Ans.** It is more reactive than phenyl hydrazine. Moreover it has low solubility and high melting point.

**Q.** **Define diazotization.**

**Ans.** It is the reaction which involves the formation of diazonium compound by the action of $HNO_2$ on primary aromatic amine.

**Q.** **Give the name of test to confirm carbohydrates.**

**Ans.** Molisch test.

**Q.** **Name the test for hydrocarbons.**

**Ans.** There is no specific test for hydrocarbons.

**Q.** **Name the compound which contains both acidic and basic groups.**

**Ans.** Aminoacetic acid (Glycine) $H_2NCH_2COOH$.

**Q.** **What is Barfoed's reagent?**

**Ans.** This reagent is used to test particularly reducing sugars. It is a solution of copper acetate in water and glacial acetic acid.

**Q.** **What is acetylating mixture?**

**Ans.** It is a mixture of equal volume of acetic anhydride and glacial acetic acid.

**Q.** **What is the difference between carbohydrates and hydrocarbons?**

**Ans.** Hydrocarbons are the organic compounds consisting of carbon and hydrogen atoms, while carbohydrates may contain C, H, and O.

# *Part Three*

# INORGANIC CHEMISTRY

# 3.1. Basis of Periodic Classification

**Q. What is periodic table?**

**Ans.** Periodic table is an arrangement of the elements by symbol in order of atomic numbers. The chief function of the periodic table is to serve as a fundamental framework for the systematic organization of chemistry.

**Q. State Mendeleef's periodic law.**

**Ans.** The properties of elements are periodic functions of their atomic weights, i.e., if the elements are arranged in the increasing order of their atomic weights, the properties of the elements are repeated after definite regular intervals.

**Q. What are the defects of Mendeleef's periodic law?**

**Ans.** The various defects in the law are:

- *(i)* The position of the hydrogen in the periodic table is anomalous.
- *(ii)* Lanthanides and actinides do not find their proper positions.
- *(iii)* Similar elements are separated while dissimilar elements are placed in the same group.
- *(iv)* Some elements of higher atomic weights precede those of lower atomic weights.

**Q. State Mosely's modern periodic law.**

**Ans.** The properties of elements are periodic functions of their atomic numbers, i.e., when the elements are listed in the order of increasing atomic numbers, elements having closely similar properties will fall at definite intervals along the list.

**Q. What is the difference between a group and a period?**

**Ans.** The vertical column shown in the periodic table is called a *group*. There are nine groups in all including VIII group consisting of three triads and zero group of inert gases.

The horizontal row shown in the periodic table is called a *period*. There are seven periods in the periodic table.

**Q. Write some general characteristics of a group.**

**Ans.** Some of the general characteristics of a group are:

- *(i)* The valencies of all the elements of the same group are the same.
- *(ii)* All the elements of a given group possess very similar physical and chemical properties.
- *(iii)* Size of atoms increases on descending a group.
- *(iv)* Number of valence electrons remain the same in a group.

**Q. Discuss some general characteristics of a period.**

**Ans.** Some of the general characteristics of a period are:

(*i*) Size of atom decreases from left to right in a period.

(*ii*) The properties of the elements of a given period differ considerably, but the elements in the two adjacent periods show marked similarities between them.

(*iii*) On moving from left to right in the periodic table, the metallic character of the elements decreases.

(*iv*) Number of valence electrons increases from 1 to 8 when we proceed from left to right in the periodic table.

**Q. What is diagonal relationship?**

**Ans.** The two elements showing similarities in properties are called *diagonal neighbours*, and across the street similarity in properties existing between the two elements of a diagonal pair is known as *diagonal relationship*. For example, lithium resembles with magnesium and beryllium with aluminium.

**Q. Discuss some merits of long form of periodic table.**

**Ans.** The long form of the periodic table has a number of merits over the mendeleef's periodic table. Some of these are:

(*i*) The classification of the elements is based on a more fundamental property viz. atomic number.

(*ii*) It explains the similarities and variations in the properties of the elements in terms of their electronic configurations and brings out clearly the trends in chemical properties across the long periods.

(*iii*) The inert gases having completely filled valence shells have been placed at the end of each period.

(*iv*) It provides a clear demarcation of different types of the elements like active metals, transition metals, non-metals, metalloids, inert gases, lanthanides and actinides.

**Q. Mention some defects of long form of the periodic table.**

**Ans.** Although the long form of the periodic table is superior to mandeleef's periodic table in many respects, it retains of the defects as such. For example:

(*i*) The problem of the position of hydrogen still remains unsolved.

(*ii*) Like the Mendeleef's table, it fails to accommodate the lanthanides and actinides in the main body of the table.

**Q. Discuss the classification of elements on the basis of their complete and incomplete electron shells.**

**Ans.** There are four types of elements based on the presence of complete and incomplete electron shells.

**Noble gases.** In the atoms of these elements the outermost shell which has $ns^2p^6$ configuration (except He) is completely filled. $ns^2p^6$ configuration is stable and hence these elements generally do not enter into ordinary chemical reactions.

**Representative elements.** In the atoms of these elements the outer most shell is partly filled while the inner shells are completely filled. The electronic configuration of these elements varies from $ns^1$ to $ns^2p^5$.

**Transition elements.** In the atoms of these elements two outermost shells (i.e., nth and (n − 1)th) are partly filled, while the remaining inner shells are completely filled.

**Inner-transition elements.** In the atoms of these elements three outermost shells (i.e., nth, (n − 1) the and (n − 2)th) are partly filled, while the remaining inner shells are completely filled.

## 3.2. Periodic Properties

**Q. What do you mean by periodicity of properties?**

**Ans.** The term periodicity of properties indicates that the elements with similar properties reappear at certain regular intervals of atomic number in the periodic table.

**Q. Why do the elements placed in the same group have similar properties? or What is the cause of periodicity of properties?**

**Ans.** If we examine the valence shell configuration of various elements, we shall find that in any group, similar valence-shell configuration of the elements reoccur after certain regular intervals of atomic number. This reoccurrence of similar valence-shell configurations of the elements at certain regular intervals of atomic number is the cause of periodicity of properties.

**Q. What is shielding effect?**

**Ans.** In a multi-electron atom, the valence-shell electrons are attracted by the nucleus and also at the same time repelled by the electrons present between the nucleus and the valence shell electrons. The combined effect of these two forces is that the actual force exerted by the nucleus on the valence-shell electrons is partially decreased by the presence of repulsive force exerted by the inner-shell electrons. This decrease in the attractive force exerted by the nucleus on the valence-shell electron is called *screening effect or shielding effect.*

**Q. Define group trend.**

**Ans.** Group trend is the tendency of the properties of elements in a group to vary in a regular way.

**Q. What is effective nuclear charge?**

**Ans.** It is due to the shielding effect of the inner electrons on the outer-electrons that the valence-electrons experience less attractive pull from the nucleus. The decrease in the attractive force reduces the nuclear charge, Z represented by the atomic number of the element. This decreased nuclear charge is called *effective nuclear charge*.

**Q. Define atomic volume.**

**Ans.** Atomic volume is defined as the volume in $cm^3$ occupied by one gram atom of the element in the solid state. It is obtained by dividing the atomic weight of the element by its density, i.e.

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{Density}}$$

**Q. What do you know about atomic radius?**

**Ans.** We know that an atom is composed of a compact nucleus surrounded by an electron cloud which does not have a sharply defined boundary because of its diffused nature. The diffused nature of the electron cloud makes it difficult for us to give an exact definition of atomic size or atomic radius. Thus the atomic radius is an arbitrary concept and is influenced by the nature of neighbouring atoms. However, it is usually considered as the distance from the centre of the nucleus to the point where the electron density is effectively zero (i.e., negligible).

**Q. What is bond length? Discuss its significance.**

**Ans.** Bond length is defined as the distance between the nuclei of two bonded atoms.

The length of a given bond is a measure of its stability. A molecule with small bond length is more stable than that with large bond length. Moreover, the bond length can be used to infer the presence of $\pi$-bonding in a molecule.

**Q. Discuss various types of radii.**

**Ans.** Because of the vague concept of atomic radius, a number of radii have been defined for an atom which pertain to different types of bonding between the atoms. Some of these radii are.

**Covalent Radius.** Covalent radius of an atom is equal to one-half of the inter-nuclear distance.

**Crystal Radius.** (*Atomic or Metallic radius*). The atomic radius as obtained from the metallic crystalline structure of a metal is referred to its crystal or metallic radius. Thus it is used for metal atoms which are assumed to be closely packed spheres in the metallic crystals. Thus crystal radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the closely packed metallic crystal.

**Van der Waals Radius.** When two non-bonded isolated atoms or two non-bonded atoms belonging to two adjacent molecules of an element in the solid state approach each other without overlapping their electron clouds to form a bond between them, they cannot come closer than a minimum distance without forming a bond. This minimum distance is called *van der Waals distance* and half of this distance is called *van der Waals radius*.

**Ionic Radius.** The ionic radius is defined as the distance between the nucleus of an ion and the point where the nucleus exerts its influence on the electron cloud.

**Q. Discuss the variation of atomic and ionic radii in a period and a group.**

**Ans. In a Period.** We know that the number of shells in all the elements of a given period remains the same, but the value of effective nuclear charge increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right. Thus in going from left to right in a period, atomic and ionic radii decrease with the increase of atomic number.

**In a Group.** In going down a group, the atomic and ionic radii both increase with the increase of atomic number. As atomic number increases, the outer-most shell electrons get farther and farther away from the nucleus and hence atomic and ionic radii increase.

**Q. Why a cation is smaller in size than its parent atom?**

**Ans.** We know that a cation is formed by the removal of one or more electrons from the atom. Thus a cation has smaller number of electrons than its parent atom. With the decrease of number of electrons, the magnitude of effective nuclear charge increases, which pulls the electron cloud of the cation nearer to the nucleus and thus makes the cation smaller in size than its parents neutral atom.

**Q. Why an anion is bigger in size than its parent atom?**

**Ans.** We know that an anion is formed by adding one or more electrons to the neutral atom. Thus an anion has more electrons than its parent atom. With the increase of number of electrons, the magnitude of effective nuclear charge decreases, which pulls the electron cloud of anion outward away from the nucleus and thus makes the anion larger in size than its parent neutral atom.

**Q. What are iso-electronic species?**

**Ans.** Iso-electronic species are the atoms or ions which have the same number of electrons and the electronic configuration, but different magnitude of electronic charge. For example, $C^{4-}$, $N^{3-}$, $O^{2-}$ $F^-$ etc.

**Q. Define bond order or bond multiplicity.**

**Ans.** Bond order or bond multiplicity is defined as the number of covalent bonds between the two bonded atoms. The bond length decreases with the increase of multiplicity.

**Q. What is ionization energy?**

**Ans.** It is defined as the amount of energy required to remove the most loosely bound electron from isolated neutral gaseous atom in its lowest energy state to form a unipositive ion.

Ionization energy is also called *ionization potential*, since it represents the amount of potential (or voltage) required to remove the most loosely bound electron from the gaseous atom of an element. It is measured in eV/atom, kilo calories per mole or kilo joules per mole.

**Q. Discuss the variation of ionization potential in a period and a group.**

**Ans. In a Period.** In general, as we move from left to right in a period, the ionization potential of the elements increases due to the successive increase in the nuclear charge and decrease in atomic size.

**In a Group.** When we proceed from top to bottom in a group, the ionization potential values of the elements go on decreasing. This decrease in the values on descending a group is due to the addition of extra-shells which result in the increase of size.

**Q. What is electron affinity?**

**Ans.** It is defined as the amount of energy released when a gaseous ground-state atom gains an electron to form an anion.

**Q. Discuss the group and periodic trends of electron affinity.**

**Ans. In a Period.** On moving from left to right in a period, the size of atoms decreases and the effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the electron. Consequently, the atom has a greater tendency to attract an extra-electron from outside towards itself and hence its electron affinity increases from left to right in a period.

**In a Group.** Electron affinity generally decreases down a group in the periodic table. This is due to progressive increase in the atomic size.

**Q. Define electronegativity.**

**Ans.** When two different atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by both the atoms. Rather, the electron pair lies nearer to one atom than the other. The relative tendency of the bonded atom in a molecule to attract the shared electron pair towards itself is termed as its electronegativity.

**Q. Discuss the periodic trends of electronegativity.**

**Ans. In a Period.** On moving from left to right in a periodic table, there is a decrease in the size of atoms. Smaller atoms have greater tendency to attract the electrons towards themselves, i.e., smaller atoms have higher electronegativity values.

**In a Group.** In going down a group, the electronegativity values decrease. As we move down a group, there is an increase in the size of atoms. With the increase in size of atoms, their electronegativity values decrease.

**Q. What is electropositivity?**

**Ans.** Electropositivity is the converse of electronegativity. It is related to the tendency to lose electron/s. The greater is the tendency to lose electron to form the cation, greater is the metallic or electropositive character.

**Q. Discuss the periodic trends of metallic character.**

**Ans.** Metallic character decreases from left to right in a period, because atomic size decreases and ionization potential increases. Now since ionization potential decreases from top to bottom in a group, the metallic character (i.e., basic character) of the elements increases in the same direction.

**Q. What is REDOX potential?**

**Ans.** Redox potential is a measure of the tendency of an element or ion to gain or lose electrons. It is a combined term involving reduction potential and oxidation potential.

**Q. Define electrochemical series.**

**Ans.** Electrochemical series of elements is the arrangement of elements in the order of increasing or decreasing electrode potentials.

**Q. Discuss some applications of electrochemical series.**

**Ans.** *(i)* We can calculate the voltage of any cell constructed by using any two elements.

*(ii)* We can determine the feasibility of a chemical reaction.

*(iii)* From the position of an element in the series, we can know the strength of an oxidizing or that of a reducing agent.

**Q. Define lattice energy.**

**Ans.** Lattice energy is the energy required to move the ions of one mole of an ionic crystal separated from each other by an equilibrium distance to an infinite distance.

## 3.3. Acids and Bases

**Q. What is Arrhenius concept of acids and bases?**

**Ans.** According to this concept, an *acid* is any hydrogen containing compound which gives $H^+$ ions in an aqueous solution and a *base* which gives $OH^-$ ions in aqueous solution.

**Q. What are the limitations of Arrhenius concept?**

**Ans.** It does not explain the acid-base reactions taking place in non-aqueous solvents such as liquid ammonia.

It also cannot explain the reactions in gas phase where no solvent is present.

**Q. Explain Lowery Bronsted Concept.**

**Ans.** According to this concept, an *acid* is defined as a species which donates a proton and a *base* is a species which accepts a proton.

**Q. Give examples of species which are regarded as acids and bases according to Lowery-Bronsted concept.**

**Ans.** The following species may be regarded as acids:

$$HCl, CH_3COOH, HSO_4^-, HCO_3^-, H_3O^+, NH_4^+$$

The following species may be regarded as bases:

$$H_2O, NH_3, OH^-, HS^-, Cl^-, [Fe(H_2O)_5OH]^{2+}$$

**Q. What is amphiprotic species?**

**Ans.** A species that acts both as a proton donor and a proton acceptor is said to be *amphiprotic*. For example, $H_2O$, $HS^-$.

**Q. Define basicity of an acid.**

**Ans.** The number of $H^+$ ions liberated by one molecule of an acid in aqueous solution is known as its *basicity*.

**Q. Define acidity of a base.**

**Ans.** The number of $OH^-$ ions liberated by one molecule of a base in aqueous solution is known as its *acidity*.

**Q. Define conjugate acid and base.**

**Ans.** Consider the reaction between HCl and $H_2O$.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

In this reaction $Cl^-$ ion (base) formed by the loss of one proton from HCl (acid), is called *conjugate base* of the acid, HCl. Thus HCl and $Cl^-$ is a conjugate acid-base pair. Similarly if we consider the reverse reaction, $H_2O$ (base) formed by the loss of one proton from $H_3O^+$ (acid) is called the conjugate base of the acid, $H_3O^+$. Thus $H_3O^+$ and $H_2O$ is another conjugate acid-base pair. $H_3O^+$ is said to be *conjugate acid* of the base, $H_2O$.

**Q. What is the behaviour of conjugate bases in case of strong and weak acids?**

**Ans.** The strong acids have weaker conjugate base and weak acids have stronger conjugate base pairs.

**Q. What is Lewis concept?**

**Ans.** According to this concept, an *acid* is defined as a species which can accept a pair of electrons and a *base* is a species which can donate a pair of electrons. An acid is an electrophile (electron loving) and a base is a nucleophile (nucleus loving).

**Q. Give some examples of Lewis acids and bases?**

**Ans.** Lewis acids: $BF_3$, $AlCl_3$, $Ag^+$, $Co^{3+}$, $CO_2$

Lewis bases: $NH_3$, $OH^-$, $Cl^-$, $H_2O$

**Q. What is the Lux-Flood concept?**

**Ans.** According to Lux-Flood concept, a *base* is any species which gives up an oxide ($O^{2-}$) ion, and an *acid* is any species which takes up oxide ion.

$$\text{Base} \rightleftharpoons \text{Acid} + \text{Oxide } (O^{2-}) \text{ ion}$$

**Q. Explain the difference between strong and weak acids and bases.**

**Ans.** Those acids and bases which ionize almost completely in solution are called *strong acids and bases*, while those which are ionized to a limited extent in solution are termed as *weak acids and bases.*

**Q. Give some examples of strong and weak acids and bases.**

**Ans.** Strong acids: $H_2SO_4$, $HNO_3$, HCl
Weak acids: $CH_3COOH$, $CH_3CH_2COOH$,
Strong bases: KOH, NaOH
Weak bases: $NH_4OH$, $(CH_3)_2NH$

**Q. What do you mean by strength of an acid or base.**

**Ans.** The strength of an acid or a base is defined as its capacity to give $H^+$ and $OH^-$ ions in equimolar solutions in water respectively.

**Q. What is the significance of dissociation constant?**

**Ans.** Dissociation constant is a measure of an acid or a base strength in aqueous solution. Thus higher the value of dissociation constant, the stronger is the acid or base.

**Q. Arrange the following acids in order of increasing strength.**

HBr, HF, HCl, HBr and
$HClO_3$, HClO, $HClO_2$, $HClO_4$

**Ans.** HF< HCl< HBr< HI (strongest acid)
HClO< $HClO_2$< $HClO_3$< $HClO_4$ (Strongest acid)

**Q. What are polyprotic acids?**

**Ans.** Acids containing one proton which can be donated are *monoprotic acids.* Those acids which contain more than one donatable proton are known as *polyprotic acids.*

For example, $H_2SO_4$, $H_3PO_4$ etc.

**Q. What is Usanovich concept?**

**Ans.** This is the most comprehensive concept of acid-base definition. According to this concept an *acid* is any chemical species which is capable of combining with anions or electrons or giving up cations. Conversely, a *base* is any chemical species which is capable of giving up anions or electrons or combining with cations.

**Q. What is leveling effect?**

**Ans.** All strong acids like $HClO_4$, $H_2SO_4$, HCl, $HNO_3$ have very close pKa values. They appear to have nearly equal strengths in aqueous solutions. This phenomenon is called *leveling effect.*

**Q. What is the strongest acid which exists in aqueous solution?**

**Ans.** $H_3O^+$ ion is the strongest acid which exists in aqueous solution.

**Q. What is the strongest base which exists in aqueous solution?**

**Ans.** The strongest base which can exist in water is $OH^-$ ion.

**Q. What is SHAB concept?**

**Ans.** SHAB is an abbreviation of soft and hard acids and bases. This concept was introduced by R.G. Pearson. He divided the Lewis acids and bases as defined below:

**Hard Bases.** Lewis bases whose donor atoms are of low polarizabilities, high electronegativities and associated with empty orbitals of high energy, e.g., $F^-$, $OH^-$, $Cl^-$ etc.

**Soft Bases.** Lewis bases whose donor atoms are of high polarizabilities, low electronegativities and associated with empty orbitals of low energy, e.g., $I^-$, $RS^-$, $R_2S$. etc.

**Hard Acids.** Lewis acids whose acceptor atoms are of high positive charge, small size and do not have outer electrons which can be easily excited, e.g; $Na^+$, $K^+$, $Al^{3+}$ etc.

**Soft Acids.** Lewis acids whose acceptor atoms are of low positive charge, large size and have several outer electrons which can be easily excited, e.g., $Cu^+$, $Ag^+$, $I^+$ etc.

**Q. What is Pearson's Principle?**

**Ans.** Pearson has suggested a simple rule for predicting the stability of the complexes formed between acids and bases: According to this rule hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.

## 3.4. Chemical Bonding

**Q. What is a chemical bond?**

**Ans.** A chemical bond is defined as the attractive force that holds two or more atoms together in a molecule or an ion.

**Q. Why do atoms combine?**

**Ans.** By a close study of atoms and molecules it has been found that atoms combine chemically for the following reasons.

- *(i)* Net attractive force between the atoms.
- *(ii)* To obey the octet rule.
- *(iii)* Lowering of energy of the combining atoms.

**Q. What is octet rule?**

**Ans.** The tendency of the atoms to have eight electrons in their outer most shell is known as *octet rule*.

**Q. Define ionic or electrovalent bond.**

**Ans.** Ionic bond is the bond which is established by the transfer of one or more valence electrons from one atom to the other. For example, NaCl and $MgCl_2$ both have ionic bond.

**Q. What are the necessary conditions for the formation of ionic bonds.**

**Ans.** *(i)* Number of valence electrons.

*(ii)* The ionization energy of the metal atom should be low.

(*iii*) Electron affinity of the non-metal atom should be high.

(*iv*) Electronegativity difference between the two atoms should be high.

**Q. Define electrovalency.**

**Ans.** Electrovalency of an element is its combining capacity in an ionic compound, i.e., when an element forms electrovalent bond, its valency is known as its electrovalency.

**Q. Why ionic compounds have high melting and boiling points?**

**Ans.** Ionic compounds have high melting and boiling points because of the strong attractive forces. These forces are not localized between two molecules but distributed among all the ions of the solid.

**Q. What is covalent bond?**

**Ans.** The chemical bond between two atoms in which the electrons are shared by both the participating atoms is called *covalent bond*. For example, $H_2$ and $Cl_2$ molecules have covalent bonds.

**Q. What is covalency?**

**Ans.** The valency of an element in a covalent compound is called its covalency.

**Q. What are the necessary conditions for the formation of covalent bonds?**

**Ans.** Following are the main factors which favour the formation of covalent bonds.

High ionization energy.

Equal electron affinities.

High nuclear charge and small internuclear distance.

Equal electronegativities.

Number of valence electrons.

**Q. Why ionic compounds have low melting and boiling points?**

**Ans.** Low melting and boiling points are due to the fact that the attractive forces between covalent molecules are weak van der Waals forces.

**Q. What is co-ordinate bond?**

**Ans.** A covalent bond which is formed by the mutual sharing of two electrons both of which are provided entirely by one of the linked atoms (or ions) is called a *co-ordinate bond.*

**Q. Define metallic bond.**

**Ans.** The attractive force that binds the metal ions to the mobile electrons is called *metallic bond.*

**Q. Why do metals not form ionic or covalent bonds?**

**Ans.** Since all the atoms in a metal crystal are similar, there is no possibility of the linking of the metals atom by ionic bond. Further, most of the metals have less than four electrons in their valence shell. With so few electrons in valence shell, it is not possible for a metal atom to be linked to other eight or twelve atoms by sharing the electrons with them.

**Q. What is the nature of hydrogen bond?**

**Ans.** Hydrogen bond is merely an electrostatic force rather than a chemical bond.

**Q. What are van der Waals forces?**

**Ans.** Van der Waals forces are very short lived intermolecular attractive forces which are believed to exist between all kinds of atoms, molecules and ions when they are sufficiently close to each other.

**Q. Discuss briefly the significance of van der Waals forces.**

**Ans.** It is the van der Waals forces between the molecules that cause substances like inert gases-halogens etc. to condense to liquids and to freeze into solids, when the temperature is considerably lowered.

**Q. What is valence shell electron pair repulsion (VSEPR) theory.**

**Ans.** This is a very useful theory to predict the geometry or shape of a number of polyatomic molecules or ions of non-transition elements. The theory says that the shape of a given species (molecule or ion) depends on the number and nature of electron pairs surrounding the central atom or ion of the species.

**Q. What is the cause of change in bond angle?**

**Ans.** The change in the magnitude of bond angle is due to the fact that (lp — lp) repulsion is greater than (lp — bp) repulsion, which in turn is greater than (bp — bp) repulsion.

**Q. What are electron deficient molecules?**

**Ans.** The class of compounds which have strong tendency to accept electrons because they have too few electrons to provide a total count of electrons required for next inert gas configuration are called *electron deficient molecules.* For example, $AlCl_3$, $BF_3$ etc.

## 3.5. Chemistry of s-Block Elements

**Q. What are S-block elements?**

**Ans.** The elements of group 1A and 11A of the periodic table constitute the S-block.

**Q. Why the elements of 1A group are called alkali metals?**

**Ans.** Group 1A of the periodic table contains six elements which are Lithium (Li), Sodium (Na), Potassium (K) Rubedium (Rb), Caesium (Cs) and Francium (Fr). These elements are collectively called *akali metals*, since they form strongly alkaline oxides and hydroxides.

**Q. Why do the alkali metals have similar physical and chemical properties?**

**Ans.** It is due to the similarity in the electronic configurations of the atoms of the alkali metals.

**Q.** **How the alkali metals are characterised?**

**Ans.** The alkali metals are characterised by the presence of one electron in outer most 's' shell.

**Q.** **Why all alkali metals have low ionization energies?**

**Ans.** We know that all alkali metals have only one electron in their outermost shell ($ns^1$ electron). This $ns^1$ electron is so weakly held with the nucleus that it can be removed very easily. Alkali metals, therefore, have low ionization energies.

**Q.** **Why do the alkali metals show strong electropositive character?**

**Ans.** The elements which have a strong tendency to lose their outermost electrons to form the cations are said to be *electropositive* or *metallic elements.* In case of alkali metals we have seen that $ns^1$ electron in these metals is weakly bound with the nucleus and hence can be easily removed from the atom to form $M^+$ cation.

$$M \longrightarrow M^+ + e^-$$

Thus these metals have strong tendency to lose their $ns^1$ electron to form $M^+$ cation and hence show strong electropositive or metallic character.

**Q.** **Why do the alkali metals show strong reducing properties?**

**Ans.** It is well known that an oxidizing agent is a substance which can accept electrons, while a reducing agent is a substance which can lose electrons. Since alkali metals have a strong tendency to lose their $ns^1$ electron, so they act as strong reducing agents.

**Q.** **Why different colours are imparted by the atoms of the alkali metals to the flame?**

**Ans.** We know that the valence shell electron ($ns^1$) of the atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the atoms or their salt into bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic radiation and hence the colour is imparted by the atom to the flame. Since the amount of energy absorbed during the excitation processes is different in different atoms, different colours are imparted by the atoms to the flame e.g., Li-crimson, Na-golden yellow, K-violet etc.

**Q.** **What is the difference between soda ash and washing soda?**

**Ans.** The anhydrous salt $Na_2CO_3$ is called *soda ash* while the hydrated salt is known as washing soda ($Na_2CO_3\ 10H_2O$).

**Q.** **Mention some uses of sodium carbonate.**

**Ans.** Sodium carbonate is used:

*(i)* for the manufacture of glass.

*(ii)* for washing purposes.

(*iii*) in paper and paint industries, and

(*iv*) for softening hard water.

**Q. What is baking soda? Give its uses.**

**Ans.** $NaHCO_3$ is known as baking soda. It is used as a medicine (*soda bicarb*) to neutralize acidity in the stomach It is largely used in baking powder and in the preparation of effervescent powders, fruit salts etc.

**Q. What are the different members of group 11A of the periodic table?**

**Ans.** Group 11A of the periodic table consists of six elements which are: Breyllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

**Q. Why the elements of 11A group are called alkaline earth metals?**

**Ans.** The oxides of three metals, viz; Ca, Sr and Ba were known much earlier than the metals themselves and were called *alkaline earths*, since they were alkaline in character and occurred in nature as earths. Later when Ca, Sr and Ba were discovered, they were named *alkaline earth metals*.

**Q. Why do the alkaline earth metals have high melting and boiling points than alkali metals?**

**Ans.** This is because the alkaline earth metals have two valence electrons and are much strongly bonded in the solid state than alkali metals.

**Q. Why Be and Mg do not give any colour to the flame?**

**Ans.** This is because the atoms are smaller and hence their electrons are most strongly attracted by the nucleus. Thus these electrons are not excited to the higher energy levels by the energy of the flame.

**Q. Give some uses of $MgSO_4$.**

**Ans.** It is used:

(*i*) as a purgative

(*ii*) in the manufacture of paints, soaps and fire proofing

(*iii*) as a filler for paper, and

(*iv*) as a mordant in dyeing and tanning industries.

**Q. How do alkali metals resemble with alkaline earth metals?**

**Ans.** The points of similarity are:

(*i*) Both are electropositive.

(*ii*) Both do not occur in the free state in nature.

(*iii*) Both are soft and silvery white metals.

(*iv*) The hydroxides of both are strong bases.

**Q. How do alkali metals differ from alkaline earth metals?**

**Ans.** The following points of difference are noteworthy.

*(i)* The alkaline earth metals are heavier and hearder than alkali metals.

*(ii)* Alkaline earth metals have high melting and boiling points than those of alkali metals.

*(iii)* Carbonates and sulphates of all alkaline earth metals are insoluble in water, but those of alkali metals are fairly soluble.

**Q.** **How Be resembles with Al?**

**Ans.** The points of similarities are:

*(i)* Both do not react with dilute nitric acid.

*(ii)* Both dissolves in caustic alkalies to form beryllates and aluminates with the evolution of hydrogen.

*(iii)* The halides of both metals are good Lewis acids.

*(iv)* Beryllium carbide and aluminium carbide liberate methane on hydrolysis.

## 3.6. Chemistry of P-Block Elements

**Q.** **What are P-block elements?**

**Ans.** Elements in which P-orbitals are in the process of filling in order to reach the inert gas configuration are called *P-block elements*. The elements have completely filled ns orbitals and have $np^{1-6}$ electronic configuration.

**Q.** **Which periodic groups belong to this block?**

**Ans.** Groups IIIA, IVA, VA, VIA, VIIA and zero group belong to this block.

**Q.** **What is the nature of P-block elements?**

**Ans.** Whereas s, d and f block elements are almost all metals, the P-block elements include metals non-metals, metalloids and inert gases.

**Q.** **How does electronegativity values vary in P-block elements?**

**Ans.** The electronegativity values of P-block elements decreases down the group and increases in a period.

**Q.** **Discuss the electropositive character of P-block elements.**

**Ans.** The electropositive character of P-block elements decreases on moving in a period, because ionization energy increases from left to right in a period and increases down the group due to decrease in ionization energy.

**Q.** **Why do P-block elements not give characteristic colour in the flame?**

**Ans.** The reason is that the excitation energy given out by the electrons, when they come back to ground state, does not appear in the visible region of the spectrum.

**Q. What is the nature of chemical bonding in P-block elements?**

**Ans.** Usually covalent bonding is present in P-block elements.

**Q. What is the nature of oxides formed by P-block elements?**

**Ans.** We know that P-block elements include metals, metalloids and non-metals. The metallic elements of P-block give basic oxides ($Bi_2O_3$), metalloids give amphoteric oxides ($As_2O_3$) and non-metallic elements give acidic oxides ($CO_2$, $SO_3$).

**Q. Write the names of group IIIA elements.**

**Ans.** Group IIIA of the periodic table consists of five elements which are: Boron (B), Aluminium (Al), Gallium (Ga), Indium (In) and Thallium (Tl).

**Q. What is the valence-shell electronic configuration of group IIIA?**

**Ans.** The valence-shell electronic configuration of group IIIA is $ns^2p^1$.

**Q. Why boron usually forms covalent compounds?**

**Ans.** Since boron atom has small size and high ionization energy, it does not lose all of its valence electrons and hence does not give $B^{3+}$ ion. It is for this reason that boron atom combines with other elements through covalent bonds, i.e., boron atom mainly gives covalent compounds.

**Q. Discuss the metallic character of boron group.**

**Ans.** All the members of this group are metals except boron which is semi-metal.

**Q. Why boron shows diagonal relationship with silicon?**

**Ans.** Some common properties showing the similarities between B and Si are given below:

*(i)* Both the elements can be prepared by reducing their oxides.

*(ii)* Chemically, both the elements are typical non-metals and are bad conductors of heat and electricity.

*(iii)* Both the elements are normally inert at room temperature.

*(iv)* Boron and silicon combine with $O_2$ at elevated temperature to form stable oxides, viz. $B_2O_3$ and $SiO_2$.

**Q. How does boron differ from silicon?**

**Ans.** The following points show dissimilarities between bronon and silicon.

*(i)* Boron has three electrons in its valence shell while silicon has four electrons.

*(ii)* Boron combines with $N_2$ to give BN, while silicon does not combine with $N_2$.

*(iii)* Boron is tri-covalent in its compounds, while silicon is tetracovalent in its compounds.

(iv) Boron is oxidized by hot cone $HNO_3$ or hot cone. $H_2SO_4$ to form $H_3BO_3$, while silicon is only attacked by HF.

**Q.** **Give some uses of boric acid.**

**Ans.** Boric acid ($H_3BO_3$) is used.

- *(i)* in the manufacture of pottery glazes, glass and enamels.
- *(ii)* in medicine as an antiseptic and as an eye lotion.
- *(iii)* as preservative in food industry, and
- *(iv)* in the manufacture of borax and pigments.

**Q.** **Give some uses of borax.**

**Ans.** Borax or sodium tetraborate ($Na_2B_4O_7010H_2O$) is a sodium salt of tetraboric acid ($H_2B_4O_7$). It is used:

- *(i)* in borax bead test for the detection of basic radicals.
- *(ii)* in the manufacture of enamels and glazes for pottery.
- *(iii)* in making optical glass and boro-silicate glass-ware.
- *(iv)* in the manufacture of washing powders and soaps.

**Q.** **Write the names of group IVA elements.**

**Ans.** Group IVA of the periodic table consists of five elements viz. Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn) and Lead (Pb). Carbon is an essential constituent of all organic matter, while silicon is the main constituent of inorganic matter.

**Q.** **What is the valence shell electronic configuration of group IVA elements?**

**Ans.** The valence-shell electronic configuration of group IVA elements is $ns^2p^2$.

**Q.** **How does carbon occur in nature?**

**Ans.** Carbon is the only element of this group which occurs in the free state as diamond, graphite and coal. In the combined state, it occurs as hydrocarbons, carbohydrates and carbon dioxide in the atmosphere.

**Q.** **How does lead occur?**

**Ans.** Lead occurs in mineral galena, PbS.

**Q.** **Discuss the metallic and non-metallic character of group IVA elements.**

**Ans.** The first two elements, viz., C and Si are distinctly non-metals; the third element viz; Ge is partly a metal and partly a non-metal (i.e., *metalloid*), while the last two elements viz; Sn and Pb are distinctly *metals*.

**Q.** **What is catenation or self-linkage?**

**Ans.** All the elements of group IVA have a tendency to link with each other and thus forms long chains of identical atoms. This type of linking of identical atoms with each other is called *catenation or self-linkage*.

**Q. What is the important characteristic of group IVA in the periodic table?**

**Ans.** Group IVA bridges the metals and non-metals on both sides of the periodic table.

**Q. Do the elements of this group show allotropy?**

**Ans.** Excepting lead, all other elements of this group show *allotropy*, i.e., these elements exist in different allotropic forms.

**Q. What ar different allotropic forms of carbon?**

**Ans.** Diamond, graphite, coal, coke, charcoal etc.

**Q. Write the names of group VA elements.**

**Ans.** Group VA of the periodic table consists of five elements, viz; Nitrogen (N), Phosphorus (P). Arsenic (As), Antimony (Sb) and Bismuth (Bi).

**Q. What is the valence shell configuration of group VA?**

**Ans.** The valence shell configuration of group VA elements is $ns^2p^3$.

**Q. Why does phosphorus not occur in the native state?**

**Ans.** Since phosphorus is very reactive and hence does not occur in the native state. Rather it occurs as phosphates in its ores:

**Q. Why do arsenic and phosphorus atoms not form $P_2$ and $As_2$ species while nitrogen atoms form $N_2$ species?**

**Ans.** The answer to this question is that it is not possible for P and As atoms to form P ⬀, P ⬀ bonds because these atoms cannot come closer to each other to form P ⬀, P ⬀ bonds due to the increased repulsions from the non-bonding electrons of penultimate shell. However, nitrogen atoms do not encounter any repulsion, since they contain $1s^2$ electrons in their penultimate shells.

**Q. Why does nitrogen differ from the other members of this group.**

**Ans.** This is because of the following inherent properties of nitrogen: *(a)* small size *(b)* higher electronegativity, and *(c)* non-availability of d-orbitals. The main points of difference are:

*(i)* Nitrogen is a gas while other elements are solids.

*(ii)* Nitrogen atom cannot expand its octet, while the other members of this group can do so.

*(iii)* Nitrogen shows a large number of oxidation states, while the other elements do not show such a variety of oxidation states.

*(iv)* Nitrogen is chemically inert due to high dissociation energy of $N \equiv N$ bond. However, other elements of the group are quite reactive.

**Q. Discuss the metallic and non-metallic character of group VA elements.**

**Ans.** Due to the decrease in the values of ionization energies from N to Bi, the metallic character of these elements increases in the same direction. For example, the first two elements viz. N and P are exclusively non-metals, the next two elements viz. As and Sb are metalloids while the last element namely Bi is definitely a metal.

**Q. What is the importance of N and P.**

**Ans.** Both the elements are essential constituents of fertilizers.

**Q. What do you mean by fixation of nitrogen?**

**Ans.** The conversion of atmospheric nitrogen into useful nitrogenous compounds by natural or artificial methods is called *fixation of nitrogen*. Nitrogen present in these nitrogenous compounds is called fixed or combined nitrogen.

**Q. What are the natural methods of nitrogen fixation?**

**Ans.** In nature nitrogen is fixed by the following methods.

**By lightning discharges.** The nitrogen and oxygen present in air combine together to form nitric oxide under the influence of lightning discharges. Nitric oxide is oxidized by excess of oxygen present in the atmosphere to form nitrogen peroxide which further combines with water to form nitric acid.

**By symbiotic bacteria.** The atmospheric nitrogen is being constantly transferred to the soil through the agency of certain bacteria called symbiotic bacteria. These grow in small nodules in roots of plants belonging to the family Leguminaceae (Pea, gram etc.).

**Q. Why nitrous oxide is called laughing gas?**

**Ans.** When this oxide is inhaled in small quantities, it produces hysterical laughter and for this reason this oxide is called *laughing gas*.

**Q. Give some uses of nitric acid.**

**Ans.** It is used:

*(i)* in the manufacture of nitrate which are important chemicals of commerce. Basic calcium nitrate is used as fertilizer. Silver nitrate is used in photography and sodium nitrate in the manufacture of gunpowder and fireworks.

*(ii)* in the manufacture of explosives like nitroglycerine, dynamite, trinitrotoluene, picric acid etc.

*(iii)* in the manufacture of artificial silk, dyes and perfumes.

*(iv)* in the manufacture of $H_2SO_4$.

*(v)* in the preparation of aqua regia.

**Q. What are nitrides and azides?**

**Ans.** The binary compounds of nitrogen with electropositive elements or with the elements which are less electronegative than nitrogen are called nitrides. While the salts of hydrazoic acid are called azides. Thus, $Na_3N$ $Ag_3N$ etc. are the examples of nitrides, while $NaN_3$, $AgN_3$ etc are the examples of azides.

**Q. What is the use of $P_2O_5$?**

**Ans.** It is extensively used as a drying and dehydrating agent.

**Q. Give some uses of phosphoric acid ($H_3PO_4$).**

**Ans.** *(i)* Pure phosporic acid has pharmaceutical applications and is used in the preparation of nervous tonics.

*(ii)* It is used for the manufacture of fertilizers, dyes, enamels and porcelain cement.

*(iii)* It is used in the dental filling.

**Q. What is microcosmic salt?**

**Ans.** Sodium ammonium hydrogen phosphate [Na $(NH_4)$ $HPO_4$ $4H_2O$] is called microcosmic salt since it is present in the urine of the "microcosm" i.e., man.

**Q. What is phossy jaws?**

**Ans.** White phosphorus has garlic odour and highly poisonous. It is used in match factories. Workers in match factories suffer from a disease called phossy jaws in which bones of jaw and teeth decay. This disease is due to white phosphorus.

**Q. What is transition temperature?**

**Ans.** It is the temperature at which one allotropic form of a substance changes into other. It has a fixed value for each pair of allotropes.

**Q. What do you know about diamond?**

**Ans.** Diamond is the hardest substance known. Among various forms of carbon, diamond is the purest and densest. It has the highest refractive index, 2.45. This property is responsible for its value as gems.

**Q. What do you know about Koh-i-Noor?**

**Ans.** Koh-i-Noor (mountain of light) is a famous diamond of large size which had the original weight of 186 carats (1 gram = 5 carats) but had to be out down to 106 carats later on.

**Q. What do you know about the conductance behaviour of diamond?**

**Ans.** The diamond is a non-conductor of electricity because of the complete utilization of valence electrons for the formation of covalent bonds.

**Q. Discuss the structure of diamond.**

**Ans.** Diamond contains carbon atoms linked together in a tetrahedral manner. Each carbon atom is surrounded by other carbon atoms (coordination number 4) in a three dimensional network.

**Q. Give some uses of diamonds.**

**Ans.** *(i)* Diamonds are both colourless and coloured. They are mostly used as jewels and gems in ornaments.

*(ii)* Black diamonds are known as *Carbonado* because of their great hardness. Thus they are used for glass cutting, rock drilling and for cutting and polishing colourless diamonds.

**Q. What do you know about graphite?**

**Ans.** Graphite is also an allotropic form of carbon. It is soft and greasy to touch. It has a grey-black colour with metallic luster.

**Q. What do you know about the conductance behaviour of graphite?**

**Ans.** Graphite is a good conductor of heat and electricity. The electrical conductivity of graphite is due to the presence of an electron remained after $SP^2$ hybridization. This single electron forms $\pi$-bond and $\pi$-electrons are mobile rendering graphite a conductor of electricity.

**Q. What do you know about amorphous carbon?**

**Ans.** Amorphous form of carbon is obtained by heating wood, starch, sugar and other organic substances rich in carbon in the absence of air. The important forms are:

**Charcoal.** The residue left after heating organic substances in absence of air is called charcoal. The most important form is *wood charcoal* which is manufactured by heating up a pile of wood in such a way that only a limited supply of air is allowed. Another form of charcoal is called *animal charcoal* which is obtained by destructive distillation of bones. Animal charcoal is employed for decolouring sugar and other organic matter.

**Coal.** It is produced by decomposition of wood and other vegetable matter in limited supply of air.

**Lampblack.** It is prepared by burning tar, petroleum and turpentine oil etc. in limited supply of air.

**Q. What are silicones?**

**Ans.** Silicones are important class of silicon compounds. They are polymeric substances with Si — O — Si linkages. They are obtained from silicon dioxide, $SiO_2$.

**Q. Discuss some uses of silicones.**

**Ans.** Silicones have remarkable heat resistance and high electrical insulating properties. So they are used as heat resistant varnishes, and insulating liquids in electrical transformers.

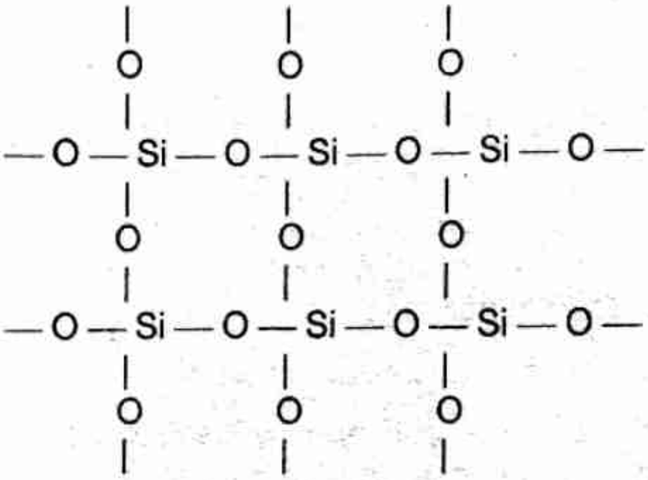
Silicone oils, silicone rubbers and silicone polymers are extensively used in industry where (i) high temperature conditions are to be maintained, (ii) electrical insulation is required and (iii) water repellant properties are to be maintained.

**Q. What is Keiselguhr?**

**Ans.** It is a siliceous earth left by remains of minute sea and other organisms. It is used as adsorbent for nitroglycerine, as wood filler etc.

**Q. Why $CO_2$ is a gas and $SiO_2$ is a solid at room temperature?**

**Ans.** The difference in physical properties of $SiO_2$ and $CO_2$ is due to the fact that the former consists of polymeric structure $(SiO_2)n$, whereas $CO_2$ exists in monomeric state. The structure of $(SiO_2)n$ can be represented as



**Q. Why do the tetravalent compounds of Si undergo hydrolysis?**

**Ans.** The tetravalent compounds of Si, Ge and Sn especially tetrahalides undergo hydrolysis and other reactions involving expansion of valence shell. Thus they can have covalencies more than four due to the involvement of d-orbitals.

**Q. Give some uses of silica, $SiO_2$?**

**Ans.** *(i)* It is used in the preparation of transparent varieties of glass.

*(ii)* The coloured varieties of quartz are used as gems.

*(iii)* The quartz glass used in delicate parts of the electrical instrument can be prepared from silica.

*(iv)* Silica is used in the manufacture of ordinary glass, porcelain cement, concrete and mortar.

**Q. What are silicates?**

**Ans.** The salts of silicic acid are called silicates. For example, sodium and potassium silicates.

**Q. What is the difference between water glass and soluble glass?**

**Ans.** The soluble silicates, e.g., sodium and potassium silicates, are known as *soluble glass*. The aqueous solution of soluble glass is known as *water glass*.

**Q. Write the names of group VIA elements.**

**Ans.** Group VIA of the periodic table consists of five elements viz., Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) and Polonium (Po). The elements O S, Se and Te ore often collectively called *chalcogens* i.e., the are forming elements.

**Q. What is the valence shell electronic configuration of group VIA elements?**

**Ans.** The characteristic valence shell configuration for these elements is $ns^2 np^4$.

**Q. Discuss the group trends of group VIA elements.**

**Ans.** *(i)* There is an overall increase in metallic character down the group.

*(ii)* The stability of 2 oxidation state decreases down the group.

*(iii)* The acidic nature of the oxides decreases down the group.

*(iv)* The tendency to form compounds containing large coordination numbers increases down the group.

**Q. Write the most common oxidation states of group VIA elements.**

**Ans.** −2, +2, +4, and +6.

**Q. Why does oxygen differ from the rest of the elements of group VIA?**

**Ans.** Oxygen, the first element of group VIA differs considerably from the rest of the elements of the group VIA because of the following inherent characteristics.

*(i)* Small size

*(ii)* Higher electronegativity

*(iii)* Non-availability of the d-orbitals

**Q. What are the main point of difference between oxygen and rest of the elements of the group?**

**Ans.** The main points of difference between oxygen and the remaining members of group VIA are:

*(i)* Oxygen is a gas while the other members are solid.

*(ii)* Oxygen is the most abundant of all the elements and constitutes 46.6% of the earth's crust.

*(iii)* Oxygen molecule is diatomic ($O_2$), while the molecules of other elements are more complex.

*(iv)* Maximum covalency of oxygen is two, while the other elements exhibit a covalency of six.

**Q. How does oxygen resemble with sulphur?**

**Ans.** *(i)* Both are non-metals

*(ii)* Both have six electrons in their valence shell

*(iii)* Both of them exist in free and combined states

*(iv)* Both show the phenomenon of allotropy

**Q. Discuss some dissimilarities between oxygen and sulphur.**

**Ans.** *(i)* Oxygen is a colourless and odourless gas, while sulphur is a pale yellow solid with a faint odour.

(ii) Oxygen occurs more abundantly in nature than sulphur.

(iii) Maximum covalency of oxygen is 2 while that of sulphur is 6.

(iv) Oxygen does not react with conc $HNO_3$, while sulphur is oxidized by conc $HNO_3$.

**Q. What is ozone?**

**Ans.** Ozone is an allotropic form of oxygen and its molecular formula is $O_3$.

**Q. What is fuming sulphuric acid?**

**Ans.** When $SO_3$ is passed through concentrated $H_2SO_4$, we get $H_2S_2O_7$, which is known as *fuming sulfuric acid* or *oleum*.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

**Q. Write down some uses of ozone.**

**Ans.** (i) As germicide and disinfectant for sterilizing water.

(ii) For bleaching oils, flour, wood pulp and textile fibre.

(iii) In destroying odours that arise from cold storage rooms, kitchens of big hotels and slaughter houses.

**Q. Discuss some uses of $H_2SO_4$.**

**Ans.** $H_2SO_4$ is used:

(i) in the manufacture of chemical manures like ammonium sulphate and calcium superphosphate.

(ii) in the manufacture of other acids like $HNO_3$, HCl and $H_3PO_4$ etc.

(iii) in refining petroleum.

(iv) in the manufacture of explosives.

(v) in the laboratory as an important reagent and as a drying and dehydrating agent.

**Q. Why addition of $H_2SO_4$ in water produces a lot of heat?**

**Ans.** Addition of $H_2SO_4$ in water produces a lot of heat because of the formation of $H_3O^+$ ions. $H_2SO_4$ has a strong affinity for water and would act as dehydrating agent.

**Q. What is hypo? Give its uses.**

**Ans.** Sodium thiosulphate ($Na_2S_2O_3\ 5H_2O$) is quite commonly used under the name `hypo' in photography. It is used:

(i) in photography. Due to its property of dissolving silver halides, it is used as fixer in photography under the name hypo. It removes the excess of silver halides.

(ii) in the laboratory for estimation of iodine and as a reagent.

(iii) in medicine.

**Q. Write the names of group VIIA elements.**

**Ans.** Group VIIA of the periodic table consists of five elements viz. Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (As).

**Q. What is the valence shell electronic configuration of group VIIA elements?**

**Ans.** The characteristic valence shell configuration of the elements of this group is $ns^2np^5$, which is one short of next inert gas configuration.

**Q. Discuss the general group trends of group VIIA elements.**

**Ans.** *(i)* All the halogens exist as covalent diatomic molecules ($X_2$ molecules) in the gaseous, liquid and crystalline state.

*(ii)* The electronegativity of the halogens decreases down the group.

*(iii)* The dissociation energy of halogen molecules decreases with increase in atomic number.

$$Cl_2 > Br_2 > I_2$$

But $F_2$ has exceptionally low value due to greater repulsion between lone-pair of electrons.

*(iv)* The oxidizing power of halogens decreases with increase in atomic number.

$$F_2 > Cl_2 > Br_2 > I_2$$

*(v)* The predominant oxidation state for halogens is -1, but compounds of halogens are known in which key show +1, +3, +5 and +7 oxidation states.

**Q. Why the term halogen is used for group VIIA elements?**

**Ans.** The term halogen is derived from the Greek halos (= salt) and genes (= born) meaning salt producers, because most of these elements exist in sea water, notably in the form of their sodium compounds.

**Q. Why do all the halogens appear coloured?**

**Ans.** All the halogens are coloured. Their colour is due to the fact that the molecules absorb light in the visible region by means of which the outer electrons are excited to higher energy level. The amount of excitation energy decreases from fluorine to iodine as the size of atom decreases. Thus there is a progressive deepening of colour from fluorine (yellow) to iodine (deep violet).

**Q. Why does fluorine differ from other members of its group.**

**Ans.** Fluorine differs from the other members of its own group due to

*(i)* its small size

*(ii)* its high electronegativity

*(iii)* non-availability of d-orbitals, and

*(iv)* low bond dissociation energy.

**Q. How does fluorine differ from other members of its group.**

**Ans.** Fluorine differs from other halogens in many respects. The following are the major points of difference.

- *(i)* Fluorine does not form oxyacids and oxysalts.
- *(ii)* It forms compounds which exhibit hydrogen bonding.
- *(iii)* It can form only one covalent bond.
- *(iv)* It possesses low bond energy.

**Q. Write the formulae and names of oxyacids of chlorine. Also mention the oxidation state of chlorine in each compound.**

**Ans.**

| Oxyacid | Name | Oxidation State |
|---|---|---|
| $HClO$ | Hypochlorous acid | +1 |
| $HClO_2$ | Chlorous acid | +3 |
| $HClO_3$ | Chloric acid | +5 |
| $HClO_4$ | Perchloric acid | +7 |

**Q. Write the sequence of oxyacids strength.**

**Ans.** The strength of oxyacids increases with increasing number of oxygen atoms. The sequence of the acid strength of oxyacid is:

$$HXO_4 > HXO_3 > HXO_2 > HXO$$

**Q. What are freons?**

**Ans.** Chloro-fluorocarbons obtained from $CCl_4$ are called freons.

$$CCl_4 + HF \longrightarrow Cl_3F + CCl_2F_2 + CClF_3 + CF_4 + HCl$$

These are used as non-toxic and non-corrosive inert refrigerants, aerosol bomb propellants and heat transfer and fire extinguishing agents.

**Q. How do freons differ from hydrocarbons?**

**Ans.** Freons differ from the hydrocarbon in that they are chemically very inert. This property makes them useful solvents, lubricants and insulators.

**Q. What is freon-12?**

**Ans.** Freon-12 is difluorodichloromethane, $CF_2Cl_2$. It is used in refrigeration and air conditioning in place of $NH_3$ and $SO_2$. It is non-toxic and non-flammable.

**Q. What do you know about Teflon?**

**Ans.** Teflon is polytetrafluoroethylene $(C_2F_4)n$. This is a plastic like inert material. It is insoluble in any solvent and is not attacked by acids, alkalies and oxidizing agents. Due to these properties, this material is used in the construction of chemical plants.

**Q. Why all the halogens are the most reactive elements as a family?**

**Ans.** The main reasons for their extreme reactivity are:

- *(i)* low dissociation energies of $X_2$ molecule, and
- *(ii)* high electron affinity values.

All the halogens have a strong tendency to add on electron to form $X^-$ ion.

**Q.** **Write down some uses of chlorine.**

**Ans.** Chlorine is employed:

(i) in the purification of water for drinking purposes.

(ii) in the manufacture of bleaching powder, chloroform, carbon tetrachloride, hypochlorite, hydrochloric acid and a number of synthetic compounds.

(iii) in the manufacture of poisonous gases like phosgene and mustard gas etc.

(iv) in the bleaching of cotton, paper and rayon.

**Q.** **Why sodium iodide is added to table salt?**

**Ans.** Sodium iodide is added to table salt (NaCl) for supplying the body needs of iodine.

**Q.** **What is Tincture of iodine?**

**Ans.** Tincture of iodine is a solution of iodine in alcohol — water solution containing potassium iodide. It is used as antiseptic and analgesic.

**Q.** **What is bleaching powder?**

**Ans.** Bleaching powder is probably not a single compound but is a mixture of salts of hydrochloric acid (HCl) and hypochlorous acid (HClO) and hence the formula $CaOCl_2$ or Ca (OCl)Cl. The formula shows that it is calcium chloro-hypochlorite.

**Q.** **What are interhalogens?**

**Ans.** The binary compounds of halogens among themselves are called interhalogen compounds. For example, $ClF_3$, $ICl_3$ and $IF_7$.

**Q.** **Why do halogens form binary compounds?**

**Ans.** Due to difference in electronegativity.

**Q.** **What are pseudohalogens?**

**Ans.** Certain radicals show behaviour analogous to halogens and are called pseudohalogens. They would form covalent dimers just like halogen molecules. For example,

Cyanogen $(CN)_2$
Thiocyanogen $(SCN)_2$
Selenocyanogen $(SeCN)_2$

**Q.** **Write the names of zero group elements.**

**Ans.** Zero group of the periodic table consists of six elements namely, Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radan (Rn). These elements are also called by other names like *inactive gases, inert gases, rare gases* and *noble gases.*

**Q. What is the valence shell configuration of noble gases?**

**Ans.** The characteristic valence shell configuration of noble gases is $ns^2p^6$.

**Q. Why are the rare gases chemically inert?**

**Ans.** The chemical inertness of these elements is due to the following reasons:

*(i)* All the atoms have saturated shells. They have, therefore, no tendency either to lose, gain or share electrons with atoms of other elements.

*(ii)* Atoms of these elements have all the electron paired.

*(iii)* The electronegativity and electron affinity of these elements are zero.

**Q. Why are these elements placed in zero group?**

**Ans.** These elements are placed in zero group, because their combining tendency or valency is zero.

**Q. Why are these elements placed in VIII group?**

**Ans.** Electronic configurations of these elements indicate that except helium, which has $ls^2$ configuration, all the elements have eight electrons in their outermost shell. Therefore, on this basis they must be placed in the VIII group.

**Q. Why are these elements called rare gases?**

**Ans.** Sometimes, they are also called rare gases because they exist only in minute quantities in the atmosphere.

**Q. How do they occur in nature?**

**Ans.** They all exist as free atoms.

**Q. Give some uses of inert gases.**

**Ans.** *(i)* Helium is used for filling balloons due to its lightness and inflammable nature.

*(ii)* Helium is also used in tyres of large aeroplanes.

*(iii)* Helium is used in scientific research to produce inert atmosphere.

*(iv)* Neon is used in neon lamps and advertisement signals.

*(v)* Argon is used in electric bulbs to keep an inert atmosphere.

*(vi)* Radon is used in radiotherapy of cancer.

**Q. What are clathrates?**

**Ans.** The inert gases argon, krypton and xenon form solid compounds with certain organic molecules such as phenol hydroquinone under pressure. In these compounds, the inert gases are enclosed into the crystal lattices of the organic molecules. These compounds are known as clathrates. These are also referred to as cage compounds.

## 3.7. Chemistry of d-block Elements

**Q. What are d-block elements?**

**Ans.** Those elements in which (n – 1)d orbital is in the process of completion are called d-block elements.

**Q. What is the valence shell configuration of these elements?**

**Ans.** The valence shell configuration of most of these elements varies from $(n-1)d^1, ns^2$ to $(n-1)d^{10}, ns^2$.

**Q. Why are d-block elements called transition elements?**

**Ans.** The d-block elements are also called transition elements, since their properties are intermediate between those of S and P block elements.

**Q. What is the nature of d-block elements?**

**Ans.** All the d-block elements consist of metals only. They are hard, malleable and ductile.

**Q. What types of bonding occurs in d-block elements?**

**Ans.** Both metallic and covalent bonding exist in these elements.

**Q. Why do the d-block elements how different oxidation states?**

**Ans.** Most of the transition metals show different oxidation states in their compounds The cause of showing different oxidation states is that these elements have several (n – 1)d and ns electrons and that the energies of (n – 1)d and ns orbitals are fairly close to each other. Hence (n – 1)d electrons are easily lost as ns electrons.

**Q. Why do Mn show the maximum number of oxidation states in 3d-series?**

**Ans.** Because it is at Mn that the number of unpaired electrons in the 3d-orbitals is maximum. Hence it shows +2, +3, +4 (+6) and +7 oxidation states.

**Q. Do the transition metal ions possess paramagnetic behaviour?**

**Ans.** Yes, the transition metal ions and their compounds usually possess unpaired electrons and would show paramagnetism and are attracted into a magnetic field.

**Q. Why do most of the transition metal ions possess a definite colour?**

**Ans.** Most of the transition metal ions possess unpaired electrons and are coloured. The colour of the ion depends upon the electronic transitions between the available d-orbitals. As different oxidation states of the same metal possess different number of unpaired electrons, different amounts of energy would be absorbed or emitted with difference in the colour of the ions.

**Q. Do transition metals possess catalytic properties?**

**Ans.** Yes, most of the transition metals and some of their derivatives act as catalyst. For example, Pd, Pt, Ni and V metals and their compounds are used as catalysts in industry. Ni is used as a catalyst for the hydrogenation of vegetable oil to vanaspati ghee.

**Q. Why do transition metals form complex compounds?**

**Ans.** The tendency of the cations of d-block elements to form complexes with the ligands is due to two reasons:

*(i)* The cations are relatively very small in size and hence have high positive charge density which makes it easy for the cations to accept the lone pair of electrons from the ligands.

*(ii)* The cations have vacant (n – 1)d orbitals which are of appropriate energy to accept lone pair of electrons from the ligands for bonding with them.

**Q. What are addition or molecular compounds?**

**Ans.** When solutions of two or more salts in simple molecular ratio are mixed together and allowed to evaporate, crystals of a new compound are obtained. This new compound is called addition or molecular compound.

**Q. What is the difference between double salts and coordination or complex compounds?**

**Ans.** Addition compounds are of two types.

**Double salts.** These compounds are stable in the solid state only but are broken into their individual compounds when dissolved in water or any other ionic solvent. The physical and chemical properties of a double salt are the same as those of these individual compounds. For example, Mohr's salt. $FeSO_4 (NH_4)_2 SO_4 . 6H_2O$ and potash alum, $K_2SO_4 Al_2(SO_4)_3 . 24H_2O$.

**Coordination compounds.** These compounds retain their identities in the solid as well as when dissolved in water. Their properties are completely different from those of their individual constituents. For example, $[Co (NH_3)_6] Cl_3$ and $[CO (NH_3)_5 Cl]Cl_2$.

**Q. What is a complex ion?**

**Ans.** Complex ion is a charged molecular species consisting of a metallic atom or ion to which is attached one or more charged or neutral molecules. For example, $[Ni (NH_3)_6]^{2+}$ ion.

**Q. What is a ligand?**

**Ans.** The neutral molecule or ion (usually anion) which is attached with the central ion in complex compound is called ligand or coordinating group. For example, $NH_3$, $H_2O$, $F^-$, $Cl^-$, CO.

**Q. Define unidentate ligand.**

**Ans.** The ligand which has only one donor atom. For example, $NH_3$, CO.

**Q. Define coordination number, and coordination sphere.**

**Ans.** Coordination number is defined as the number of donor atoms establishing coordinate bonds to the central metal atom or ion.

The formulae of coordination complexes are written using square brackets [ ], called coordination sphere.

**Q. What is chelate?**

**Ans.** When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, we get a complex compound which contains one or more rings in its structure and hence is called a chelate or chelated complex.

**Q. Do the coordination compounds show isomerism?**

**Ans.** Yes, coordination compounds show two types of isomerism namely structural isomerism and stereo-isomerism.

**Q. Explain outer orbital and inner orbital complexes.**

**Ans.** Outer orbital complexes or high spin complexes are the coordination compounds in which the central metal atom uses its "outer" d-orbitals for coordination linkage with the ligands. Such complexes usually show paramagnetic behaviour (attracted by external magnetic field). For example, $[CoF_6]^{3-}$ ion.

Inner orbital complexes or low spin complexes are the coordination compounds in which central metal atom uses its "inner" d-orbitals for coordination linkage with the ligands. These usually show diamagnetic behaviour (repelled by external magnetic field). For example $[CO(NH_3)_6]^{3+}$ ion.

**Q. Explain effective atomic number rule.**

**Ans.** Sidgwick pointed out that during the formation of coordination compounds, the central metal atoms have tendency to attain the electronic configuration of next inert gas. In otherwords, the effective atomic number of the central metal atom becomes equal to the atomic number of next inert gas after complex formation. This is called effective atomic umber (E.A.N) rule.

**Q. What is crystal field splitting?**

**Ans.** The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting. This concept makes the basis of CFT. This energy difference arises because of the difference in electrostatic field exerted by the ligands on two sets of orbitals of the central metal cations.

**Q. What are degenerate orbitals?**

**Ans.** The orbitals which have the same energy are called degenerate orbitals.

**Q. What factors affect the crystal field splitting?**

**Ans.** The extent of crystal field splitting depends on several factors. The nature of the ligand is an important factor. With the same metal ion, the ligands with large negative charge which can approach the metal orbitals closely should provide greater crystal field splitting. Small and more electronegative ions will have less crystal field splitting, e.g. F- ion.

The crystal field splitting ability of ligands is found to decrease in the following order

$$CO, CN^- > NO_2^- > NH_3 > H_2O > F^- > OH^- > Cl^- > Br^- > I^-$$

| strong field ligands | intermediate field ligands | weak field ligands |
|---|---|---|

**Q. What is the major achievement of CFT.?**

**Ans.** The major achievement of CFT is its success in interpreting the colours and absorption spectra of transition-metal complexes.

**Q. Write formulae and names of some coordination compounds.**

**Ans.**

| | |
|---|---|
| $[CO(NH_3)_6]Cl_3$ | Hexamminecobalt (III) chloride |
| $[CO(NH_3)_4Cl_2]Cl$ | Dichlorotetramminecobalt (III) chloride |
| $Ni(CO)_4$ | Tetracarbonylnickel (O) |
| $K_4[Fe(CN)_6]$ | Potassium Hexacyanoferrate (II) |
| $[Ni(DMG)_2]$ | Bis (dimethylglyoximato) nickel (II). |

**Q. How does CFT treat the bonding between metal atom and ligands?**

**Ans.** According to CFT, the interaction between the metal cation and the ligands is regarded as purely electrostatic, i.e., the metal-ligand bond is considered to be 100% ionic.

## 3.8. Chemistry of f-block Elements

**Q. What are f-block elements?**

**Ans.** The elements in which the extra electron enters (n – 2)f orbitals are called f-block elements.

**Q. Why are f-block elements called inner transition elements?**

**Ans.** Since (n – 2)f orbitals lie comparatively deep within the kernel (being inner to the penultimate shell), these elements are also called inner transition elements.

**Q. What are 4f-block elements?**

**Ans.** The elements in which 4f orbital is in the process of completion. 4f-block elements are also called *lanthanides, lanthanones* or *rare earths*. The first two names are given because of their strong resemblance to lanthanum. The name rare earths was given to them because they were originally extracted from oxides for which ancient name was earth and which were considered to be rare.

**Q. What is the valence shell configuration of lanthanides?**

**Ans.** The valence shell configuration of lanthanides is

$$(n-2)f^{0,2\ldots\ldots14}\,(n-1)d^{0,1}\,ns^2$$

**Q. What is the composition of monazite mineral.**

| | | |
|---|---|---|
| Monazite<br>(Ce)$PO_4$ | 49 — 74 % | Ce-earths (as oxides) |
| | 1 — 4% | Y-earths (as oxides) |
| | 5 — 9% | $ThO_2$ |
| | 1 — 2% | $SiO_2$ |
| | 20 — 30% | $P_2O_5$ |
| | Traces | U |

**Q. Write the composition of euxenite mineral.**

**Ans.** Euxenite — Y (Nb, Ta) $TiO_6 \cdot X\ H_2O$

| | |
|---|---|
| 13 — 35% | Y-earths (as oxides) |
| 2 — 8% | Ce-earths (as oxides) |
| 20 — 23% | $TiO_2$ |
| 25 — 35% | $(Nb, Ta)_2O_5$ |

**Q. What is the common oxidation state of lanthanides?**

**Ans.** +3 is the common oxidation.

**Q. Why La, Gd and Lu show only +3 oxidation state?**

**Ans.** It is a general rule that empty, half filled and completely filled 4f-orbitals are highly stable. So $La^{3+}$ ($4f^{0}$) $Gd^{3+}$ ($4f^{7}$) and $Lu^{3+}$ ($4f^{14}$) ions are stable.

**Q. How are rare-earths separated from each other?**

**Ans.** The following methods are used for the separation of rare-earths.

(*i*) Fractional crystallization.

(*ii*) Fractional precipitation.

(*iii*) Oxidation-reduction.

(*iv*) Ion-exchange.

(*v*) Solvent extraction.

**Q. What are mish metals?**

**Ans.** Alloys of lanthanides are known as mish metals. The major constituent of mish metals are Ce (45%), La (20%) Nd (5%) and small quantities of other lanthanides and Fe and Ca impurities.

Mish metals are used for the production of different brands of steel like heat resistant, stainless and instrumental steel.

**Q. What is the basis of absorption spectra of lanthanides?**

**Ans.** The absorption spectra of lanthanide cations result from f-f transition in a manner analogous to d-d transitions of transition metals.

**Q. What is lanthanide contraction?**

**Ans.** The steady decrease in the atomic and ionic radii in the lanthanide series is called *lanthanide contraction*.

**Q. What is the cause of lanthanide contraction?**

**Ans.** As we proceed from one element to the next in the series, the nuclear charge increases by +1 at each next element and the addition of extra electron takes place in the 4f orbital. Due to negligible amount of mutual shielding effect between 4f electrons, the increase in nuclear charge by +1 at each next element brings the valence shell near to the nucleus and hence the size of $M^{3+}$ cations goes on decreasing as we move from one element to the next one in the series.

**Q. What are the consequences of lanthanide contraction?**

**Ans.** *(i)* There is a decrease in the basic strength of the hydroxides of lanthanides with increase in atomic number.

*(ii)* There is a decrease in the basic strength of the oxides with the increase in atomic number.

*(iii)* Post-lanthanide elements have similar properties, e.g. Zr — Hf, Nb — Ta etc. have almost similar size.

*(iv)* Occurrence of Y with heavy lanthanides.

**Q. Give some uses of lanthanide compounds.**

**Ans.** *(i)* Mish metals are used for the production of different brands of steel.

*(ii)* $CeO_2$, $La_2O_3$, $Nd_2O_3$ and $Pr_2O_3$ are widely used for decolourizing glass.

*(iii)* CeS is used in the manufacture of a special type of crucibles which are used for melting metals.

*(iv)* Lanthanide oxides are used as abrasive for polishing glasses.

*(v)* $Ce(SO_4)_2$ is used as an oxidizing agent in volumetric titrations.

**Q. What are actinides?**

**Ans.** The elements is which 5f-orbitals are in the process of completion are called actinides.

**Q. What are transuranium elements?**

**Ans.** The elements which are lying beyond uranium in the periodic table are known as trans-uranium elements.

**Q. What is the valence shell configuration of actinides?**

**Ans.** The valence shell configuration of actinides is

$$5f^{0,1,2 \ldots\ldots 7,9 \ldots\ldots 14}\ 6d^{0,1,2}\ 7s^2$$

**Q. What is the nature of actinides?**

**Ans.** All the actinides are radioactive.

**Q. What is the most stable oxidation state for actinides?**

**Ans.** Actinides show a variety of oxidation states, but +3 is the most stable oxidation state.

**Q.** **What are uranates?**

**Ans.** The salts of uranic acid are called uranates. For example, $Na_2U_2O_7$, $Na_2UO_4$, $Li_2UO_4$ etc.

**Q.** **How do lanthanides resemble with actinides?**

**Ans.** *(i)* In both the series, the (n – 2)f orbitals are in the process of completion.

*(ii)* The elements of both the series show +3 oxidation states.

*(iii)* Both the series show contraction in their atomic and ionic radii.

*(iv)* Most of the lanthanide and actinide cations are paramagnetic.

*(v)* Elements of both the series have low electronegativity and are very reactive.

**Q.** **How do lanthanides differ from actinides?**

**Ans.** *(i)* In lanthanides, 4f orbitals is in the process of completion, while in actinides 5f-orbital is involved.

*(ii)* The compounds of lanthanides are less basic, while the compounds of actinides are more basic.

*(iii)* Lanthanides show only +2, +3 and +4 oxidation states, while actinides show a variety of oxidation states like +2, +3, +4, +5, +6 and +7.

*(iv)* Most of the tripositive cations of lanthanides are colourless while tripositive and tetrapositive actinide cations are coloured.

*(v)* Except Pm, all the lanthanides are non-radioactive while all the actinides are radioactive.

## 3.9. Qualitative and Quantitative Analysis

**Q.** **What is a salt?**

**Ans.** It is a neutralization product of an acid and a base.

**Q.** **What do you mean by an 'ion'?**

**Ans.** An ion is a atom or a group of atoms having positive or negative charge.

**Q.** **What are deliquescent substances?**

**Ans.** These are the substances which absorb moisture from the air. For example, NaOH, $P_2O_5$ etc.

**Q.** **How would you perform charcoal cavity test?**

**Ans.** This test is performed by fusing the salt with anhydrous sodium carbonate in a cavity made of charcoal. The heating is done by reducing the flame of a blow pipe. The metallic residue is examined and the result is inferred.

**Q.** **Write the formula of borax.**

**Ans.** Sodium tetraborate, $Na_2\,B_4O_7.\,10H_2O$.

**Q.** **Can you perform borax bead test for colourless salts?**

**Ans.** No. This test is only performed for coloured salts because none of the colouress salt gives a characteristic bead with borax.

**Q. What is the compound formed which appears as a bead in borax bead test?**

**Ans.** It is due to the formation of metaborate.

**Q. What are the colours of Cu, Fe, Co, Ni, Cr and Mn beads?**

**Ans.** Cu = blue, Fe = light yellow, Co = blue, Ni = pale red,
Mn = violet.

**Q. Why is platinum wire used in the borax bead test?**

**Ans.** Only platinum wire is used in the borax bead test because it has high melting point and imparts no colour to the flame.

**Q. How would you perform filter ash test?**

**Ans.** Take the powdered substance in a test tube and shake it with cobalt nitrate solution. Dip a piece of filter paper in this liquid and dry it over a burner. Then burn it and note the colour of the ash.

**Q. Name the basic radicals which give filter ash test.**

**Ans.** Sn, Al, Mg and Zn.

**Q. Can you perform filer ash test for a coloured salt.**

**Ans.** No, this test is performed only for colourless salts.

**Q. How would you perform flame test?**

**Ans.** Make a thin paste of the given salt with conc HCl in a clean watch glass. Take aplatinum wire, dip it in cone. HCl contained in a clean watch glass and heat it in a flame till the wire does not impart any colour to the flame. Now dip this clean platinum wire in the paste and place in the clean bunsen flame, observe the colour as long as it lasts.

**Q. Why do we use platinum wire for performing flame test?**

**Ans.** Because it has high melting point and imparts no colour to the flame.

**Q. Why do you make a paste with conc HCl?**

**Ans.** The salts are moistened with cone HCl in order to convert them into the chlorides, which being more volatile, can easily impart the characteristic colour to the flame.

**Q. Can we make a paste of the salt in conc $H_2SO_4$ instead of conc HCl?**

**Ans.** No, if a paste of the given salt is prepared with con $H_2SO_4$, it will change to sulphate which are not as volatile as chlorides. Therefore characteristic colour will not be imparted to the flame easily.

**Q. What colours are imparted to the flame by slats of K, Na, Ca, Ba, Sr, Zn and Cu?**

**Ans.** Na = golden yellow
K = violet
Ca = Brick red
Ba = Apple green
Sr = Crimson
Zn = Green
Cu = Bluish green.

**Q. Why is it necessary to note the colour of the flame through the blue glass?**

**Ans.** A blue glass absorbs a part of light and hence flame colouration suffers a characteristic change which helps in distinguishing between similar flames like Ca and Sr or to detect the presence of a particular radical in the presence of other, e.g., K in the presence of Na.

**Q. What is dry test?**

**Ans.** It is a test which is applied to the salt in the dry state.

**Q. What do you mean by a wet test?**

**Ans.** It is a test which is applied to the salt after forming its solution.

**Q. Name basic radicals of group I.**

**Ans.** Silver ($Ag^+$), mercurous ($Hg^+$), Plumbous ($Pb^{++}$).

**Q. What is the group reagent of group I ?**

**Ans.** Dilute HCl.

**Q. How the basic radicals of group I are precipitated?**

**Ans.** Basic radicals of group I are precipitated as their chlorides, e.g. AgCl, HgCl, $PbCl_2$.

**Q. Can we use dil $H_2SO_4$ in place of dil. HCl as group reagent in first group of basic radicals?**

**Ans.** No, because in that case basic radicals of other groups will also be precipitated as sulphates in the first group, e.g., $BaSO_4$, $SrSO_4$ etc.

**Q. Name basic radicals of group II.**

**Ans.** IIA $Cd^{2+}$, $Hg^{2+}$, $Bi^{3+}$, $Cu^{2+}$
IIB $As^{3+}$, $Sb^{3+}$, $Sn^{2+}$

**Q. What is the group reagent for II group?**

**Ans.** $H_2S$ in the presence of dil. HCl.

**Q. How the radicals of II group are precipitated?**

**Ans.** They are precipitated as their sulphides.

**Q. What is the colour of CdS, $Bi_2S_3$ and CuS?**

**Ans.** CdS = Yellow, $Bi_2S_3$ = Brownish black, CuS = Black.

**Q. What is the formula of yellow amm. sulphide?**

**Ans.** $(NH_4)_2S_x$

**Q. Why yellow amm. sulphide is called as yellow?**

**Ans.** The yellow colour is due to excess of sulphur.

**Q. Why yellow amm. sulphide is used?**

**Ans.** It is used in the II group of basic radicals to distinguish between basic radicals of IIA and IIB groups.

**Q. What is the colour of anhydrous $CuSO_4$?**

**Ans.** Colourless (White).

**Q. Why do we add dil. HCl before passing $H_2S$ gas in the II group?**

**Ans.** $H_2S$ is a weak electrolyte and cannot ionize completely in the presence of common H+ ions from HCl which is a strong electrolyte.

$$H_2S \rightleftharpoons 2H + S^{2-}$$
$$HCl \rightleftharpoons H^+ + Cl^-$$

This low concentration of sulphide ions would precipitate basic radicals of II group only, whereas it would be insufficient to precipitate radicals of other groups because their sulphides are comparatively soluble.

**Q. Sometimes a turbid solution is obtained when the mixture is dissolved in water, what is that due to?**

**Ans.** Due to Bi and Sb salts which hydrolyse to form BiOCl and SbOCl. It may be avoided by adding few drops of dil. $HNO_3$ , which will prevent hydrolysis.

**Q. Why is necessary to dissolve IIA precipitates in $HNO_3$ of moderate concentrations (i.e. 45%) instead of conc $HNO_3$?**

**Ans.** Con. $HNO_3$ is not used because if Pb is present in the mixture, it will be converted into insoluble $PbSO_4$.

**Q. What is `red lead' and white lead?**

**Ans.** Red lead = $Pb_3O_4$, White lead = $2PbCO_3$, $Pb(OH)_2$.

**Q. What is Blue vitriole?**

**Ans.** $CuSO_4 . 5H_2O$.

**Q. What is aqua-regia?**

**Ans.** It is a mixture of two acids i.e., conc HCl and conc, $HNO_3$ having ratio 3:1

**Q. Name basic radicals of III group.**

**Ans.** $Fe^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$.

**Q. Why do you add 1-2 drops of conc. $HNO_3$ in the III group?**

**Ans.** 1-2 drops of conc. $HNO_3$ are added only if the salt is of light green colour. Conc. $HNO_3$ oxidizes $Fe^{2+}$ into $Fe^{3+}$.

**Q. What is group reagent for III group?**

**Ans.** Solid ammonium chloride and $NH_4OH$.

**Q. What would happen if a ferrous salt is given but conc. $HNO_3$ is not added in the III group?**

**Ans.** In the absence of conc. $HNO_3$, ferrous salt will be precipitated as ferrous hydroxide $Fe(OH)_2$, which is of green colour and it will create confusion with the ppt. of chromium which is of dirty green colour.

**Q. How can you distinguish between ferrous and ferric salt?**

**Ans.** Add potassium sulphocyanide (KSCN) to the original solution, a blood red colouration shows that presence of ferric ($Fe^{3+}$). No blood red colouration shows ferrous ($Fe^{2+}$).

**Q. Why $NH_4Cl$ is added along with $NH_4OH$?**

**Ans.** The cations of III group are precipitated as insoluble hydroxides, if $NH_4Cl$ is not added other cations may also precipitate as hydroxides. In the presence of $NH_4Cl$, the ionization of $NH_4OH$ is suppressed so that the __$OH^-$ ions in the solution are just sufficient to precipitate the radicals of the III group only and not others.

**Q. What is green vitriole?**

**Ans.** $FeSO_4$ $7H_2O$.

**Q. What is alum?**

**Ans.** It is a double salt of potassium and aluminium having the formula $K_2SO_4$ Al2$(SO_4)_3$. $24H_2O$.

**Q. Why is it necessary to boil off $H_2S$ from the filtrate of II group before the addition of conc. $HNO_3$?**

**Ans.** It is essential to boil off $H_2S$ gas, otherwise it will be oxidized, at least partly, to $H_2SO_4$.

$$H_2S + 8HNO_3 \longrightarrow H_2SO_4 + 4H_2O + 8NO_2$$

If the mixture contains Ba and Sr, they will form insoluble sulphates and get precipitated in the III group.

**Q. What difficulty may come across when the III group is precipitated from a cold solution and an excess of $NH_4OH$ has been added?**

**Ans.** Chromium may not be precipitated, but may pass on into the filtrate as a complex compound $[Cr\ (NH_3)_6]^{3+}$. Its colour resembles the pink colour $[Co\ (NH_3)_4]^{2+}$ and the students may suspect the presence of Co.

**Q. Name those acid radicals which interfere in the regular analysis of basic radicals.**

**Ans.** Oxalates, Tartrates, Phosphates, Chromates, Dichromates, Permanganates, Silicates, Arsenates, Borates etc.

**Q. How will you detect the presence of oxalate, tartrate and phosphate?**

**Ans.** *(i)* Heat the dry mixture in a test tube, charring indicates *tartrate*.

*(ii)* Take a few drops of the solution before proceeding to group III, add a few drops of acidified $KMNO_4$ solution. decolouration with evolution of $CO_2$ indicates *oxalate*.

*(iii)* To the original solution, add conc. $HNO_3$ and freshly prepared ammonium molybdate solution, boil and allow to stand, yellow ppt or colour indicates *phosphate*.

**Q. Why is it necessary to detect and eliminate the interfering radicals before proceeding to the precipitation of III group?**

**Ans.** It is necessary because if one or more of them are present in the mixture, then addition of $NH_4OH$ solution for III group will not precipitate Al, Fe and Cr only but also the bases of the IV, V groups and Mg as salts of these acids. The salts of these acids with the bases of III, IV, V groups and Mg are insoluble in water or water containing $NH_4OH$, even in the presence of $NH_4Cl$. This is why it is necessary to detect and eliminate the interfering radicals.

**Q. Why do the interfering radicals not interfere in I and II groups?**

**Ans.** They do not interfere in I and II groups due to the fact that they are soluble in acidic medium.

**Q. Whether the elimination of interfering radicals is always necessary?**

**Ans.** Elimination is not always necessary. Take the filtrate of II group and boil off $H_2S$ completely. Then add $NH_4OH$ drop wise till the medium is alkaline. If there is any precipitate, the removal of interfering radicals is necessary. On the other hand, if there is no precipitation by the addition of $NH_4OH$, then removal of interfering radicals is not required. Moreover, the cations of group III to V and $Mg^{2+}$ are absent, and directly examine $Na^+$, $K^+$ and $NH_4^+$

**Q. How will you eliminate oxalates and tartrates?**

**Ans.** Evaporate the filtrate of group II with a few drops of conc. $HNO_3$ to almost dryness twice until the black residue is completely oxidized. (Do not heat the residue too strongly as Fe, Al and Cr may be converted to $Fe_2O_3$-$Al_2O_3$ and $Cr_2O_3$ which are insoluble in dil. HCl) Extract the residue with 10 drops of dil HCl and proceed with regular analysis.

**Q. How will you eliminate phosphates?**

**Ans.** Take the filtrate from group II and evaporate it to a small volume. Add 3ml of HCl and 0.5 gram of $NH_4Cl$. Shake or heat the solution to dissolve $NH_4Cl$ and then add zirconyl nitrate or chloride drop by drop with constant stirring to complete precipitation. Boil, cool and centrifuge. Reject the precipitate and proceed for analysis of group III to VI with the filtrate.

**Q. Name the cations of IV group.**

**Ans.** IV group of basic radical contains $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Mn^{2+}$.

**Q. What is the group reagent for IV group?**

**Ans.** The group reagent is $H_2S$ in ammonical solution ($NH_4OH$).

**Q. Why the medium is made alkaline before passing $H_2S$ gas?**

**Ans.** Medium is made alkaline before passing $H_2S$ gas for the precipitation of IV group in order to increase the concentration of sulphide ions. In alkaline solution, the concentration of sulphide ion from $H_2S$ is increased and brings about the precipitation of IV group.

$$H_2S \rightleftharpoons 2H^{+} + S^{2}$$

$$NH_4OH \rightleftharpoons NH_4^{+} + OH$$

$OH^{-}$ ions remove $H^{+}$ ions in the form of unionized water and thus increase the ionization of $H_2S$.

**Q. How the basic radicals of IV group are precipitated?**

**Ans.** They are precipitated as their sulphides.

For example,

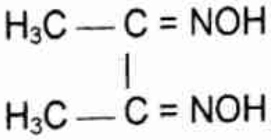
NiS = Black
MnS = Pink or flesh colour
CoS = Black
ZnS = Grayish white

**Q. What is the usual colour of Co, Mn, Ni and Zn salts?**

**Ans.** Ni-salts = Green
Co-salts = Dark pink
Mn-salts = Light pink
Zn-salts = Colourless.

**Q. Write the formula of dimethylglyoxime.**

**Ans.** The formula of dimethylglyoxime is



$$\begin{array}{l} H_3C - C = NOH \\ \quad\quad\;\; | \\ H_3C - C = NOH \end{array}$$

**Q. What are the cations of group V ?**

**Ans.** $Ba^{2+}$, $Ca^{2+}$ and $Sr^{2+}$.

**Q. What is the group reagent for V group?**

**Ans.** $(NH_4)_2 CO_3$ in the presence of $NH_4Cl$ and $NH_4OH$.

**Q. How the basic radicals of V group are precipitated?**

**Ans.** Basic radicals of V group are precipitated as their carbonates.

**Q. Name some of the carbonates which are insoluble in water.**

**Ans.** $CaCO_3$, $SrCO_3$, $BaCO_3$.

**Q. What is the colour of the slat of V group?**

**Ans.** The salts of V group are colourless.

**Q. Name some insoluble sulphate.**

**Ans.** $PbSO_4$, $BaSo_4$, $SrSo_4$.

**Q. Why is it necessary to add $NH_4OH$ before the addition of $(NH_4)_2Co_3$ for the precipitation of group V radicals?**

**Ans.** $(NH_4)_2CO_3$ reagent used in the laboratories usually contains a high percentage of $NH_4HCO_3$ which will give a little precipitate with the metals of group V if $NH_4OH$ is not added.

$$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$$

**Q. Sometimes it is expected that calcium does not get precipitated in group V. What is this due to ?**

**Ans.** This happens because Ca forms $Ca(HCO_3)_2$ instead of $CaCO_3$ on the addition of $(NH_4)_2CO_3$ solution. $Ca(HCO_3)_2$ is soluble and passes into the filtrate of V group.

**Q. Why is it necessary to add ammonium sulphate and ammonium oxalate solution to the filtrate of V group and to boil before adding ammonium phosphate for the precipitation of Mg?**

**Ans.** Ca, Ba and Sr may not be precipitated completely as their carbonates are slightly soluble in the presence of an excess of ammonium ions. Hence $(NH_4)_2 SO_4$ and $(NH_4)_2 C_2O_4$ precipitate more effectively than $(NH_4)_2 CO_3$.

**Q. Name the cations of VI group.**

**Ans.** $Mg^{2+}$, $Na^+$, $K^+$ and $NH_4^+$.

**Q. What is the group reagent for VI group?**

**Ans.** There is no common group reagent for the cations of VI group. Hence they are confirmed individually.

**Q. Why $NH_4^+$ is confirmed from the original salt?**

**Ans.** $NH_4^+$ is placed in VI group of basic radicals. Proceeding from group 1 to group V, $NH_4^+$ ion is continuously added as group reagent in different groups. For this reason $NH_4^+$ ion is confirmed from original salt.

**Q. Why Mg is placed in VI group although it belongs to alkaline earth metals?**

**Ans.** Mg belongs to alkaline earth metals but it differs from them in forming a soluble carbonate and thus cannot be precipitated by $(NH_4)_2CO_3$ in the presence of $NH_4OH$.

**Q. Why $NH_4^+$ is placed in VI group ?**

**Ans.** Ammonium forms similar compounds like that of K and Na.

**Q. What is the usual colour of Na md K salts?**

**Ans.** Colourless (white).

**Q. Name some coloured salts of Na and K.**

**Ans.** $Na_2CrO_4$ = Yellow $K_2CrO_4$ = Yellow

$KMnO_4$ = Pink $K_2Cr_2O_7$ = Orange red.

**Q. What is table salt?**

**Ans.** Sodium chloride.

**Q. What is the formula of Nessler's reagent.**

**Ans.** $K_2HgI_4$.

**Q. What happens when an ammonium salt is heat with NaOH?**

**Ans.** Smell of $NH_3$ gas which gives white fumes with HCl.

**Q. Write the formulae of quick lime, slaked lime and soda lime.**

**Ans.** Quick lime = $CaO$

Slaked lime = $Ca(OH)_2$

Soda lime = $(CaO + NaOH)$

**Q. Write the formulae of baking soda and washing soda.**

**Ans.** Baking soda = $NaHCO_3$

Washing soda = $Na_2CO_3$

**Q. What is Epsum salt?**

**Ans.** $MgSO_4 . 7H_2O$.

**Q. What is the Glauber's salt?**

**Ans.** $Na_2SO_4 . 10H_2O$.

**Q. What is the difference between an acid radical and a basic radical?**

**Ans.** An acid radical may be defined as the radical which is contributed by an acid during salt formation. While the basic radical is contributed by a base during salt formation.

**Q. What is the difference between the detection of basic radicals and acid radicals?**

**Ans.** The basic radicals are detected and confirmed by the formation of colour or precipitate, while the acid radicals are generally detected by the confirmation of their volatile product.

**Q. Name the gas evolved when a salt containing carbonate or bicarbonate is treated with dil. HCl.**

**Ans.** Carbon dioxide ($CO_2$).

**Q. Ho will you differentiate between $SO_3^{2-}$ and $S_2O_3^{2-}$?**

**Ans.** Add dil. $H_2SO_4$ to the salt. A colourless gas with burning sulphur smell which turns $K_2Cr_2O_7$ solution green indicates both sulphite and thiosulphate. Note the colour of the contents of the test tube.

Yellow contents = Thiosulphate

Transparent = Sulphite

**Q. Why lime water turns milky on passing $CO_2$ through it?**

**Ans.** When $CO_2$ is passed through lime water $Ca(OH)_2$, insoluble $CaCO_3$ is produced as white milky suspensions.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

**Q. If an excess of $CO_2$ gas is passed through the above milky precipitate, the milky precipitate disappears and a clear solution is formed why?**

**Ans.** On passing excess of $CO_2$, the precipitate gets dissolved due to the formation of $Ca(HCO_3)_2$

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

**Q. Is there any gas like $CO_2$, which turns lime water milky?**

**Ans.** Yes, $SO_2$ turns lime water milky due to the formation of insoluble $CaSO_3$.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

**Q. How will you distinguish between $CO_3^{2-}$ and $HCO_3^-$?**

**Ans.** Dissolve the salt in water, if the salt is insoluble, it means the presence of insoluble carbonate. But if the salt is soluble in $H_2O$, then add $MgSO_4$ to this solution, formation of white ppt, in cold state shows the presence of soluble carbonate. If not white ppt, is formed in cold state, then heat the above solution. Formation of white precipitate on heating shows the presence of $HCO_3$-.

**Q. Name some insoluble carbonates.**

**Ans.** All carbonates are insoluble in water except those of sodium, potassium and ammonium. For example, $CaCO_3$, $SrCO_3$, $BaCO_3$ etc.

**Q. Name the acid radicals of dilute acid group.**

**Ans.** Bicarbonate ($HCO_3^-$), Carbonate ($CO_3^{2-}$), Sulphide ($S^{2-}$), Sulphite ($SO_3^{2-}$), Thiosulphate $S_2O_3^{2-}$, Nitrite ($NO_2^-$).

**Q. Name the acids which are used for the detection of acid radicals belonging to the dilute acid group.**

**Ans.** Dil. HCl or dil. $H_2SO_4$.

**Q. What is the colour and smell of $SO_2$ and $H_2S$ gases?**

**Ans.** $SO_2$ is a colourless gas which has a burning sulphur smell. $H_2S$ is a colourless with a rotten egg smell.

**Q. Does nitrite gives "ring test"?**

**Ans.** Nitrite also gives ring test similar to that of nitrates but the acid used should be dil. acetic acid or dil. $H_2SO_4$ instead of conc. $H_2SO_4$.

$$2NaNO_2 + 2CH_3COOH \longrightarrow 2CH_3COONa + 2HNO_2$$

$$3HNO_2^- \longrightarrow H_2O + HNO_3 + NO$$

$$FeSO_4 + NO \longrightarrow [Fe(NO)]SO_4$$

Nitroso-ferrous sulphate (ring)

**Q. Can we use conc. HCl in place of conc. $H_2SO_4$ in concentrated acid group like dilute acid group?**

**Ans.** No, we cannot use conc. HCl in conc. acid group because this group contains $Cl^-$ ion so it will create confusion because we are introducing $Cl^-$ ions ourself in the form of conc. HCl.

**Q. What is chromyl chloride test?**

**Ans.** It is a confirmatory test for $Cl^-$ and is performed as. Take small quantity of solid salt and solid $K_2Cr_2O_7$ in a test tube. Add conc. $H_2SO_4$ in the test tube and heat the mixture. Pass the gas through NaOH solution and then add acetic acid and lead acetate. Yellow ppt. of $PbCrO_4$ is obtained.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \xrightarrow[\text{Heat}]{\Delta} KHSO_4 + 4NaHSO_4 + 5H_2O + 2CrO_2Cl_2$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$$

**Q. What is the nature of chromyl chloride?**

**Ans.** It is a volatile liquid which on heating is converted into gas. It is reddish brown in colour.

**Q. What is the physical state of chlorine, bromine and iodine?**

**Ans.** Chlorine is a yellow green gas.

Bromine is an orange red fuming liquid.

Iodine is a violet solid.

**Q. What happens when conc. $H_2SO_4$ is added to NaBr NaI and NaCl salts?**

**Ans.** When a salt containing chloride, bromide or iodide is heated with conc. $H_2SO_4$, initially HCl, HBr and HI are formed. But HBr and HI formed are oxidized by the conc. $H_2SO_4$ to $Br_2$ and $I_2$, whereas HCl is a strong reducing agent and is not easily oxidized by conc. $H_2SO_4$.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

**Q. How the reddish brown vapours of $Br_2$ and $NO_2$ are distinguished?**

**Ans.** Bromides give the brown vapour of bromine while nitrate that of $NO_2$. If the addition of cu-turnings, increases the intensity of brown fumes, then nitrate is indicated and if there is no change in vapour's densness on the addition of cu-turnings, then bromide is present.

**Q. How bromides and iodides are distinguished?**

**Ans.** When treated with $AgNO_3$ solution, pale yellow ppt. of iodine and bromide is not distinguished by naked eye. For this layer test is performed. Violet layer indicates iodide, while brown shows the presence of bromide.

**Q. What is vinegar?**

**Ans.** Vinegar is a dilute solution of $CH_3COOH$.

**Q. By what methods $SO_4^{2-}$ and $PO_4^{3-}$ are confirmed?**

**Ans.** The confirmation of these two radicals differs from others in the fact that they are confirmed by the method of precipitation and not by volatile products.

**Q. Why do we heat the mixture/salt with strong solution of $Na_2CO_3$ for the preparation of solution of acid radicals?**

**Ans.** We heat the mixture/salt with strong solution of $Na_2CO_3$ so that double decomposition reaction may take place. The anion remain in the solution while cations of heavy metals are replaced by sodium and are precipitated as neutral or basic carbonates and in some cases hydroxides. For example,

*(i)* $BaSO_3 + Na_2CO_3 \longrightarrow BaCO_3\downarrow + Na_2SO_3$

*(ii)* $2CuSO_4 + 2N_2CO_3 + H_2O \longrightarrow (CuOH)_2CO_3\downarrow + 2Na_2SO_4 + CO_2\uparrow$

*(iii)* $2AlCl_3 + 3Na_2CO_3 + 3H_2O \longrightarrow 2Al(OH)_3\downarrow + 6NaCl + 3CO_2\uparrow$

**Q. What is a standard solution?**

**Ans.** A solution of known concentration is called a standard solution. 1NHCl, 2M $H_2SO_4$ etc.

**Q. Define equivalent weight of a substance.**

**Ans.** It is the amount of a substance which combines with or displaces 1 part of hydrogen, or 8 parts of oxygen or 36.5 parts of chlorine.

**Q. What is dehydrating agent?**

**Ans.** Dehydrating agent is a substance which is used for removing moisture from a substance.

**Q. Define the term solubility.**

**Ans.** It is the maximum weight in grams of a substance which is dissolved in 100 grams of the solvent to form a saturated solution at a given temperature.

**Q. What is solubility product?**

**Ans.** It is the product of ionic concentration in a saturated solution at a fixed temperature.

**Q. What is common ion effect?**

**Ans.** Common ion effect is a phenomenon in which the degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte having common ion.

**Q. Define acidity and basicity?**

**Ans.** The number of replaceable OH groups in alkalies is called acidity, while the number of replaceable H-atoms in acid is called its basicity.

**Q. What is meant by reducing agent?**

**Ans.** The substance that donates electrons is called reducing agent. For example, oxalic acid, ferrous sulphate, ferrous ammonium sulphate.

**Q. Write the formula of Mohr's salt.**

**Ans.** $FeSO_4\,(NH_4)_2SO_4.\,6H_2O$.

**Q. Why dilute $H_2SO_4$ is used in redox titrations?**

**Ans.** Due to the fact that $KMnO_4$ behaves as oxidizing agent in the presence of dilute $H_2SO_4$.

**Q. Why heating is necessary when oxalic acid is titrated against $KMnO_4$ solution?**

**Ans.** The oxidation of oxalic acid occurs at a temperature ranging between 70-80°C and hence heating is needed.

**Q. What is oxidizing agent?**

**Ans.** The substance that accepts electrons is called oxidizing agent. For example, $KMnO_4$, $K_2Cr_2O_7$, etc.

# *Part Four*

# ANALYTICAL CHEMISTRY

## 4.1. Introduction and Scope

**Q. Define Analytical Chemistry.**

**Ans.** Analytical chemistry is basically concerned with the determination of the chemical composition of matter. So far this was the main goal of the analytical chemists. However, identification of a substance, the elucidation of its structure and quantitative analysis of its composition are the aspects covered by modern analytical chemistry.

**Q. Briefly discuss the importance of analytical chemistry.**

**Ans.** Chemical analysis holds an important position in our modern society. A knowledge of analytical procedures has become essential in practically all the arts and sciences as well as the technical operations of the industry. The discovery of new medicines, new fabrics, new alloys, and other materials would not be possible without the services of the analytical chemists. Analytical chemistry is such an important part of our industrial structure and advancing science that without it our present day economy could not exist.

**Q. What causes are responsible for expanding interest of analytical chemistry?**

**Ans.** The last twenty five years have witnessed an expanding interest in the problems and methods of chemical analysis. This has been the result of many causes :

(*i*) The great increase in industrial production, the great number and variety of industrial products, the more careful control that is required in the manufacture of these products.

(*ii*) Many companies that in the past were able to succeed without analyzing their raw materials or their products, have recently found that it is now essential to make analyses in order to maintain quality and uniformity.

(*iii*) Another element in expanding the analytical picture has been the demand caused by recent wars for substances urgently needed for military purposes. The atomic energy project alone has required a large amount of research in analytical methods.

**Q. Discuss some applications of analytical chemistry in various fields.**

**Ans.** No other branch of science finds so extensive applications as analytical chemistry purely for two reasons — one it finds numerous applications in various disciplines of chemistry such as inorganic, organic, physical and biochemistry and secondly it finds large applications in other fields of sciences. It would be worthwhile to consider one or more examples in each area of research.

**Agriculture.** Agriculture has been aided with increased yields and enhanced soil fertility through accurate chemical analysis by adjusting the composition of fertilizers. The analysis of pesticides or insecticides from crops by gas chromatography or high performance liquid chromatography is also the instance of use of analytical chemistry in agricultural sciences.

**Environmental Sciences.** In environmental sciences, the monitoring of air and water pollution is an important problem. The continuous monitoring of $SO_2$, $CO_2$ and CO can be done by fluorescence or infrared spectroscopy, while analysis of dissolved oxygen or chlorine from water can be done by potentiometry or colorimetry.

**Biomedical Research.** An enormous number of chemical analyses is made daily in the laboratories of hospitals for purposes of diagnosis and treatment. Analyses of blood, urine, etc, are absolutely essential in order that proper treatment may be prescribed. An excess or deficiency of sugar, calcium, potassium, iodine or other substances may be the cause of a pathological condition. Poisons may be identified by analysis and often their source is indicated. Similarly one can cite several examples like presence of arsenic in hair and nail by spectroscopic methods, analysis of cobalt in vitamin $B_{12}$ etc.

**Miscellaneous.** Training in analytical chemistry serves as a sound basis for studies in other branches of chemistry and other sciences. The laboratory work of physical chemistry requires the quantitative skills that are developed in the analytical course. Work in biology, geology and physics may be accomplished at a higher level of understanding and ability with a background of the principles and techniques acquired in a course in quantitative analysis.

**Q. What are the important steps in chemical analysis?**

**Ans.** The two important steps in chemical analysis are:

*(i)* Identification, and

*(ii)* Estimation of constituents of a compound.

**Q. What is the difference between qualitative and quantitative analysis?**

**Ans.** Qualitative analysis is concerned with the identification and separation of chemical substances and the chemical principles on which such procedures are based.

Quantitative analysis is concerned with the estimation of the amount of a chemical substance present either alone or in a simple or complex mixture of other substances. Unlike qualitative analysis, there is no general scheme of separation but rather a scheme of experimental techniques that find general use after the isolation of the particular substance to be determined.

**Q. What are the types of quantitative analytical methods?**

**Ans.** Quantitative analytical methods may be broadly divided into two general groups.

**Group I** consists of those methods in which the final measurement of the substance sought is made by direct or indirect measurements of the volume and weight after proper treatment of a measured portion of the material to be analyzed. For example, gravimetric methods and titration methods.

**Group II** consists of those methods in which the final measurement is made upon the system as a whole. These methods involving sophisticated instruments can be termed as modern methods of analysis. For example, atomic and molecular absorption spectroscopy, conductometry, potentiometry, voltametry, molecular luminescence etc.

**Q. What factors determine the selection of a particular analytical methods?**

**Ans.** The choice of a particular analytical method is determined by several factors such as speed, convenience, accuracy, sensitivity, selectivity, availability of the instruments, amount of sample, level of analysis.

**Q. What are the various steps in quantitative analysis?**

**Ans.** The steps involved in quantitative analysis are:

*(i)* Procurement of samples.

*(ii)* Conversion of desired constituent to measurable form.

*(iii)* Measurement of desired constituent.

*(iv)* Calculation and interpretation of analytical data.

**Q. What are well-recognized rules and regulations for successful quantitative analysis?**

**Ans.** Success in the laboratory work of quantitative analysis is dependent on the following well-recognized rules and regulations.

*(i)* All the glassware should be kept clean, apparatus should be kept in an orderly fashion in the locker, and the working space on the bench should be carefully wiped clean of all puddles of liquid and spilled solids before any operation is started and after it is completed.

*(ii)* Side shelf reagents should be returned to their proper place after use, and any spilled should be promptly cleaned up.

*(iii)* Knowledge for all procedures should be read in advance to be sure that the necessary apparatus and reagents are available before the beginning of the laboratory period.

*(iv)* Each operation should be performed with extreme care, some operations may be quite time consuming, but speed develops as one gains in experience.

**Q. What are desk equipments?**

**Ans.** In addition to the standard items of glassware and other apparatus, certain other items are required in quantitative work.

These include:

(i) **A wash bottle.** It is used to wash precipitates and rinse off reagents from glassware.

(ii) **Desiccator.** It purpose is to provide a storage place of low moisture content for dried sample and crucibles. The bottom is charged with fresh drying material of suitable nature. Anhydrous calcium chloride is commonly used. Other desiccants include conc. sulphuric acid, phosphorus pentoxide, etc.

(iii) **Porcelain crucible.** It is used to ignite precipitates that are collected on filter paper.

(iv) **Filtering crucible.** It is used in filtering precipitates by suction where the precipitate may be either dried or ignited at moderate temperature.

(v) **Crucible holders.** These are used to hold a filtering crucible during the process of filtration by suction.

(vi) **Weighing bottles.** These are small, glass-stoppered vessels that are used for the storing of samples prepared for analysis.

(vii) **Glass funnels.** These are used in filtering operations involving the use of filter paper.

In addition to the above, the required volumetric glassware include pipets, burets, volumetric flasks, stirring rods, glass hooks etc.

**Q. What is the function of muffle furnace and drying oven?**

**Ans.** Muffle furnace is used for heating operations that require an ignition at high temperatures (up to 1000°C). It gives the best temperature range and control.

Drying ovens are used for drying samples and certain precipitates at some fixed temperature. The useful operating range is about 90° – 120°C.

## 4.2. Evaluation of Analytical Data

**Q. What factors are taken into consideration by an analyst about the chemical analysis?**

**Ans.** The function of an analyst is to obtain a result as nearer to the true value as possible by correct application of the analytical procedure employed. To be confident about the result, the analyst should have the knowledge of following facts:

(i) Errors and sources of errors.

(ii) Accuracy and precision of the method.

(iii) Chemistry involved in the process.

(iv) The statistical methods employed to derive conclusions to boost the confidence in the result.

**Q. Explain the term error in chemical analysis.**

**Ans.** The numerical value obtained in every scientific measurement contains certain degree of uncertainty. In very accurate work, the uncertainty may be very small, but it is still present. This uncertainty is called the error of measurement.

The term error as used in chemical analysis refers to the numerical difference between a measured value and true value. In the right sense, true value is a value in which the uncertainty is less than in something else with which it is compared. In chemistry standard values supplied by standard reputed laboratories are considered as true values.

**Q. What is the relation between error of measurement and accuracy?**

**Ans.** Usually the error of a measurement is an inverse measure of accuracy of that measurement, i.e., smaller is the error greater is the accuracy of an analysis.

**Q. How are errors generally expressed?**

**Ans.** The error, observed value and the true value in any chemical analysis is related by the following equation.

$$E = O - T \qquad \text{..... 4.1}$$

Where $E$ = absolute error

$O$ = observed value

$T$ = true value

The errors are generally expressed relatively as

$$\text{Percentage } \left(\frac{E}{T} \times 100\right) = \%\text{ error} \qquad \text{..... 4.2}$$

$$\text{Per thousand } \left(\frac{E}{T} \times 1000\right) = \text{ppt} \qquad \text{..... 4.3}$$

From the knowledge of error, we can easily differentiate between the two terms generally used viz. *Precision* and *accuracy*.

**Q. What do you mean by precision and accuracy?**

**Ans.** The term precision is used to describe the reproducibility of the result. It can be defined as the extent of agreement of the individual values among themselves. The mean or average deviation or the relative mean deviation is a measure of precision.

The accuracy of a measured quantity may be defined as the closeness between the measured value and its true or most probable value. The true value cannot be measured exactly, however, in many cases it can be estimated very closely. Accuracy is expressed in terms of errors i.e., absolute and relative errors.

Note the difference between precision and accuracy. Accuracy involves a comparison with respect to a true or accepted value. Precision compares a result with other measurements made in the same manner. Precision always accompanies accuracy, but a high degree of precision does not always imply accuracy. An accuracy without precision is not at all possible.

**Q.** **Briefly discuss different types of errors encountered in chemical analysis.**

**Ans.** The errors which affect an experimental result may be classified into two groups namely determinate or systematic errors and indeterminate or random errors.

(*i*) **Determinate errors.** These errors have definite values and at least in principle definite cause. The analyst can determine the magnitude of these errors and can fix the cause. The determinate error is generally unidirectional with respect to the true value, and leads, with equal probability, to both high or low results.

(*ii*) **Indeterminate errors.** These errors possess indefinite values and follow no law and invariably have fluctuating values. They arise from uncertainties in a measurement that are unknown and over which analyst has no control.

**Q.** **What are different types of determinate errors?**

**Ans.** The determinate errors are of four kinds depending upon their origin.

(*i*) Operational and personal errors.
(*ii*) Instrumental and reagent errors.
(*iii*) Methodic errors.
(*iv*) Additive and proportional errors.

**Q.** **What are the causes of determinate errors?**

**Ans.** There can be many reasons, which can cause the determinate errors. Some of the reasons are :

(*i*) A poorly calibrated pipet or buret.
(*ii*) An impurity in the reagent used.
(*iii*) An appreciable solubility of a precipitate.
(*iv*) A side reaction interfering with main reaction.
(*v*) A reaction is not being allowed to complete etc.

**Q.** **Define average value.**

**Ans.** An average is a single value which is intended to represent a set of data or a distribution as a whole.

**Q.** **Explain the terms mean and median.**

**Ans.** The mean, arithmetic mean and average ( $\bar{X}$ ) are similar terms, their numerical value is obtained by dividing the sum of a set of replicate measurements by the number of individual results in the set.

Suppose in certain experiments, the replicate measurements are 10.06, 10.20, 10.08 and 10.10. Then the mean $X^-$ will be

$$\bar{X} = \frac{10.06 + 10.20 + 10.08 + 10.10}{4} = 10.11$$

The median value of a set is that result about which all others are equally distributed, half being numerically greater and half numerically smaller half smaller. If the set consists of an odd number of measurements, the selection of median may be made directly. However, if the set contains even number of measurements, then the average of central pair is taken.

Let us again take the set of replicate measurements from the previous experiment (10.06, 10.08, 10.09, 10.10 and 10.20). Since the set has odd number of measurements, hence the median value will be 10.09.

**Q. What do you mean by deviation?**

**Ans.** Deviation is defined as the difference between the individual value and average value. Mathematically,

$$\Delta = X - \bar{X} \qquad \text{..... 4.4}$$

Where $\Delta$ = deviation
$X$ = individual value
$\bar{X}$ = mean vlue or averge value

**Q. How is accuracy usually expressed?**

**Ans.** Accuracy is usually expressed in terms of error i.e., absolute and relative error.

So absolute error is nothing but deviation ($\Delta$), which is the difference between individual value (true value) X and mean value X⁻.

$$\Delta = X - \bar{X}$$

However, the criterion of the accuracy of the result is the relative means error (e). It is the ratio of the absolute error and true value.

$$e = \frac{X - \bar{X}}{X} \qquad \text{..... 4.5}$$

It is expressed in percentage or part per thousand.

**Q. How is precision usually expressed?**

**Ans.** There are many different ways to express the precision of a set of a data. Of these, only a few have any statistical basis, causing these expressions now to be recommended.

(*i*) **The range.** This is merely the numerical difference between the highest and the lowest value of a set of results.

The other methods for expressing precision are based on the absolute difference between each particular piece of data and the average of the set. This difference is known as the deviation of a particular piece of data. A deviation has no sign, being obtained by subtracting the datum from the average of the set.

*(ii)* **The average or mean deviation.** The average deviation is nothing more than the average of all of the deviations for the members of the set of a data taken without regard to sign.

Mathematically,

$$a = \frac{\Sigma(X_i - m)}{n} \qquad \text{..... 4.6}$$

Where

$a$ = average deviation

$X_i$ = any given measurement

m = arithmetic mean

n = total number of pieces of data in the set

Statistically, the average deviation has no importance.

*(iii)* **Relative mean deviation.** The relative mean deviation is the mean deviation divided by the mean. This may be expressed in percentage or part per thousand.

*(iv)* **Standard deviation.** It is a meaningful statistical term used to express precision. The standard deviation is defined as the square root of the sum of the squares of the deviations divided by one less than the number of pieces of data in the set namely,

$$S = \sqrt{\frac{\sum_i (X_i - m)^2}{n-1}} \qquad \text{..... 4.7}$$

n-1 is used for finite number of samples.

*(v)* **The variance $S^2$.** For certain statistical tests, it is more convenient to use the square of the standard deviation, instead of the standard deviation. This term is called the variance, and it is defined as the sum of the square of the deviations divided by one less than the number of pieces of the data. Mathematically,

$$S^2 = \sum_i \frac{(X_i - m)^2}{n-1} \qquad \text{..... 4.8}$$

*(vi)* **Relative standard deviation (coefficient of variation).** Usually the value of the mean of the data set is given along with the standard deviation, which does enable one to estimate the relative magnitude of the S. When the S is expressed as the fraction of the mean of the set of data, a better feeling for the proportionality of the error is obtained. The relative S is nothing more than the S divided by the mean of the set.

Relative standard deviation = $\frac{S}{m} \times 1000$ ppt.

**Q. What is confidence limit or interval?**

**Ans.** This is a statistical term used to define the distance on either side of the mean value of a set of data, within which one may expect to find, with stated probability, the true value. Thus the 95% confidence interval or limit is the distance on either side of the average within which the true value will be found with 95% of the time

**Q. What are significant figures?**

**Ans.** Significant figures are the digits necessary to express the results of a measurement to the precision with which it is made. The general rule used in chemistry states that the last digit of a number, has certain uncertainty in it, while all of the other digits in the number contain no uncertainty. For example, in weighing an object on an analytical balance, the figures 10.476 can be recorded with certainty. The fourth decimal is estimated by reading a pointer scale and the final weight recorded as 10.4763. The last digit is uncertain, probably to ±1 in a single reading. The six digits in this weight are all significant figures.

**Q. What do you know about the F-test?**

**Ans.** The F-test provides a simple method for comparing the precision of two sets of identical measurement. It is based upon the null hypothesis, which assumes that the two means are identical i.e., precisions are identical.

Mathematically, $$F = \frac{S_1^2}{S_2^2} \qquad \text{..... 4.10}$$

Where $S_1^2$ and $S_2^2$ are the variance of the two measurements. The value of F obtained is then compared with significant values given in the statistical tables of F values.

When the calculated F is larger than the tabulated value, then the difference between two sets of data is highly significant.

If the calculated F is smaller than the tabulated value, then the difference between the precisions is not significant.

**Q. What is the criteria for rejection of data?**

**or**

**What do you know about Q-test?**

**Ans.** In any chemical analysis a number of replicate values are obtained. When the number of replicate values is large, the question of rejecting one of the values is not so much significant. However, for smaller number of values, various methods and rules are devised to assess, whether the obtained data is to be retained or rejected. Out of these the most simple statistical method is called Q-test.

The steps involved in Q-test are as follows:

*(i)* Calculate the range of results.

*(ii)* Find the difference between the suspected result and its nearest neighbour.

(*iii*) Divide the difference from step 2 by the range from step 1 to get the value of rejection quotient Q.

(*iv*) Consult a table of Q-values. If the computed value of Q is greater than the value given in the table, the result can be discarded with 90% confidence.

## 4.3. Standard Solutions — Definitions and Preparation of Solutions of Various Strength

**Q. What is a true solution?**

**Ans.** A true solution is defined as a homogeneous mixture of two or more substances that form a single phase.

**Q. What are the characteristics of a true solution?**

**Ans.** A true solution has the following characteristics.

(*i*) The various components of the solution can not be distinguished.

(*ii*) The components do not settle under the effect of gravity.

(*iii*) The components can be obtained by processes like crystallization, distillation, evaporation etc.

(*iv*) The components of the solution show their properties to prove their presence.

**Q. Explain the terms solute and solvent.**

**Ans.** The components of a solution are generally referred to as solute and solvent. A solute is frequently a substance that dissolves and a solvent is one in which dissolution takes place.

**Q. What is the difference between a dilute and a concentrated solution?**

**Ans.** A dilute solution is one in which the quantity of solute is very small as compared to that of solvent. A concentrated solution contains relatively higher amount of solute.

**Q. What is a binary solution?**

**Ans.** A solution containing only two components is called a binary solution.

**Q. What are the different concentration units for a solution?**

**Ans.** Any quantitative study of solutions requires that we know the amount of solute dissolved in a solvent or the concentration of a solution. Chemists employ several different concentration units in their work, each one having its own advantages and limitations.

(*i*) Mass percent.

(*ii*) Volume percent.

(*iii*) Molarity.

(*iv*) Molality.

(*v*) Normality.

(vi) Formality.

(vii) Mole fraction.

**Q. What is the difference between amount and concentration?**

**Ans.** A measured or weighed quantity of any substance is called its amount. When this amount is dissolved in a unit volume (say 1 dm$^3$) of a solution (or in a unit amount of solvent), then it is known as concentration.

**Q. What is a standard solution?**

**Ans.** A standard solution is one whose strength or concentration is known, e.g. 1M HCl, 2N $HNO_3$ etc.

or

A reagent of known concentration upon which a volumetric method is based.

**Q. What are the requirements of an ideal standard solution?**

**Ans.** The ideal standard solution for volumetric analysis should

(i) be sufficiently stable, so that its concentration remains unchanged.

(ii) react rapidly with the analyte (substance to be analyzed) so that satisfactory end points are realized

(iii) and undergo a selective reaction with the analyte that can be described by a simple balanced equation.

**Q. What is a percent solution (%)?**

**Ans.** Percent solution is that which is based on the mass or volume of the components of the solution per 100 parts. It is usually expressed in the following way.

$$\text{Mass percent (W/W)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 \text{..... 4.11}$$

$$\text{Volume percent (V/V)} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100 \text{..... 4.12}$$

Mass-Volume percent (W/V)

$$= \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100 \text{..... 4.13}$$

For example:

A solution is 1% (W/W), when it contains 1g of solute and 99 g of solvent to make 100 g of solution.

A solution is 1% (V/V), when it contains 1 cm$^3$ of solute and 99 cm$^3$ of solvent to make 100 cm$^3$ of solution.

Similarly a solution is 1% (W/V), when it contains 1g of solute per 100 cm$^3$ of the solution.

**Q. How would you prepare the following solutions?**

- **(i) 10% NaOH**
- **(ii) 5% $C_2H_5OH$**
- **(iii) 200 $cm^3$ of 10% NaOH**
- **(iv) 500 $cm^3$ of 5% $C_2H_5OH$**
- **(v) 50 $cm^3$ of 10% NaCl**
- **(vi) 10 $cm^3$ of 10% NaCl**

**Ans. (i) 10% NaOH.**

Dissolve 10g of NaOH in some distilled water and make the volume up to 100 $cm^3$ in a volumetric flask or measuring cylinder.

**(ii) 5% $C_2H_5OH$**

Take 5 $cm^3$ of $C_2H_5OH$ and 95 $cm^3$ of distilled water to make 100 $cm^3$ of solution.

**(iii) 200 $cm^3$ of 10% NaOH**

100 $cm^3$ of solution requires salt = 10 g

1 $cm^3$ of solution requires salt $= \frac{10}{100}$

200 $cm^3$ of solution requires salt $= \frac{10}{100} \times 200 = 20$ g

So take 20 g of NaOH in some quantity of distilled water and make the volume up to 200 $cm^3$ in a volumetric flask.

**(iv) 500 $cm^3$ of 5% $C_2H_5OH$**

100 $cm^3$ of solution requires $C_2H_5OH$ = 5 $cm^3$

1 $cm^3$ of solution requires $C_2H_5OH = \frac{5}{100}$

500 $cm^3$ of solution requires $C_2H_5OH$ $= \frac{5}{100} \times 500$

$= 25\ cm^3$

So take 25 $cm^3$ of $C_2H_5OH$ and 475 $cm^3$ of distilled water to make 500 $cm^3$ of 5% $C_2H_5OH$.

**(v) 50 $cm^3$ 10% NaOH**

100 $cm^3$ of solution requires salt = 10 g

1 $cm^3$ of solution requires salt $= \frac{10}{100}$

50 $cm^3$ of solution requires salt $= \frac{10}{100} \times 50 = 5$ g

So dissolve 5g of NaOH in some quantity of distilled water and make the volume up to 50 $cm^3$ in a volumetric flask.

*(vi)* **10 $cm^3$ of 10% NaCl.**

100 $cm^3$ of solution requires salt = 10 g

1 $cm^3$ solution requires salt = $\frac{10}{100}$

10 $cm^3$ of solution requires salt = $\frac{10}{100} \times 10 = 1$ g

So dissolve 1 g of NaCl per 10 $cm^3$ of solution.

**Q. What is the %age composition of the following solutions?**

- *(i)* **2 g of NaOH is dissolved per 50 $cm^3$ of solution.**
- *(ii)* **4 g of NaOH is dissolved per 1000 $cm^3$ of solution.**
- *(iii)* **1 g of NaOH is dissolved per 10 $cm^3$ of the solution.**

**Ans.** *(i)* 50 cm3 of solution contains NaOH = 2 g

1 $cm^3$ of solution contains NaOH = $\frac{2}{50}$

100 $cm^3$ of solution contains NaOH= $\frac{2}{50} \times 100 = 4$g

So the solution of NaOH is 4%

*(ii)* 1000 $cm^3$ of solution contains NaOH = 4 g

1 $cm^3$ of solution contains NaOH = $\frac{4}{1000}$

100 $cm^3$ of solution contains NaOH = $\frac{4}{1000} \times 100 = 0.4$ g

So the solution of NaOH is 0.4%

*(iii)* 10 $cm^3$ o the solution contains NaOH = 1 g

1 $cm^3$ o the solution contains NaOH = $\frac{1}{10}$

100 $cm^3$ o the solution contains NaOH = $\frac{1}{10} \times 100 = 10$ g

So the composition of the solution is 10%.

**Q. Write the formula which is used for dilutions purposes.**

**Ans.** The formula used for dilution purposes is

$$C_1V_1 = C_2V_2 \qquad \text{..... 4.14}$$

(Given Solution) (Required Solution)

Where $C_1$ = Concentration of the standard solution.

$C_2$ = Concentration of the solution to be prepared.

$V_1$ = Volume of the standard solution used for dilution purposes.

$V_2$ = Volume of the solution to be prepared.

**Q. How would you prepare the following solutions from 10% solution of sucrose?**

**(i) 100 cm³ of 4% sucrose solution.**

**(ii) 10 cm³ of 5% sucrose solution.**

**Ans.** *(i)*

$$C_1V_1 = C_2V_2$$

$$10 \times V_1 = 4 \times 100$$

$$V_1 = \frac{4 \times 100}{10} = 40 \text{ cm}^3$$

Take 40 cm³ of standard solution (10%) of sucrose and make the volume up to 100 cm³.

*(ii)*

$$C_1V_1 = C_2V_2$$

$$10 \times V_1 = 5 \times 10$$

$$V_1 = \frac{5 \times 10}{10} = 5 \text{ cm}^3$$

Take 5 cm³ of the standard solution and make the volume up to 10 cm³ with distilled water.

**Q. Define molar solution.**

**Ans.** A molar solution is one which contains one mole (gram molecular weight) of the solute per dm³ of the solution at a specified temperature. Molar concentration is represented by *M* and is sometimes spoken as molarity.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume in dm}^3 \text{ of the solution}} \quad \text{..... 4.15}$$

$$\text{Nole} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute}} \quad \text{..... 4.16}$$

$$\text{Number of moles of solute} = M \times V \text{ (in dm}^3\text{)} \quad \text{..... 4.17}$$

Molar mass of NaOH = 40

Molar mass of HCl = 36.5

1 mole of NaOH = 40 g

1 mole of HCl = 36.5 g

**Q. How would you prepare the following solutions?**

**(i) 1 *M* solution of NaOH (Molar Mass - 40).**

**(ii) 0.1 *M* solution of NaOH.**

**(iii) 100 cm³ of 1 *M* solution of NaOH.**

**(iv) 100 cm³ of 0.1 *M* solution of NaOH.**

**(v) 2 dm³ of 2 *M* solution of NaOH.**

**Ans.** *(i)* Dissolve 1 mole (40g) of NaOH per $dm^3$ of the solution.

*(ii)* 1 *M* solution contains NaOH = 40 g

0.1 *M* solution contains NaOH = $40 \times 0.1 = 4$ g

So dissolve 4 g of NaOH per $dm^3$ of solution.

(iii) 1000 $cm^3$ (1 $dm^3$) of 1 *M* solution = 40 g contains NaOH

$$1\ cm^3 \text{ of } 1\ M \text{ solution contains NaOH} = \frac{40}{1000}$$

$$100\ cm^3 \text{ of } 1\ M \text{ solution contains NaOH} = \frac{40}{1000} \times 100 = 4\ g$$

So dissolve 4 g of NaOH per 100 $cm^3$ of solution.

(iv) 1 *M* solution contains NaOH = 40 g

0.1 *M* solution contains NaOH = $40 \times 0.1 = 4$ g

1000 $cm^3$ 0.1 *M* solution contains NaOH = 4 g

$$1\ cm^3\ 0.1\ M \text{ solution contains NaOH} = \frac{4}{1000}$$

$$100\ cm^3\ 0.1\ M \text{ solution contains NaOH} = \frac{4}{1000} \times 100$$

$$= 0.4\ g$$

So dissolve 0.4 g per 100 $cm^3$ of the solution.

(v) 1 *M* solution contains NaOH = 40 g

2 *M* solution contains NaOH = 2  40 = 80 g

100 $cm^3$ of 2*M* solution contains NaOH = 80 g

$$1\ cm^3 \text{ of } 2M \text{ solution contains NaOH} = \frac{80}{1000}$$

$$1000\ cm^3\ (2\ dm^3) \text{ of } 2M \text{ solution contains NaOH} = \frac{80}{1000} \times 2000 = 160\ g$$

So dissolve 160 g of NaOH per 2 $dm^3$ of solution.

**Q. Calculate the molarity of following solutions.**

***(i)* 4 g of NaOH dissolved per 100 $cm^3$.**

***(ii)* 4 g of NaOH dissolved per 2 $dm^3$.**

***(iii)* 4 g of NaOH dissolved per 500 $cm^3$.**

**Ans.** *(i)*

$$\text{Number of moles} = \frac{4}{40} = 0.1$$

$$\text{Volume} = 100\ cm^3 = 0.1\ dm^3$$

$$M = \frac{0.1}{0.1} = 1$$

(*ii*) Number of moles $= \frac{4}{40} = 0.1$

Volume = 2 $dm^3$

$$M = \frac{0.1}{2} = 0.05$$

(*iii*) Number of moles $= \frac{4}{40} = 0.1$

Volume = 500 $cm^3$ = 0.5 $dm^3$

$$M = \frac{0.1}{0.5} = 0.2$$

**Q. How would you prepare the following solutions from the 10 *M* HCl solution?**

**(*i*) 100 $cm^3$ of 2 M HCl.**

**(*ii*) 500 $cm^3$ of 1 M HCl.**

Ans. (*i*)

$$M_1V_1 = M_2V_2$$

$$10 \times V_1 = 2 \times 100$$

$$V_1 = \frac{2 \times 100}{10} = 20\ cm^3$$

Take 20 $cm^3$ of the standard solution and make the volume up to 100 $cm^3$ in a volumetric flask.

(*ii*)

$$M_1V_1 = M_2V_2$$

$$10 \times V_1 = 1 \times 500$$

$$V_1 = \frac{1 \times 500}{10} = 50\ cm^3$$

Take 50 $cm^3$ of the standard solution and make the volume up to 500 $cm^3$ in a volumetric flask.

**Q. What mass of NaOH is required to prepare 200 $cm^3$ of 5.0 *M* solution?**

**Ans.** Number of moles of the solute $= M \times V$ (in $dm^3$)

$= 5.0 \times 0.2$

$= 1.0$

Mass of the solute = Number of moels × Molar mass

$= 1.0 \times 40 = 40$ g

So take 40 g of NaOH and dissolve per 200 $cm^3$ to get 5.0 *M* solution.

**Q. What do you know about formality and formal solutions?**

**Ans.** In case of solutes which exist as giant molecules (e.g. NaCl) or as associated molecules (e.g. $(HF)_2$), the term molar mass loses its significance as no definite molecule exists as such. There is a trend to express the concentration of the solution of such substances in terms of formality.

Therefore, formal solution is defined as that solution which contains one gram formula weight of the solute per dm³ of the solution at a specified temperature. For example, 1F solution of NaCl contains 58.5 g NaCl per dm³ of the solution.

Similarly, 1 F solution of $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$ contains 392 g of the substance per dm³.

**N.B.** Both molarity and formality are based on the volume of the solution; hence these are sensitive to temperature changes.

**Q. What is a molal solution?**

**Ans.** A solution that contains one mole of the solute dissolved per kilogram (1000 g) of the solvent is called a molal solution.

**Q. What is the effect of temperature on the molality of a solution?**

**Ans.** Molal solution is based on the mass of the solvent; hence it is a temperature independent quantity (provided that the solution in question is not of a gas as it will evolve on heating).

**Q. When concentration is expressed in molality?**

**Ans.** Whenever, measurements are to be made over a wide range of temperatures, the concentration is usually expressed in terms of molality.

**Q. How would you prepare the following solutions?**

***(i)*** **1 *m* NaOH**

***(ii)*** **0.1 *m* NaOH**

***(iii)*** **0.5 *m* NaOH**

**Ans.***(i)* Dissolve 40 g of NaOH per Kg of solvent.

*(ii)* Dissolve 4 g of NaOH per Kg of solvent.

*(iii)* Dissolve 20 g of NaOH per Kg of solvent.

**Q. What do you know about normality and normal solution?**

**Ans.** The normality of a solution is defined as the number of gram equivalents of solute dissolved per dm³ of the solution at a specified temperature.

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume (in dm}^3\text{) of the solution}} \quad ..... 4.18$$

A normal solution is one that contains one gram equivalent of solute per dm³ of the solution.

**Q. Why do we need this new unit?**

**Ans.** A new unit is not absolutely necessary. Let us justify defining this new unit. It is introduced to shorten our work and clarify our thinking. Consider this. One dm$^3$ of 1 $M$ $H_2SO_4$ does not react completely with just 1 dm$^3$ of 1 $M$ NaOH; it reacts with 2. And, in general equal volumes of solutions of equal molarities do not necessarily react with one another completely. This new unit of concentration is defined in such a way that equal volumes of solutions of equal concentration (in this unit) exactly neutralize one another.

**Q. What is equivalent weight?**

**Ans.** Equivalent weight of a substance is the weight that reacts with 8 g of oxygen or its equivalent. (The reason 8 g of oxygen was chosen is that with a smaller weight of oxygen, the weight of hydrogen would be less than 1 g. We wish to avoid numbers smaller than unity). It can also be defined as that weight equivalent in reacting power to an atom of hydrogen.

**Q. How would you determine the equivalent weight of different substances?**

**Ans.** (*i*) Equivalent weight of an atom = $\frac{\text{Atomic weight}}{\text{Valence}}$

e.g., H = 1.008, Mg = 12.16, Na = 23.00, Al = 8.99

(*ii*) Equivalent weight of an acid = $\frac{\text{Molecular weight of the acid}}{\text{Number of replaceble H atom}}$

e.g., Eq. weight of HCl = $\frac{36.5}{1} = 36.5$

Eq. weight of $H_2SO_4 = \frac{98}{2} = 49$

Eq. weight of $H_3PO_4 = \frac{98}{3} = 32.7$

(*iii*) Equivalent weight of a base = $\frac{\text{Molecular weight of the base}}{\text{Number of replacable OH groups}}$

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

Eq. weight of $Ba(OH)_2 = \frac{90}{2} = 45$

Eq. weight of $Al(OH)_3 = \frac{78}{3} = 26$

(*iv*) Equivalent weight of a salt = $\frac{\text{Molecular weight of the salt}}{\text{Total valence of +Ve or Ve group}}$

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

Eq. weight of $MgSO_4 = \frac{120}{2} = 60$

Eq. weight of $Al_2(SO_4)_3 = \frac{342}{6} = 57$

(v) Equivalent weight of an oxidizing agent

$$= \frac{\text{Molecular weight of O.A.}}{\text{Change in oxidation number of reduced ion}}$$

$2KMnO_4 + 4H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

Change in oxidation number $= 7 \quad 2 = 5$

Hence the equivalent weight of $KMnO_4$ in acidic medium will be $158/5 = 31.6$.

(vi) Equivalent weight of reducing agent

$$= \frac{\text{Molecular weight of R.A.}}{\text{Change in oxidation numebr of the oxidized ion}}$$

**Q. How would you prepare the following solutions?**

**(i) 1 *N* NaOH**

**(ii) 1 *N* HCl**

**(iii) 1 *N* $H_2SO_4$**

**(iv) 1 *N* $H_3PO_4$**

**Ans.** (i) Dissolve 1 gram equivalent (40 g) of NaOH per $dm^3$ of the solution.

(ii) Dissolve 1 gram equivalent (36.5 g) of HCl per $dm^3$ of the solution.

(iii) Dissolve 1 gram equivalent (49 g) of $H_2SO_4$ per $dm^3$ of the solution.

(iv) Dissolve 1 gram equivalent (32.7 g) of $H_3PO_4$ per $dm^3$ of the solution.

**Q. What is the normality of the following solutions?**

**(i) 60 g of NaOH dissolved per $dm^3$.**

**(ii) 20 g of NaOH dissolved per 500 $cm^3$.**

**Ans.** (i) Number of gram equivalents $= \frac{\text{Mass of the solute}}{\text{Molar mass}}$

$$= \frac{60}{40} = 1.5$$

$$\text{Volume} = 1\ \text{dm}^3$$

$$N = \frac{1.5}{1} = 1.5$$

(*ii*) Number of gram equivalent $= \dfrac{\text{Mass of the solute}}{\text{Molar mass}}$

$$= \frac{20}{40} = 0.5$$

$$\text{Volume} = 500\ \text{cm}^3 = 0.5\ \text{dm}^3$$

$$N = \frac{0.5}{0.5} = 1$$

**Q. What mass of $H_2SO_4$ is required to prepare 100 cm³ of 2 *N* solutions?**

**Ans.** Number of equivalents $= N \times V\ (\text{in dm}^3)$

$$= 2 \times 0.1 = 0.2$$

Mass of the solute = Number of equivalents × Equivalent weight

$$= 0.2 \times 49 = 9.8\ \text{g}$$

**Q. What volume of 2*N* $H_3PO_4$ can be prepared from 147 g of $H_3PO_4$?**

**Ans.** Equivalent weight of $H_3PO_4$ $= \dfrac{98}{3} = 32.7$

1 *N* solution contains $H_3PO_4$ $= 32.7$ g

2 *N* solution contains $H_3PO_4$ $= 65.4$ g

65.4 g of $H_3PO_4$ makes the volume $= 1\ \text{dm}^3$

1 g of $H_3PO_4$ makes the volume $= \dfrac{1}{65.4}$

147 g of $H_3PO_4$ makes the volume $= \dfrac{1}{65.4} \times 147$

$$= 2.25\ \text{dm}^3$$

**N.B:** Similarly different types of solutions and their dilutions can be prepared as given under the molarity and formality.

**Q. What is the relationship between normality and molarity?**

**Ans. Rule 1.** Knowing the molar concentration, *M*, to find the normality, *N*, multiply *M* by the number of gram equivalents in one gram mole of the solute. The product is the number of gram equivalents per dm³ and is, therefore, *N*, by definition.

$$n\,M = N \qquad \text{..... 4.19}$$

Where n = 1, 2, 3......

**Rule 2.** Knowing $N$, to find $M$, divide $N$ by the number of gram equivalents in one gram mole of the solute. This quotient is the number of mole per $dm^3$ and is molarity.

$$M = \frac{N}{n} \qquad \text{..... 4.20}$$

Where n = number of gram equivalents in one mole of the solute

**N.B.** $M$ is never greater than $N$. It is equal to $N$ when the gram equivalent weight is equal to the gram molecular weight of the solute.

**Q. What is the normality of a 3M solution of $H_3PO_4$, $H_2SO_4$ and HCl?**

**Ans.** Apply rule 1

For $H_3PO_4$, $N = 3 \times 3 = 9$

For $H_2SO_4$, $N = 2 \times 3 = 6$

For HCl, $N = 1 \times 3 = 3$

**Q. Why sometimes concentrations are expressed in mole fractions?**

**Ans.** When the components of a solution are not easily designated as the solute and the solvent, the concentration of each individual constituent is expressed in mole fractions.

The mole fraction of any constituent of a solution or mixture is defined as the no. of moles of that constituent per mole of the solution.

e.g. Mole fraction of A = $X_A = \frac{n_A}{n_A + n_B}$ ..... 4.21

e.g., Mole fraction of B = $X_B = \frac{n_B}{n_A + n_B}$

**Q. An aqueous solution containing 10 g of NaOH and 90 g of water had a density of 1.12 Kg $dm^{-3}$. Calculate *(i)* mass percent of NaOH *(ii)* molality *(iii)* mole fraction *(iv)* molarity and *(v)* normality.**

**Ans.***(i)* Mass percent of NaOH = $\frac{10}{10 + 90} \times 100 = 10\%$

*(ii)* Number of moles of NaOH = $\frac{10}{40} = 0.25$

Number of moles of $H_2O$ = $\frac{90}{18} = 5$

Molality = $\frac{0.25}{90} \times 1000 = 2.78$ m

*(iii)* $X_{NaOH} = \frac{0.25}{5 + 0.25} = 0.0476$

*(iv)* Volume of solution $V$, corresponding to $100 \times 10^{-3}$ kg of solution is

$$V = \frac{M}{d} = \frac{100 \times 10^{-3}\ \text{Kg}}{1.12\ \text{Kg dm}^{-3}} = 89.3 \times 10^{-3}\ \text{dm}^3$$

Hence molarity $= \dfrac{0.25}{89.3 \times 10^{-3}} = 2.8\ M$

*(v)* Normality of the solution is equal to its molarity.

**Q. What do you know about ppm concentrations?**

**Ans.** In dealing with concentrations of very dilute solutions, percent composition becomes awkward to use because of the number of zeros needed to place the decimal point,. Under these conditions the concentrations can be conveniently expressed in terms of parts per million (ppm). ppm-means 1 part in total one million parts (including 1 part of the substance as well).

$$\text{ppm} = \frac{\text{Weight of the solute}}{\text{Weight of the solution}} \times 1{,}000{,}000 \ \text{.....}\ 4.22$$

**Q. How ppm concentration could be expressed?**

**Ans.** ppm can be expressed in the following way as:

*(i)* ppm

*(ii)* mg $\text{dm}^{-3}$

*(iii)* mg $\text{kg}^{-1}$

*(iv)* μg $\text{cm}^{-3}$

**Q. How would you prepare the following solutions?**

***(i)*** **1 ppm of NaCl**

***(ii)*** **1000 ppm of NaCl**

***(iii)*** **1000 ppm solution of Na from NaCl salt.**

**Ans.***(i)* Dissolve 1 mg of NaCl per $\text{dm}^3$ of the solution.

*(ii)* Dissolve 1000 mg (or 1 g) of NaCl per $\text{dm}^3$ of the solution.

*(iii)* Formula weight of NaCl = 23 + 35.5 = 58.5 g

58.5 of NaCl contains 23 g of Na.

23 g of Na is present in = 58.5 g NaCl

1 g of Na will be present in $= \dfrac{58.5}{23} = 2.54$g NaCl

2.54 g NaCl = 1 g of Na = 1000 mg of Na.

So dissolve 2.54 g of NaCl per $\text{dm}^3$ of the solution and the concentration of the solution will be 1000 ppm.

**Q. What is the concentration of a solution in ppm that is 0.0003% by weight ?**

**Ans.** 0.0003% means 0.0003 g per 100 $\text{cm}^3$.

100 $\text{cm}^3$ of the solution contains = 0.0003 g

$$1\ \text{cm}^3 \text{ of the solution contains} = \frac{0.0003}{100}$$

$$1000\ \text{cm}^3 \text{ of the solution contains} = \frac{0.0003}{100} \text{🔔} 1000$$

$$= 0.003\ \text{g}$$

$$0.003\ \text{g} = 3\ \text{mg} = 3\ \text{ppm}$$

**Q. How would you prepare the following solutions from 1000 ppm stock solution of Na?**

**(i) 100 cm$^3$ of 100 pm.**

**(ii) 100 cm$^3$ of 10 ppm.**

**Ans.** *(i)*

$$C_1V_1 = C_2V_2$$

$$1000 \times V_1 = 100 \text{🔔} 100$$

$$V_1 = \frac{100\ \Pi \times 100}{1000} = 10\ \text{cm}^3$$

So take 10 cm$^3$ of the stock solution and make the volume up to 100 cm$^3$.

*(ii)*

$$C_1V_1 = C_2V_2$$

$$1000 \times V_1 = 10 \times 100$$

$$V_1 = \frac{10 \times 100}{1000} = 1\ \text{cm}^3$$

So take 1 cm$^3$ of the stock solution and make the volume up to 100 cm$^3$.

**Q. Glacial acetic acid is 100% $CH_3COOH$ by weight and has a specific gravity of 1.05. Describe the preparation of the following solutions.**

**(i) 1 *N* $CH_3COOH$**

**(ii) 0.5 *N* $CH_3COOH$**

**(iii) 300 cm$^3$ of 0.5 *N* $CH_3COOH$.**

**Ans.** *(i)* Equivalent weight of acid = 60

Specific gravity (density) = 1.05

$$D = \frac{m}{V}$$

or

$$V = \frac{m}{d} = \frac{60}{1.05} = 57.14\ \text{cm}^3$$

Dissolve 57.14 cm$^3$ of glacial actic acid per dm$^3$ to get 1 *N* solution.

*(ii)* 1 N $CH_3COOH$ solution contains = 57.14 cm$^3$

0.5 N $CH_3COOH$ will contain = 57.14 × 0.5 = 28.57 cm$^3$

So dissolve 28.57 $cm^3$ of glacial acetic acid per $dm^3$ to get 0.5 *N* solution.

(*iii*) 1000 $cm^3$ of 0.5 *N* solutions glacial $CH_3COOH$ = 28.57 $cm^3$

1 $cm^3$ of 0.5 *N* solutions glacial $CH_3COOH = \frac{28.57}{1000}$

300 $cm^3$ of 0.5*N* solutions glacial $CH_3COOH = \frac{28.57}{1000} \times 300$

$= 8.57 \text{ cm}^3$

So dissolve 8.57 $cm^3$ per 300 $cm^3$

**Q. Concentrated $H_2SO_4$ is 96% $H_2SO_4$ by weight and has a density of 1.84. Calculate the amount of $H_2SO_4$ required to prepare 100 $cm^3$ of 1 N $H_2SO_4$.**

**Ans.** Equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$

$$V = \frac{M}{d} = \frac{49}{1.84} = 26.63 \text{ cm}^3$$

Dissolve 26.63 $cm^3$ of conc. $H_2SO_4$ per $dm^3$ of the solution to get 1 N solution.

1000 $cm^3$ of 1*N* solution contains conc. $H_2SO_4$ = 26.63 $cm^3$

1 $cm^3$ of 1*N* solution contains conc. $H_2SO_4 = \frac{26.63}{1000}$

100 $cm^3$ of 1*N* solution contains conc. $H_2SO_4$

$$= \frac{26.63}{1000} \times 100 = 2.663 \text{ cm}^3$$

Since the acid is not 100% pure, so we have to make further calculations.

96 $cm^3$ conc. $H_2SO_4$ = 100 $cm^3$ commercial $H_2SO_4$

1 $cm^3$ conc. $H_2SO_4 = \frac{100}{96}$

2.663 $cm^3$ conc. $H_2SO_4 = \frac{100}{96} \times 2.663 = 2.77 \text{ cm}^3$

If 2.77 $cm^3$ of conc. $H_2SO_4$ is dissolved per 100 $cm^3$, then the solution will be of required strength.

**Q. Write %age purity, specific gravity and normality of the commercial concentrated solutions of acids and bases.**

**Ans.**

| **Compound** | **MW** | **Sp. gravity** | **% age W/W** | **Approx. *N*** |
|---|---|---|---|---|
| HCl | 36.5 | 1.19 | 37 | 12.1 |
| $HNO_3$ | 63.0 | 1.42 | 70 | 15.8 |
| $H_2SO_4$ | 98.0 | 1.84 | 96 | 35.2 |
| $H_3PO_4$ | 98 | 1.71 | 85 | 44.5 |

| | | | | |
|---|---|---|---|---|
| $CH_3COOH$ | 60 | 1.06 | 100 | 17.4 |
| $HCOOH$ | 46.0 | 1.20 | 86 | 24 |
| $NH_3$ | 17.0 | 0.91 | 28 | 14.8 |

## 4.4. pH and Buffers

**Q. What do you understand by pH value?**

**Ans.** pH may be defined according to Sorensen (1909) as the negative logarithm of hydrogen ion concentration expressed in molarity i.e.,

$$pH = -\log [H^+] \qquad \text{..... 4.23}$$

It is realized that activity rather than concentration of an ion determines the e.m.f. of a galvanic cell of the type commonly employed to measure pH. Hence pH may be defined more accurately as

$$pH = -\log a_{H^+}$$

**Q. What is the physical significance of pH value?**

**Ans.** The pH scale is a series of numbers which expresses the degree of acidity or alkalinity of a solution, as contrasted with the total quantity of an acid or a base in some material.

**Q. What is the difference between activity and concentration?**

**Ans.** Concentration is the amount of solute dissolved per unit volume of the solution. The effective concentration is known as activity. Both these terms are related as

$$a = fc \qquad \text{..... 4.24}$$

Where f is activity coefficient.

**Q. How pH of a solution is determined?**

**Ans.** The pH of a solution is determined by the following methods.

(i) Taste
(ii) Litmus paper
(iii) Hydrion paper
(iv) Indicators
(v) pH-meter

**Q. What is the most accurate method of determining pH value?**

**Ans.** Potentiometric (pH-meter) method is the most accurate method for determining pH value.

**Q. Briefly discuss the theory of potentiometry.**

**Ans.** When a metal M is dipped into a solution containing its own ions $M^{n+}$, an electrode potential is established, the value of which is given by Nerst equation:

$$E = E^\circ + \frac{RT}{nF} \ln a_{M}^{n+} \qquad ..... 4.25$$

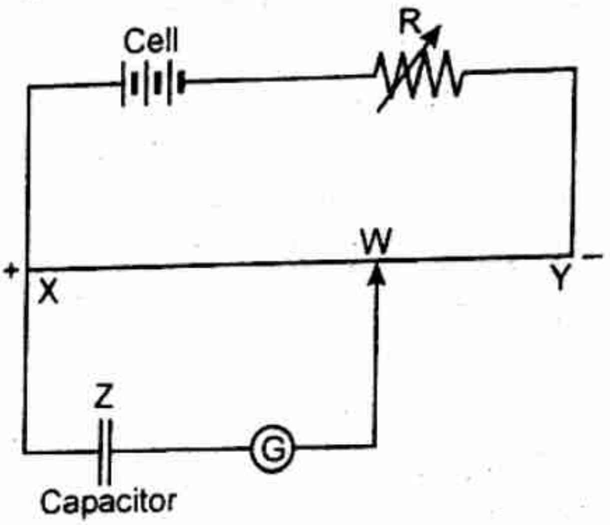
Where E° is the standard electrode potential of the metal. E is measured by combining the electrode with reference electrode. The Nerst equation gives a simple relationship between the relative potential of an electrode and concentration of corresponding ionic species in the solution. Thus measurement of the potential of a reversible electrode permits calculations of the activity or concentration of a component of the solution.

**Q. What is the principle of potentiometer?**

**Ans.** A potentiometer is a device which is used to measure e.m.f. of a cell. It operates on the Poggendorff compensation principle. The principle of this method is to balance the unknown e.m.f or potential difference against a known e.m.f., which can easily be varied. When these two e.m.f's are exactly equal, no current will flow through a galvanometer placed in the circuit. The galvanometer is therefore employed as a null instrument.

**Q. Draw a circuit diagram of a potentiometer.**

**Ans.**



A storage battery sends a current through the wire XY and the variable resistance R. The value of R is adjusted accordingly to potential across XY. Now on sliding W the potential across XW and WY is in the same proportion as the length of the distance from one end of the wire. To measure potential of unknown cell, it is connected in series with galvanometer (G) between X and sliding point (W). Now W is moved till galvanometer gives null deflection. Now XW distance represents the potential of the cell and can be determined by measurement of distance.

**Q. How does a pH meter differ from a simple potentiometer?**

**Ans.** A simple potentiometer is entirely satisfactory for measurement of the potential of cells with resistance of less than about 10,000 ohms, but it is totally unsuited for the voltage determination with systems that include membrane electrodes e.g. glass electrode. The resistance of such an electrode typically ranges from 50 to 500 mega ohms. Thus the currents in such circuits can not be detected with even the best galvanometer. Here some kind of electronic current amplification is required and several instruments with this feature have been developed.

In principle, a potentiometric pH meter differs from the ordinary potentiometer only to the extent that the galvanometer is replaced by an electronic circuit that amplifies the current in the circuit by a factor of $10^9$ or more.

**Q. Briefly discuss the principle of a pH meter.**

**Ans.** A pH meter is a special type of millivolt potentiometer designed to measure the e.m.f. of a cell in which the electrolyte contains $H^+$ ions. The e.m.f. (E) of a galvanic cell can be related by means of the Nerst equation to the activity of $H^+$ ions in the solution. The voltage produced by the cell is converted by the potentiometer (pH meter) to a current which is proportional to the pH of the sample. This current is translated into a pH reading on a dial. A glass electrode is employed as a measuring electrode and a calomel electrode is needed as a reference electrode.

**Q. What is the significance of pH measurements?**

**Ans.** *(i)* Large number of qualitative and quantitative analyses are carried out at a definite pH values.

*(ii)* pH has got a great importance in agriculture. Soils are often tested to determine whether acidic or basic fertilizers are required for a particular crop.

*(iii)* Food preservation needs definite pH.

*(iv)* It has also got a great importance in biochemical reactions such as digestion of food, working of enzymes etc.

**Q. Define a buffer solution.**

**Ans.** A solution which resists any change in its pH value on dilution or an addition of an acid or alkali is called a buffer solution and it keeps its pH value fairly constant.

**Q. What are the components of a buffer solution?**

**Ans.** A buffer solution consists of a weak acid and its salt with a strong base, e.g. $CH_3COOH$ and $CH_3COONa$.

or

It consists of a weak base and its salt with a strong acid. e.g. $NH_4OH$ and $NH_4Cl$.

**Q. What is the principle of common ion effect?**

**Ans.** Common ion effect is a phenomenon in which the dissociation of a weak acid or a base is cut down in the presence of common ion furnished by the salt of that acid or base.

**Q. How does a buffer solution work?**

**Ans.** Consider a buffer system consisting of $CH_3COOH$ and $CH_3COONa$. Suppose a small amount of concentrated $OH^-$ ions is added to this buffer solution. It combines immediately with $H^+$ ions to form water. If no buffer were present, this would dramatically lower the H+ ions concentration and thus raise the pH value. The buffer however,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$H^+ + OH^- \rightleftharpoons H_2O \text{ (Neutral)}$$

provides a means of replenishing the consumed $H^+$ by the ionization of $CH_3COOH$ to $CH_3COO^-$.

Conversely, if a small amount of conc. HCl is added to the buffer system, the $H^+$ ions will combine with $CH_3COO^-$ ions to form $CH_3COOH$ which is again a weak acid and hence does not alter pH.

$$HCl \longrightarrow H^+ + Cl^-$$

$$H^+ + CH_3COO \longrightarrow CH_3COOH \text{ (weak acid)}$$

**Q. Why do strong acids and bases not form buffer solutions?**

**Ans.** Strong acids and bases seldom form buffers because they dissociate completely and neutralized one another e.g.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

**Q. What is buffer capacity?**

**Ans.** The buffer capacity may be defined as the number of moles of acid (base) which when added to one dm³ of the buffer solution changes its pH by unity.

**Q. Briefly discuss the significance of Henderson's equation.**

**Ans.** Henderson's equation helps us to calculate the pH value of a buffer system if the concentration of the acid and its salt is known.

$$pH = pKa + \log\frac{[Salt]}{[Acid]} \qquad .....4.26$$

Moreover, a solution of any pH can be prepared from this equation.

**Q. Describe the preparation of 1 dm³ of 0.1 M Phosphate buffer having pH = 7 (pKa = 6.86).**

**Ans.** A buffer solution of any pH can be prepared from Henderson's equation. An acid is chosen such

$$pH = pKa + \log\frac{[Salt]}{[Acid]}$$

that its pKa is near to the desired pH. Since we have phosphate buffer, therefore.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-}$$

Using the above equation.

$$7 = 6.86 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$0.14 = \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Taking antilog on both sides.

$$\frac{1.38}{1} = \frac{[\text{Salt}]}{[\text{Acid}]}$$

Total = 1.38 + 1 = 2.38

Molarity of the salt ($HPO_4^{2-}$) = $\frac{1.38}{2.38} \times 0.1 = 0.058$ M

Molarity of the salt ($H_2PO_4^-$) = $\frac{1}{2.38} \times 0.1 = 0.042$ M

Number of moles = V ($dm^3$) × M

Number of moles of salt = 1 × 0.058 = 0.058

Number of moles of acid = 1 × 0.042 = 0.042

Weight in gram of salt ($K_2HPO_4$)

= No. of moles × molecular weight

= 0.058 × 174 = 10.09 g.

Weight in grams of acid ($KH_2PO_4$) = 0.048 × 136 = 6.53 g

Therefore, to prepare 1 $dm^3$ of the phosphate buffer, dissolve 10.09 g of salt and 6.53 g of acid per $dm^3$ of the solution.

**Q. Describe the preparation of buffers having pH 1 to 11.**

**Ans. Sodium acetate-Hydrochloric acid Buffer.** 1.0 M $CH_3COO$ Na. 10 M HCl. Take 20 $cm^3$ of $CH_3COO$ Na solution and the following quantities ($cm^3$) of distilled water and HCl.

| **pH** | **HCl** | **$H_2O$** |
|---|---|---|
| 1.0 | 29.6 | 50.4 |
| 2.0 | 21.0 | 59.0 |
| 3.0 | 19.6 | 60.4 |
| 3.5 | 18.4 | 61.6 |
| 4.0 | 15.6 | 64.4 |

**Acetic acid-Sodium acetate Buffer.**

(0.2 M $CH_3COOH$, 0.2M $CH_3COONa$)

| **pH** | **Acid, $cm^3$** | **Sodium acetate $cm^3$** |
|---|---|---|
| 4 | 82 | 18 |
| 5 | 30 | 70 |
| 5.5 | 12 | 88 |

**Phosphate Buffer** (M/15 $KH_2PO_4$, M/15 $Na_2HPO_4$)

| pH | $KH_2PO_4$ cm$^3$ | $Na_2HPO_4$ cm$^3$ |
|---|---|---|
| 6 | 98 | 12 |
| 7 | 38 | 62 |
| 7.5 | 15 | 85 |
| 8 | 6 | 94 |

**Borate Buffer.** (0.05 M Borax; 0.2 M Boric Acid)

| pH | Borax cm$^3$ | Boric acid cm$^3$ |
|---|---|---|
| 7 | 6.0 | 94.0 |
| 8 | 27.5 | 72.5 |
| 9 | 80.0 | 20.0 |
| 10.0 | 97.5 | 2.5 |
| 11.0 | 98.4 | 1.6 |

## 4.5. Gravimetric and Volumetric Analyses

**Q. What is gravimetric analysis?**

**Ans.** Gravimetric analysis is the most important classical method of analysis which is based upon obtaining the weight of a precipitate. The large proportion of the determinations in gravimetric analysis is concerned with the transformation of element or radical into stable pure compound which can be readily converted into a form suitable for weighing. The weight of the element is readily calculated from the knowledge of the formula of the compound and atomic weights of the constituent elements.

**Q. What are the various steps of gravimetric analysis?**

**Ans.** In general, a gravimetric method of analysis consists of the following steps:

*(i)* The sample weight is determined and it is dissolved in a proper solvent.

*(ii)* a sequence of chemical reactions is carried out to obtain a suitable product.

*(iii)* the weight of the product of the reaction is determined.

*(iv)* this weight in conjunction with the knowledge of the product is used to calculate the quantitative composition of the sample.

**Q. What chemical reaction is involved in gravimetric methods?**

**Ans.** The key chemical reaction involved in gravimetric methods is almost always a precipitation, because it can be a highly selective means for separating the components of interest from the matrix, and the product weighed is almost always a precipitate, because it can be weighed readily.

**Q. What are the general requirements of a gravimetric method?**

**Ans.** For gravimetric analysis, the precipitation reaction should have the following criteria:

(i) It should precipitate only the compound of interest.

(ii) The precipitation should be quantitative.

(iii) The particle size of the precipitate should be large enough so that it could be washed, filtered or dried with little difficulty.

(iv) The precipitate should be a compound of known composition or it should be readily converted into such a compound.

**Q. What are the general requirements of a precipitate?**

**Ans.** The precipitate must itself be a stoichiometric compound that is easy to weight, it should be nonvolatile, nonhygroscopic, nonefflorescent, inert to reaction with air, or it should be easily convertible into such a compound by drying or ignition.

**Q. What are the optimum condition for precipitation?**

**Ans.** The general rules are as follows:

(i) High dilution of the sample solution.

(ii) Use of dilute solutions of reagents.

(iii) Presence of minimal excess of any common ions.

(iv) Precipitation at elevated temperature, provided the precipitate is stable at high temperature.

(v) Extensive washing of precipitates.

**Q. How are precipitates separated?**

**Ans.** The solid liquid phase separation may be achieved by decantation, filtration, centrifugation or a combination of these procedures.

**Q. What is the difference between co-precipitation and post-precipitation?**

**Ans.** Contaminations may be classified into two groups: Those due to co-precipitation and those caused by post-precipitation.

The contamination of the precipitate by substances which are normally soluble in mother liquor is termed as co-precipitation. It is concerned with the adsorption at the surface of the particle exposed to solution and occlusion of foreign substances during the process of crystal growth from primary particles.

Post-precipitation is the precipitation which occurs on the surface of first precipitate after its formation. It occurs with the sparingly soluble substances which form supersaturated solutions.

**Q. Why pure water is rarely used as wash solution?**

**Ans.** The objective of washing the precipitate is to remove the contamination on the surface. Pure water is rarely used as wash solution due to the following reasons:

(*i*) solubility losses are maximized in pure water.

(*ii*) water tends to remove all ions, which in case of colloidal precipitates causes peptization.

**Q. What is the objective of drying and ignition?**

**Ans.** Once obtained, collected, and washed with a suitable liquid, the precipitate is freed from water by drying or ignition. During this heat treatment, the precipitate may undergo physical or chemical changes which influence its weight and composition.

**Q. Write the names of some organic precipitants.**

**Ans.** Several organic reagents are used extensively in gravimetric analysis e.g.

(*i*) Dimethylglyoxime for nickel

(*ii*) Quinaldic acid for copper

(*iii*) 8-hydroxyquinoline for magnesium etc.

**Q. What is volumetric analysis?**

**Ans.** Volumetric (titrimetric) analysis is a very widely used method of analysis. It depends upon the accurate measurement of volumes of solutions of substances which react with the constituents being determined.

or

Volumetric analysis is a method of analysis is which a substance to be analysed is allowed to react with another substance with known concentration from buret in the form of solution. The concentration of unknown is then calculated.

**Q. What are the advantages of volumetric analysis over the direct instrumental evaluation?**

**Ans.** Volumetric analysis has the following inherent advantages over the direct instrumental evaluation of a physico-chemical property.

(*i*) Accuracy.

(*ii*) Reliability.

(*iii*) Base and rapidity of performance.

(*iv*) Specificity through adjustment of conditions.

(*v*) Simplicity of interpreting the results.

**Q. What are the general requirements of a titrimetric method?**

**Ans.** A titrimetric method should:--

*(i)* be accurate and precise.

*(ii)* be simple to use.

*(iii)* work under a wide range of conditions.

*(iv)* be rapid, and

*(v)* have practical applications.

**Q. What are the general requirements of a volumetric reaction?**

**Ans.** A volumetric reaction should:

*(i)* go essentially to completion.

*(ii)* be exceeding rapid.

*(iii)* be stoichiometric.

*(iv)* be free from side reactions.

*(v)* be specific for the substance to be determined.

**Q. Explain important terms of volumetric analysis.**

**Ans. 1. Titration.** We may define the titration as a process which involves the careful addition of the reagent solution to the solution containing the constituent (or some other substance with which quantitative reaction takes place) until the amounts of reagent and constituent are exactly equivalent.

**2. Standard Solution.** A standard solution is one whose strength or concentration is known.

**3. Titre.** A titre is defined as the weight of the solute contained in 1 $cm^3$ of the solution or the weight of any substance which will react with or be equivalent to 1 $cm^3$ of the solution. The relationship between titre and normality is given as

$$\text{Normality} = \frac{\text{Titre} \times 1000}{\text{Gram equivalent weight of the substance}} \quad \text{..... 4.27}$$

It is seen that the titre of a normal solution is its milliequivalent weight.

**4. Equivalence point.** The point at which just adequate reagent is added to react completely with substance is called as the equivalence point.

**5. Indicator.** It is that substance which indicates the physico-chemical condition of a chemical reaction. Indicator indicates the end point generally by a change of colour of the solution.

**6. End point.** When the reaction between the two solutions is completed, then the slight excess of one solution is revealed by the colour change in the solution. This stage of reaction is known as end point.

or

The point at which colour change of an indicator becomes apparent to the eye, is called as an end point

or

The point at which the reaction is complete, is termed the end point.

The equivalence point (or stoichiometric point) and end point are not same.

**7. End point error.** The actual difference between end point and equivalence point is called end point error. It is a random error which is different for different systems.

**Q. What are primary standards?**

**Ans.** The substances which are available in pure form with definite chemical composition are called as primary standards. All primary standards must be obtainable in pure form. They must react only under the condition of titrations and no side reaction be present. They must not change weight during exposure to atmosphere. The equivalent weight should be pretty high to reduce error due to weighing. Moreover they should be readily prepared, stable, easily dried and highly nonhygroscopic.

**Q. Write down names of some primary standards.**

**Ans.** **Acids:** Potassium hydrogen phthalate, oxalic acid dihydrate sulfamic acid, benzoic acid, constant boiling HCl.

**Bases:** $Na_2CO_3$, $Na_2B_4O_7$

**Oxidizing agents:** $K_2Cr_2O_7$, $KBrO_3$

**Reducing agents:** $Na_2C_2O_4$, $K_4[Fe(CN)_6]$.

**Q. What are secondary standards?**

**Ans.** These are the substances which may be used for standardizations and whose contents of active substance have been found by comparison against a primary standard e.g. NaOH, KOH, HCl, $H_2SO_4$ etc.

**Q. What is cleaning solution?**

**Ans.** Chromic-sulfuric acid mixture is known as cleaning solution. It is prepared by adding conc. $H_2SO_4$ to $Na_2Cr_2O_7$ and allowing it to stand for sometime before use. Glassware to be cleaned is brought in contact with the mixture and allowed to stand for a period of 10-15 minutes. When the dark colour of the mixture turns green, it should be discarded.

**Q. Briefly discuss the classification of volumetric analysis.**

**Ans.** The volumetric methods have been broadly classified into four categories as:

(a) **Acid-base titrations.** Those exercises involving strong or weak acid or base.

(b) **Redox titrations.** Those titrations which largely involve simultaneous oxidation-reduction reaction.

(c) **Precipitation titrations.** Those titrations in which the titration reaction results in the formation of a precipitate or a slightly soluble salt.

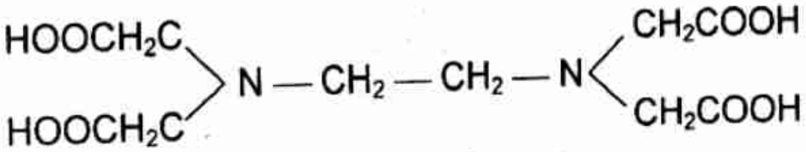
(d) **Complexometric titrations.** Those titrations which are based on the reaction of a metalion with a ligand to form a soluble complex and in which one of the two reactants is used as a titrant.

**Q. What is the difference between a chelatometric titration and a chelometric titration?**

**Ans.** A complexometric titration which involves the formation of a soluble chelate, it is known as a `chelatometric titration' and when a 1:1 chelate is formed, it is known as chelometric titrations.

**Q. What do you know about EDTA?**

**Ans.** EDTA (Ethylene diaminetetra acetic acid) is the most common complexing agent. It is also known by several other names such as Versene, Nullapon, Trilon B etc.



Structure of EDTA

EDTA has the following advantages and is most commonly used.

(i) It dissolves readily in water.

(ii) It is obtainable in high degree of purity.

(iii) Dihydrate can be used as the primary standard.

**Q. Briefly discuss the ionization of EDTA.**

**Ans.** EDTA may be assigned the formula $H_4Y$; the disodium salt is therefore $Na_2H_2Y$ and in solution yield the ion H2Y2-. The reaction with cation such as $M^{2+}$ may be represented as.

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$

For trivalent and other ions, we may write

$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^- + 2H^+$$

$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{n-4} + 2H^+$$

## 4.6. Solvent Extraction

**Q. What is the principle of solvent extraction?**

**Ans.** Amongst the various methods of separation, solvent extraction also called as liquid-liquid extraction is considered to be most versatile and popular method of separation. It is based on the principle that a solute can distribute itself in a certain ratio between two immiscible or partially miscible solvents such as benzene, water or chloroform.

**Q. Why solvent extraction is considered as a useful separation technique?**

**Ans.** The main reason for its usefulness is that separations can be carried out on macro-level as well as on micro-level. Moreover, one does not need any sophisticated apparatus or instrumentation execpt a separatory funnel.

**Q. What are the applications of solvent extraction?**

**Ans.** This technique can be used for the purpose of preparation, purification, enrichment, separation and analysis on all scales of working. It is an elegant, simple and rapid technique.

**Q. What is Nerst distribution law?**

**Ans.** When a solute `A' is shaken with two immiscible solvents 1 and 2, the solute distributes itself between these two liquids and a dynamic equilibrium is established:

$$A_1 \rightleftharpoons A_2$$

Where $A_1$ and $A_2$ are the concentrations of the solute A in solvent 1 and 2 respectively. If the solute exists in the same ionic or molecular form in both the solvents, Nerst law states that

$$K_D = \frac{A_1}{A_2} \qquad \text{..... 4.28}$$

Where $K_D$ is a constant at a particular temperature known as distribution or partition constant.

**Q. What are the limitations of the distribution law?**

**Ans.** *(i)* The two solvents should be immiscible.

*(ii)* The solutions should be dilute.

*(iii)* Molecular state of the solute should be same in both the phases.

**Q. Write the formula if solute undergoes association in one of the phases.**

**Ans.** When a solute undergoes association in one of the phases, then the distribution law is written as

$$K = \frac{A_1}{\sqrt{A_2}} \qquad \text{..... 4.29}$$

**Q. What is distribution ratio (D)?**

**Ans.** In the practical applications of solvent extraction we are not interested whether the solute, in any of the solvent, is in the association or dissociated form, but our primary interest is to know the fraction of total solute in one or the other solvent. Hence the term distribution ratio (D) or extraction coefficient (E) is used which is given by.

$$D = \frac{(C_A)_1}{(C_A)_2} \qquad \text{..... 4.30}$$

Where $(C_A)_1$ = total concentration of A in solvent 1.

$(C_A)_2$ = total concentration of A in solvent 2.

**Q. Mention one important analytical application of solvent extraction.**

**Ans.** The most important type of analytical application of solvent extraction involves metal chelates which are readily soluble in organic solvents but only sparingly soluble in water. For example, by adding dimethylglyoxime to an aqueous solution of Ni(11) at pH between 5-12, nickel dimethylglyoxime is quantitatively precipitated which can be extracted with chloroform. The red solution in chloroform so obtained is examined photometrically and the amount of Ni present in the sample solution can be determined.

**Q. Briefly discuss various techniques of extraction.**

**Ans.** The two liquids may be brought in contact with one another discretely or continuously, giving rise to three common ways of carrying out an extraction. These are:

*(i)* **Batch Extraction.** In batch extraction, a liquid (usually $H_2O$) containing the dissolved solute sample is shaken with another liquid (usually organic) in a closed container until equilibrium has been established. The two immiscible phases are allowed to settle and separated mechanically. When the value of D for the desired compound is greater that 10 and considerably different from other components of the mixture, a batch extraction is preferred.

*(ii)* **Continuous Extraction.** The continuous extraction is used when the distribution ratio is relatively small ($D<1$), so that large number of batch extractions would normally be necessary to affect quantitative separation. In this technique, the extracting liquid (lighter of heavier) is passed continuously through or over the stationary liquid containing the solute. The two phases are then separated physically and one containing unextracted desired solute is again treated for continuous extraction.

*(iii)* **Counter Current Extraction.** In such type of extraction, the solvent and the liquid which is being extracted move continuously in opposite directions and thus the solute distributes in two oppositely moving phases. When the extraction is complete, the two phases are separated physically. Equilibrium is not attained in this technique.

## 4.7. Chromatography

**Q. What is chromatography?**

**Ans.** Chromatography is a modern analytical technique which is used for the examination and separation of closely related compounds. It facilitates the purification, isolation and comparison of components of a mixture It may be employed with all kinds of volatile and soluble substances, organic and inorganic, polar and non-polar etc.

**Q. What do you know about M. Tswett?**

**Ans.** Mikhail Tswett was a Russian botanist who is generally credited with the discovery of chromatography. He provided the basic nomenclature and note the fundamental process underlying the method. Chromatography is taken from the Greek word **'Chroma'** for colour and **'graphy'** to write.

**Q. What do you know about stationary phase and mobile phase?**

**Ans.** In every chromatographic separation, there is a stationery phase which remains fixed in a system and it consists of packing within the column. The other phase, called the mobile phase, percolates over the surface of the fixed layer.

**Q. What is the general principle of chromatography?**

**Ans.** All separations by chromatography depend on the fact that the substances to be separated, distribute themselves between the mobile and the stationary phases in proportions which vary from one substance to another. Chromatographic separations are dependent upon multiple partition and adsorption process.

**Q. How would you classify the chromatographic methods?**

**Ans.***(a)* Chromatographic processes may be classified on the basis of the physical states of the two phases. The stationary phase may be either liquid or solid and the mobile phase either gas or liquid. Thus the processes may be classified, naming the physical state of the mobile phase first, as

*(i)* Liquid-liquid Chromatography.
*(ii)* Liquid-solid Chromatography.
*(iii)* Gas-liquid Chromatography, and
*(iv)* Gas-solid Chromatography.

*(b)* Chromatographic processes may alternatively be classified on the basis of the mechanism whereby the components of a test sample are distributed between the two phases, regardless of whether the mobile phase is a liquid or a gas. On this basis, there are three major classes of the chromatographic separations:

*(i)* adsorption chromatography.
*(ii)* partition chromatography.
*(iii)* ion exchange chromatography.

*(c)* Chromatographic methods can also be classified on the basis of molecular geometry. The stationary phase consists of porous particles

with a fixed pore size. Mobile phase is liquid. This type of criterion forms the basis of molecular exclusion chromatography which are of two types:

- *(i)* gel filtration chromatography.
- *(ii)* gel permeation chromatography.

**Q. Explain the terms elution, eluent and eluate.**

**Ans.** The process of causing the components of the test sample to move through the column, by the continuous flow of the mobile phase, is called elution. The solvent gas or liquid chosen for the mobile phase is the eluent. The eluate is whatever emerges from the column, that is the eluate is the eluent plus whatever component of the test sample it contains at any particular time.

**Q. Define partition chromatography.**

**Ans.** It is a type of chromatography in which the solute is distributed or partitioned between the two phases such as in a liquid-liquid extraction e.g. paper chromatography, column chromatography etc.

**Q. What do you know about paper chromatography?**

**Ans.** Paper chromatography is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bonded to cellulose network (inert support) of the paper. The mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds between these two liquid phases. The mobile phase travels by capillary action through the paper.

Depending upon the way, the solvent travels on the paper, there are three types of paper chromatography as given below:

- *(i)* **Ascending paper chromatography.** The mobile phase moves up on paper strip in this case.
- *(ii)* **Descending paper chromatography.** The mobile phase in this case moves down the paper strip.
- *(iii)* **Circular paper chromatography.** The mobile phase moves horizontally along a circular sheet of paper here.

**Q. What is a chromatogram?**

**Ans.** Chromatorgram is a sheet of filter paper on which the sample components (colour zones) appeared after development.

**Q. What is a chromatographic tank?**

**Ans.** It is a cylindrical jar or cabinet which is used for suspending the paper sheet.

**Q. What do you mean by development?**

**Ans.** Development is a process in chromatography in which the mobile phase is allowed to move through the paper by capillary action.

**Q. What are the basis of detection for monitoring the progress of separation?**

**Ans.** The measurement of almost any physico-chemical property of a solute-solvent system including the thermal and electrical conductivity, radioactivity, colour and other spectral characteristics, can be made the basis of a detection device for monitoring the progress of a separation.

**Q. What is $R_f$ value?**

**Ans.** It is defined as the ratio of the distance travelled by the solute (sample component) to that of solvent front.

$$R_f = \frac{\text{Distance travelled by the solute (cm)}}{\text{Distance travelled by the solvent front (cm)}}$$

$R_f$ stands for retention factor or retardation factor. It is constant for a particular compound at a particular temperature for a given solvent:

In actual practice standard reference compounds are applied individually with the sample. Their $R_f$ value are calculated and compared with the unknown for their identification.

**Q. What important points are considered for paper chromatography?**

**Ans.** When it is proposed to attempt a separation by paper chromatography, the following points have to be considered:

*(i)* method (ascending, descending, or horizontal).

*(ii)* type of paper.

*(iii)* selection and preparation of the solvent.

*(iv)* equilibrium in the selected apparatus.

*(v)* preparation of the sample.

*(vi)* method of detection and identification.

**Q. What is elutropic series?**

**Ans.** It is a series in which the polarity of the solvents is expressed. The solvents are arranged in order of increasing polarity as indicated by their dielectric constant.

**Q. Briefly discuss various solvents for paper chromatography.**

**Ans.**

| Separation | Solvent | Proportions |
|---|---|---|
| Amino-acids | n-butanol/acetic acid/ water | 4:1:5 |
| | n-butanol/ pyridine/ water | 1:1:1 |

| | | |
|---|---|---|
| Sugars | ethyl acetate/ pyridine/ water | 2:1:2 |
| | ethyl acetate / acetic acid/ water | 14:3:3 |
| Fatty acids | n-butanol/1.5 M $NH_3$ | sat. soln. |
| Co, Mn, Ni, Cu Fe (Chlorides) | acetone/con. HCl/water | 87:8:5 |

**Q. What are locating reagents?**

**Ans.** The success of a chromatographic separation method depends ultimately on the detection process. Coloured substances are visible as separate patches at the end of the run. Colourless ones require physical or chemical detection. It should be a routine that chromatograms are examined under UV light before and after the application of any other method.

The locating agents are the reagents which give a colour reaction with as many of the substances present as possible.

| | |
|---|---|
| **Metals locating reagents.** | Rubeanic acid, ammonium sulphide, diphenylcarbazide. |
| **Amino acids locating reagents.** | Ninhydrin, isatin, sakaguchi |
| **Sugars locating reagents.** | Silver nitrate, anisaldehyde, aniline phthalate. |

**Q. What are the applications of paper chromatography?**

**Ans.** There is hardly any field in which paper chromatography has not found some use. Some of the principal uses are given below:

(*i*) Analysis of polymers.

(*ii*) Detection and estimation of metals in soils.

(*iii*) Investigation of phenolic material in plant extracts.

(*iv*) Separation of steroids and alkaloids.

(*v*) Separation of amino acids and peptides.

(*vi*) Examination of urine and body fluids for sugars and amino acids.

**Q. What is thin layer chromatography (TLC)?**

**Ans.** Thin layer chromatography is a kind of adsorption chromatography, carried out on glass plates coated with a thin layer of adsorbent. In this technique, a solution of the sample in a volatile solvent is applied via a pipet to the bottom of a uniform layer of inert adsorbent such as silica, alumina, which has been uniformly spread over a suitable supporting plate of a material dried under standard conditions. When the spot has dried, the plate is placed vertically in a suitable tank. The solvent rises by capillary action, resolving the sample mixture into discrete spots.

**Q. How does TLC differ from paper chromatography?**

**Ans.** TLC is faster, more reproducible and versatile (wide range of stationary phases and solvent), and in most cases has better resolution, than paper chromatography. Corrosive reagents such as $H_2SO_4$ which cannot be applied on paper, can be used in TLC for spot detection. A further and very important advantage of TLC is that it can be used to separate hydrophobic substances, such as lipids and hydrocarbons, which are difficult to deal with on a paper.

**Q. Briefly mention various adsorbents for TLC.**

**Ans.**

| Adsorbent | Uses. |
|---|---|
| Silica gel | Amino acids, alkaloids, lipids, fatty acids, essential oils, inorganic anions and cations, steroids, terpenoids. etc. |
| Alumina | Alkaloids, food dyes, phenols, steroids, vitamins, carotenes, amino acids. etc. |
| Kielselguhr | Sugars, oligosaccharides, amino acids, steroids, fatty acids etc. |
| Celite | Steroid, inorganic cations. |

**Q. What is silica gel?**

**Ans.** Silica gel is the most commonly used adsorbent in TLC studies. It is prepared by the hydrolysis of sodium silicate to polysilicic acid which an further condensation and polymerisation yields silica gel material. A binder is commonly added to silica gel to confer greater mechanical strength to the layer and to enhance adhesion to the packing plate e.g. gypsum.

**Q. How many methods are for applying thin layer to its support?**

**Ans.** There are four principal ways for applying thin layer to its support.

- Spreading.
- Pouring.
- Spraying.
- Dipping

**Q. Name the binder added in the slurry and what is their function.**

**Ans.** The binder added in the slurry are Gypsum, plastics of Paris etc. the function of binder is to strengthen the plate and to help the slurry to adhere the backing material.

**Q. How are many types of TLC?**

**Ans.** There are many types of TLC but on the basis of sample application they are of three types.

- Micro TLC also called analytical TLC (sample size 1 - 5μg/μl).
- Preparative TLC (sample size 4mg).
- Semiprepratative TLC (sample size 250mg).

**Q. Why the chemical method for the locating the spots are not oftenly used?**

**Ans.** Chemical method of locating reagent is destructive because chemical reagent reacts with the compounds and changes their nature.

**Q. What is the important point considered for solvent in TLC?**

**Ans.**

- Solvent should be of low polarity.
- Cheap and highly pure
- Not too volatile.

**Q. What is meant by activation of plate in TLC?**

**Ans.** The method of removing water from the slurry after pouring on the plate in the oven at 100°C for 30 minutes and then placing it in the desiccators is known as activation of plate.

**Q. What is reversed phase chromatography?**

**Ans.** As the name implies, the phases used in liquid-liquid partition chromatography (paper chromatography) are reversed. In normal chromatography, the stationary phase, being aqueous, is more polar than the mobile phase. The technique where the mobile phase is more polar is called reversed phase chromatography. The mobile phase is not necessarily water, although the mixtures used normally contain some water.

A number of substances have been employed as supports for the stationary phase, among them are rubber latex, olive oil, silicone oils etc.

**Q. What is column chromatography?**

**Ans.** In column chromatography, a solid phase (adsorbent) is held in a vertical tube, the mixture to be separated is placed on the top of the column of adsorbent and a solvent (eluent) is allowed to flow down through the column. At all times, a certain fraction of each component of the mixture will be adsorbed by the solid and the remainder will be in solution. A substance that is relatively strongly adsorbed will have a greater fraction of its molecules adsorbed at any one time and thus any given molecule will spend more time sitting still and less time moving through the column. On the contrary, a weakly adsorbed substance will have a smaller fraction of its molecules adsorbed at any one time, and hence any given one molecule will spend less time in sitting on the column and more time moving.

**Q. Define partition column chromatography.**

**Ans.** In partition chromatography, the solid adsorbent is replaced by a packing comprising a support material coated with a stationary phase. The stationary phase should be insoluble or sparingly miscible in the mobile phase. Thus partition chromatography is a technique which utilizes the ability of a solute to distribute itself between the two phases, to an extent determined by its partition coefficient.

**Q. What are the advantages and limitations of column chromatography?**

**Ans. Advantages.**

*(i)* It is useful for the separation of large amount of sample.

*(ii)* It is mostly used for the separation of polyphenols, phospholipids, steroids etc.

**Limitations.**

*(i)* The process is slow.

*(ii)* Column packing is difficult.

*(iii)* The resolution is slow as compared to other techniques.

*(iv)* It is not useful for the separation of polar compounds.

**Q. What are the advantages and limitations of TLC?**

**Ans. Advantages.**

*(i)* Small amount of sample is required.

*(ii)* Simple and cheaper apparatus is used.

*(iii)* Better resolution is achieved.

*(iv)* Quick method and gives better quantitative determination of the components of a mixture.

**Limitations.**

*(i)* Uniform coating on the plates is a difficult job.

*(ii)* Due to exposure to air, adsorption of water takes place and instead of adsorption phenomenon, the partition may occur.

**Q. What are the advantages and limitations of paper chromatography?**

**Ans. Advantages.**

*(i)* It is used for the separation of inorganic ions.

(ii) It is useful for the separation of amino acids.

(iii) Investigation of phenolic materials in plants and separation of alkaloids is possible.

(iv) One of the major advantages of paper chromatography is its sensitivity. Amounts as little as 0.1 microgram of some compounds can be detected.

**Limitations.**

(i) Low speed.

(ii) Does not give better resolution.

(iii) Does not give quantitative determination of components of a mixture.

(iv) Cannot be used in the separation of volatile substances such as hydrocarbons and volatile fatty acids.

**Q. Briefly discuss gas Chromatography (GC).**

**Ans.** Gas chromatography is similar to liquid-liquid and liquid-solid chromatography except that in gas chromatography, the mobile phase is a gas rather than a liquid. Gas chromatography, as its name suggests, is particularly suited for the separation of gases and volatile liquids and solids in the gaseous state.

**Q. How does GLC differ from GSC?**

**Ans.** In gas-solid chromatography (GSC), the column is packed with an adsorbent such as active carbon and the components of the mixture distribute themselves between the gas phase and the adsorbed phase, that is, on the surface of the solid. Separation is due to differences in adsorptive behaviour.

In gas-liquid chromatography (GLC), the column is packed with a porous solid coated with a thin layer of involatile liquid as the stationary phase. Separation is due to differences in solution behaviour. Components of the mixture distribute themselves between the gas phase and the stationary liquid phase according to their partition coefficients. The solid functions only as a support for the liquid stationary phase.

**Q. What types of gases are used in GC?**

**Ans.** Gases which are inexpensive, readily available and not hazardous are used, such as helium, nitrogen, hydrogen and argan.

**Q. What are different types of detectors used in GC?**

**Ans.** The purpose of detectors is to monitor the column effluent, measuring variations in its composition. They do not, however, identify the components of a mixture. The various types of detectors used are:

(i) Katharometer

(ii) Gas density balance

(iii) Flame ionization detectors etc.

**Q. Briefly describe the working mechanism of a gas chromatograph.**

**Ans.** In practice a small amount of the material being examined is injected into a stream of an inert gas which carries it into a column containing a suitable medium capable of retarding the flow by varying degrees of the individual components of the sample as they flow through the column. The separated components then emerge from the column at discrete intervals (charoacterstic of each component) and pass through some form of detector. Differences in adsorption or partition of the material in the column is again the factor which makes separation possible.

**Q. What are the different components of a gas chromatograph?**

**Ans.** A typical gas chromatograph consists of:

(*i*) gas cylinder

(*ii*) sample injector

(*iii*) column

(*iv*) an oven (for temperature control)

(*v*) a suitable detector

(*vi*) recorder for display of results

**Q. Briefly discuss the scope and limitations of gas chromatography.**

**Ans.** Compared with the other chromatographic methods, gas chromatography requires fairly complicated and expensive apparatus, but the advantages more than compensate for these drawbacks. Mixtures, whose separation is extremely tedious by other methods, can be resolved quickly and efficiently by gas chromatography. The advantages of gas chromatography depend mainly on two properties of gas, low viscosity and rapid attainment of equilibrium.

Gas chromatography is applicable to any substance that is easily vaporized which limits its use mainly to liquid samples. Some solid samples that have high vapour pressures at room temperature can also be subjected to GC, but they must first be dissolved in volatile solvents. In some instances non-volatile substances may be converted to their derivatives which are vaporizable under the given conditions.

Since it is necessary to heat most materials to maintain them in the gas phase, it is essential that the compounds be thermally stable and not undergo any chemical change at the elevated temperature. Hence heat sensitive samples cannot be analyzed by GC. This technique is now particularly used for the analysis of fatty acids, steroids and pesticides. For other most compounds, both volatile and non-volatile (inorganic, proteins, dyestuffs etc.) and heat sensitive compounds, an other technique developed recently is the high performance (or pressure) liquid chromatography (HPLC).

**Q. How many types of columns are used in GC?**

**Ans.** Mainly there are two types of column, packed column and capillary columns, also know as open tubular columns. A packed column is one that contains a particular packing material whereas a capillary column is that does not contain a particular packing material.

**Q. What is the difference between walls coated open tubular column and support coated open tubular column?**

**Ans.** In wall coated open tubular columns, the stationary phase is coated on the column wall whereas in support coated open tubular column, the stationary phase is coated on a solid support i.e., attached to the column wall.

**Q. What is meant by column bleed in GC?**

**Ans.** The tendency of stationary phase to elute from the column is known as column bleeds.

**Q. What is cryogenic focusing in GC?**

**Ans.** The process of concentrating volatile solutes by cooling the column inlet below room temperature to maintain efficiency is known as cryogenic focusing.

**Q. What is the difference between split injection and split less injection?**

**Ans.** In split injection only a small portion of the sample enters the column but in split less we can inject the higher percentage of the sample to the column.

**Q. What is on column injection?**

**Ans.** The direct injection of thermally unstable samples onto a capillary column is known as on column injection.

**Q. How non-volatile analytes are analyzed in GC?**

**Ans.** Non volatile analytes must be chemically converted to a volatile derivative before analysis e.g. to analyze amino acids, the amino acids are reacted with 1-butanal and acetyl chloride to produce esterified amino acid. Subsequent treatment with trifluoroacetic acid give the amino acid's volatile N-trifluoroacetyl-n-butylester derivatived which is than analyzed by GC.

**Q. What is the function of molecular sieves in GC?**

**Ans.** For optimum result, the gas is dried before use by passing through tubes containing a material known as molecular sieve. The function of molecular sieves is to remove water vapors from the gas.

**Q. Explain the terms retention time and retention volume?**

**Ans.** The retention time for a component of a mixture is the time required for it to pass through the column, measured from the time of injection of the test sample to the time of its peak response on the measuring device.

The retention volume for a component is the volume of the mobile phase which must flow to cause that component to pass through the column. If flow rate is constant, the retention volume is the product of the retention time and flow rate.

The numerical values of the retention time and retention volume vary from one component to another, which is really the reason why the substances may be separated by chromatography.

**Q. What are the basis of high performance liquid chromatography (HPLC).**

**Ans.** Gas chromatography is an elegant chromatographic method which overcame many of the problems associated with classical liquid chromatography (LC) and thin layer chromatography (TLC). The essential prerequisite for the analysis of mixture by GC is that each of the sample components has an appreciable vapour pressure at the operating temperature of the column. Nevertheless, there still remains a large number of compounds, such as pharmaceuticals, polymers, proteins and dyestuffs, which cannot be volatilized or even heated without decomposition and which therefore cannot be analyzed by GC.

**Q. What is HPLC?**

**Ans.** HPLC stands for high performance (or pressure) liquid chromatography. In ordinary column liquid chromatography, the mobile liquid phase moves down the column slowly through the stationary phase under the influence of gravity, this requires much time for the separation of various components. In HPLC, the eluent (mobile liquid phase) is pumped through the column packed with the adsorbent, hence separation becomes much more rapid. The basic principle of this procedure is the same as for adsorption or partition chromatography.

The pressure mechanical pump ensures the rapid solvent flow. The flow rate of the solvent affect the resolution of the sample components. As each component passes through the column, the detector notes its elution and gives signal to the recorder.

**Q. Is HPLC is applicable both for adsorption and partition type chromatography?**

**Ans.** Yes, both adsorption and partition type chromatography can be carried out by high pressure technique. The stationary solid phase for adsorption chromatography may be any suitable adsorbent, which allows the smooth flow of solvent under high pressure conditions. Micro-particulate silica gels are the commonly used adsorbents.

Partition chromatography requires a stationary liquid phase that is adsorbed on the solid support (as in GLC).

**Q. What are the components of HPLC?**

**Ans.** A typical HPLC consists of:

- *(i)* a packed column
- *(ii)* a high pressure pump
- *(iii)* a solvent reservoir
- *(iv)* an injection port
- *(v)* a detector
- *(vi)* a recorder.

**Q. Briefly describe the working mechanism of HPLC.**

**Ans.** The operation of HPLC instrument involves the column equilibration with the solvent (mobile phase). This requires the solvent to flow through the column for a few minutes. At the same time, the detector is turned on and a base line is established on the recorder. Then the sample dissolved in least possible polar solvent is injected by a microlitre syringe. The solvent (mobile phase) is allowed to flow. Elution of each component of the sample appeared as a peak on the recorder. A computing integrator can also be connected to the detector to print the composition of the sample mixture.

**Q. What is the difference between isocratic elution and gradient elution?**

**Ans.** In isocratic elution, the resolution of the sample mixture is affected by using a solvent of constant composition, while the gradient elution technique involves the varying composition of the solvent.

**Q. What are different types of detectors for HPLC?**

**Ans.** Most commonly used detectors are:

- *(i)* UV, visible, IR absorption detectors.
- *(ii)* differential refractometer.

**Q. Compare GLC with HPLC.**

**Ans.** It would be interesting at this state to compare GLC with HPLC. From the view point of speed and simplicity of equipment GLC is better. For isolation of nonvolatile substances including inorganic ions and thermally unstable materials HPLC is preferable. Both techniques as a matter of fact are complimentary, efficient, highly selective, needing small sample which can he handled by nondestructive testing and applicable for the quantitative analysis. The special feature of HPLC is that it can accommodate thermally unstable, nonvolatile and inorganic ions. However, it is very expensive technique due to the use of highly pure solvents.

**Q. What are different solvents used in HPLC?**

**Ans.** The eluents employed for HPLC separations may comprise water, aqueous buffer solutions, organic solvents such as methanol and acetonitrile or a mixture of the above.

**Q. What is bonded stationary phase in HPLC?**

**Ans.** A liquid stationary phase that is chemically bonded to a particular packing material is known as bonded stationary phase. The use of boned stationary phase is to prevent the column bleed.

**Q. What is the difference between normal phase chromatography and reverse phase chromatography?**

**Ans.** In normal phase chromatography, the stationary phase is polar and mobile phase is non polar and vice versa.

**Q. What is the loop injection in HPLC? And why we use it?**

**Ans.** A mean to injection of samples in which the sample is loaded into a short section of tubing and injected onto the column by re-directing the mobile phase through the loop. The typical operating pressure of HPLC is sufficiently high so it is impossible to inject the sample in the same manner as in GC. So we use loop injection method.

**Q. What is the function of ion suppress column in ion exchange chromatography?**

**Ans.** To minimize the mobile phase's contribution to conducting, an ion suppressor column is placed between the analytical column and the detector. This column selectively removes mobile phase electrolyte ions without removing solute ions.

**Q. What is molecular exclusion chromatography?**

**Ans.** Molecular exclusion chromatography is also a separation technique. The separation of various constituents by taking the advantage of difference in the size and geometry of the molecule is the basis of exclusion chromatography By virtue of difference in size, certain particles move faster while other moves slower creating, thereby differential migration front. The stationary phase consists of porous particles with a fixed pore size. Mobile phase is a liquid. It has two types.

*(i)* Gel permeation or gel filtration.

*(ii)* Ion exclusion and retardation.

**Q. What is gel permeation chromatography? Briefly discuss its working mechanism.**

**Ans.** Gel permeation or gel filtration is technique that fractionates substances largely according to their molecular size. It is based upon inclusion and exclusion of the solutes through a stationary phase which consists of porous particles with a fixed pore size. It may be soft gels (gel filtration) or semi-rigid gels (gel permeation). A column of any of these porous materials is prepared. The sample mixture is added to the column along with a suitable solvent (mobile phase). Sample component with large molecular size, which cannot enter the pores, are excluded and immediately swept from the column with liquid mobile phase. On the other hand, sample components having smaller molecules enters the pores and pass through the column at a lower rate. The larger molecules are therefore collected first, followed by the smaller ones according to their size.

**N.B.** Some people say that gel permeation is not a type of chromatography since it does not affect separations on the basis of molecular size and is, in fact, a filtration or sieving procedure.

**Q. Briefly mention some applications of gel permeation.**

**Ans.** *(i)* It is principally used for the analysis of mixtures of the molecules of different molecule weight, e.g. separation of maltose, rafinose and glucose.

*(ii)* It is also possible to separate molecules of same molecular weight by proper selection of gel type and column height

*(iii)* Molecular weights of various bio-chemical compounds can be estimated.

*(iv)* Generally this technique is employed to remove impurities from an analytical sample.

*(v)* It is also used for copolymerization studies to study whether one has obtained pure copolymer or a mixture of homopolymers.

**Q. What is ion exclusion?**

**Ans.** Ion exclusion is a process for separating ionic materials from nonionic materials based on inherent differences in the distribution of two types of solutes between an ion-exchange resin phase and a true aqueous solution.

**Q. Briefly mention some applications of ion exclusion method.**

**Ans.** *(i)*Sugar and salt cannot be easily separated by other methods but ion exclusion permits such separation because the size and relative inability of sucrose and glucose molecule to diffuse rapidly into the resin phase.

*(ii)* The separation of strong electrolytes from neutral molecules can be best achieved by ion exclusion, e.g. purification of commercial glycerine when high ionic concentrations are overcome.

*(iii)* The separation of NaCl and ethylene glycol, HCl and $CH_3COOH$, $CH_3COOH$ and $ClCH_2COOH$, NaCl and ethanol etc.

**Q. Briefly discuss ion-exchange chromatography.**

**Ans.** As the name implies, ion-exchange chromatography is based on ion-exchange phenomenon. This technique involves the use of an ionized stationary phase which selectively binds charged molecules present in the sample. Usually the stationary phase is in the form of a particulate ion exchange resin which can be used to pack a glass column. The sample is applied to the top of the column and a solvent, or a series of solvents, is used to wash through the various components of the sample.

**Q. What are ion-exchange resins?**

**Ans.** The ion exchange resins are complex organic polymers. By varying the structure and functional groups of these polymers, the properties of the resins can be controlled in regard to the rate of exchange, exchange capacity and selectivity Both cation and anion exchange resins can be used.

**Q. What are cation and anion exchange resins?**

**Ans.** Most of the cation exchange resins contain sulphonic or carboxylic acids which exchange their $H^+$ ions with other cations.

Anion exchange resins generally contain substituted amines as functional groups. A primary amine in aqueous solution reacts to form a hydroxy compounds, the hydroxyl ions then react with other anions.

**Q. Briefly discuss the working mechanism of ion-exchange chromatography.**

**Ans.** In this type of chromatography, the ions in the sample solution are held by the charged groups as the particles of the stationary phase. As solvent passes over the solid phase, weakly held ions are swept away more quickly than those which are tightly bound. The extent of exchange of ions between an ion exchange resin and a solution depends upon a number of factors e.g. valency, atomic number, nature of resin, solvent, temperature and concentration.

**Q. Briefly mention some applications of ion-exchange chromatography.**

**Ans.** This technique is used in a large number of operations e.g.

*(i)* Separation of fission products.

*(ii)* Separation of lanthanides and actinides series.

*(iii)* Water softening.

*(iv)* metal concentrations and separations etc.

**Q. What is Supercritical fluid chromatography?**

**Ans.** It is a separation technique in which the mobile phase is supercritical fluid is known as supercritical fluid chromatography. The most common mobile phase in supercritical fluid chromatography is carbon dioxide.

**Q. What are the supercritical fluids?**

**Ans.** A supercritical fluid is defined as a substance above its critical temperature and pressure.

**Q. What are the forces responsible for the separation of solute components?**

**Ans.** There are two opposing sets of forces which get to work as the solvent moves on the paper. These are, Propelling forces which act to shift the substance from their point of origin and displaces them in the direction of solvent flow. They are also of two types ,

Solvent flow.

Solubility of each substance in the solvent.

Retarding forces are of two types,

Adsorption

Partition

**Q. What are the specific and non specific locating reagents?**

**Ans.**

- Specific reagent. The reagent which react with the compound that contain particular functional groups are called specific reagent. For example dinitrophenyl hydrazine is used to locate the compound having carbonyl functional group. The specific reagent not only locates the compound but also help in their identification.
- Non-Specific reagent. Those reagents, which produce colour spots with various classes of organic compound, are known as non-specific reagent. Example are iodine, Rhoda mine B, fluorescein and sulphuric acid. But $H_2SO_4$ is not used in TLC.

**Q. What is single column ion chromatography?**

**Ans.** Ion exchange chromatography in which conditions are so adjusted that an ion suppressor column is not needed is known as single column chromatography.

**Q. What is inclusion limit in size exclusion chromatography?**

**Ans.** In size exclusion chromatography, the smallest solute that can be separated from other solutes is known as inclusion limit; all smaller solutes elute together.

**Q. What is exclusion limit?**

**Ans.** In size exclusion chromatography, the largest solute that can be separated from other solutes is known as inclusion limit; all largest solutes elute together.

**Q. What is fronting and tailing?**

**Ans.** A tail at the beginning of a chromatographic peak due to injecting too much sample is known as fronting whereas a tail at the end of chromatographic peak due to the presence of highly active sites in the stationary phase is known as tailing.

**Q. What is band broadening?**

**Ans.** The increase in a solute's baseline width as it moves from the point of injection to the detector is called band broadening.

**Q. What are theoretical plates?**

**Ans.** A quantitative means of evaluating column efficiency that treats the column as though it consists of a series of small zones or plates, in which partitioning between the mobile and stationary phases occurs.

**Q. Define capacity factor?**

**Ans.** A measure of how strongly a solute is retained by the stationary phase is known as capacity factor.

**Q. What is void time?**

**Ans.** The time required for unreacted solutes from point of injection to the detector is called void time.

**Q. What is void volume?**

**Ans.** The volume of mobile phase needed to move an unreacted solute from the point of injection to the detector.

**Q. What is resolution?**

**Ans.** The separation between two chromatographic bands is known as resolution.

**Q. What is base line width?**

**Ans.** The width of solute's chromatographic band measured at the base line is termed as baseline width.

**Q. What is adjusted retention time?**

**Ans.** The difference between as solute's retention time and column void time is known as adjusted retention time.

## 4.8. Conductometry

**Q. What is conductimetry?**

**Ans.** Conductimetry is one of the important electro-analytical techniques used in physico-chemical analysis. It can be defined as a technique of analysis which is based on the measurement of electrical conductance.

**Q. What are conductors and insulators?**

**Ans.** Those substances which permit the passage of current through them, are called conductors, while substances which do not conduct electricity are known as insulators.

**Q. How do metallic conductors differ from electrolytic conductors?**

**Ans.** In metallic conductors, electrons carry electric current, while in electrolytic conductors ions act as carriers of current.

**Q. How does resistance differ from conductance?**

**Ans.** Resistance is a property of conductors due to which they retard the flow of electric current. It is represented by R and has unit ohm.

The reciprocal of the resistance is known as conductance. It is represented as

$$L = \frac{1}{R} \qquad \text{..... 4.31}$$

The units of conductance is $ohm^{-1}$ or siemen.

**Q. Define specific resistance and specific conductance.**

**Ans.** Specific resistance is the resistance which a centimetre cube of a conductor offers to the flow of current.

The reciprocal of the specific resistance is known as specific conductance. It is defined as the conductance of $1 cm^3$ volume of a solution. Mathematically.

$$Ls = L\frac{l}{a} \qquad \text{..... 4.32}$$

It has the units $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$.

**Q. State Ohm's law.**

**Ans.** The law states that the quantity of current flowing through a conductor is directly proportional to the potential difference and inversely proportional to the resistance.

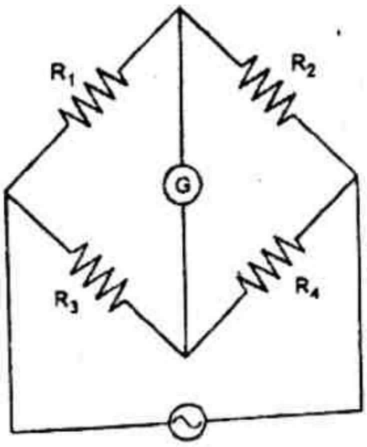
$$I = \frac{V}{R} \qquad \text{..... 4.33}$$

**Q. What is the principle of conductivity meter?**

**Ans.** The measurement of resistance and hence conductance of an electrolyte solution is usually performed with a modified Wheatstone bridge circuit as shown below

According to Wheatstone bridge principle, if there is no flow of current through the circuit as indicated by detector G the following relationship exists.

$$\frac{R_1}{R_3} = \frac{R_2}{R_4}$$



If the values of the resistance of three conductors, i.e., $R_2$, $R_3$ and $R_4$ are known, then the value of fourth resistance can be calculated.

$$R_1 = \frac{R_2}{R_4} \times R_3 \qquad \text{..... 3.34}$$

Knowing $R_1$, the conductance and specific conductance can be determined.

**Q. What is cell constant? Give its significance.**

**Ans.** Cell constant is a factor which stands for the ratio of the specific conductance of a solution to its measured conductance in the cell.

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}} \qquad \text{..... 4.35}$$

Cell constant is used to measure specific conductance of a solution.

**Q. Define molar and equivalent conductance.**

**Ans.** Molar conductance is the conducting power of all the ions produced by dissolving one mole of the electrolyte at a given dilution and temperature. It is measured in S cm$^2$ mol$^{-1}$. Mathematically,

$$\Lambda_m = \frac{L_s \times 1000}{C} \qquad \text{..... 4.36}$$

Equivalent conductance is the conducting power of all the ions produced by dissolving one gram equivalent of the electrolyte at a given dilution and temperature. It is measured in S cm$^2$ equiv-1. Methematically.

$$\Lambda_m = \frac{L_s \times 1000}{C} \qquad \text{..... 4.37}$$

where 'C' represents concentrations in gram equivalent per dm$^3$.

**Q. How cell constant is determined?**

**Ans.** Cell constant is usually determined by using KCl solution of known concentrations at a given temperature. The conductance of KCl solution is measured with conductivity meter, them its specific conductance is consulted from the literature.

**Q. Why KCl solution is used for cell constant determination?**

**Ans.** *(i)* KCl is available in pure form as compared to other electrolytes.

*(ii)* The ionic conductances of $K^+$ and $Cl^-$ ions are comparable.

*(iii)* Values of specific conductance at different concentrations and temperatures are available.

**Q. What is the effect of concentration on specific and equivalent/molar conductance?**

**Ans.** Since specific conductance is the conductance of a unit volume of the solution, hence it increases with increasing concentration and vice versa. The equivalent/molar conductance increases on dilution due to increase in the degree of ionization (weak electrolytes) or increase in the ionic mobility (strong electrolytes).

**Q. What is conductivity water? How is it prepared?**

**Ans.** Ordinary distilled water possesses some conductance due to the materials dissolved from the container and due to $CO_2$ and $NH_3$ dissolved from air. Such water cannot be used for preparing solutions of conductance experiments. Hence water is specially purified before it can be used. Such water is known as conductivity water. It is prepared by redistilling good quality distilled water after adding $KMnO_4$ and NaOH in a pyrex distillation unit. Conductivity water should have a conductance not more than $1 \times 10^{-6}$ S $cm^{-1}$.

**Q. Write some applications of conductance measurements.**

**Ans.** *(i)* Dissociation constant can be determined.

*(ii)* Degree of dissociation can be determined.

*(iii)* Solubility of a sparingly soluble salt can be determined.

*(iv)* Ionic product of water can be studied.

*(v)* Rate constant of a reaction can be studied.

*(vi)* End point of titration can be determined.

## 4.9. Refractometry

**Q. What is refraction of light?**

**Ans.** When a ray of light travels obliquely from one medium to another, it is bent or refracted at the surface separating the two media. This change of direction is known as refraction of light. It depends upon the nature of the two media and the direction in which the light travels.

**Q. Why does refraction occur?**

**Ans.** The refraction occurs because light travels at slightly different velocities in different media; thus at the interface between media there is a slight change in wavelength.

**Q. Explain the terms incident ray, refracted ray and normal.**

**Ans.** The ray before refraction is termed the incident ray; on being refracted it becomes the refracted ray. A line perpendicular to the refracting medium at the point where the incident perpendicular ray enters it is the normal.

**Q. What are the laws of refraction?**

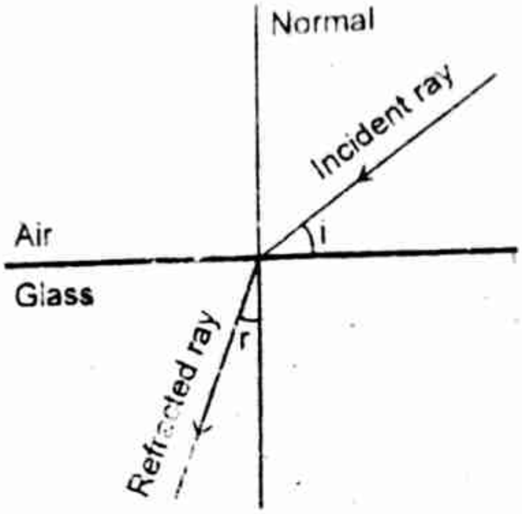
**Ans.** *(i)* The incident ray, the refracted ray and the normal to the surface of separation of the two media at the point of incidence lie in the same plane.

*(ii)* Snell's law. The ratio of the sine of the angle of incidence to the sine of the angle of refraction is a constant for any pair of media.

**Q. Define refractive index of a medium.**

**Ans.** It is defined as the ratio of the sine of the angle of incidence to the sine of the angle of refraction when light is refracted from a vacuum (or, to a very close approximation, from air) into the medium. This is equivalent to the fundamental definition: the ratio of the velocity of light in the free space to that in the medium.

$$n_{med} = \frac{\text{Sin } i}{\text{Sin } r} \qquad ..... 4.38$$



**Q. What factors affect the refractive index?**

**Ans.** The refractive index of any substance/medium depends upon the nature of the medium, temperature and wavelength of light used.

**Q. What is the significance of refractive index?**

**Ans.** Refractive index is a physical characteristic of a substance which is used to identify a substance. By knowing the refractive index, we can check the purity of a substance.

**Q. What is a refractometer?**

**Ans.** A refractometer is a device which is used to measure the refractive index of a substance.

**Q. What is the difference between critical angle and grazing anlge?**

**Ans.** During the phenomenon of refraction as the angle of incidence (i) increases, the angle of refraction (r) also increases, when 'i' becomes equal to 90°, it is called grazing angle, then 'r' approaches its maximum value and is known as critical angle.

**Q. Briefly discuss the principle of Abbe's refractometer.**

**Ans.** A refractometer works on the principle that when an incident ray of light is made to strike an interface at the grazing incidence, i.e., the angle of incidence(i) is 90°, then

$$n_{med} = \frac{1}{\text{Sin } r_c} \qquad ..... 4.39$$

where $r_c$ is the critical angle for the pair of media under question. Eq. (4.39) forms the basis of refractometry. If `i' is greater than 90°, the ray is totally reflected at the surface of separation.

**Q. Write the names of some important refractometers.**

**Ans.** Abbe's refractometer.

Pulfrich refractometer.

Immersion refractometer.

**Q. What does the symbol $n_D 25$ signify?**

**Ans.** The symbol means the refractive index for D-lines of sodium measured at 25°C.

**Q. What is the difference between specific and molar refraction?**

**Ans.** The refractive index of a liquid varies with temperature. It decreases with an increase of temperature, as the number of molecules in the path of light is changed. But a quantity known as specific refraction is independent of the temperature. It depends only on the nature of a liquid and is defined as

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \qquad \text{..... 4.40}$$

In order to compare the refracting powers of different substances, the specific refraction is multiplied by their molecular mass, the resulting term is called molar refraction.

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \qquad \text{..... 4.41}$$

**Q. Write some applications of refractometry.**

**Ans.** *(i)* We can identify a substance.

*(ii)* We can check % age purity of a substance.

*(iii)* % age composition of a binary solution can be determined.

*(iv)* Sugar concentrations can be estimated.

*(v)* The number of theoretical plates for distillation column can be evaluated from the refractive index measurements.

**Q. Write refractive indices of some compounds/substances.**

**Ans.**

| **Substance** | **Refractive indices** |
|---|---|
| Diamond | 2.4173 |
| Glass | 1.5 — 1.7 |
| Ethanol (25°C) | 1.359 |
| Water (25°C) | 1.332 |
| Air (0°C, 760mm) | 1.000293 |

## 4.10. Polarimetry

**Q. What is polarimeter?**

**Ans.** A polarimeter is a device which is used to measure angle of rotation caused by an optically active substance. It is also known as polariscope.

**Q. What is optical activity?**

**Ans.** Optical activity or optical rotation refers to the ability of certain compounds (solid or in solution) to rotate the plane of polarized light. Such substances which rotate the plane of polarized light are called optically active. For example, sugar solution, lactic acid, quartz etc.

**Q. What is plane polarized light?**

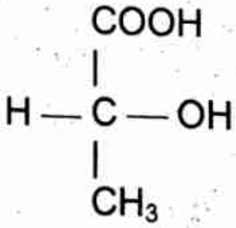
**Ans.** The light which vibrates only in one plane and direction is known as plane polarized light. It is obtained by passing the ordinary light through a Nicol prism.

**Q. What is monochromatic light?**

**Ans.** The light radiation consisting of only one wavelength or frequency is known as monochromatic light. For example, sodium vapour lamp emits monochromatic light.

**Q. Define an asymmetric carbon atom.**

**Ans.** A carbon atom which is attached to four different atoms or groups is called asymmetric carbon atom, e.g. lactic acid contains an asymmetric carbon atom.



$$H-\overset{\displaystyle COOH}{\underset{\displaystyle CH_3}{C}}-OH$$

**Q. What is the cause of optical activity?**

**Ans.** The optical activity in the substance is due to some asymmetric properties. Compounds containing at least one asymmetric centre and having no plane of symmetry show optical activity. There are some compounds which show optical activity but they have no asymmetric centre, e.g. allenes and spiro compounds.

**Q. Briefly describe the principle of polarimeter.**

**Ans.** It works on the principle that when plane polarized light is passed through an optically active substance, it rotates the plane of polarized light. The degree and direction of rotation depends on the nature of the compound and its concentration. Mathematically,

$$\alpha = [\alpha]_{\lambda}^{t}\, l \,.\, d \qquad \text{..... 4.42}$$

Where $\alpha$ = observed rotation in degrees.

$[\alpha]_\lambda^t$ = the specific rotation of the compound at fixed temperature and wavelength (generally the D-line of sodium 5893Å).

d = density of the substance in g/cm$^3$.

*l* = the light path length (in dm$^3$).

**Q. How does polarimeter differ from saccharimeter?**

**Ans.**(*i*) Polarimeter uses monochromatic light, usually the sodium D-light. In contrast to this, saccharimeter employees white light usually supplied by tungsten lamp.

(*ii*) In polarimeter the rotation of polarized light is measured by rotating the second Nicol prism (analyser). On the other hand, the analyser is permanently crossed with the polarizer in the Saccharimeter and quartz wedges (which are also optically active and can rotate the light in a direction opposite to the sample) measure the rotation.

(*iii*) The scale of Saccharimeter measures the sugar percentage directly, while polarimeter measures the rotation in degrees.

**Q. What are the components of a polarimeter?**

**Ans.** A simple polarimeter consists of the following major components:

(*i*) A light source.
(*ii*) Two Nicol prisms (polarizer and analyser)
(*iii*) Sample tube
(*iv*) A circular scale to measure angle
(*v*) An eye-piece

**Q. What factors affect the angle of rotation?**

**Ans.** The angle of rotation depends on the following factors:

(*i*) The nature of the substance.
(*ii*) The nature of the solvent.
(*iii*) The length of the tube, containing the sample solution.
(*iv*) The temperature.
(*v*) The wavelength of light used.

**Q. Define specific and molar rotation.**

**Ans.** Specific rotation is defined as the rotation in degrees produced by 1 dm length of solution having one gram of the substance per cm$^3$, at a given temperature and wavelength.

If the solution of an optically active substance contains C' g of the substance per 100 cm$^3$ of the solution, then the specific rotation is given by

$$[\alpha]_{\lambda}^{t} = \frac{\alpha \times 100}{l \times C} \qquad \text{..... 4.43}$$

The molar rotation is defined as the product of specific rotation and molar mass of the substance. Hence

$$[M]_{\lambda}^{t} = \frac{[\alpha]_{\lambda}^{t} \times M}{100}$$

$$= \frac{\alpha \times M}{l \times C} \qquad \text{..... 4.44}$$

**Q. What is the physical significance of specific rotation?**

**Ans.** The specific rotation is a physical constant, characteristic of a substance. It is an inherent property of a substance and its measurement is useful to identify a substance. We can determine the purity of a substance if the concentration is known. Conversely, if the identity of the substance is known, then concentration of the substance can be determined.

**Q. What are dextro-rotatory and levo-rotatory substances?**

**Ans.** All optically active compounds in solution show the property of optical rotation, i.e., a beam of polarized light will be rotated when it passes through the solution. If the light is rotated towards right, the compound is said to be dextro-rotatory and this property is designated by the symbol (+). Conversely, rotation to the left is referred to as levo-rotatory and designated as (–).

**Q. What is the difference between polarizer and analyser?**

**Ans.** The prism (Nicol) which is fixed near the light source and makes the light plane polarized is known as polarizer. Analyser is also a Nicol prism, but it is movable and measures the rotation.

**Q. Briefly describe the working mechanism of polarimeter.**

**Ans.** The two Nicol prisms (polarizer and analyser) are arranged in such a way that the light passes readily through them and the eye piece is uniformely illuminated. Switch `on' the polarimeter and observe a bright field through the eyepiece. Then place the sample solution .n the tube between the two prisms. Since the solution rotates the plane of polarized light, it will not pass through the second Nicol prism and the field of view will become dark. The analysing Nicol prism is them rotated until the field of view is again uniformely illuminated. The number of degrees through which the prism is rotated represents the extent of rotation of the plane polarized light by the sample solution.

**Q. Briefly discuss the applications of polarimetry.**

**Ans.**(*i*) The most extensive application of analysis by optical rotation is in the food industries. An important example of that of sugar industry. Sucrose (in the absence of others) can be determined quantitatively.

*(ii)* If, however, other common sugars are present, then hydrolysis of sucrose with an acid is done. The resulting mixture of glucose and fructose is called invert sugars and the reaction inversion. By measuring the rotation before and after inversion it is possible to calculate the amount of sucrose present. In similar manner, sugars in juices, ice creams, cold drinks, jams, jellies and related products can be readily estimated by polarimeter.

*(iii)* We can study acid catalyzed hydrosis of an optically active ester, acetal, glycoside etc.

*(iv)* In modern organic chemistry, optical rotatory dispersion (ORD) is used in molecular structure investigation.

## 4.11. Colorimetry and Spectrophotometry

**Q. What is colorimetry?**

**Ans.** Colorimetry is an important analytical technique which deals with the determination of the concentration of a substance by measurement of the relative absorption of light or transmittance with respect to a known concentration of the substance.

Colorimetry refers to the measurement of the intensities of colours. The intensity of the colour is related to the concentration of coloured compounds in solution. Such compounds have the property to absorb light. The absorption of light increases with the intensity of colour, and hence with the concentration of compounds in solution.

**Q. What are electromagnetic radiations?**

**Ans.** Radiations which consist of electric and magnetic fields are known as electromagnetic radiations. All electromagnetic radiations travel with same speed i.e., $3 \times 10^8$ $ms^{-1}$. For example, X-rays, γ-rays, uv-visible, infrared and microwaves, all are electromagnetic radiations.

**Q. What is a photon or quantum?**

**Ans.** A discrete unit or packet of energy is known as photon or quantum having energy where γ is the frequency of light radiation.

$$E = h\nu \qquad \text{..... 4.45}$$

**Q. Describe the relationship between wavelength and frequency of radiation.**

**Ans.** The wavelength (λ) and frequency (*v*) are inversely proportional to each other, i.e.,

$$\nu \propto \frac{1}{\lambda}$$

**Q. what is the range of UV-visible region of electromagnetic radiations?**

**Ans.** The visible spectrum is usually considered to be 380 – 770 nm and the ultraviolet region is normally defined as 200 – 380 nm.

**Q. What is spectroscopy?**

**Ans.** Spectroscopy is the study of the interaction between electromagnetic radiation and matter.

**Q. What is the relationship between m, nm, cm and Å?**

**Ans.** $1\ \text{nm} = 10^{-9}\ \text{m} = 10^{-7}\ \text{cm} = 1\ \text{m}\mu = 10\ \text{Å}$

**Q. How we can use the radiant energy for analytical purpose?**

**Ans.** When an atom, ion or a molecule absorbs a photon (or quantum), the added energy results in a transition alteration of state; the species is then said to be excited. Excitation may involve any of the following processes:

*(i)* Transition of an electron to a higher energy level.

*(ii)* A change in the mode of vibration of the molecule.

*(iii)* Alteration in its mode of rotation.

Each of these transitions require a definite quantity of energy; the probability of occurrence for a particular transition is the greatest when the absorbed photon supplies precisely this quantity of energy.

**Q. What is colorimeter?**

**Ans.** The colorimeter is an instrument which compares the light transmitted by a solution with that transmitted by a standard solution. It is also known as colour comparator.

In visual colorimetry, natural or artificial white light is generally used as a light source. When the eye is replaced by a photoelectric cell, the instrument is termed as photoelectric colorimeter.

**Q. What is the principle of colorimetry?**

**or**

**What are the fundamental laws of colorimetry?**

**Ans.** Colorimetry is based on the absorption of light, which is governed by two important laws:

*(i)* Lambert's law and

*(ii)* Beer's law.

**Lambert's Law:** The proportion of incident light absorbed by a transparent medium is independent of the intensity of the light (provided that those is no other physical or chemical change in the medium). Therefore successive layers of equal thickness will transmit an equal proportion of the incident light.

**Beer's Law:** The absorption of light is directly proportional to concentration of the absorbing medium.

These two laws are usually combined and are spoken as the Beer-Lambert law which states that the absorption of light is directly proportional to both the concentration of the absorbing medium and the thickness of the absorbing medium in the light path.

**Q. Write mathematical statement of Beer-lambert law and explain the various terms involved.**

**Ans.** Mathematically, Beer-Lambert law can be written as

$$A = \text{Log}\,\frac{I_o}{I} = \varepsilon c l \qquad \text{..... 4.47}$$

Where A = absorbance

ε = molar extinction coefficient

c = concentration of the absorbing solution (molar)

*l* = light path in the absorbing material (cm).

**Q. What is the difference between absorbance and transmittance?**

**Ans.** For a uniform medium, the proportion of the radiation passing through it is called the transmittance, T, where

$$T = \frac{I}{I_o} \qquad \text{..... 4.48}$$

Whre $I_o$ = intensity of incidnet radiation

I = intensity of transmitted radiation.

The extent of radiation absorption is more commonly referred to as the absorbance (A) or extinction (E) which are equal to the logarithm of the reciprocal of the transmittance, i.e.,

$$A = E = \log\frac{I}{T} = \log\frac{I_o}{I} \qquad \text{..... 4.47}$$

**Q. How extinction and transmittance are usually expressed?**

**Ans.** Extinction has no units and varies from 0 to ∞.

Transmittance is usually expressed on a range 0 to 100% but is rarely used.

**Q. What is optical density (D)?**

**Ans.** Optical density is a historic term for extinction.

Now-a-days it should not be used.

$$A = E = D$$

**Q. What do you know about molar extinction coefficient E or specific absorption (extinction) coefficient, Es or absorbancy index, *a*?**

**Ans.** According to Beer-Lamber law

$$A = a \times c \times l$$

or

$$A = \varepsilon \times c \times l$$

Here α or ε is a constant for the absorbing medium. If c is expressed in mol/dm$^3$ and *l* in cm, then *a* is given the symbol ε and is called molar absorption coefficient or molar absorptivity (formerly called the molar extinction coefficient).

The specific absorption coefficient, Es, may be defined as the absorption per unit thickness and unit concentration. It is also known as absorbancy index.

Since the molar extinction coefficient, $\varepsilon$, of a compound may be extremely large, an alternative is to quote the extinction given by a 1 cm thick sample of a 1% solution of the compound, i.e., $E_{1cm}^{1\%}$.

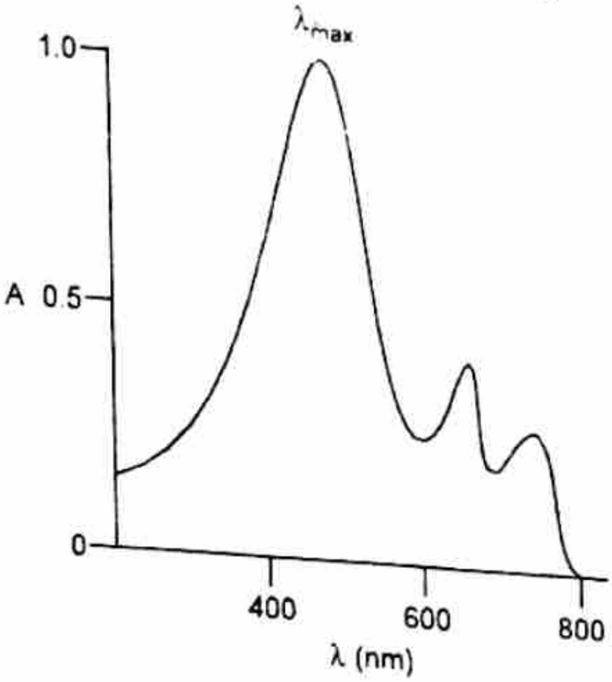
**Q. What is the physical significance of molar absorption coefficient?**

**Ans.** Molar absorption (or extinction) coefficient is constant for a particular absorbing medium. It depends upon the nature of the solute, solvent, wavelength of light used and temperature. It is independent of concentration. It is a physical characteristic which is used to identify a compound. If its value is known, we can determine the unknown concentrations.

$$\varepsilon = \frac{A}{c \times l} \qquad \text{..... 4.50}$$

**Q. What is absorption spectrum?**

**Ans.** Absorption spectrum of a compound may be shown as a plot of the light absorbed (extinction) by that compound against wavelength.

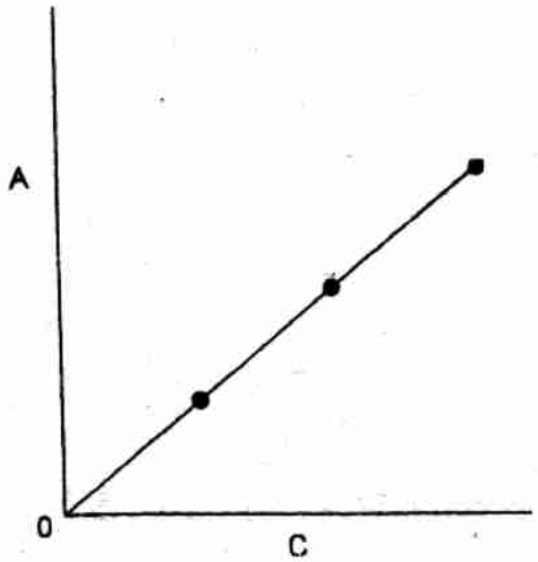


**Q. What is $\lambda_{max}$?**

**Ans.** Solutions that exhibit colour do so because some component in the solution absorbs some of the wavelengths of white light. This wavelength which depends upon its nature is known as $\lambda_{max}$ for that substance. Maximum absorption of light occurs at this wavelength.

**Q. How would you test the validity of Beer-Lambert law?**

**Ans.** The validity of Beer-Lambert law can be tested by plotting a graph between absorbance and concentrations. A straight line shows the validity of the law.



**Q. What are the limitations of Beer-Lambert law?**

**Ans.** Often the Beer-Lambert law may not be applicable to a system for a number of reasons. Firstly, the specimen may ionize or polymerise at higher concentrations, or it may coagulate to give a turbid solution, which may increase or decrease the extinction apparently. Furthermore, the instrument may be susceptible to stray radiation a well as being capable of producing beams of radiation of finite waveband only.

**Q. What are the components of a colorimeter?**

**Ans.** A photoelectric colorimeter consists of the following components:

*(i)* A light source, usually tungsten lamp

*(ii)* Slit

*(iii)* Condenser lens

*(iv)* Filter

*(v)* Cuvette

*(vi)* Photoelectric cell

*(vii)* Amplifier

*(viii)* Galvanometer

**Q. What is photoelectric cell?**

**Ans.** It is a device which converts radiant energy into electric current, that is directly proportional to the intensity of light. It is superior to the human eye in assessing the degree of absorption of a colour.

**Q. What are primary colours?**

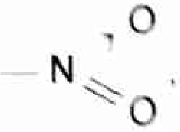
**Ans.** The primary colours of light are blue, green and red. These colours when combined, gave white light or visible light. The apparent colour of a solution is the complement of the colour absorbed. Thus, a yellow solution absorbs in the blue region of the spectrum, a red in green region and a green in red etc.

**Q.** **What is the basis of colorimetric analysis?**

**Ans.** The variation of the colour of a system with change in concentration of some component, forms the basis of colorimetric analysis.

**Q.** **What is a chromophore?**

**Ans.** Any chemical group, such as the azo group, that causes a compound to have distinctive colour. Some of the more common chromophore groups are:



$-N\overset{\nearrow O}{\underset{\searrow O}{}}$, $-N=O$, $-N=N-$ etc.

**Q.** **What is spectrophotometry? Briefly describe the advantages of this technique.**

**Ans.** Spectrophotometry is one of the most widely used and versatile of all bio-chemical analytical tools. It also deals with the analysis of system by measuring light absorption or transmittance, but unlike colorimetry, it includes UV-visible and 1R region of spectrum. Moreover, it is based on the same absorption laws i.e., Beer and Lambert laws.

This technique has definite advantages. It is a non-destructive method, unless a photochemical reaction occurs, which is not common, and it offers selectivity in that each compound has a characteristic spectrum. Often a particular component in a solution or a group in a molecule can be signaled out for observations. It averages the properties of a system over a short time interval, $10^{-14}$ sec. Finally, probably the most important fact is that measurement of high accuracy can be made in a short time using minute quantities of the substance.

**Q.** **What is spectrophotometer? How does it differ from colorimeter?**

**Ans.** A spectrophotometer is a device which is used for measuring light absorption or transmittance as a function of wavelength. It includes UV-visible and 1R region of radiation. It is a sophisticated type of colorimeter where monochromatic light is provided by a grating or prism, instead of filter. The wavelength band of the light from the filter used in colorimeter is quite broad. This makes it difficult to distinguish between two compounds of closely related absorption maxima with a colorimeter. A spectrophotometer is useful in such cases, which makes use of the light of a definite wavelength. This modern instrument has displayed improved resolution, greater sensitivity and versatility as compared to the colorimeter.

**Q.** **What is the difference between a spectrometer and a photometer?**

**Ans.** The function of spectrometer is to provide a beam of radiation of a selected wavelength and that of photometer is to measure the intensity of transmitted radiation. When combined in the spectrophotometer, the spectrometer and photometer are employed conjointly to produce a signal corresponding to the difference between the transmitted radiation of a reference material and that of a sample at selected wavelength.

**Q. Write some applications of colorimetery and spectrophotometry.**

**Ans.** Colorimeter and spectrophotometer are excellent devices for determining the concentration of substances that absorb light. They have been used for both the qualitative and quantitative analysis of several biochemical compounds, such as chlorophylls, carotenoids, proteins, amino acids, sugars steroids etc. Enzyme assays are usually performed by spectrophotometers. Mineral elements such as P and Fe in food and biological specimens are usually determined by these instruments. They can also be used to determine some of the chemical and physical properties of the substances. Properties such as rate of reactions, the nature of complex ions and the ionization constants of weak acids and bases can be determined.

## 4.12. Voltametery and Polarography

**Q. What is voltametery?**

**Ans.** It is a group of electroanalytical methods that are based upon the potential current behavior of electrode in the solution being analyzed.

**Q. Describe the basic principle of voltametery?**

**Ans.** In voltametery a measured small potential is impressed across a pair of electrodes, one of which is a non-polarizable reference electrode and other is polarizable inert electrode. The current which flows through the solution depends upon composition of solution.

In other words, voltametery and voltametric analysis are concerned with the study of current voltage relation at a microelectrode, called working electrode.

**Q. How working electrode in chosen for a particular analysis?**

**Ans.** The choice of working electrode largely depends on the range of potentials it is desired to investigate. Inert platinum electrode (working electrode) is more suitable for potentials more positive than the reference saturated calomel electrode (SCE).

**Q. What are the dimensions of working electrode?**

**Ans.** In order to ensure polarization of working electrode, its dimensions are usually kept small. This is also the reason the electrode is so called micro electrode (having surface area of few square millimeters). This electrode may be of some inert metal, such as mercury or gold.

**Q. What are the dimensions of reference electrode?**

**Ans.** The reference electrode may be of any conventional form, since it does not carry current.

**Q. Can we use three electrodes in voltametric analysis?**

**Ans.** In general voltametric analysis a three electrode cell is preferred due tom its more accuracy and less interferences. The third (auxiliary) electrode can be a simple wire of platinum or silver, or mercury pool.

**Q. What is polarography?**

**Ans.** In voltametric analysis the term polarography is used when working electrode is polarizable dropping mercury electrode (DME). It is an instrumental technique which consisit in measurement of potential difference as current flows in solutions and results so obtained cab be interpreted in terms of nature and behavior of many substances and systems.

**Q. Describe basic principle of polarography?**

**Ans.** When solution containing various ions is electrolyzed with a steadily increasing voltage, ions with lower discharge potentials will discharge first in preference to those whose discharge potential is higher.

**Q. Who developed polarography?**

**Ans.** Heyrovesky in 1922 developed this important technique and was awarded noble prize in 1959.

**Q. What do you known about supporting electrolyte?**

**Ans.** The electrolyte is an electroactive dilute solution of material under examination in a suitable medium containing an excess of indifferent electrolyte, called base of ground solution or supporting electrolyte.

**Q. What is residual current and charging current?**

**Ans.** Residual current is the sum of total current due to the reduction of traces of impurities like iron, copper or oxygen and a so called charging current which results from the fact that the mercury solution acts like a capacitor of continuously increasing area.

**Q. What is migration current?**

**Ans.** The electroactive spices should not act as a current carrier except after passage of the decomposition potential. If electroactive species are current carriers prior to decomposition potential, the resulting current is called as migration current.

**Q. How migration current is minimized?**

**Ans.** In order to minimize the migration current, a supporting electrolyte is added to solution in large concentrations in relative to electroactive species. The supporting electrolyte should be chemically inactive in the potential range to be studied and it must be free of even traces of active interfering ions.

**Q. How will you distinguish between the cathodic and anodic polarography?**

**Ans.** It is possible to carry out oxidation as well as reduction on DME. In the case of reduction, working electrode (DME) is made the cathode and technique is known as cathodic polarography, while in case of oxidation DME is anode may be regarded as anodic polarography.

**Q. What is meant by polarogram?**

**Ans.** A plot of current as function of the potential applied to polarographic cell is called a polarogram. A poargram provides both qualitative as well as quantitative information regarding the composition of the solution in which electrodes are immersed?

**Q. Why polarography offers attractive possibility for selective analysis?**

**Ans.** Because polarographic behavior of any species is unique for a given set of experimental contions.

**Q. What is amperometry?**

**Ans.** Amperometry is similar to voltametery, except both electrodes in former may be polarizable.

## 4.13 X-Ray Methods

**Q. How will you define X-rays?**

**Ans.** The interaction of radiation with matter results in elastic collisions in which potential energy of target species is raised. A common type is one in which electron is excited to higher energy level. When electron comes back to its ground state, energy is released as electromagnetic radiation, which may be visible light ($\lambda$ = 400-800 nm), ultraviolet ($\lambda$=10-400nm) or X-rays ($\lambda$=0.005-10nm).

So in simple words X-ray is that type of electron spectroscopy in which emitted radiations fall in $\lambda$=0.005-10nm.

**Q. What is the basic principle of X-rays?**

**Ans.** When a beam of high energy electrons or X-ray photons impinges on a target material (usually metal), a sufficient energy knock out a planetary electron of target atom completely. Then another electron falls into vacancy from higher orbital (outer orbital) to emit X-ray radiation with a wave length dependent on the energy levels, and hence the characteristic of the element.

**Q. What is Bremsstrahlung?**

**Ans.** When electrons from some source collide with electrons of target material these are slow down by multiple interaction with the electrons of the target. The energy lost is converted into a continuum of X-radiation, called Bremsstrahlung, meaning breaking radiation.

**Q. Differentiate between Kα and Kβ ?**

**Ans.** X-rays due to transitions from the L to the K shell are called Kα X-rays. $K\alpha_1$ and $K\alpha_2$ corresponding to electrons originating in different sublevels of the L-shell. X-rays due to transition from the M to K-shell are called Kβ, and so on.

**Q. How for analytical purposes X-rays are obtained?**

**Ans.** For analytical purposes, X-rays are obtained in three ways.

a. Bombardment of a metal target with a beam of high energy electrons.

b. By exposure of a substance to a primary beam of X-rays inorder to generate a secondary beam of fluorescent rays, and

c. By a radioactive source whose decay process results in X-ray emission.

**Q. What analytical information is provided by X-rays?**

**Ans.** For analytical purposes x-rays can be utilized in several different ways. For example,

a. Absorption of X-rays gives information about the absorbing material, just as in other spectral regions.

b. The diffraction of X-rays permits analysis of crystalline materials with a high degree of accuracy and specificity.

c. Wavelength measurement identifies the element in the excited state samples.

d. Measurement of radiant power at given wavelength can be quantitative indicator of the composition of the sample.

**Q. Which instrument can be used for X-rays measurement and what are its components?**

**Ans.** The instrument used for X-ray studies is the X-ray spectrometer-absorptiometer. It consists of a high intensity X-ray tube, a sample chamber, a goniometer with collimator and analyzer crystal and a detector.

In both emission and absorption, the X-rays must be transmitted from the X-ray tube target to the counting volume of the detector.

**Q. What detectors are being used in X-rays absorption and emission analysis?**

**Ans.** There are three types of detectors X-rays absorption and emission analysis. These are:

a. Photographic detectors

b. Gas ionization detector

c. Scintillation detectors

**Q. Make a comparison between X-ray absorption and X-ray emission.**

**Ans.**

1. For general elemental analysis the X-ray emission is more versatile than X-absorption. Emission has advantages of spectral line specificity and sensitivity of one or two orders of magnitude greater than absorption.

2. X-ray emission is applicable to a wide range of elements without changing any instrumental parameter other than Bragg angle.
3. X-ray emission methods are applicable to all elements having atomic number 11 to 92, with some practical and theoretical limitations, especially in the case of low atomic number elements.
4. A unique advantage of the absorption edge method over emission is the elimination of matrix effect which is inherent in emission analysis.
5. Concentration can be calculated from absorption edge measurement without recourse to the use of standards.
6. The lower limit of detection by emission method is a function to peak to back ground ratio and the number of photons counted.

**Q. What do you know about X-ray diffraction?**

**Ans.** In this analytical technique X-rays are employed in investigating the interior of a crystal to certain the special arrangement of the structural units of a substance in crystalline state.

**Q. Why crystals diffract X-rays?**

**Ans.** It might be possible to diffract X-rays by means of crystals, because

a. The crystals act as a three dimensional natural grating for X-rays.
b. X-rays act as a part of electromagnetic radiation.
c. X-rays are actually the radiation of very small wavelength probably of the order of $10^{-8}$ cm.

**Q. Define Bragg law?**

**Ans.** X-ray diffraction is explained best by Bragg's law, which states"As the atoms in a crystal are orderly arranged, a beam of X-rays is reflected from plane of atoms similar to the reflection of light wave from a plane mirror."

$$n\lambda=2d\sin\theta$$

Where,

n is an integer 1,2,3 etc, known as order of reflection.

d is inter planar distance of crystal/

$\lambda$ is wavelength.

**Q. What are the most important requirements of diffraction?**

**Ans.** The most important requirements of diffraction are:

a. The spacing between the layers of atoms must be roughly the same as the wavelength of radiation.
b. The scattering centre must be specially distributed in a highly regular way.

**Q. What are advantage and disadvantage of X-ray methods?**

**Ans.** Advantages of X-ray methods

1. X-ray methods are non-destructive in nature.

2. X-ray analysis can be applied to amorphous or crystalline samples in any physical state of sub-division.
3. There is no consideration of electrical and mechanical properties of samples.

Disadvantages of X-ray methods

1. The accuracy of method depends upon the surface preparation, reliability of standards, stability of the X-ray tube output and number of X-ray photons counted.
2. At one percent concentration level the line intensity and line to background ratio is sufficiently high.
3. Instrumental and sample variables affect the analysis. Three variables can, however, be reduced to less than 1% using standardized techniques and modern instruments.

## 4.14 Thermoanalytical Methods

**Q. What are thermometric or thermoanalytical methods of analysis?**

**Ans.** These are methods in which some property of system is measured as function of temperature.

**Q. What are the distinct types of thermometric or thermoanalytical methods of analysis?**

**Ans.** It involves techniques such as thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), differential thermal analysis (DTA) and thermometric titrations (also called enthalpy titrations).

**Q. Summarize the main properties of thermoanalytical methods?**

**Ans.** It can be summarized as follows:

| **Thermoanalytical methods** | | |
|---|---|---|
| Designation | Property measured | Apparatus |
| Thermogravimetric analysis (TGA) | Change in weight | Thermobalance |
| Derivative thermogravimetric analysis (DTG) | Rate of exchange of weight | Thermobalance |
| Differential thermal analysis (DTA) | Heat evolved or absorbed | DTA apparatus |
| Thermometric titrations (TT) | Change of temperature | Titration calorimeter |

**Q. Define thermogravimetric analysis (TGA)?**

**Ans.** This technique involves change in the weight of a system under examination as the temperature is increased at a predetermined rate and preferably at a linear rate. In simple words thermogravimetric analysis (TGA) is concerned with an analysis of sample weight change curve.

**Q. Define differential thermogravimetric analysis (DTG)?**

**Ans.** When thermogram of substance under consideration is being compared with its first derivative the method is known as differential thermogravimetric analysis (DTG).

**Q. Define derivative thermogravimetric analysis (DTG)?**

**Ans.** It is the technique in which the temperature difference between the sample and a thermally inert reference substance is continuously recorded as a function of furnace temperature or time.

**Q. Define thermometric titrations (TT)?**

**Ans.** The thermometric titrations utilize heats of reaction to obtain titration curves which are obtained by plotting changes in solution temperature against the volume of titrant.

**Q. Describe the basic principle of thermometric titrations?**

**Ans.** Thermometric titrations involve the measurement of the temperature change of a system as a function of time of volume or titrant. This technique consists in the detection and measurement of the change in temperature of solution as titrant is added to it, under nearly as adiabatic conditions as possible.

**Q. Why it is possible to follow the course of a reaction by observing the heat evolved or absorbed in thermometric titrations?**

**Ans.** Because practically all chemical reactions are accompanied by a heat effect.

**Q. What are the important requirements of a good recording thermobalance?**

**Ans.** These are accuracy, reproducibility, sensitivity, capacity, rugged construction, and insensitivity to ambient temperature changes.

**Q. What are important characteristics of a thermobalance?**

**Ans.** These include:

a. It should have adjustable range of weight change.

b. It should have high degree of electronic and mechanical stability.

c. It should be able to respond rapidly to changes in weight.

d. It should be relatively unaffected by vibrations.

e. It should be simple to operate and verstale, so it can used for varied applications.

**Q. Describe applications of thermoanalytical methods?**

**Ans.** The applications are:

a. Automatic analysis cab be performed in short period of time.
b. Determination of composition of complex mixtures.
c. Discovery of new methods of separation.
d. Evaluation of suitable standards.
e. Testing of sample purity.
f. Study of drying and ignition temperatures.
g. Heat of reaction can be measured.
h. Determination of moisture contents can be done.
i. Effect of radiation on polymeric and other substance can be studied.
j. Enthalpy change can be measured.

## 4.15. MOSSBAUER SPECTROSCOPY

**Q. What is mossbauer effect?**

**Ans.** It is the phenomenon of resonance fluorescence of gamma ray. It is comparable to resonance fluorescence in optical regions, but involves intra nuclear rather than electronic energy levels. An important characteristic of this radiation, under optimum conditions of measurement, is extreme sharpness of the lines.

**Q. Who discovered mossbauer effect?**

**Ans.** R.L.Mossbauer (1958).

**Q. What is Lamb Mossbauer factor?**

**Ans.** The recoilless of $\gamma$- rays emitted from a source imbedded in a solid lattice is called Lamb Mossbauer Facor (f) and is given by

$$F = \exp(-E/h\omega_E)$$

Where,

$\omega_E$ is the angular frequency of the oscillator and E is the free recoil energy.

**Q. Are all the nuclide which emit $\gamma$- rays are suitable for mossbauer study?**

**Ans.** No.

**Q. What are the important characteristics the nuclide should to be used for mossbauer study?**

**Ans.** The nuclide should posses following important characteristics:

a. The energy of $\gamma$-radiation should be in the range 10-200 keV.

b. The half life of the parent nuclide generating the $\gamma$-emitter nuclide should be an order of a year so that the same source with reasonably constant activity made available for a series of experiments.

c. The $\gamma$-emission half life of the excited source should be within the limits $10^{-6}$ s $>\Gamma>10^{-10}$s.

d. The conversion coefficient should be as low as possible so that most decays are via $\gamma$-emission.

e. The absorber nuclide should be present in high isotopic abundance. Samples enriched in the relevant isotopes are sometimes used in those cases where greater sensitivity is required.

**Q. How mossbauer nuclides form?**

**Ans.** The mossbauer nuclides are in excited state, which return to the ground state with very short half lives of a few microseconds or even less. They are correctly indicated as $^{57}Fe^*$, $^{119}Sn^*$ etc.

**Q. What are the applications of mossbauer spectroscopy?**

**Ans.** It has following application:

a. It is used for isomeric shift or chemical shift.

b. Coordination chemistry of iron cyanides can be studied.

c. It is used to determine quadruple splitting due to asymmetry.

d. Structure determination can be done.

e. Used for biochemical studies.

f. It is used for determination of curie point.

**Q. What is curie point?**

**Ans.** The transition temperature below which paramagnetic substance get converted into ferromagnetic because of large domains of spin aligning. in parallel orientation is called curie point.

**Q. In healthy human blood iron is ferrous not the ferric?**

**Ans.** Because it is in low spin state when oxygenated and in high spin when de-oxygenated.

# *Part Five*

# ENVIRONMENTAL CHEMISTRY

## 5.1. Basic Concepts

**Q. What is environmental chemistry?**

**Ans.** Environmental chemistry deals with the study of the various chemical phenomena taking place in the environment. In broader terms, it is the study of the chemical species existing in various segments of the environment, their sources, pathways, reactions and their consequences on the activities of human beings and other life forms. Thus, environmental chemistry may be considered as a multi-disciplinary study, involving physical and life sciences, meteorology, agriculture, public health, engineering etc.

**Q. What is the objective of environmental education?**

**Ans.** The objective of environmental education is to enlighten the public, particularly students, about the importance of protection and conservation of our environment and the need to restrain human activities which lead to indiscriminate release of pollutants into the environment.

**Q. Define environmental pollution.**

**Ans.** Environmental pollution may be defined in a number of ways.

Environmental pollution means destabilizing the balance of atmospheric composition.

or

It is an undesirable change in the environment due to its physical, chemical and biological changes, which is harmful for the human life and other species present on the earth.

or

It means removal of certain ingredients from air, soil or water and also the addition of extraneous substances into them.

It is defined as contamination of air, water or soil with undesirable material, heat or sound.

**Q. What is the most serious problem for humanity today?**

**Ans.** Environmental pollution is the most serious problem that humanity is facing today. Badly polluted air can cause illness and even death whereas polluted water kills marine life. Pollution of soil reduces the amount of land available for growing food. It also brings ugliness to our beautiful land. Our earth is a heaven and we should keep it as a sacred property that God donated to man for maintaining it.

**Q. How may the environmental pollution be reduced?**

**Ans.** If we follow the law of nature and adopt the suggested measures, environmental pollution may be reduced to a great extent.

**Q. What are the different kinds of environmental pollution?**

**Ans.** There are several kinds of environmental pollution. Major of them are as follows:

- *(i)* Water pollution
- *(ii)* Air pollution

*(iii)* Industrial pollution
*(iv)* Agricultural pollution
*(v)* Food pollution
*(vi)* Noise pollution
*(vii)* Radiation pollution (Radioactive pollution)
*(viii)* Thermal pollution
*(ix)* Health pollution
*(x)* Warfare pollution

**Q. What is pollutant?**

**Ans.** A pollutant is a substance which may alter environmental constituents or cause a pollution.

or

A substance present in nature, in greater than natural abundance due to human activity, which ultimately has a detrimental effect on the environment and therefore on living organisms and mankind.

or

The pollutant may also be defined as a constituent in the wrong amount at the wrong place or at the wrong time.

*Examples:* Lead, mercury, sulphur dioxide, carbon dioxide etc.

**Q. How does a contaminant differ from a pollutant?**

**Ans.** A contaminant is a material which does not occur in nature, but is introduced by human activity into the environment, affecting its composition.

A contaminant is classified as a pollutant when it exerts a detrimental effect.

**Q. Explain the terms receptor and sink.**

**Ans.** The medium which is affected by a pollutant is known as receptor. For example, man is the receptor of photochemical smog causing irritation of the eyes and respiratory tract.

A sink is the medium which retains and interacts with a long-lived pollutant. For example, a marble wall will act as a sink for atmospheric sulphuric acid and ultimately get damaged.

**Q. What do you mean by pathways of a pollutant?**

**Ans.** The mechanism by which the pollutant is distributed from its source into the environmental segments.

For example,

$$Pb(C_2H_5)_4 \text{ (in gasoline)} \xrightarrow{\text{Auto exhausts}} PbCl_2 + PbBr_2 \text{ (Air)}$$

$$\rightarrow PbCl_2 + PbBr_2 \text{ (Soil)} \longrightarrow \text{To food chain}$$

**Q. What do you mean by speciation?**

**Ans.** The different chemical forms or species of inorganic, organic or organometallic compounds present in the environment. It is important to identify the chemical species of a pollutant since some species are more toxic than others.

**Q. What are the different segments of environment?**

**Ans.** The environment consists of the following four segments.

(*i*) **Atmosphere.** The atmosphere is a protective blanket of gases surrounding the earth which sustains life on earth and saves it from the hostile environment of outer space.

(*ii*) **Hydrosphere.** The hydrosphere includes all types of water resources-oceans, seas, rivers, lakes, streams, reservoirs, polar ice caps and ground water.

(*iii*) **Lithosphere.** This is the outer mantle of the solid earth, consisting of minerals occuring in the earth crust and the soil.

(*iv*) **Biosphere.** This is the region of earth where life exists and includes a global girdle extending from about 10,000 m below sea level to 6,000m above sea level.

**Q. Briefly discuss the role of atmosphere in our environment.**

**Ans.** The atmosphere plays a vital role in maintaining the heat balance on the earth. It absorbs most of the cosmic rays from outer space and a major portion of the electromagnetic radiation from the sun. It transmits only near UV, visible, near 1R and radio waves while filtering out tissue-damaging UV radiation (below 300nm).

**Q. Write the average composition of the atmosphere.**

**Ans.** The composition of clear, dry air, near sea level is given in the following table.

| **Contents** | **Contents % by Volume** | **PPM.** |
|---|---|---|
| **(a) Major Components** | | |
| Nitrogen ($N_2$) | 78.09 | 780900 |
| Oxygen ($O_2$) | 20.94 | 209400 |
| Water Vapours ($H_2O$) | 0.1 – 5 | 1000 – 50000 |
| **(b) Minor Components** | | |
| Argon (Ar) | 0.934 | 9340 |
| Carbon dioxide ($CO_2$) | 0.032 | 3.20 |
| **(c) Trace Components** | | |
| Neon (Ne) | 0.00182 | 18.2 |
| Helium (He) | 0.000524 | 5.24 |
| Methane ($CH_4$) | 0.00018 | 1.8 |

| | | |
|---|---|---|
| Krypton (Kr) | 0.00011 | 1.1 |
| Nitrous oxide ($N_2O$) | 0.000025 | 0.25 |
| Hydrogen ($H_2$) | 0.00005 | 0.5 |
| Xenon (Xe) | 0.0000087 | 0.087 |
| Sulphur dioxide ($SO_2$) | 0.0000002 | 0.002 |
| Nitrogen dioxide ($NO_2$) | 0.0000001 | 0.001 |
| Ammonia ($NH_3$) | 0.00001 | 0.01 |
| Carbon monoxide (CO) | 0.000012 | 0.12 |
| Ozone ($O_3$) | 0.000002 | 0.02 |
| Iodine ($I_2$) | Traces | Traces |

**Q. What is dissolved oxygen (DO)?**

**Ans.** Oxygen dissolved in water has been an important vital species which gets consumed by oxidation of organic matter/reducing agent etc. It is regarded as an important water quality parameter. The optimum value for good water quality is 4-6mg/ $dm^3$ of DO, which ensures healthy aquatic life in a water body. Lower DO values indicate water pollution.

**Q. What is biochemical oxygen demand (BOD)?**

**Ans.** It is a water quality parameter for organic matter in water, which is empirical in nature. It is measured by the quantity of oxygen utilized by suitable aquatic microorganisms during a five day period. It is expressed as mg of oxygen per $dm^3$. BOD is not a pollutant but an indicator.

**Q. What is chemical oxygen demand (COD)?**

**Ans.** This is an index of the organic content of water and is an important water quality parameter. It may be defined as the amount of oxygen required by organic matter in a sample of water for its oxidation by a strong chemical oxidant, and is expressed as ppm of oxygen taken from a solution of $K_2Cr_2O_7$ in two hours.

COD is more scientific than the traditional empirical concept of BOD. This test is based on the chemical oxidation of material in water by $K_2Cr_2O_7$ in 50% $H_2SO_4$.

**Q. Define threshold limit value (TLV).**

**Ans.** Threshold limit value indicates the permissible level of a toxic pollutant in atmosphere to which a healthy industrial worker is exposed during an eight-hours day without any adverse effect.

**Q. What are the concentrations units of pollutants?**

**Ans.** Concentrations of pollutants have been usually expressed by fractions. A concentration of one part per million (1ppm) means one part pollutant per one million parts of the gas, liquid or solid mixture. More recently, gaseous pollutants and particulate matter in the atmosphere are expressed as $\mu g/m^3$.

**Q. What are particulates?**

**Ans.** Small solid particles and liquid droplets are collectively called particulates. Many different chemical substances can enter the atmosphere in particulate form, e.g. iron (as $Fe_2O_3$ or $Fe_3O_4$), magnesium (as MgO), aluminium (as $Al_2O_3$) etc.

## 5.2. Air Pollution

**Q. Define air pollution.**

**Ans.** Air pollution may be defined as the presence in the outdoor atmosphere of one or more contaminants in such quantities and of such duration as may be or may tend to be injurious to human, plant or animal life, or property.

Air pollution turns the clear and odourless air into a poisonous gas that harms health, kills plants and damages property.

**Q. What are the sources of air pollution?**

**Ans.** The sources of air pollution may be classified as:

*(i)* **Combustion.** It includes fuel burning, transportation and refuse-burning.

*(ii)* **Agriculture.** This includes field burning and crop spraying.

*(iii)* **Manufacturing Processes.** It includes chemical plants, metallurgical plants and waste recovery.

*(iv)* **Solvent-usage.** This includes spray painting, solvent extraction inks and solvent cleaning.

*(v)* **Nuclear.** This includes fuel fabrication, ore preparation, nuclear device testing and spent fuel processing.

**Q. What are the important air pollutants?**

**Ans.** The most common air pollutants are:

*(i)* Sulphur dioxide ($SO_2$)
*(ii)* Carbon monoxide (CO)
*(iii)* Carbon dioxide ($CO_2$)
*(iv)* Nitrogen Oxides ($NO_x$)
*(v)* Particulates
*(vi)* Hydrocarbons.
*(vii)* Photochemical smog.
*(viii)* Hydrogen sulphide etc.

**Q. What are the sources of CO emission. Discuss its effects.**

**Ans. Sources.**

*(i)* Incomplete combustion of fuels

(*ii*) automobile exhausts
(*iii*) Jet engine emissions
(*iv*) Blast furnaces, and
(*v*) Mines and tobacco making.

**Typical Effects.**

(*i*) It has toxic effects on animal and human beings. This is due to reversible combination of CO with haemoglobin in the blood, which decreases the oxygen carrying capacity of the blood.

(*ii*) CO also decreases the dissociation of oxyhaemoglobin.

(*iii*) It causes T.B. lungs cancer and respiratory diseases in human beings and animals.

**Q. Discuss the sources and typical effects of $SO_2$ as pollutant.**

**Ans. Sources.**

(*i*) Combustion of coal
(*ii*) Combustion of petroleum products
(*iii*) Burning of refuse
(*iv*) Petroleum industry and oil refining
(*v*) Power houses and metallurgical operations etc.

**Typical effects.**

(*i*) It is the most dangerous gas to human life. It affects lungs, heart and liver.

(*ii*) It absorbs moisture from air and changes into sulphuric acid which causes decolorization and physical deterioration of building materials.

(*iii*) It has corrosive action and affects the surface of steel, iron and zinc.

(*iv*) The high concentration of $SO_2$ produces leaf injury such as *necrosis* in plants and brownish colouration in the tips of pine needles.

**Q. Briefly discuss the sources and typical effects of oxides of nitrogen ($NO_x$).**

**Ans. Sources**

(*i*) Automobile exhausts
(*ii*) Coal fired and gas fired furnaces
(*iii*) Power stations
(*iv*) Explosive industries
(*v*) Fertilizer industries
(*vi*) Combustion of wood and refuse etc.

**Typical effects.**

(*i*) Oxides of nitrogen produce photochemical smog (*ii*) The manufacture and use of nitrogen fertilizers, increase the amount of $N_2O$ in atmosphere, which acts as a catalyst, converting ozone to oxygen.

(*iii*) The nitrogen oxides fade the textile dyes, damage the cotton and wool.

(*iv*) At the concentration of 15 to 50 ppm $NO_2$ has severe effects on lungs, liver, heart and kidney.

**Q. What are the sources and effects of particulate matters?**

**Ans.** The particulate matters are the solid and liquid aerosols suspended in the atmosphere. Their sources of emission are as follows:

(*i*) Volcano eruptions and the blowing of dust and soil by wind.
(*ii*) Asbestos particulates from construction and factories
(*iii*) Mining activities and power stations
(*iv*) Metallurgical industries, factory stacks
(*v*) Glass and cement industries
(*vi*) Foundries and incomplete combustion processes etc.

**Typical Effects.**

(*i*) The aerosols containing fluoro-carbons reduce the ozone layer by as much as 10%.

(*ii*) Jet aeroplanes are the important emitters of aerosols. These emit oxides of sulphur and nitrogen, which also reduce the ozone level.

(*iii*) The particulate matters have toxic effects on human being and animals. The toxic effects are of intrinsic toxicity due to chemical properties, interference with clearance mechanism in the respiratory tracts, toxicity due to absorbed toxic substances.

(*iv*) The dust particles can work as a carriers of micro-organisms and other infective agents and thereby spread diseases.

(*v*) They also cause *silicosis* and *asbestosis* from specific dust.

**Q. Discuss the sources and typical effects of lead (Pb) as a pollutant.**

**Ans. Sources.**

(*i*) Automobile emissions
(*ii*) Lead smelters
(*iii*) Burning of coal and oil
(*iv*) Lead arsenate pesticides
(*v*) Smoking, mining and plumbing.

**Effects**

(*i*) Absorption through gastrointestinal and respiratory tract and deposition in mucous membranes, cause liver and kidney damage

(*ii*) Mental retardation in children

(*iii*) Abnormalities in fertility and pregnancy.

**Q. Discuss the sources and typical effects of chromium (Cr) as a pollutant.**

**Ans. Sources.**

*(i)* Metallurgical and chemical industries

*(ii)* Processes using chromate compounds

*(iii)* Cement and asbestos units.

**Effects.**

*(i)* Toxic to body tissues, can cause irritation, dermatitis, ulceration of skin, perforation of nasal septum.

*(ii)* Carcinogenic action suspected.

**Q. What are the sources of cadmium (Cd)? Also discuss its effects.**

**Ans. Sources.**

*(i)* Cadmium producing industries, electroplating, welding.

*(ii)* By-product from refining of Pb, Zn and Cr.

*(iii)* Fertilizer industry and pesticide manufacture.

*(iv)* Cadmium-nickel batteries.

*(v)* Nuclear fission plants etc.

**Typical Effects**

*(i)* Inhalation of fumes and vapours causes kidney damage, brochitis, gastric and intestinal disorders, cancer, disorder of heart, liver and brain.

*(ii)* Chronic and acute poisoning may result.

*(iii)* Anaemia, hypertension, bone-marrow disorder.

**Q. Briefly discuss the sources of mercury (Hg) and mention its important effects.**

**Ans. Sources.**

*(i)* Mining and refining of mercury.

*(ii)* Organic compounds containing mercury (pesticides).

*(iii)* Laboratories using mercury.

**Effects**

*(i)* Inhalation of mercury vapours may cause toxic effects and protoplasmic poisoning.

*(ii)* Organic compounds containing mercury are highly toxic and may cause irreversible damage to nervous system and brain.

**Q. What is photochemical smog? How is it formed?**

**Ans.** When the atmosphere is loaded with large quantities of automobile exhausts during warm sunny days with gentle wind and low inversion, then the exhaust gases are trapped by the inversion layers with stagnant air masses and simultaneously exposed to intense sunlight. Then a number of photochemical reactions involving $NO_2$, hydrocarbons and other organic compounds and free radicals take place leading to the formation of peroxides and other photochemical oxidants. This gives rise to the phenomenon of photochemical smog.

**Q. What is Los Angeles Smog?**

**Ans.** Photochemical smog was observed in some parts of Los Angeles and Denver in USA and that is why it is sometimes referred to as "Los Angeles smog".

**Q. What is photochemical oxident?**

**Ans.** It is a substance which oxidizes materials not readily oxidized by gaseous oxygen.

**Q. How does photochemical smog differ from reducing smog?**

**Ans.** Photochemical smog is an oxidizing smog. While reducing smog forms due to the combination of smoke and fog.

**Q. What are the effects of photochemical smog?**

**Ans.** Photochemical smog is characterized by the formation of aerosols that reduce visibility, generation of brown hazy fumes that irritate the eyes and lungs and which cause extensive damage to vegetation and rubber goods.

**Q. How the formation of noxious photochemical pollutants in the atmosphere be controlled?**

**Ans.** For controlling the formation of noxious photochemical pollutants in the atmosphere, the emission of primary pollutants, viz. hydrocarbons and NOx should be controlled.

**Q. How ozone is formed in photochemical smog?**

**Ans.** A simplified scheme for ozone formation is:

$$N_2 + O_2 \longrightarrow 2NO \text{ (engine cylinder)}$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 \longrightarrow O_3$$

## 5.3. Water Pollution

**Q. What is water pollution?**

**Ans.** When the toxic substances like industrial wastes or effluents, chemicals, wastes of human society, raw sewage, garbage, low level radioactive substances go into water, it gets polluted. This type of pollution is known as water pollution.

Any human activity that impairs the use of water as a resource may be called water pollution.

**Q. Briefly discuss the importance of water.**

**Ans.** Like air, water is essential for plants, animals and human life. Water played an important role in the evolution of earth and in the life of our planet. It is a versatile solvent. We can survive for many days without food but not without water. Water erosion can turn fertile soil into a desert, and water can transform the desert into a flower garden.

**Q. What factors are responsible for water pollution?**

**Ans.** The important factors responsible for water pollution are:

*(i)* Exploding population
*(ii)* Increasing industrialisation
*(iii)* Urbanisation.

**Q. What are the polluting sources of water?**

**Ans.** The following are the main water pollutants:

*(i)* Organic sewage and industrial wastes.
*(ii)* Organic chemicals — detergents, herbicides, pesticides.
*(iii)* Inorganic chemicals, such as metals, metal compounds, salts and acids.
*(iv)* Infectious agents from hospitals, slaughter houses, tanneries and large cities.
*(v)* Plant nutrients.
*(vi)* Nitrates and phosphates.
*(vii)* Radioactive materials.

**Q. Write some physical characteristics of waste waters?**

**Ans.** Waste waters are characterized on the basis of following physical characteristics:

*(i)* Colour
*(ii)* Odour
*(iii)* Dissolved oxygen (DO).
*(iv)* Insoluble substances.
*(v)* Radioactive.

**Q. Write some chemical characteristics of the waste waters?**

**Ans.** *(i)* Chemical oxygen demand (COD)
*(ii)* Acidity or alkalinity
*(iii)* Hardness
*(iv)* Total dissolved solids.
*(v)* Chlorine demand.
*(vi)* Known organic and inorganic components such as $Cl^-$, $S^{2-}$, $SO_4^{2-}$, phenols; hydrocarbons etc.

**Q. What are the biochemical characteristics of waste water?**

**Ans.** Biochemical oxygen demand (BOD), presence of pathogenic bacteria etc; and toxicity to man, aquatic organisms, plants and other forms.

**Q. What is DO?**

**Ans.** DO represents the dissolved oxygen. The determination of DO is the basis for BOD

**Q. Why DO is determined?**

**Ans.** *(i)* To calculate BOD value

*(ii)* For maintaining aerobic conditions in the receiving waters.

*(iii)* For aerobic treatment of sewage and industrial waste water.

**Q. What is the significance of BOD?**

**Ans.** BOD is considered as the major characteristic used in stream pollution control. It gives very valuable information regarding the purification capacity of streams and serves as a guide-line for the Regulatory Authorities to check the quality of effluents discharged into such bodies.

**Q. Briefly discuss the effects of water pollution.**

**Ans.** *(i)* Nutrient rich sewerage causes depletion of dissolved oxygen and ultimately causes death of aquatic animals.

*(ii)* During sixties, the lakes in the Scandanavian countries became totally devoid of marine life due to pollution.

*(iii)* 60 percent of infant deaths are due to infection of parasitic diseases, most of them are water borne.

*(iv)* Vegetables grown from waste water have serious bacteriological contamination problems.

*(v)* Pollution of river water has cut its fish production by 5000 tons per years.

*(vi)* Water pollution causes live stock death and contaminates a large tract of cultivated land.

**Q. How preliminary treatment of waste water is done?**

**Ans.** The principal objective of preliminary treatment is the removal of gross solids, i.e; the large floating and suspended solid matter. Removal of gross solids is generally accomplished by passing waste water through different types of screens.

**Q. What is primary treatment of waste water?**

**Ans.** After the removal of gross solids, gritty materials and excessive quantities of oils and grease, the next step is to remove the remaining suspended solids as much as possible. The primary treatment involves the sedimentation process. The suspended matter can be removed efficiently and economically by this process.

**Q. What is secondary treatment of waste water?**

**Ans.** In secondary treatment, dissolved and colloidal organic matter present in waste waters is removed by biological processes involving bacteria and other micro-organism. These processes may be aerobic or anaerobic. The following sequential changes are obtained:

*(i)* Coagulation and flocculation of colloidal matter.

*(ii)* Oxidation of dissolved organic matter to $CO_2$, and

*(iii)* Degradation of nitrogenous organic matter to $NH_3$, which is then converted into nitrite and eventually to nitrate.

**Q. Briefly discuss the tertiary treatment of waste water.**

**Ans.** Tertiary treatment is the final treatment, meant, for "polishing" the effluents from the secondary treatment processes, to improve its quality further. The major objectives of tertiary treatment are:

*(i)* Removal of fine suspended solids.

*(ii)* Removal of bacteria.

*(iii)* Removal of dissolved inorganic solids.

*(iv)* Removal of final traces of organics, if it is felt necessary.

**Q. How the removal of fine suspended solids is achieved?**

**Ans.** Removal of finely divided suspended solids can be achieved with the help of micro-strainers and sand filters.

**Q. How bacteria are removed?**

**Ans.** Removal of bacteria, particularly of faecal origin, can be achieved by retaining the effluents from secondary biological treatment plants in maturation ponds for specified periods of time. The final effluent is chlorinated if necessary.

**Q. How the dissolved inorganic solids are removed?**

**Ans.** Removal of dissolved inorganic solids is a major problem with waste waters from industries such as fertilizers, textile processing, tannery and electroplating. The following treatment methods can be applied:

*(i)* Evaporation

*(ii)* Ion-exchange

*(iii)* Adsorption

*(iv)* Electrodialysis

*(v)* Reverse osmosis

**Q. What is Electrodialysis?**

**Ans.** This is a process in which colloidal or dissolved species are exchanged between two liquids through selective ion-exchange membrances. An electromotive force brings about the separation of the species according to their charge. The semipermieable membranes allow the passage of certain charged species while rejecting the passage of oppositely charged species.

**Q. Define reverse osmosis. Write its applications.**

**Ans.** This is essentially a process in which a semipermeable membrane allows water molecules through and retains the ions. Applications of reverse osmosis include recovery of valuable components from effluents, recovery of water for reuse, pollution control, recycling of waste waters and spent chemicals etc.

## 5.4. Noise Pollution

**Q. What is noise?**

**Ans.** The term "noise" may be defined as an unwanted sound at a wrong time and a wrong place. Although noise is undesirable, it could he meaningful or meaningless.

**Q. Explain the difference between meaningful and meaningless noise.**

**Ans.** A meaningful noise is generally meant for inviting attention or expecting a consequent response such as the cry of a baby. On the contrary, a meaningless noise is disturbing and annoying.

Whether a given sound is wanted or unwanted may depend upon the person involved, the loudness, the rhythm, and the length of time for which one is exposed to it.

**Q. Why noise is considered as a pollutant?**

**Ans.** Noise is a very troublesome pollutant in the urban areas. It is a by-product of human activity. It is found to cause some kind of physical, physiological or psychological harm or stress to human beings. Due to these reasons, it is also considered as a pollutant.

**Q. Write some physical properties of sound.**

**Ans.** Sound has several physical properties among which "Frequency" and "Intensity" are most relevant. Sound frequency is the rate at which compression waves arrive at or pass a fixed point. Sound intensity is the acoustical power (i.e., the energy delivered by sound) per unit area.

**Q. Explain the difference between "Pitch" and "Loudness".**

**Ans.** Pitch is the human perception of sound frequency (and also intensity to some extent).

Loudness is the human perception of the sound intensity (and also frequency to some extent).

**Q. What is Hertz?**

**Ans.** Hertz (Hz) or cycles per second is a measure of sound frequency. Human beings can hear only sounds ranging from 20Hz to 20,000 Hz.

**Q. What is the range of frequencies of human speech?**

**Ans.** The range of frequencies of human speech is 200 to 3000 Hz, which is best heard by humans.

**Q.** **What is the difference between "ultrasound" and "infrasound".**

**Ans.** Sound which has high frequency (above 20,000 Hz) is called ultrasound and that which is too low in frequency (below 20 Hz) is called infrasound.

**Q.** **What is "decibel" (dB)?**

**Ans.** The loudness is expressed in terms of a unit called decibel (dB). In terms of sound, a 'decibel' (dB) is ten times the logarithm of the ratio of two sound intensities, one being the intensity of any sound of interest and the other being a reference sound.

**Q.** **What is the dB range of normal conversation?**

**Ans.** A normal conversation is done at 60 dB sound levels.

**Q.** **Write the dB scale for some familiar sound sources.**

**Ans.**

| Sound Source | Decibel, dB |
|---|---|
| Space rocket | 170 |
| Jet plane at takeoff | 150 |
| Threshold of pain | 140 |
| Motor Cycle | 117 |
| Alarm clock | 80 |
| Living room | 45 |
| Library | 35 |
| Threshold of hearing | 0 |

**Q.** **Write some psychological and physical effects at different Decibel levels.**

**Ans.**

| Decibel, dB | Effects |
|---|---|
| 135 | Painful |
| 110 | Discomfort |
| 88 | Hearing impairment on prolonged exposure |
| 80 | Annoying |
| 65 | Intrusive |

**Q.** **Briefly discuss the effects of noise pollution.**

**Ans.** *(i)* It affects sense of hearing.

*(ii)* It causes anxiety, depression, blood pressure and nervousness.

*(iii)* Wildlife also suffers from noise pollution.

*(iv)* It can affect sight and impair the ability to judge distance.

*(v)* It interferes with proper rest and sleep. It lessens efficiency and increases rate of accidents.

**Q. How noise pollution be controlled?**

**Ans.** The following four approaches are available for noise control:

*(i)* Modifying some of the present practices and procedures in order to minimise the noise, e.g., reducing automobile traffic, outlaying sirens, discouraging stereos without headsets etc.

*(ii)* Shielding the sources of noise generation, e.g; use of sound absorbing motor mountings, better installation, better design, use of motor enclosures etc.

*(iii)* Shielding the noise receiver, e.g; using earplug, control booths, etc.

*(iv)* Shifting noisy sources and things away from people, e.g; isolating airports, industrial complexes etc.

**Q. What are Mufflers or Silencers?**

**Ans.** A muffler or a silencer is a pipe or duct treated or shaped for reducing sound transmission while at the same time allowing the free flow of a gas. Silencers are classified as:

*(i)* **Dissipative silencers.** They are also known as absorptive silencers. They work on the principle of absorbing noise. They make use of acoustical absorbant linings.

*(ii)* **Reactive silencers.** They work on the principle of reflection, and thus containing sound within them.

## 5.5. Major Effects of Environmental Pollution

**Q. What are the major effects of environmental pollution?**

**Ans.** Following are the major effects of environmental pollution.

*(i)* Depletion of ozone layer.

*(ii)* Acid rain.

*(iii)* Green House effect (Global warming).

**Q. What do you know about ozone layer?**

**Ans.** The ozone layer is a naturally occurring zone found in the stratosphere, situated between 20 to 40 Km above the surface of earth. At an altitude of about 30 Km its concentration is about 10 ppm. Ozone is a naturally component of the atmosphere.

**Q. What is the function of ozone layer?**

**Ans.** Ozone layer acts as a shield against ultraviolet rays which are being emitted continuously by the Sun. Ultraviolet rays are the radiations of wavelengths less than those of visible light. If these rays reach on the surface of earth, they will end all life on it. Ozone layer functions as a natural umbrella that protects us from the harmful effects of UV radiations. Ozone absorbs the UV radiations in the region 220-330 nm.

**Q. How ozone is formed in stratosphere?**

**Ans.** Ozone is formed in the stratosphere by photochemical reaction:

$$O_2 + h\nu\ (242\ \text{nm}) \longrightarrow O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

Where M is a third body such as $N_2$ or $O_2$ which absorbs the excess energy liberated by the above reaction, and thereby the ozone molecule is stabilized. Thus, ozone layer is constantly formed in the stratosphere.

**Q. How does the depletion of ozone layer take place?**

**Ans.** Ozone layer is destroyed by chlorine, released due to volcanic activity and also by reaction with *(a)* Nitric oxide *(b)* Atomic oxygen and *(c)* Reactive hydroxyl radical which are also present in the atmosphere, by the following reactions:

*(i)* $O_3 + NO \longrightarrow NO_2 + O_2$

*(ii)* $O_3 + O \longrightarrow O_2 + O_2$

*(iii)* $O_3 + HO^\circ \longrightarrow HO_2 + HOO^\circ$

$HOO^\circ + O \longrightarrow HO^\circ + O_2$

The depletion is also caused by certain highly stable synthetic chemicals which are the product of petrochemical industries. These include chlorofluorocarbons (CFC's), which are used as coolants in refrigerators, air-conditioners, propellants in aerosol sprays and in plastic foams. The CFC molecules decompose to release chlorine in the ozone layer (by photodissociation), and each atom of chlorine, thus liberated, is capable of attacking several ozone molecules.

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

**Q. What do you know about "ozone hole"?**

**Ans.** It is not a hole-only a thinning of the ozone layer. It was detected over the Antarctica (South Pole) during September to November in 1985.

**Q. What are the effects of ozone layer depletion?**

**Ans.***(i)* Increase risk of melanoma.

*(ii)* Skin cancer

*(iii)* Incidents of optic ailments

*(iv)* Suppression of human immune system

*(v)* Major field crops are adversely affected

**Q. Briefly discuss some protective measures for ozone layer.**

**Ans.***(i)* Use of ceiling fans instead of air conditioners.

*(ii)* CFC's are used in refrigeration with the trade name Freon. It should not be released in the atmosphere.

*(iii)* Replacement of CFC,s with HFC's and methyl cylohexane (MCH).

**Q. What is green-house effect?**

**Ans.** The earth is heated by sunlight and some of the heat that is absorbed by the earth is radiated back into space. However, some of the gases in the lower atmosphere, acting like glass in the greenhouse, allow the solar radiations (in the range 300 to 2500nm), but do not allow the earth to re-radiate the heat into space. In other words, these gases in the atmosphere are transparent to sun light coming in but they strongly absorb the infra-red radiations, which the earth sends back as heat. A part of the heat so trapped in these atmospheric gases is re-emitted to the earth's surface. The net result is the heating of the earth's surface by this phenomenon called "Greenhouse effect".

**Q. What is global warming?**

**Ans.** Scientists have discovered that the average temperature of the earth's atmosphere has increased by 0.5°C (0.9°F) since accurate records began. This may seem to be a very small increase in absolute terms but the rate of temperature change — which is now faster than at any time in the past — is significant. This trend is called global warming.

**Q. What are the latest predictions about global warming?**

**Ans.** The latest predictions for global warming given at European meetings of climatologists and policy makers say that the temperature of the earth could increase by 1.5 to 4.5°C by the year 2100.

**Q. What gases are responsible for greenhouse effect?**

**Ans.** Emission of twenty gases may possibly cause green house effect. The major gases are:

- *(i)* $CO_2$
- *(ii)* Water Vapours
- *(iii)* $CH_4$
- *(iv)* CFCs
- *(v)* Nitrous Oxide
- *(vi)* Ozone

**Q. Briefly discuss the significance of greenhouse gases.**

**Ans.** The greenhouse gases (particularly $CO_2$ and water vapours) are responsible for keeping our planet warm and thus sustaining life on the earth. If the greenhouse gases are very less or totally absent then the average temperature on the earth would have been at sub-zero levels. But however, if the concentrations of greenhouse gases are larger, they may trap too much heat, which may threaten the very existence of life on the earth.

**Q. What are the major sources of greenhouse gases?**

**Ans.** The major sources of greenhouse gases are:

- *(i)* Burning fossil fuels
- *(ii)* Furnaces
- *(iii)* Motor engines

*(iv)* Automobile exhaust

*(v)* Coal combustion

*(vi)* Agriculture fertilizers

*(vii)* Rotten plants

*(viii)* Garbage

*(ix)* By various hydrocarbons and nitrous oxide.

**Q. Briefly discuss the future impacts of global warming.**

**Ans.** It is thought that the impact of global warming on the planet would be unevenly distributed. The southern hemisphere, with its extensive oceans, would suffer less increase in temperature, as the seas would be able to absorb more heat than the land masses of northern hemisphere. The Arctic region may become, on average, 8 °C warmer than at present by 2100. As a result some of the polar ice caps would melt, causing a rise in sea level, of 20-30 cm by the middle of 21st century with predictions of a 60-100 cm rise by 2100. This would threaten very low lying areas such as Maldives, New York, London, Leningrad Rotterdam etc.

**Q. Write some possible measures to minimize greenhouse effect.**

**Ans.***(i)* Reduction in the use of fossil fuels

*(ii)* Encouraging the use of alternative sources of energy, e.g., solar, geothermal, wind, bio-gas etc.

*(iii)* Conservation of forests

*(iv)* Reduction in the use of automobiles.

*(v)* Ban on CFC's and nuclear explosions.

*(vi)* Effective check on the growth of population.

*(vii)* Imparting of non-formal and formal environmental reduction.

**Q. What is acid rain?**

**Ans.** When sulphur dioxide and various oxides of nitrogen are released into air, they react with moisture, sunlight and oxygen. As a result of these reactions, $H_2SO_4$, and $HNO_3$ are produced in the air and mixing with rain, these acids fall on earth. This rain is called acid precipitation or acid rain.

**Q. What is the pH of rain (natural)?**

**Ans.** Rain tends to be naturally acidic with pH of 5.6 to 5.7 due to the reaction of atmospheric $CO_2$ with $H_2O$ to produce $H_2CO_3$. This small amount of acidity is sufficient to dissolve minerals in earth's crust and make them available to plant and animal life, yet not acidic enough to cause any damage.

**Q. What are the different species present is the acid rain?**

**Ans.** Analysis of acid rain samples showed the following species.

**Cations:** $H^+$, $NH_4^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$

**Anions:** $SO_4^{2-}$, $NO_3^-$, $Cl^-$

**Q. Briefly discuss the effects of acid rains.**

**Ans.** *(i)* Kill flora and fauna.

*(ii)* Destroy Buildings (e.g. Taj Mahal)

*(iii)* Pollute river, Lakes and Ponds.

*(iv)* Kill fish and other animals.

*(v)* Increase acidity of soil.

*(vi)* Branches of tree become bare as leaves fall off.

**Q. Write some protective measures for acid rain.**

**Ans.** *(i)* Creating awareness of the source of emission of $SO_2$ and NO.

*(ii)* Conservation of energy.

*(iii)* Reducing of motor vehicles.

*(iv)* Introducing the effective transport system.

# *Part Six*

# APPLIED/INDUSTRIAL CHEMISTRY

## 6.1. Water Treatment

**Q. Briefly discuss the significance of water in daily life.**

**Ans.** Water is most abundant and most useful natural compound. It is used for industrial and municipal purposes. It is essential for all living beings. The largest water requirement is for municipal use but the standard of purity required for this purpose is quite different from that demanded for industrial and commercial uses. In industry more than half the water is used in chemical plants for the purpose of cooling. A large volume of water is also used for the purpose of dilution and making solutions.

The availability of water, both in quantity and quality, is one of the prime factors in deciding the growth of towns and cities as well as industries.

**Q. What are the sources of water?**

**Ans.** In nature water occurs abundantly as:

*(i)* Water vapours in the atmosphere.

*(ii)* As liquid water in land waters and the ocean.

*(iii)* As ice in polar regions, and

*(iv)* As water of hydration in many rocks and minerals in the earth crust.

**Q. Write some characteristic properties of water.**

**Ans.** Water freezes at O°C and boils at 100°C at NTP. This is in sharp contrast to the melting and boiling points of its higher analogues, $H_2S$, $H_2Se$ etc. Moreover, the latter are bad smelling gases at room temperature. Water also has higher surface tension and dielectric constant. Liquid water shows a maximum density at 4°C, unlike all other substances. The specific heat as well as latent heat of fusion and evaporation of water are all abnormally high. All these facts are explained by attributing to water molecules the tendency to associate, giving rise to polymer of the type $(H_2O)n$ as a result of hydrogen bonding.

Pure water is virtually a non-conductor of electricity. It also takes part in a variety of chemical reactions.

**Q. What are the important factors which decide the location of a chemical industry?**

**Ans.** The most important factors deciding the location of a chemical industry are:

*(i)* Raw materials

*(ii)* Power

*(iii)* Water

*(iv)* Transport

But as regards water, every industry has its own special requirements and sometimes that which is suitable for one is fatal to another.

**Q. Write some principle requisites of water for important industries.**

**Ans. Boiler feed water** — should be as soft as possible and should not contain much nitrate or organic matter so as to avoid incrustations or corrosions of the boiler plates.

**Water for paper mills** — the presence of iron is injurious and any excess of lime and magnesia decomposes the resin soaps.

**Water for sugar factories** — if water rich in sulphates and alkaline carbonates and especially in nitrates is used, crystallisation becomes more difficult, molasses are more abundantly obtained and the sugar becomes deliquescent on exposure. Water rich in microorganisms partially decomposes the sugar.

**Water for dyeing** — should be clear, free from iron and should possess little hardness.

**Water for cooking** — should contain little hardness, otherwise the vegetables do not cook easily.

**Q. What are the sources of impurities in water?**

**Ans.** The sources of impurities are the followings:

*(i)* Water takes up impurities from the ground, or soil with which it comes into contact.

*(ii)* Water becomes impure when it comes in contact with the sewage or industrial wastes.

*(iii)* Organic impurities in water are generally introduced by the decomposition of plants and animals remains.

*(iv)* Certain micro-organisms and bacteria are also responsible for certain organic impurities.

**Q. What is the nature of impurities in water?**

**Ans.** The common impurities present in water are:

*(i)* **Dissolved gases:** Like $O_2$, $CO_2$, $H_2S$ etc.

*(ii)* **Suspended matter:** Insoluble minerals such as clay, sand etc.

*(iii)* **Microscopic matter:** Bacteria, algae, fungi etc.

*(iv)* **Dissolved mineral salt:** Dissolved salts are mainly the carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron, sodium and potassium.

**Q. What is meant by hard and soft water?**

**Ans.** Water is classified as hard or soft, depending upon its behaviour towards soap solution.

Water that easily forms a lather of films and froths when agitated with a soap solution is known as soft water.

Water that reacts with soap solution to form a white scum only without producing a lather easily, is said to be hard water.

**Q. What is the cause of hardness of water?**

**Ans.** The hardness of water is due to the presence of dissolved salts of metals (except the salts of alkali metals), notably those of calcium, magnesium and iron, in water.

**Q. How hard water is classified?**

**Ans.** For convenience, hard water is classified as temporary and permanent.

**Temporary hardness** is due to the presence of soluble bicarbonates of calcium, magnesium and iron in water.

**Permanent hardness** is caused by the presence of chlorides and sulphates of calcium and magnesium in water.

**Q. How temporary hardness is removed?**

**Ans.** Temporary hardness can be removed by:

*(i)* Boiling the water

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

*(ii)* Adding slaked lime which precipitates the insoluble carbonates.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

**Q. How permanent hardness is removed?**

**Ans.** Permanent hard water is softened by the addition of $Na_2CO_3$ to water, when insoluble $CaCO_3$ and $MgCO_3$ precipitate.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 + NaCl$$

**Q. What is water conditioning or softening?**

**Ans.** Water conditioning is the process by which hard water, both temporary and permanent, is made soft (by total reduction or reducing the proportion of chemicals causing hardness) to be suitable for use as boiler feed water.

**Q. What is the objective of water softening?**

**Ans.** The main objective of water softening is to get maximum out put of steam and to protect the life of boiler bodies, tubes and pipes by prevention of scale formation and corrosion.

**Q. Briefly discuss various water conditioning processes?**

**Ans.** Modern methods to soften hard water are the following.

*(i)* **Soda-lime process:** This procedure removes both permanent and temporary hardness. Hard water is treated with slaked lime and soda ash when the calcium and magnesium are precipitated as $CaCO_3$ and $Mg(OH)_2$.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + MgCO_3 + 2H_2O$$

Since $MgCO_3$ is fairly soluble, it reacts with excess of lime, precipitating $Mg(OH)_2$.

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3$$

For non-carbonate hardness, the chemical reactions are:

$$MgCl_2 + Na_2CO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3 + NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

*(ii)* **Phosphate Conditioning.** Various phosphates are added to boiler water to precipitate the calcium ions.

$$3CaSO_4 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3Na_2SO_4$$

Sodium hexa-meta phosphate (Calgon) is also used for water softening.

*(iii)* **The base exchange process.** This is the modern and most effective method of removing both temporary and permanent hardness. The base exchange material permutit may be formulated as $Na_2Ze$ where Ze is the zeolite radical $(Al_2H_4Si_3O_{12})$. In this process the hard water is allowed to percolate through a bed of ground permutit. The calcium and magnesium salts react with permutit forming insoluble calcium and magnesium aluminium silicates which are retained in the filter bed.

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe\downarrow + 2NaHCO_3$$

$$Na_2Ze + MgSO_4 \longrightarrow MgZe\downarrow + Na_2SO_4$$

**Q. Briefly discuss the effects of problems/troubles associated with boiler using hard water.**

**Ans.** Water for raising steam in boilers must be soft and must not contain too much dissolved or suspended matter, so as to avoid the following troubles.

*(i)* **Scale formation.** It is a deposit of mainly $CaCO_3$ which is formed on the walls of the boiler. The formation of this hard heat insulating crust causes a much greater consumption of the fuel and also a rapid deterioration of the boiler due to overheating.

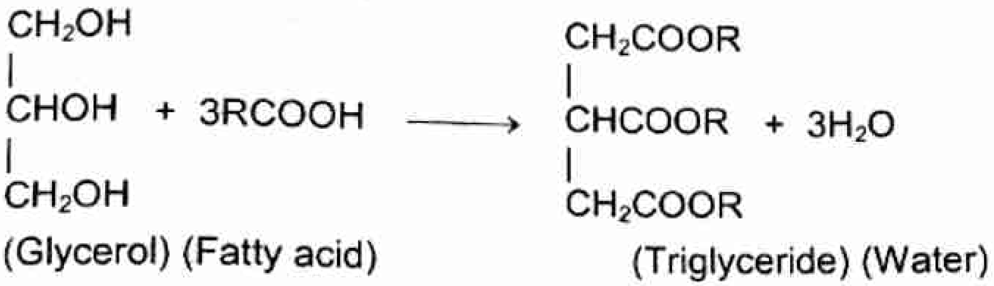
*(ii)* **Corrosion.** Continuous deposition of scales on the walls of the boiler causes corrosion, that is the material of the body is corroded and damaged. The boiler body thus gets weaker and may burst.

*(iii)* **Foaming.** Too much of dissolved matter in boiler water causes foaming and frothing. This prevents the formation and escape of steam.

## 6.2. Oils, Fats and Waxes

**Q. What is the chemical nature of oils and fats?**

**Ans.** Fats and oils are esters of fatty acids and glycerol. Three molecules of fatty acid are essential for esterification with a molecule of glycerol to form a triglyceride.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH \longrightarrow \begin{array}{l} CH_2COOR \\ | \\ CHCOOR \\ | \\ CH_2COOR \end{array} + 3H_2O$$

(Glycerol) (Fatty acid) (Triglyceride) (Water)

**Q. How an ester is formed?**

**Ans.** An ester is formed by the combination of an alcohol and an acid, with the elimination of water.

$$RCOOH + ROH \longrightarrow RCOOR + H_2O$$

**Q. What is the difference between oils and fats?**

**Ans.** Both fats and oils are triglycerides. The main difference is the relatively high content of saturated fatty acids in the fats, which are solid at room temperature. In contrast to this, oils contain more unsaturated fatty acids, and are liquid at room temperature.

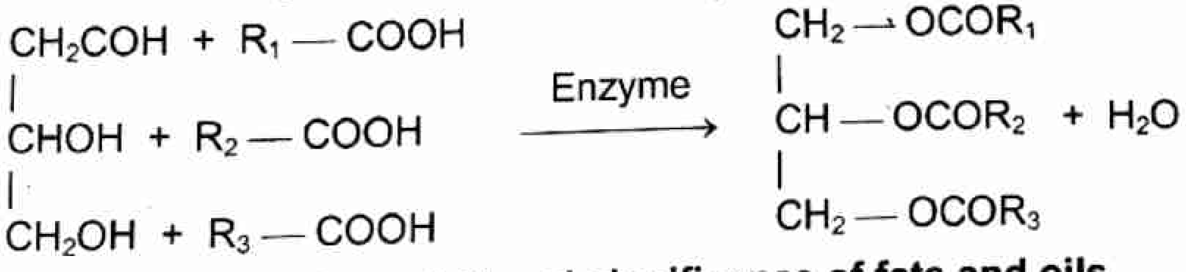
**Q. What are simple and mixed triglycerides?**

**Ans.** Fats and oils may be classified as simple and mixed triglycerides. Those which are made up of three similar molecules of fatty acids are called simple glycerides. For example, tristearin and tripalmitin.

In most naturally occurring oils and fats, three different fatty acids are found in the same molecule. These are called mixed triglycerides. For example, palmityl-distearin and caproyl-lauryl-olein.

**Q. Briefly discuss the synthesis of oils and fats.**

**Ans.** Synthesis of oils and fats takes place in oil seeds such as cotton seeds, groundnuts, caster seeds etc. or in fruits such as coconut, olive, almonds and in animals such as cow, goats, human etc. under the effect of enzyme.



$$\begin{array}{l} CH_2COH + R_1-COOH \\ | \\ CHOH + R_2-COOH \\ | \\ CH_2OH + R_3-COOH \end{array} \xrightarrow{\text{Enzyme}} \begin{array}{l} CH_2 \rightarrow OCOR_1 \\ | \\ CH-OCOR_2 \\ | \\ CH_2-OCOR_3 \end{array} + H_2O$$

**Q. Briefly discuss the nutritional significance of fats and oils.**

**Ans.** Fats and oils are the most concentrated source of energy. They provide more energy than both carbohydrates and proteins. In addition to their function as source of energy, fats and oils are important constituents of protoplasm and body tissues. They serve as an insulating materials in the subcutaneous tissues and around certain organs. Some fats are also vitamin carriers especially vitamin A and D.

**Q. Briefly discuss the various kinds of oils.**

**Ans.** There are three kinds of oils:

*(i)* **Fatty oils:** These are glycerides of monobasic organic acids, called fatty acids. These acids may contain both saturated and unsaturated residual parts.

*(ii)* **Essential oils:** These are volatile oils, with pleasant odour and are obtained from various plants and flowers by steam distillation. They contain unsaturated alcohols, unsaturated aldehydes and esters etc.

*(iii)* **Mineral oils:** These are saturated hydrocarbons or paraffins containing the number of C atoms ranging from $C_5$ to $C_{30}$. They are obtained from crude petroleum by distillation.

**Q. Classify the oils on the basis of proportion of unsaturation.**

**Ans.** On the basis of unsaturation, the oils are generally classified as:

*(i)* **Drying oils:** These contain a high proportion of unsaturated acids, e.g., linseed oil, tung oil etc.

*(ii)* **Semi-drying oils:** These contain intermediate proportion of unsaturated acids, e.g; maize oils, cotton seed oil etc.

*(iii)* **Non-drying oils:** These contain least proportions of unsaturated acid, e.g. almond oil, palm oil, olive oil etc.

**Q. Write names, formulae and sources of common fatty acids.**

**Ans.**

| Fatty acid | Formula | Source |
|---|---|---|
| Butyric Acid | $CH_3(CH_2)_2$ COOH | Butter |
| Caproic Acid | $CH_3(CH_2)_4$ COOH | Butter |
| Lauric Acid | $CH_3(CH_2)_{10}$ COOH | Butter, coconut and palm oil. |
| Myristic Acid | $CH_3(CH_2)_{12}$ COOH | Animal and plant fats |
| Palmitic Acid | $CH_3(CH_2)_{14}$ COOH | Animal and plant fats |
| Stearic Acid | $CH_3(CH_2)_{16}$ COOH | Animal fat |
| Caproleic Acid | $C_9H_{17}$ COOH | Milk fat |
| Myristoleic Acid | $C_{13}H_{25}$ COOH | Animal fat |
| Oleic Acid | $C_{17}H_{33}$ COOH | Plants and animals |
| Linoleic Acid | $C_{17}H_{31}$ COOH | Linseed and other |
| Linolenic Acid | $C_{17}H_{29}$ COOH | Oil seeds. |

**Q. Write three important physical constants which are used to characterise oils and fats.**

**Ans.**
- *(i)* Melting point
- *(ii)* Specific gravity
- *(iii)* Refractive index.

**Q. What are chemical constants of oils and fats?**

**Ans.** The important chemical constants of fats and oils used to test their quality and industrial value are:

- *(i)* Acid value
- *(ii)* Saponification value
- *(iii)* Iodine value
- *(iv)* Reichert — Meissel and Polenske values

**Q. Define iodine value. Give its significance.**

**Ans.** Iodine value is the number of centigrams of iodine absorbed by 1 g of fat. It measures the degree of unsaturation of the constituent fatty acids in an oil and fat.

$$—CH=CH— + I_2 \longrightarrow —CHI—CHI—$$

**Q. Define saponification. What does it indicate?**

**Ans.** Saponification value indicates the mean molecular weight of a fat or oil. It is the number of mg of KOH required to saponify the fatty acids in 1 g.

**Q. Briefly discuss the significance of acid value.**

**Ans.** This value is sometimes also called as free fatty acid value. It is defined as the number of mg of KOH required to neutralize the free fatty acids present in 1 g of fat/oil.

During storage, hydrolysis of fat may occur with the release of fatty acids. The amount of free acids expressed as acid value indicates the extent of hydrolysis which is related to the age and quality of fat. It roughly indicates the index of freshness.

**Q. Define Reichert-Meissel and Polenske values.**

**Ans.** Reichert-Meissel (R.M) value is defined as the number of ml of 0.1 N NaOH required to neutralize the volatile soluble fatty acids distilled from 5 g of fat.

Th Polenske value is the number of ml of 0.1N NaOH required to neutralize the volatile insoluble fatty acids distilled from 5 g of fat.

**Q. What is meant by hydrogenation of oils.**

**Ans.** Hydrogenation is the process of converting an oil into a fat. Oils are unsaturated, so by breaking the double bond and adding the hydrogen in the presence of particular catalyst, they can be converted into fat.

**Q. What is the importance of hydrogenation.**

**Ans.** *(i)* To improve the taste of bad odour oils e.g. linseed, cotton seed etc.

(ii) To obtain margarine or artificial butter from animal oils.

(iii) To obtain good hard soaps from cotton seed oil and whale oil etc.

**Q. What are the disadvantages of hydrogenation?**

**Ans.** Due to hydrogenation, the fatty acids become saturated and their boiling points are increased. Due to increased boiling points, the resulting cholesterol esters are very solid and hard which deposit in the arteries causing high blood pressure and heart diseases. Hence vegetable oils are nutritionally and medically better than Vanaspati Ghee.

**Q. What is the difference between slip point and soften point?**

**Ans.** The temperature at which a fat begins to travel on metallic surface is known as slipping or slip point. While the temperature at which a fat expands before melting is known as softening point.

**Q. Explain smoke, flash and fire point.**

**Ans.** The smoke point is the temperature at which a fat or oil gives off a thin bluish smoke. The temperature at which a mixture of fat or oil vapours and air ignite is known as flash point. The fire point is the temperature at which a fat or oil will sustain continue combustion.

**Q. What are waxes?**

**Ans.** Waxes are esters of fatty acids and contain monohydric alcohols of higher molecular weight. Of the fatty acids present in the oils and fats, usually palmitic, stearic and cerotic are present in waxes.

**Q. How do waxes differ from oils and fats?**

**Ans.** Waxes differ from oils and fats in the alcohol which forms the ester. In all the oils and fats, the alcohol is the same, i.e., glycerol (trihydric). But the ester forming alcohol in different types of waxes may differ.

**Q. Write some alcohols present in the waxes.**

**Ans.** The alcohols present in waxes are cetyl alcohol, octodecyl alcohol, ceryl alcohol, lanolin alcohol, cholesterol phytosterol etc.

**Q. What are different types of waxes?**

**Ans.** Broadly speaking waxes are classified into two classes.

**1. Solid waxes:**

(i) Spermaceti
(ii) Bees wax.
(iii) Chinese wax
(iv) Wool wax

**2. Liquid Waxes:**

Obtained from bladder and head cavity of sperm whale, e.g., Jojoba oil.

## 6.3. Fertilizers (or Manures)

**Q. What are fertilizers or manures?**

**Ans.** Fertilizers or manures are the substances that are added to the soil to increase its fertility and to provide the elements necessary for plant growth.

**Q. Write the names of different elements required by the plants for proper growth.**

**Ans.** **Major elements:** Nitrogen, phosphorus and potassium

**Trace elements:** Mn, Mg, I, Co, Zn

**Minor elements:** Ca, Na, S

**Q. Why fertilizers are necessary for proper growth?**

**Ans.** Fertilizers are necessary because:

*(i)* They help to maintain the pH of the soil in the vicinity of 7 to 8.

*(ii)* They stimulate and act as substrate in the process of metabolism.

*(iii)* They give an additional supply of tonic and good food so the plant become healthy and produce a better yield.

**Q. How would you classify fertilizers?**

**Ans.** Fertilizers may be classified into two classes, i.e., farm manure or natural fertilizers and synthetic or chemical fertilizers.

**Q. How do natural fertilizers differ from chemical fertilizers?**

**Ans.** *(i)* The composition of the natural fertilizers is not precisely known while the composition of chemical fertilizers is exactly known.

*(ii)* Excess of natural fertilizers may not be harmful for plants, while the excess of synthetic fertilizers is harmful for the plants.

*(iii)* Natural fertilizers contain micro-organisms which play very important role in uptake of fertilizer elements. While the synthetic fertilizers do not contain micro-organism but rather may be harmful for some micro-organisms.

**Q. What are stimulants?**

**Ans.** Stimulants are the substances which make the availability of fertilizers to the plants easily.

**Q. What are mixed fertilizers?**

**Ans.** The fertilizers containing N, P and K, particularly N and P are known as mixed fertilizers. They give better results in terms of maintenance and growth of plants and higher yield of produce, e.g. Nitrophos.

**Q. How nitrogen is fixed naturally.**

**Ans.** During electric discharge in the atmosphere, nitrogen is converted into nitric oxide, which is then oxidized by the excess of oxygen into nitrogen dioxide. This reacts with rain water forming nitric acid which is washed down by rain to the soil where it is converted into nitrates by bases present in the soil.

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$$

**Q. Briefly discuss the importance of nitrogenous fertilizers.**

**Ans.** Nitrogenous fertilizers containing nitrogenous compounds are used in the synthesis of plant enzymes and harmones which act as organic catalysts for carrying out the metabolic biochemical processes. Moreover, nitrogen is a constituent element of proteins and amino acids which are the chief agricultural produce (e.g. grains, seeds etc.) affecting its quality and quantity.

**Q. Write the names of some important nitrogenous fertilizers.**

**Ans.** Urea 46% N

Ammonium nitrate 35% N

Ammonium sulphate 21% N

Calcium ammonium nitrate 21% N

**Q. Briefly discuss the importance of phosphatic fertilizers.**

**Ans.** Phosphorus is a constituent element of phosphatic enzymes which are responsible for energy metabolism (A.T.P. etc) in the plants and animals. Moreover, phosphorous is the component of plants stems.

**Q. Write the names of phosphatic fertilizers.**

**Ans.** *(i)* Super phosphate $Ca(H_2PO_4)_2$

*(ii)* Triple superphosphate $3Ca(H_2PO_4)_2$

**Q. What is the % age of phosphorous in the above fertilizers?**

**Ans.** Super phosphate contains 16-18% available phosphorous as $P_2O_5$, while triple super phosphate contains 48-49% $P_2O_5$.

**Q. What is the raw material for phosphatic fertilizers?**

**Ans.** *(i)* Phosphate rock — tricalcium phosphate with varying amount of impurities.

*(ii)* Sulphuric acid — 70%

*(iii)* Phosphoric acid.

**Q. What is fluorapetite?**

**Ans.** Phosphate rock is known as Fluorapetite. It is mainly tricalcium phosphate, $Ca_3(PO_4)_2$.

**Q. What do you know about potassic fertilizers?**

**Ans.** In the order of importance, potassic fertilizers come after N and P keeping Pakistani soils and crops into considerations. By and large Pakistani soils are not deficient in potassium, however for sandy soils or chalky soils it has a very favourable effect particularly for crops like cotton, coffee, corn, clover, potato etc.

There is abundance of potassium salts in Pakistan, therefore there is practically no manufacture of K-fertilizers in Pakistan. KCl and $KNO_3$ are important fertilizers.

## 6.4. Cement Industry

**Q. Define Cement.**

**Ans.** Cement may be defined as a material obtained by burning an intimate mixture of calcarious (lime bearing) and the argillaceous (clayer) material at a sufficiently high temperature to produce clinker by incipient fusion and subsequently grinding the resulting clinker to a fine powder.

**Q. What is Portland Cement?**

**Ans.** The name "Portland Cement" was given by Joseph Aspdin, because the cement he made in 1824 yielded stones resembling those found in quarries near Portland, England. His cement was the prototype of the present Portland Cement.

**Q. What is the composition of the Portland Cement?**

**Ans.** An average composition of the Portland Cement is

| | |
|---|---|
| Lime ($CaO$) | 62% |
| Silica ($SiO_2$) | 22% |
| Alumina ($Al_2O_3$) | 7.5% |
| Magnesia ($MgO$) | 1.5% |
| Iron oxide ($Fe_2O_3$) | 2% |
| Sulphur trioxide ($SO_3$) | 1% |
| Alkali oxide ($K_2O$, $Na_2O$) | 1.5% |

**Q. What are the essential constituents of Portland Cement?**

**Ans.** The essential constituents of Portland Cement are:

- *(i)* Lime
- *(ii)* Silica, and
- *(iii)* Alumina

These are combined to form tricalcium silicate $3CaO. SiO_2$ tricalcium aluminate, $3\,CaO\,Al_2O_3$ and dicalcium silicate $2\,CaO\,SiO_2$

**Q. Briefly discuss the various steps involved in the manufacturing process.**

**Ans.** The manufacturing process consists of the following steps:

- *(i)* Grinding and mixing of the raw materials.
- *(ii)* Burning of the mixture at specified temperature.
- *(iii)* Grinding the burnt product called clinker along with gypsum into fine powder.

**Q. How does wet process differ from dry process?**

**Ans.** The specific feature of the wet process is that the raw materials are prepared in water whereas in dry process the materials are ground and mixed dry. Dry process although cheaper needs excessive fine grinding.

**Q. What factors determine the choice of wet or dry process?**

**Ans.** The choice between wet and dry processes depends on certain factors.

*(i)* Physical conditions of the raw materials.

*(ii)* The price of the fuel, and

*(iii)* The local climatic conditions of the factory.

**Q. What do you mean by setting of cement?**

**Ans.** Cement has unique property by virtue of which it combines with water; the resulting mass becomes hard and very resistant to pressure. This process is known as setting of cement.

**Q. Write some physical tests which are used to test the quality of a cement.**

**Ans.** *(i)* Setting time

*(ii)* Compression strength

*(iii)* Tensile strength

*(iv)* Specific gravity

**Q. What is Concrete?**

**Ans.** It is a mixture of cement with sand and crushed stone, gravel, blast furnance slage etc., all made up to paste with water. It sets into a very hard solid mass and is extensively used in the construction of building.

**Q. What is X-rays spectrometer?**

**Ans.** It is a device which is used to determine the crystal structure. It works on Braggs law.

$$n\lambda = 2d \sin\theta$$

Where $\lambda$ = Wavelength of X-rays

$d$ = Internuclear distance

$n$ = an integer

## 6.5. Sugar Industry

**Q. Briefly discuss the nutritional significance of sugar.**

**Ans.** Sugar or sucrose is one of the basic food materials for human beings which not only furnishes sweet taste but also is a source of energy.

**Q. What is sugar cane?**

**Ans.** Sugar cane is one of the two important sources of sugar which is a tropical crop with several feet long stem containing from 10–17% sucrose contents. In Pakistan it is the principal raw material which is widely grown in Punjab, Sindh and N.W.F.P.

**Q. What do you know about sugar beet?**

**Ans.** Sugar beet is another important source of sugar. It grows in temperate climinate under the surface of earth. In Pakistan it is mostly grown in N.W.F.P. Its sugar contents are 15-20% but contains considerable colouring matter.

**Q. How juice is extracted from sugar cane and sugar beet?**

**Ans.** The freshly cut cane is shredded and transported to the factory where it is passed through a series of roller mills to squeeze out the juice.

The juice is extracted from beets by cutting them into slices which are soaked in running hot water when sugar diffuses out in the water. This extraction is based on counter-current principle.

**Q. What types of impurities are present in the juice?**

**Ans.** The extracted juice contains 15 – 20% sucrose and such impurities as,

(*i*) Organic acids — oxalic, tartaric and citric acids
(*ii*) Mineral matter — inorganic phosphate
(*iii*) Nitrogenous matter — proteins etc, and
(*iv*) Colouring matter.

**Q. What is bagasse? Discuss its uses.**

**Ans.** The cellulosic material left after the extraction of juice is called bagasse. It is used (i) as boiler fuel and (ii) as a raw material for the manufacture of insulating material called celutex, good quality paper and board (called hard board or chip board).

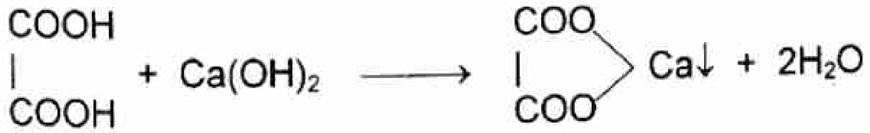
**Q. How juice is purified?**

**Ans.** The juice is purified by the following processes:

(*i*) Defecation
(*ii*) Carbonation
(*iii*) Sulphitation
(*iv*) Extra bleaching

**Q. What is defecation?**

**Ans.** It is a process in which the juice is treated with 2-3% $Ca(OH)_2$ solution or lime water and heated with steam. This process removes organic acids as insoluble calcium salts and phosphates as insoluble calcium phosphate.



$$\begin{array}{l}COOH\\|\\COOH\end{array} + Ca(OH)_2 \longrightarrow \begin{array}{l}COO\\|\\COO\end{array}\Big\rangle Ca\downarrow + 2H_2O$$

$$2K_3PO_4 + 3Ca(OH)_2 \longrightarrow 6KOH + Ca_3(PO_4)_3\downarrow$$

Nitrogenous and colouring matter are coagulated and come to the top of the juice as "*scum*". Both the scum and precipitates are removed by filtration.

**Q. What is carbonation?**

**Ans.** The defecated juice contains excess lime and calcium sucrate. To neutralize excess lime and to recover sucrose from calcium sucrate, carbonation is done which includes the treatment with $CO_2$ gas in a cylindrical vessel.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$C_{12}H_{22}O_{11} + 3CaO + 3CO_2 \longrightarrow 3CaCO_3\downarrow + C_{12}H_{22}O_{11}$$

**Q. What are the objectives of sulphitation?**

**Ans.** Sulphitation involves the treatment of juice with $SO_2$ gas. The objectives of sulphitation are:

*(i)* Neutralization of any $Ca(OH)_2$ still left in the juice.

*(ii)* Bleaching of colouring matter of the juice left after defecation.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3\downarrow + H_2O$$

$$C_{12}H_{22}O_{11} + 3CaO + SO_2 \longrightarrow 3CaSO_3\downarrow + C_{12}H_{22}O_{11}$$

**Q. What is the use of activated carbon or Fullers earth in sugar industry?**

**Ans.** In order to get extra white crystals of sugar the juice is treated with activated carbon or Fullers earth.

**Q. How purified juice is concentrated?**

**Ans.** The purified juice is concentrated by boiling under reduce pressure in multiple effect evaporators.

**Q. What is massecuite?**

**Ans.** As the concentration of sugar contents in the juice increases, crystals separate out. When proper size of crystals are formed, the contents of the pans are called massecuite.

**Q. What is molasses?**

**Ans.** It is a thick liquid which is obtained after one or two crops of sugar crystals. It constitutes about 30% of the total sugar contents. It contains 50% sugar in the form of sucrose which is uncrystallizable due to the presence of about 45% glucose and fructose which are not easily crystallizable.

**Q. How sucrose is converted into glucose and fructose?**

**Ans.** Sucrose can be converted to glucose and fructose by hydrolysis in the presence of mineral acid.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + HOH \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

This conversion is also possible in the presence of an enzyme invertase.

**Q. What do you know about glucose?**

**Ans.** Glucose, a hexose, is the most important of the monosaccharides. It is widely distributed in nature in the free or combined state. It is manufactured from starchy materials such as rice, potato, maize etc. These materials are crushed to a coarse powder and heated with dil HCl (0.5%) under 4-5 atmosphere for 1½ hours to effect hydrolysis.

**Q. Write some uses of glucose.**

**Ans.** Glucose is extensively used in beverage, confectionary and baking. It is also a good food for patients. Many other important chemicals, e.g., sorbitol, vitamin C, etc., are made from glucose.

**Q. What is starch?**

**Ans.** Starch is a polysaccharide and is formed in the green cells of plants by photosynthesis.

$$nCO_2 + nH_2O \longrightarrow (CH_2O)_n + nO_2$$

Wheat contains 60 – 70%, rice about 75%, maize 65 – 70% and potato 15-20% of starch.

**Q. Write some uses of starch.**

**Ans.** Starch is mainly used as food (boiled rice, bread, corn-flour, potato etc.). Crystalline glucose and corn syrup are also manufactured from starch. In laundry toilet powder, adhesives, sizing of paper and cotton textiles, large quantities of starch are used. It is also used for making various sweets and for making blasting explosives.

## 6.6. Paints, Varnishes and Pigments

**Q. Define a paint.**

**Ans.** A paint is a protective and/or decorative coating on some suitable surface. Paints are mixtures of organic and inorganic chemicals, obtained to form a product which when spread on a surface, dries to give a new surface. The new surface has high covering capacity.

**Q. What are the constituents of a paint?**

**Ans.** The constituents of a paint are:

- *(i)* Pigment
- *(ii)* Vehicle or medium
- *(iii)* Drier
- *(iv)* Thinner
- *(v)* Filler

**Q. What are pigments write the names and composition of some important pigments.**

**Ans.** Pigments are the chemicals (organic and inorganic) which impart characteristic colour to the paint film and the surface coated by the paint. They also impart opacity to the paint and therefore reflect destructive U.V. radiation, thus give to some extent protection to the paint. Moreover, they also give strength to the paint film.

The basic pigments are all inorganic. Some important pigments are:

| Name | Colour | Composition |
|---|---|---|
| White lead or Safeda | White | $Pb(OH)_2\ 2PbCO_3$ |
| Red lead or Sindhoor | Red | $Pb_3O_4$ |
| Chrome yellow | Yellow | $PbCrO_4$ |
| Chrome red | Orange | $PbCrO_4\ PbO$ |
| Lithophone | White | $BaSO_4 + ZnS$ |

**Q. How would you classify the pigments?**

**Ans.** Pigments may be classified as:

*(i)* Natural or mineral pigments, e.g., chalk, barytes etc.
*(ii)* Synthetic or chemical pigments, e.g., white lead, zinc oxide etc.
*(iii)* Reactive or soap forming pigments, e.g., red lead, zinc oxide etc.
*(iv)* Inert pigments like titanium dioxide.

**Q. What are the characteristics of a good pigment.**

**Ans.** *(i)* A pigment should be economical.
*(ii)* It should have low toxicity
*(iii)* It should be chemically inert
*(iv)* It should have opacity and good covering power

**Q. What is vehicle in the paint?**

**Ans.** The vehicle in a paint is liquid constituent which on exposure to air gets oxidised and forms a hard, tenacius film on the coated surface. This film serves to protect the surface and to hold the pigment. Linseed oil is the most commonly used vehicle.

**Q. What are driers?**

**Ans.** Driers are oxygen carriers. They accelerate the drying of the oil films through oxidation and polymerization. Driers also act as catalysts. Oxides of manganese, cobalt and nickel act as driers.

**Q. What is the function of thinners?**

**Ans.** Thinners are cheap liquids added to make the paint thin so that it can be applied easily. Turpentine oil is the most popular thinner. It has marked solvent properties and a low cost.

**Q. What is the function of fillers?**

**Ans.** Fillers are cheap inert materials, such as limestone, barium sulphate, gypsum, which are added to give the paint more bulk without increasing its price.

**Q. What are the properties of a good paint?**

**Ans.** A good paint should be consistent and its pigments must be finely powdered and thoroughly dispersed in the vehicle. It should have a large covering power, should dry fairly rapidly, and should be lasting.

**Q. Define a varnish.**

**Ans.** A varnish may be defined as a transparent or semi-transparent solution of a resinous substance either in linseed oil, turpentine oil or alcohol and is used as protective and/or decorative coatings.

**Q. How does warnish differ from a paint?**

**Ans.** A varnish is the modified form of a paint. But it differs from paint in respect that it contains no pigments and is harder and more impervious to moisture than paint film. A varnish consists of a resin dissolved or dispersed in colloidal form in a drying oil or a thinner or both.

**Q. What are the important types of varnish?**

**Ans.** The following are the important types of varnishes.:

*(i)* Oil varnish
*(ii)* Spirit varnish
*(iii)* Asphalt varnish
*(iv)* Water varnish

**Q. What are the ingredients of varnish?**

**Ans.** The following are ingredients of varnishes.

*(i)* Resinous substance or resins — Copal, Lac, Rosin etc.
*(ii)* Driers — turpentine oil.
*(iii)* Solvents — Linseed oil, turpentine oil, methylated spirit etc.

**Q. Write some characteristics of a good varnish.**

**Ans.** A good varnish has the following properties:

*(i)* It offers resistance to weathering effects.
*(ii)* It dries quickly.
*(iii)* It provides a brilliant and decorative covering on wooden materials.
*(iv)* It provides a hard and tough film.

**Q. Write a note on lacquers.**

**Ans.** A lacquer is a solution of a resin in an organic solvent. The lacquer dries as a result of the evaporation of the solvent and not due to oxidation as in the case of paints and oils varnishes.

Lacquers are complex coating agents and contains:

*(i)* Cellulose nitrate or cellulose acetate.
*(ii)* Synthetic resin like glyceryl phthalate.
*(iii)* Plasticizer like di-butyl phthalate.
*(iv)* Solvent like alcohol, esters.
*(v)* Diluent like toluene or xylene.
*(vi)* Pigment.

**Q. Write some uses of lacquers.**

**Ans.** Lacquers find extensive use in the manufacture of numerous articles of glass, wood and metals, where it provides the protection and decoration.

**Q. What are toners?**

**Ans.** The toners are insoluble organic dyes. They can also be used as pigments. They are durable and have high colouring power, e.g., para red, lemon yellow toner etc.

**Q. What are lakes?**

**Ans.** These are inorganic pigments which are dyed. The inorganic portion is an extender such as clay, barytes etc. Organic dye is precipitated over an inorganic pigment.

## 6.7. Polymers

**Q. What is a polymer?**

**Ans.** A polymer is a large molecule built up by the repetition of small, simple chemical units.

**Q. What is meant by polymerization?**

**Ans.** The fundamental process by which low molecular weight compounds are converted into high molecular weight compounds is called polymerization. For polymerization high temperature and/or pressure and/or catalyst is used.

**Q. What are the different types of polymerization?**

**Ans.** The polymerization process may be divided into 3 categories on the basis of the type of a reaction taking place.

*(i)* Condensation polymerization (step polymerization)

*(ii)* Addition polymerization (chain polymerization)

*(iii)* Ring opening polymerization.

**Q. Define the term addition polymerization.**

**Ans.** It is the process of formation of addition polymers when small molecules join together under the stimulus of a catalyst, heat or radiation to form a linear polymer usually without the elimination of a small molecule. This process is of three types.

*(i)* **Free-radical addition polymerization:** In this process chains are initiated by a free-radical such as phenyl radical.

*(ii)* **Cationic addition polymerization:** The active species which initiates the addition polymerization is a cation such as a proton.

*(iii)* **Anionic addition polymerization:** The initiating species in this case is an anion such as $NH_2^-$.

**Q. What is condensation polymerization?**

**Ans.** It is the process of formation of polymers from polyfunctional monomers of organic molecules with the elimination of some small molecules such as water, HCl, $NH_3$ etc. This is also called step-growth polymerization.

**Q. What is meant by ring opening polymerization?**

**Ans.** It is the process of formation of polymers by the opening of rings such as those of ethers or lactans e.g. formation of Nylon-6 from caprolactan.

**Q. Define the following terms.**

**Ans.** *(i)* **Coordination Polymerization:** It is the essential feature of coordination complex. There are a number of coordination catalysts (such as combination of aluminium trialkyl and vanadium or titanium chloride) which will polymerize olefenic compounds to yield a steriospecific polymer.

*(ii)* **Stereoselective Polymerization:** In this type of polymerization one type of ordered structure is preferentially formed in contrast to the other.

*(iii)* **Stereospecific Polymerization:** The polymerization which yields ordered structures is called stereospecific polymerization.

**Q. What is meant by pedant group?**

**Ans.** Group attached to the main polymer chain is called pedant group. e.g. -$CH_3$ group in polypropene.

**Q. What is the difference b/w isotactic and syndiotactic polymers?**

**Ans.** A polymer in which all the pedant groups are arranged on the same side of the polymer backbone is called *isotactic polymer* while a polymer in which pedant groups are arranged alternately on each side of the polymer backbone is called *syndiotactic polymer* (The arrangement of pedant groups in space is called *tacticity*).

**Q. What is the difference b/w amorphous and crystalline polymers?**

**Ans.** A polymer with an ordered structure, which has been allowed to disentangle and form a crystal is called *crystalline polymer* while a non-crystalline polymer or non-crystalline areas in a polymer are called *amorphous*.

**Q. Define Degree of polymerization.**

**Ans.** It is the average number of repeating unit in a macromolecule (polymer). It is denoted by DP or P. It is obtained by dividing the (average) molecular weight by the molecular weight of the monomer.

**Q. Define the terms monomers and oligomers.**

**Ans.** All high polymers are formed by joining together of many molecular units. The repeated unit of a polymer is called a *monomer*, while, a polymer containing a very few repeating units, usually b/w 2 and 10 is called an *oligomer*.

**Q. What are the two broad classes of polymers?**

**Ans.** Polymers can be divided into two classes.

(i) **Natural polymers:** These are naturally occurring polymers. These are also called biopolymers e.g. cotton, cellulose.

(ii) **Synthetic polymers:** These polymers are synthesized from organic (most commonly) and inorganic compounds which join together and form large molecule in which small and simple chemical units are repeated.

**Q. What are copolymers?**

**Ans.** A long chain polymer composed of at least two different monomers, joined together in an irregular sequence is called copolymer.

**Q. What are the different types of condensation polymers?**

**Ans.** The different types of condensation polymers are:

(i) Poly (ester)
(ii) Poly (amides)
(iii) Poly (ethers)
(iv) Poly (urethanes)

**Q. What is glass transition temperature?**

**Ans.** This is the temp. at which an amorphous polymer starts exhibiting the characteristic properties of the glassy state, stiffness, brittleness and rigidity. It is denoted by $\tau_g$.

**Q. What is crystalline melting point?**

**Ans.** This is the range of melting temp. of the crystalline domain of a polymer sample and is accompanied by change in polymer properties. It is the first-phase transition when the solid and liquid phases are in equilibrium. It is denoted by $\tau_m$.

**Q. What are thermoplastics?**

**Ans.** Thermoplastics are those plastics which soften a reversible physical process under the influence of heat and pressure, and can be moulded into different shapes under this condition. They retain their shapes on cooling. They can be remoulded into different shapes on heating.

**Q. What are thermosetting resins?**

**Ans.** These soften under the influence of heat and pressure and can be moulded into different shapes. They become hard and infusible on account of chemical change and cannot be remoulded.

**Q. What is compression and injection moulding?**

**Ans.** A fabrication technique of moulding a thermosetting polymer by means of heating and applying pressure is called *compression moulding*.

A fabrication process in which a heat softened polymer is forced continuously through a die by means of a piston is called *injection moulding*.

**Q. What is extrusion moulding?**

**Ans.** A fabrication technique by which a heat softened polymer is forced continuously by a screw through a die is called extrusion moulding.

**Q. Define critical chain length.**

**Ans.** The minimum chain length required for the entanglement of the polymer chains is called critical chain length.

**Q. What is vulcanization?**

**Ans.** It is the process by which cross-links between linear elastomer (synthetic or natural rubbers) chains are introduced. e.g. introduction of sulphur cross link in natural rubber by heating it with sulphur.

**Q. What is meat by theta temperature?**

**Ans.** It is a temperature at which a polymer of infinite molecular weight starts to precipitate from a solution.

**Q. What is an inhibitor?**

**Ans.** It is an additive which reacts with a chain forming radical to produce non-radical products or radicals of low reactivity, incapable of adding fresh monomer units.

**Q. What is the function of a plasticizer?**

**Ans.** A plasticizer is an additive which reduces the inter-molecular forces between polymer chains and thus acts as an internal lubricants. These are added to improve flow properties and reduce the brittleness of the products.

**Q. What is an "atactic polymer"?**

**Ans.** The polymer in which there is a random arrangement of pedant groups on each side of the chain is called *atactic polymer*.

**Q. What is the difference between configurations and conformations?**

**Ans.** The arrangements arising from rotation about single bonds, including the manifold forms that the polymer chain may have in solution are known as *conformations* e.g. in ethane molecule, if one C atom is kept stationary and other is rotated, by one degree, this would constitute a second conformation of ethane. Only those conformations are considered in actual practice which are energetically favourable.

The arrangements fixed by the chemical bonding in the molecules (e.g. cis & trans or D- & l- forms) are known as *configurations:* The configuration of a polymer chain cannot be altered unless chemical bonds are broken and reformed.

**Q. What is meant by threshold molecular weight?**

**Ans.** Threshold molecular weight is the minimum molecular weight a polymer must attain to develop the properties needed for a particular application e.g if a polymer has high molecular weight, it becomes tough and intractable and cannot be easily handled.

**Q.** **What types of intermolecular bonds are present in polymers?**

**Ans.** The intermolecular bonds formed in polymers are of following types.

*(i)* Dipole-dipole bonds.

*(ii)* Coordinate covalent bonds.

*(iii)* Hydrogen bonding.

*(iv)* Metallic bonds.

*(v)* Ionic bonds.

**Q.** **What are the different factors upon which the flexibility of a polymer chain depends?**

**Ans.** The flexibility of a polymer chain depends on the following factors.

*(i)* Potential energy barrier to rotation.

*(ii)* Molecular weight of the polymer.

*(iii)* The size of the substituents.

*(iv)* Cross-link density.

*(v)* Temperature.

**Q.** **What is meant by calendering?**

**Ans.** It is the process of making polymeric sheets by means of a machine containing counter-rotating rolls.

**Q.** **What is degradation of a polymer?**

**Ans.** Degradation of a polymer can be defined as the undesirable change that occurs in a polymer affecting its physical and chemical properties.

**Q.** **What physical methods are used in the study of degradation process?**

**Ans.** There are four important physical methods which can be used in the study of polymer degradation processes.

*(i)* Determination of molecular wt. during degradation.

*(ii)* Thermal analysis

*(iii)* Spectroscopy. (UV, IR, NMR etc. techniques)

*(iv)* Chromatography. (GLC, TLC etc.)

**Q.** **What are antioxidants?**

**Ans.** Polymer materials can suffer deterioration by thermal, photo and oxidative degradation, leading to ageing, weathering and fatigue. Additives which counteract these effects are known as antioxidants.

**Q. What is the function of a fire retardant?**

**Ans.** To minimize fire hazards, fire retardant chemicals are added to polymers as additives during processing. Six elements are particularly associated with fire retardance. These are B, Al, P, Sb, $Cl_2$, $Br_2$.

**Q. What preliminary tests are used for the identification and characterization of polymers?**

**Ans.** The preliminary tests include

*(i)* Visual examination

*(ii)* Cutting

*(iii)* Heating tests (heating in spatula, on Cu wire and on hard glass tube).

*(iv)* Fusion test. (Metallic Na. fusion test for $N_2$ & halogens. & $KNO_3/K_2CO_3$ fusion test for P).

**Q. Define the term "Rheology".**

**Ans.** The branch of science dealing with the study of deformation and flow of materials is known as rheology. (Greek words Rheos-flow & Logos-Study).

**Q. Define the following terms:**

**Ans. Relaxation time:** Time required for the stress of a polymer under constant strain to decrease to 1/e or 0.37 of its original value.

**Retardation time:** Time required for the stress of a deformed polymer to decrease to 0.63 of the original value.

**Creep:** Cold flow of a polymer or the slipping of polymer chains over a long period of time.

**Bingham plastic:** A plastic that does not flow until the external stress exceeds a critical threshold value. (So). (OR) When small stresses are applied, structural plastics resist irreversible deformation and behave as elastic solids. These plastics are called "Bingham plastics" or "ideal plastics".

**Q. Why cellulose is stronger than amylose?**

**Ans.** Cellulose is stronger than amylose because of the presence of intermolecular hydrogen bonding in cellulose.

**Q. Define isoelectric point.**

**Ans.** This is the pH at which the protein does not migrate to either of the two poles.

**Q. What is coacervation?**

**Ans.** The phenomenon of the coexistence of two liquid phases, one of which is a dilute solution and the other nearly pure solvent, is called coacervation.

**Q. Why molecular weight of a polymer is actually average molecular weight?**

**Ans.** Polymer usually is a complex mixture of molecules of different molecular weights, i.e. they are polydisperse and hetrogeneous in composition. Therefore, the molecular weight of a polymer is actually an average of the molecular weights of constituent molecules.

**Q. What are different average molecular weights of polymers?**

**Ans.** Different averages are obtained depending on the method of measurement of the molecular weight.

*(i)* **The number average molecular weight ( $\bar{M}n$):** It is obtained by the measurement of the colligative properties of a polymer by osmometry or end group analysis. It is obtained by dividing the sum of molecular weights by the number of molecules i.e.

$$\bar{M}n = \frac{\sum NiMi}{\sum Ni}$$

*(ii)* **The weight average molecular weight ( $\bar{M}w$):** It is obtained from light scattering measurements. It is the second power average of molecular weight in a polydisperse polymer. It is defined as

$$\bar{M}w = \frac{\sum NiMi^2}{\sum MiNi}$$

*(iii)* **Z-average molecular weight ( $\bar{M}z$):** It is the third power average of molecular weight in a polydisperse polymer. It is defined as

$$\bar{M}z = \frac{\sum NiMi^3}{\sum MiNi^2}$$

*(iv)* **Viscosity average Molecular Weight (Mv):** It is obtained by viscosity measurements and it is defined as

$$\bar{M}v = \left(\frac{\sum NiMi^{(1+\alpha)}}{\sum NiMi}\right)^{1/\alpha}$$

Where $\alpha$ is the exponent in Mark-Howink-Sakurada equation $[\eta] = KM^{\alpha}$, and its value lies b/w 0.6 and 0.8. and values b/w 0.5 and 1.0 are possible.

**Q. What is meant by Polymer fractionation?**

**Ans.** Separation of a polymer sample into fractions which are more homogenous is known as polymer fractionation.

**Q. What are the different methods of determining $\bar{M}n$?**

**Ans.** *(i)* Osmometry

*(ii)* End group analysis

(iii) Vapour phase osmometry. (This method is useful in measuring Mn upto 40,000).

**Q. What are the different methods of determination of Mw?**

Ans. (i) Light Scattering measurements.

(ii) Light Scattering measurements by using laser radiation sources.

**Q. What are the general methods of determination of molecular weight of polymers?**

**Ans.** (i) Functional group or end group analysis.

(ii) Colligative property measurement. (Vapour phase osmometry, gryoscopy (ebulliometry, membrane osmometry).

(iii) Light Scattering.

(iv) Solution viscosity and molecular size.

(v) Ultracentrifugation.

(vi) Polyelectrolytes. (Polymers with ionizable groups along the chain).

# *Part Seven*

# BIO-CHEMISTRY

# 7.1 Carbohydrates

**Q.** **What are carbohydrates?**

**Ans:** Carbohydrates are polyhydroxy aldehydes and ketones which contain hydrogen and oxygen in the ratio of water (2:1) or those substances which are converted into polyhydroxy aldehydes and ketones after hydrolysis. Their general fomula is $Cx(H_2O)y$.

**Q.** **What are major classes of carbohydrates?**

**Ans:** There are three major classes of carbohydrates which are:

*(i)* Monosaccharides
*(ii)* Polysaccharides
*(iii)* Oligosaccharides

**Q.** **What are monosaccharides?**

**Ans:** Monosaccharides are the carbohydrates which cannot be further broken down into simple units by acid hydrolysis e.g., erthyrose, glucose, fructose, etc.

**Q.** **What are oligosaccharides?**

**Ans:** Oligosaccharides are the carbohydrates which after acid hydrolysis yield two or ten units of monosaccharides per molecule hydrolysed e.g., sucrose, maltose, etc.

**Q.** **What are polysaccharides?**

**Ans:** Polysaccharides are the carbohydrates which are formed by natural condensation of a very large number of molecules of monosaccharides e.g., cellulose, starch etc.

**Q.** **What are major functions of carbohydrates?**

**Ans:** *(i)* They are major source of energy.
*(ii)* They are used in making structures of cells.
*(iii)* They comprise large portions of nucleotides.
*(iv)* They play a role in lubrication and immunity.

**Q.** **What are sugars & non-sugars?**

**Ans:** Monosaccharides and oligosaccharides are sugars as they are sweet in taste while polysaccharides are not sweet so called as non-sugars.

**Q.** **What is the difference between 'd' & '*l*' monosaccharides?**

**Ans:** The 'd' monosaccharides are dextrorotatory while '*l*' monosaccharides are levorotatory as former rotates the plane-polarized light to right and the latter to left.

**Q.** **What type of isomerism is present in carbohydrates?**

**Ans:** *(i)* Optical isomerism
*(ii)* Stereo isomerism

**Q.** **Which carbohydrate is obtained from milk?**
**Ans:** Lactose

**Q.** **Define reducing & non-reducing sugars?**
**Ans:** Carbohydrates having a free aldehydic or ketonic group are called as reducing sugars while those having no free aldehyde or ketonic group are called non-reducing sugars e.g., sucrose.

**Q.** **What are amino-sugars?**
**Ans:** Amino-sugrs have a hydroxyl group replaced by an amino or acetylamino group e.g., glucosamine and glactosamine.

**Q.** **What is nature of blood-group antigens?**
**Ans:** Blood group antigens are specific class of oligosaccharides that may be bound to proteins or lipids.

**Q.** **Write down any two biochemical reactions of carbohydrates?**
**Ans:** Glycolysis, Kreb's Cycle, Pentose phosphate cycle, etc.

**Q.** **Give any two chemical reactions used to confirm the presence of carbohydrates?**
**Ans:** Tollen's test, Fehling's test and Molish test.

**Q.** **How are disaccharides taken in diet converted to monosaccharides?**
**Ans:** As a result of enzymatic hydrolysis.

**Q.** **What is normal concentration of glucose in body?**
**Ans:** Normal conc. of glucose in the blood is 60-90mg/100 ml.

**Q.** **How excess glucose is utilized in body?**
**Ans:** Excess glucose is converted into fat which is stored in the fat deposits.

**Q.** **What are glycosides?**
**Ans:** Alkyl or aryl derivatives of glucose are called as glycosides.

## 7.2 Lipids

**Q.** **Define lipids?**
**Ans:** Lipids are a group of naturally occuring non-polar, water insoluble and hydrophobic substances.

**Q.** **What are main constituents of this group?**
**Ans:** This group includes fatty acids, naturally occuring fatty acid products and many other allied natural products such as steroids, terpens and fat-soluble vitamins.

**Q.** **What is the commercial importance of lipids?**
**Ans:** Commercially they are being used in manufacture of soaps, detergents, grease & paints etc.

**Q. What is the principle component of lipids?**

**Ans:** The principle component associated with the lipid is the fatty acid that contains even number (4-30) in straight chains and may be saturated or unsaturated.

**Q. What are main classes of lipids?**

**Ans:** Lipids have been divided into three main classes.

*(i)* Simple lipids
*(ii)* Compound lipids
*(iii)* Derived lipids.

**Q. What is physical state of fatty acids?**

**Ans:** Acids with small chain length and high unsaturation are liquids at room temperature.

**Q. What is the importance of hydrogenation of fatty acids?**

**Ans:** Unsaturated fatty acids are hydrogenated by Pt, Pd, Ni or Cu. With this process vegetable oil is converted into vegetable fat. (Ghee).

**Q. Define phospholipids?**

**Ans:** Phospholipids are the lipids which contain phosphorus atoms. In addition glycerol, fatty acids and a nitrogen base are key compounds.

**Q. What are essential fatty acids?**

**Ans:** The fatty acids which are essential for sustaining life and which cannot be synthesized by humans are called as essential fatty acids e.g., linoleic and linolenic acid.

**Q. What are steroids?**

**Ans:** Steroids are lipids which contain four fused carbon rings that form the steroid nucleus, cyclopentanoperhydrophenanthrene.

**Q. What are lipoproteins?**

**Ans:** These are complexes of protein and lipids held together by non-covalent bonds, for example plasma.

**Q. Give two structural aspects of fatty acids?**

**Ans:** *(i)* Non polarity
*(ii)* Geometrical Isomerism

**Q. What is distinguishing factor found in naturl fatty acids?**

**Ans:** Most of them has cis-configuration.

**Q. What are waxes?**

**Ans:** Waxes are esters of fatty acid with monohydric alcohols of high molecular weight e.g., sperm oil, candles etc.

**Q. Give biological function of waxes?**

**Ans:** Their major biological role is to serve as protective chemical coating on surface of animals and plants.

**Q.** **How any body gets lipids?**

**Ans:** Main source of lipids is diet (exogenous lipids) including fats and oils, obtained from animals and oil seeds while endogenous sources of lipids are degradation products of proteins and carbohydrates.

**Q.** **Which is main enzyme helping in digestion of lipids?**

**Ans:** Lipase.

**Q.** **What are main biological functions of lipids?**

**Ans:**
- *(i)* They act as lubricants in alimentary canal.
- *(ii)* They are important constituents of cells and tissues.
- *(iii)* They form primary transport systems of non-polar materials through biological fluids.
- *(iv)* They play important role in functioning of nervous system.
- *(v)* They provide essential fatty acids through the diet.

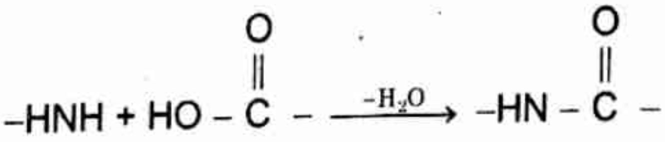
## 7.3 Proteins

**Q.** **What are proteins?**

**Ans:** Proteins are complex nitrogenous compounds of high molecular weight formed in nature by condensation of large number of amino acids through peptide bonds.

**Q.** **How peptide bond is formed?**

**Ans:** The peptide bond is established by condensation of amino group and carboxylic acid group with elimination of a water molecule i.e.,



$$-HNH + HO-\overset{\overset{\displaystyle O}{\|}}{C}- \xrightarrow{-H_2O} -HN-\overset{\overset{\displaystyle O}{\|}}{C}-$$

**Q.** **What is nature of peptide bond?**

**Ans:** They are polar bonds.

**Q.** **What is total number of amino acids found?**

**Ans:** Twenty

**Q.** **What are major functions of proteins?**

**Ans:**
- *(i)* They are fundamental components of all enzymes and some of hormones.
- *(ii)* They are structural units of skin, bone & cytoskeleton.
- *(iii)* The dietry proteins are important energy sources of body.
- *(iv)* Immune defense system is composed of proteins.

**Q. What is composition of amino acids?**

**Ans:** Amino Acids are composed of amino group, a carboxyl group, a hydrogen atom and a distinctive side chain, all bonded to carbon atom.

**Q. What is acid hydrolysis product of protein?**

**Ans:** Amino acids are generally obtained by hydrolysis of proteins.

**Q. On what factors the type of protein depends?**

**Ans:** The type of protein depends upon the number, type & sequence of amino acids involved in its structure.

**Q. Write down the type of proteins on the basis of structure?**

**Ans:** Proteins are found in three types of structure.

*(i)* Primary
*(ii)* Secondary
*(iii)* Tertiary
*(iv)* Quaternery

**Q. Give distinguishing features of each type of structure?**

**Ans:** In primary structure, there is a linear sequence of amino acids. Secondary structure contains protein resulting from hydrogen bond interaction b/w amino acids which are very close to each other. Tertiary structure refers to polypeptide chains forming complex after coiling and folding. Quaternery structure defines the structure resulting from interactions between separate polypeptides units having more than one subunits.

**Q. What are major classes of proteins on the basis of functions?**

**Ans:**
*(I)* Structural proteins (Collagen)
*(ii)* Storage proteins (Ferritin)
*(iii)* Contractile proteins (Myosin)
*(iv)* Allyl Enzymes
*(v)* Protective proteins (Fibrinogen)
*(vi)* Transport proteins (Haemoglobin)
*(vii)* Growth hormones
*(viii)* Toxins.

**Q. What are derived proteins?**

**Ans:** These are degradation products of simple & conjugated proteins e.g., peptides, peptones etc.

**Q. Write down at least two examples of oxygen-transporting proteins.**

**Ans:** *(i)* Myoglobin *(ii)* Haemoglobin

**Q. What are blood proteins?**

**Ans:** These are present in blood plasma. These include serum, albumin, glyco proteins etc.

**Q.** **How proteins may be separated?**

**Ans:** Proteins may be separated by a number of means e.g., dialysis, ultracentrifugation, HPLC, electrophoresis and gel filteration etc.

## 7.4 Nucleic Acids

**Q.** **What are nucleic acids?**

**Ans:** Nucleic acids are biopolymers of high molecular weight with repeating unit mononucleotide.

**Q.** **What are major types of nucleic acids?**

**Ans:** Nucleic acids are found in two basic structural form.

*(i)* Deoxyribonucleic acid (DNA)
*(ii)* Ribonucleic acid (RNA)

**Q.** **What are nucleotides?**

**Ans:** Nucleotides are monomers and each of which consists of a pentose sugar, a nitrogenous base and a phosphate group.

**Q.** **What types of nitrogen bases are present?**

**Ans:** There are two types of nitrogenous bases.

*(i)* Purines = having two rings i.e., a linked five membered and six membered ring. They include adenine & guanine.

*(ii)* Pyrimidines = only one ring which is six membered. It includes cytosine, thiamine & uracil.

**Q.** **Which type of sugars are found in nucleic acids?**

**Ans:** Two types of sugars are found in nucleic acid

*(i)* Ribose sugars

*(ii)* Deoxyribose sugar.

**Q.** **How different nucleotides are linked together in nucleic acids?**

**Ans:** Nucleotides are linked together by phosphodiester bond formed between a sugar molecule of one and phosphate molecule of other nucleotide.

**Q.** **Where DNA and RNA occur in cell?**

**Ans:** Over 98% of total DNA in Eukaryotic cell is found in nucleus while RNA occurs in multiple forms and is present both in nucleus & many other cell organelles.

**Q.** **What is chromatin?**

**Ans:** 'Chromatin' is the name of a complex form in which DNA is found. It is formed by binding of DNA with histones.

**Q.** **What is most important function of DNA?**

**Ans:** It serves as genetic material.

**Q.** **What functions are performed by RNA?**

**Ans:** RNA serves as carrier of genetic information to site of protein synthesis. It is essential component of ribosomes and of some enzymes.

**Q.** **What is structure of DNA?**

**Ans:** DNA has a double helical structure. Double helixes of structure are held together by complementary base pairing joined together by hydrogen bonds.

**Q.** **What are structural differences b/w DNA & RNA?**

**Ans:** *(i)* DNA contains Adenine, Thymine, Cytosine & Guanine while RNA has Adenine, Uracil, Cytosine and Guanine.

*(ii)* DNA has deoxyribose while RNA has ribose sugars.

*(iii)* DNA is double stranded while RNA is single stranded.

**Q.** **What are types of RNA?**

**Ans:** Three types of RNA are found which are:

*(i)* Messenger RNA

*(ii)* Ribosomal RNA

*(iii)* Transfer RNA.

**Q.** **Can DNA by separated?**

**Ans:** Yes, it can be separated by concentrated phenol and detergent as in this reaction proteins are denatured while nucleic acids are soluble in liquid phase.

**Q.** **Is there any evidence of double stranded RNA?**

**Ans:** Double stranded RNA is found in a few viruses.

**Q.** **What is size of human DNA?**

**Ans:** The longest human chromosome is estimated to contain a single DNA molecule with $240 \times 10^6$ base pairs.

**Q.** **Define denatuaration & melting of DNA?**

**Ans:** The hydrogen bonds that hold the two strands of a double helix together can be broken with an increase in temperature or on treatment with alkali. When all the hydrogen bonds holding together the strands are broken, the strands get separated. This process is called "denaturation" or if the separation is caused by a change in temperature, then called as melting.

## 7.5 Enzymes

**Q.** **What are enzymes?**

**Ans:** An enzyme is a protein that is synthesized in living cell and catalyzes or speeds up a thermodynamically possible reaction so that rate of reaction is compatibles with biochemical process essential for maintenance of a cell.

**Q.** **In what way enzymes differ from chemical catalyst?**

**Ans:** Enzymes are invariably proteins. They are highly specific for reactions and produce only expected products. They function within a moderate pH and temperature range.

**Q.** **How an enzyme loses its activity?**

**Ans:** Being a protein, an enzyme loses its activity if subjected to agents like heat acids or bases, organic solvents or other conditions which denature protein.

**Q.** **What is unit of enzyme activity and specific activity?**

**Ans:** A unit of enzyme activity is usually equivalent to amount of enzyme that catalyzes the transformations of one $\mu$ mole of substrate/min under optimal conditions of measurement.

Specific activity is the number of units of enzyme activity per milligram of total proteins present.

**Q.** **What are major classes of enzymes?**

**Ans:** Enzymes are calssified into six major classes.

| | |
|---|---|
| *(i)* Oxidoreductases | *(ii)* Transferases |
| *(iii)* Hydrolases | *(iv)* Lyases |
| *(v)* Isomerases | *(vi)* Ligases. |

**Q.** **Explain enzyme-action in simplest way?**

**Ans:** Enzyme + Substrate $\rightleftharpoons$ Complex $\rightleftharpoons$ Enzyme + Product

i.e., $E + S \rightleftharpoons ES \rightleftharpoons E + P$

**Q.** **What is specificity of enzyme action?**

**Ans:** Enzymes are specific in action, they act on specific substrate.

**Q.** **What is enzyme inhibition?**

**Ans:** The presence of certain substances in an enzyme catalysed reaction may reduce the reaction rate by interfering with formation or breakdown of enzyme-substrate complex. This phenomenon is called as enzyme-inhibition.

**Q.** **What are major types of inhibition?**

**Ans:** There are two major types of enzyme inhibition.

(i) Competitive inhibition.

(ii) Non–competitive inhibition.

**Q.** **Write down some of enzyme inhibitors?**

**Ans:** Mercury, Penicillin, Aspirin, Sarin etc.

**Q.** **What are Isozymes?**

**Ans:** Isozymes are different molecular forms of enzymes that may be isolated from the same or different tissues.

**Q.** **Write down any of two enzymes which are helpful in clinical diagnosis?**

**Ans:** *(i)* Alkaline phosphate helping in diagnosis of liver disease.
*(ii)* Acid phosphatase helping in diagnosis of prostate cancer.
*(iii)* Creatine kinase is used in diagnosis of heart attacks.

**Q.** **Define co-factors?**

**Ans:** A large number of enzymes require an additional component before the enzyme protein can carry out its catalytic function. The general term 'co-factor' encompasses this component.

**Q.** **What is major division of cofactors?**

**Ans:** They are divided into three main groups.
*(a)* Prosthetic group
*(b)* Co-enzymes
(c) Metal activators.

**Q.** **What are monomeric & oligomeric enzymes?**

**Ans:** The enzymes with only one polypeptide chain in which active site resides are called as "monomeric enzymes". While oligomeric enzymes are those which have at least two and as many as sixty associated to form catalytically active enzyme protein.

**Q.** **Give any two of enzyme catalysed body functions?**

**Ans:** *(i)* Trypsinogen $\xrightarrow{\text{Enterokinase}}$ Trypsin
*(ii)* Lactate $\xrightleftharpoons{\text{Lactate dehydrogenase}}$ Pyruvate

## 7.6 Vitamins

**Q.** **What are vitamins?**

**Ans:** Vitamins are organic compounds that human tissues cannot synthesize but that are required for normal growth and development and must be included in diet.

**Q.** **Write down some important sources of vitamins for a human body?**

**Ans:** Vitamins are supplied both by animal and plant sources. Some of the important sources are: vegetables, egg yolk, milk, fish, oils, whole-grain cereals, yeast, liver, wheat, grams, meat and fruits.

**Q.** **What are main classes of vitamins?**

**Ans:** Vitamins are classified into two main classes.
*(i)* Water-soluble , e.g., biotin, niacin, vitamin B & C.
*(ii)* Fat-soluble , These include vitamins A, D, E and K.

**Q.** **Define co-enzymes?**

**Ans:** Vitamins and their derivatives often serve as cofactors for enzymes. Vitamin cofactors are called as co-enzymes.

**Q.** **Does antibiotic therapy affect vitamins?**
**Ans:** It causes deficiency of vitamins.

**Q.** **Write the name of co-factors required for function of vitamin Niacin and Riboflavin?**
**Ans:** Niacin requires Nicotinamide-adenine dinucleotide and its phosphate i.e., NAD and NADP as cofactors.

Riboflavin needs flavin mononucleotide & flavin dinucleotide (FMN & FDN) as co–factors.

**Q.** **What is ascorbic acid?**
**Ans:** It is cofactor of vitamin C.

**Q.** **What are co-enzymes forms of vitamin A, thiamin, biotin and folic acids?**
**Ans:** TPP, Biocyatin, THF and retinal are coenzyme forms of thiamin, biotin, folic acid & vitamin A respectively.

**Q.** **What are diseases caused by deficiency of Vitamin D, E and K respectively?**
**Ans:** Vitamin D = Poor muscular development, Rickets.
Vitamin E = Anemia, Male sterlity Malfunction of nervous system.
Vitamin K = Slow blood clotting.

**Q.** **Where biosynthesis of biotin takes place?**
**Ans:** It takes place in intestine by intestinal micoorganism.

**Q.** **Which of the fat-soluble vitamin is synthesized by human tissue?**
**Ans:** Vitamin D.

**Q.** **What are important functions performed by vitamin C?**
**Ans:** It is a protective agent and acts as antioxidant. It helps in biosynthesis of collagen and hormones.

**Q.** **What are important sources of nicotinic acid?**
**Ans:** Sources of nicotinic acid include yeast, liver, legumes and meals.

## 7.7 Genetic Engineering

**Q.** **What is genetic engineering?**
**Ans:** This term refers to most nucleic acid technologies, which have been developed over the past 25 years. More specifically it refers to techniques that are used to manipulate, move, recombine & propagate DNA.

**Q.** **What will be impact of this technology on modern medicine?**
**Ans:** It will have tremendous impact on modern medicine. Not only will increase our knowledge of gene expression and cause of many diseases, but it will also help to lead to new approaches for diagnosis & treatment of many diseases.

**Q.** **What is heart of recombinant DNA?**

**Ans:** The heart of recombinant DNA is nucleic acid enzymes.

**Q.** **Define restriction enzyme?**

**Ans:** Bacteria contain enzymes that restrict the ability of bacteriophage to infect them, these enzymes are called as restriction enzymes.

**Q.** **Write down some of enzymes used in this technology?**

**Ans:**
*(i)* DNA Ligase
*(ii)* Terminal Transferase
*(iii)* Alkaline phosphatase
*(iv)* Exonuclease III.

**Q.** **What is cloning?**

**Ans:** In biological sense, a clone refers to cells with an identical genotype. As used in recombinant DNA, a clone specifically refers to identical host cells that carry identical recombinant DNA molecule.

**Q.** **What are various steps involved in DNA cloning?**

**Ans:** DNA cloning involves separating a specific gene or segment of DNA from its larger chromosome and attacking it to a small molecule of carrier DNA, then replicating this modified DNA thousands or even millions of times. The result is a selective amplification of that particular gene or DNA-segment.

**Q.** **Define vector?**

**Ans:** It is a DNA molecule known to replicate autonomously in a host cell to which a segment of DNA may be spliced to allow its replication, for example,.a plasmic or a temperate phage DNA.

**Q.** **Give briefly essential features of vector?**

**Ans:**
*(i)* It should be able to replicate within host cell.
*(ii)* It must be capable of interaction into host cell.
*(iii)* It must have a selectable marker.
*(iv)* It must contain a site for interaction of target DNA.

**Q.** **What are plasmids? Also give their significance?**

**Ans:** Plasmids are extrachromosal circular pieces of DNA that are found in bacteria. The first cloning vector was a plasmid. Plasmids remain key cloning vectors in recombinant DNA.

**Q.** **What are bacteriophages?**

**Ans:** These are the viruses that infect bacteria. The DNA of bacteriophages can be used as vector.

**Q.** **What is cloning cDNA?**

**Ans:** It means cloning of a double-stranded copy of an RNA.

**Q. Define Genomic library?**

**Ans:** Genomic library or bank refers to a library of clones that contains every sequence from the genome of a specific organism. These banks are used as a sources for clones of genes from a particular organism.

**Q. Write down significance of Eukaryotic cell cloning?**

**Ans:** For research, drug production and therapeutic purpose, transfer of Eukaryotic cells with recombinant DNA is required. It has following important uses:

*(i)* For treatment of hemophilia B, familal hypercholesterolemia

*(ii)* Germ line cells can also be mad to take up recombinant DNA which then becomes heritable DNA. Such eggs or cells can be implanted into pseudopregnant females, where they continue normal fetal development. Upon birth, their somatic and germline cells carry transfected genes.

**Q. Write down at least five analytical techniques based on this technology?**

**Ans:** *(i)* Southern blot analysis.

*(ii)* Northern blot analysis

*(iii)* RELP Linkage analysis

*(iv)* DNA fingerprinting

*(v)* (Polymerase Chain Reaction) PCR

*(vi)* DNA Sequencing.

**Q. What is use of PCR?**

**Ans:** *(i)* Genes in which mutations are known to cause disease may be sequenced by PCR.

*(ii)* It may be used quickly to detect bacterial or viral infections.

**Q. Define DNA finger printing?**

**Ans:** In this technique, analysis probe hybridizes to sequence between restriction enzyme sites that are highly polymorphic.

**Q. Give uses of DNA finger printing?**

**Ans:** *(i)* Forensic identification.

*(ii)* Identifying parentage.

*(iii)* For evaluation of success of bone marrow transplant

## 7.8 Fermentation

**Q. What is fermentation?**

**Ans:** Fermentation is a process in which chemical transformations of organic substances are accomplished through the activity of the enzymes produced by the microorganisms.

**Q. What are the common types of fermentation?**

**Ans:** There are two important types of fermentation:

*(i)* Aerobic fermentation

*(ii)* Anaerobic fermentation

**Q. What is anaerobic fermentation?**

**Ans:** Anaerobic fermentation involves the anaerobic degradation of organic nutrients e.g., glucose to obtain energy in the form of ATP and produce various products. Anaerobic fermentation is carried out in the presence of anaerobic organisms and in the absence of oxygen.

**Q. What are the organisms used in fermentation?**

**Ans:** The organisms which are commercially exploited to produce industrially important products are:

***Yeasts:*** Produce ethanol and other products

***Molds:*** Produce organic acid and antibiotics

***Bacteria:*** Produce various organic acids

**Q. What is the difference between alcoholic and lactic acid fermentations?**

**Ans:** Both ethanolic and lactic acid fermentations are anaerobic types of fermentation the lactic acid fermentation, is carried out by the bacteria and no evolution of $CO_2$ occurs and ethanolic fermentation is carried out in presence of yeast with the evolution of $CO_2$.

**Q. What is ethanolic fermentation?**

**Ans:** Ethanolic fermentation is anaerobic type of fermentation (i.e., incomplete oxidation of organic substances to ethanol) in the presence of microorganism to produce energy.

$$C_6H_{12}O_6 \xrightarrow[\text{decomposition}]{\text{Anaerobic}} 2C_2H_5OH + 2CO_2 \quad \Delta H = -22 \text{ kcal/mol}$$

**Q. Who discoverd the ethanolic fermentation?**

**Ans:** Lactate and ethanolic fermentations were discovered by Chain Westmen in 1910. He also discovered a bacterium clostridium acctobacterium which carried out these fermentations.

**Q. What raw material is required for the fermentation process?**

**Ans:** Most common raw materials are carbohydrates used to drive energy e.g., starches, cellulose, glucose, lactose are the common carbohydrates.

**Q. What are the requirements for fermentation?**

**Ans:** Following are the requirements for fermentation:

*(i)* Raw material
*(ii)* Microorganism
*(iii)* Optimal conditions
*(iv)* Product recovery

**Q. Which microorganism is mostly used for ethanolic fermentation?**

**Ans:** Sacchromyces cerevisiae is most commonly used for ethanolic fermentation which is a yeast.

**Q. What organic acids are produced by fermentation process?**

**Ans:** Important organic acids produced by the fermentation are acetic acid, lactic acid and citric acid, which are used in food industry and in medicines. They are the products of mold and bacterial fermentation.

**Q. What are the antibiotics produced by fermentation?**

**Ans:** Antibiotics are the substances produced by one type of microbial species which are injurious to the growth of other types. A number of antibiotics such as penicillin, streptomycin, tetracyclins, chloromycetin etc. are being commercially produced by making use of molds which produce them by fermentation.

**Q. What are the common products of fermentation?**

**Ans:** A large no. of products are obtained from the fermentation process, such as alcohols, organic acids, antibiotics, aminoacids, steroids, vitamiins etc. Energy is also produced, microbial cell, microbial enzyme with primary metabolites.

**Q. What type of organisms are used for fermentation process?**

**Ans:** The micro–organisms of fermentation are unable to manufacture their food by the ordinary process of photosynthesis as they lack chlorophyll. They are colourless and grow most actively in darkness or diffused sunlight. The organisms are generally chemohetrotrophs which drive their food and energy by metabilizing organic compounds.

**Q. What is aerobic fermentation?**

**Ans:** The degradation of organic nutrients in the presence of oxygen and some microorganism is called aerobic fermentation.

**Q. What primary steps are involved in fermentation?**

**Ans:** The different fermentations mostly involve the following two primary stages:

*(i)* The splitting of glucose molecule into two molecules of pyruvic acid with the elimination of 2H atom pairs in the form of reduced co-enzymes ($NADH+H^+$). This splitting is called glycolysis.

*(ii)* The reduction of pyruvic acid or another appropriate product at the expense of H the H–atoms produced in stage *(i)* to produce different compounds.

# *Part Eight*

# SPECTROSCOPIC TECHNIQUES

## 8.1. Introduction to Spectroscopy

**Q.** **What is spectroscopy?**

**Ans.** It is the study of interaction of electromagnetic radiations with matter.

**Q.** **How does atomic spectroscopy differ from molecular spectroscopy?**

**Ans.** Atomic spectroscopy is concerned with the interaction of electromagnetic radiations with atoms which are most commonly in their lowest energy state known as ground state.

Molecular spectroscopy is concerned with the interaction of electromagnetic radiations with molecules. In this case transitions occur between rotational and vibrational energy levels in addition to electronic transitions.

**Q.** **What is electromagnetic radiation?**

**Ans.** It is a form in which energy can be transferred from one point to another through empty space.

**Q.** **Why is the term electromagnetic radiation?**

**Ans.** When an electric current passes from one point to the other in a conductor, a magnetic field in its vicinity is produced. Similarly, a changing magnetic field can produce an electric current in a suitable conductor. It thus follows that both these effects are interrelated. Moreover, like radiation, both these effects can be transmitted through space, no material medium is required.

In 1864, J.C. Maxwell showed that certain electrical disturbances are accompanied by the emission of electric waves. Since the electric and magnetic effects are interrelated, it is now considered that an electric field will be accompanied by a magnetic wave. Therefore, electromagnetic radiation can now be considered as waves of energy propagating from a source in space and consists of oscillating electric and magnetic fields at right angles to each other as well as to the direction of propagation of the wave motion.

**Q.** **What is the nature of electromagnetic radiation?**

**Ans.** Electromagnetic radiation possesses dual nature. In some types of interaction, it is treated as wave. In other interaction, corpuscular (i.e., particle) nature of radiation is required. The dual nature of the radiation is not mutually exclusive.

**Q.** **What types of phenomenon explain the wave nature of radiation?**

**Ans.** Interference, Diffraction, Reflection, Refraction etc.

**Q.** **What types of phenomenon explain the particle nature of radiation?**

**Ans.** Photoelectric effect, Compton effect, Pair production etc.

**Q. What component of electromagnetic radiation interacts with matter?**

**Ans.** It is the electrical vector of radiation that interacts with atoms and molecules of the medium. The nature of the interaction depends upon the properties of matter and may lead to transmission, absorption or scattering of radiation.

**Q. What phenomenon likely to occur when radiations interact with matter?**

**Ans.** Some of the phenomenon that are likely to occur when electromagnetic radiations pass through matter are those of dispersion, reflection, refraction, scattering, absorption, polarization etc.

**Q. How do electromagnetic radiations differ from matter waves?**

**Ans.** Electromagnetic radiations consist of electric and magnetic fields while matter waves do not consist of these components.

Electromagnetic radiations require no medium for their propagation while matter waves require certain medium for their propagation.

All electromagnetic radiations move with the velocity of light while velocity of matter waves depends on the nature of medium.

**Q. What parameters are associated with wave properties of radiations?**

**Ans.** Waves are characterized by the following parameters:

**Wavelength:** It is defined as the distance between two successive crests or troughs of a wave. It is reprsented by $\lambda$ (lambda) and is measured in terms of centimetre (cm), metre (m), micrometre ($\mu$m), nanometre (nm) and angstrom ($\overset{o}{A}$) units.

$$1\overset{o}{A} = 10^{-10}\ \text{m} = 10^{-8}\ \text{cm}$$

$$1\mu\text{m} = 10^{-6}\text{m}$$

$$1\text{nm} = 10^{-9}\text{m}$$

**Frequency:** It is defined as the number of waves or cycles which pass a given point in one second. It is represented by $\nu$(nu) and is measured in terms of cycles per second or Hertz (Hz).

$$\nu = \frac{c}{\lambda} \qquad \text{(c is constant).}$$

**Wavenumber:** It is defined as the number of wavelengths which can be accommodated in one centimeter. It is measured in terms of $cm^{-1}$.

$$\bar{\nu} = \frac{l}{\lambda}$$

**Energy:** Electromagnetic radiation can also be characterized in terms of energy possessed by each photon of radiation. The unit commonly used for energy is Joule.

$$E = h\nu$$

when $h$ = Planck's constant

$\nu$ = frequency of radiation.

**Q. What is photon?**

**Ans.** A quantum of electromagnetic radiation which has zero rest mass and energy equal to the product of the frequency of radiation and Planck's constant. In some contexts it is convenient to regard a photon as an elementary particle.

**Q. Convert the following wavenumbers to microns (μ)**

**(i) 3600 $cm^{-1}$ (ii) 1200 $cm^{-1}$**

**Ans.** (i) 2.78 μ

(ii) 8.23 μ.

(Hint: $\bar{\nu} = \frac{1}{\lambda}$ ; $1\mu = 10^{-4}$cm)

**Q. Convert the following wavenumbers to angstrom (Å)**

(i) 3600 $cm^{-1}$ (ii) 1200 $cm^{-1}$

**Ans.** (i) 27,800 Å

(ii) 83,300 Å

(Hint: 1Å = $10^{-8}$cm)

**Q. What do you mean by electromagnetic spectrum?**

**Ans.** The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is known as electromagnetic spectrum.

**Q. What are different types of electromagnetic radiations?**

**Ans.** Cosmic rays, gamma rays, X-rays, ultraviolet, visible (light that we see) infrared, microwaves and radiowaves (used in communication) are all different forms of electromagnetic radiations.

**Q. What wave parameter is common in electromagnetic radiations?**

**Ans.** All electromagnetic radiatons move with same speed.

**Q. Which types of radiations have highest and lowest energy?**

**Ans.** Cosmic rays carry high energy while radiowaves are least energetic.

**Q. Which types of radiations have longest and shortest wavelength?**

**Ans.** Radiowaves have longest wavelength while cosmic rays carry shortest wavelength.

**Q. Write the wavelength, frequency and energy of ultraviolet, visible, infrared and microwave radiations.**

**Ans.**

| Radiation | Wavelength (nm) | Frequency (Hz) | Energy (J $mol^{-1}$) |
|---|---|---|---|
| Ultraviolet | 200 – 380 | $10^{16}$ | $10^6 - 10^7$ |
| Visible | 380 – 750 | $10^{13}$ | $10^5 - 10^6$ |
| Infrared | $10^4 - 10^5$ | $10^{13}$ | $10^3 - 10^5$ |
| Microwave | $10^6 - 10^7$ | $3 \times 10^{10}$ | $10 - 10^3$ |

**Q. What is the principle of spectroscopy?**

**Ans.** When electromagnetic radiations (emr) fall on the compound some of the radiations are absorbed by the molecules of the sample depending upon the energy levels present in the molecule. The radiations which are not absorbed are transmitted and recorded a spectrum indicating % transmittance versus wavelength of electromagnetic radiation. From the spectrum the energies of the missing radiations and thus the energy levels in the molecule can be understood.

**Q. What are different ways in which a molecule can store various energies?**

**Ans.** The energy of a molecule will have a component due to the transitional motion; a component due to the rotation about the centre of gravity of the molecule; a component due to vibration of the atoms; and finally, the energy of the electrons in the molecule.

**Q. What is translational energy?**

**Ans.** Any moving object has kinetic energy as a result of its motion through space. This is known as translation energy. The object is free to more in the three perpendicular directions x, y and z.

**Q. Write some important techniques of spectroscopy.**

**Ans.**
(i) Microwave spectroscopy.
(ii) Infrared spectroscopy.
(iii) Ultraviolet and visible spectroscopy.
(iv) Raman spectroscopy.
(v) Nuclear magnetic resonance spectroscopy.
(vi) X-ray spectroscopy.
(vii) Electron spin resonce spectroscopy.

**Q. What are the major advantages of using spectroscopic methods?**

**Ans.** *(i)* These take very little time to provide the required information.

*(ii)* Only a very small quantities of the substance is required.

*(iii)* These methods are highly reliable in establishing identity of the compounds.

*(iv)* It is possible to detect almost all groups and other structural features of a compound by using these methods.

**Q. What is the significance of Boltzmann law?**

**Ans.** The relative population of molecules in the allowed molecular energy levels can be calculated by using Boltzmann distribution law. The knowledge of population of energy levels is quite essential for spectroscopic studies.

**Q. What is the difference between absorption line and absorption band?**

**Ans.** Absorption line is the record of absorption of radiation of only one frequency whereas absorption band is the record of absorption of radiations of very close frequencies by a group of atoms or molecules.

## 8.2. Microwave Spectroscopy

**Q. What is microwave spectroscopy?**

**Ans.** The spectroscopy in the microwave region (100μm to 1cm) is concerned with the study of rotating molecules. Since it is concerned with the pure rotational motion of molecules it is also known as rotational spectroscopy.

**Q. Which types of molecules give rotational spectra?**

**Ans.** All molecules having a permanent dipole moment are said to be microwave active. Thus interaction can occur for such molecules, energy can be absorbed or emitted, and the rotation gives rise to a spectrum e.g. $CHCl_3$, HCl, etc.

**Q. Which molecules are microwave inactive?**

**Ans.** Those molecules which do not possess any resultant dipole moment are called microwave inactive. No interaction is possible for such molecules. e.g. $H_2$, $Cl_2$ etc.

**Q. What are spherical tops?**

**Ans.** Molecules which have all the three moment of Inertia identical are called spherical tops e.g. $CCl_4$, $CH_4$ etc.

$$I_A = I_B = I_C$$

**Q. What are asymmetric tops?**

**Ans.** These molecules have all the three moment of inertia different e.g. $H_2S$, $H_2O$.

$$I_A \# I_B \# I_C$$

**Q. What is rigid rotor approximation?**

**Ans.** A treatment which assumes that the molecular dimensions are independent of molecular vibrations and undisturbed by molecular rotation.

**Q. What are selection rules for rotational spectroscopy?**

**Ans.** (i) A rotating molecule must have a dipole moment for interaction with the oscillating electric field that is associated with electromagnetic radiation.

(ii) $\Delta J = \pm 1$ i.e., molecule can increase or decrease its rotational energy only to the next higher or lower energy level when it absorbs or emits a quantum of radiation.

**Q. What is moment of Inertia?**

**Ans.** Moment of inertia is defined as

$$I = \mu r^2$$

Where I = moment of inertia

$\mu$ = reduced mass ($\mu = m_1 m_2 /(m_1 + m_2)$)

r = bond length.

**Q. What is the source of microwaves in this technique?**

**Ans.** The source of microwaves is an electronic device known as klystron valve. An applied voltage accelerates electrons in a cavity in the tube, and this can be made to cause the cavity to emit radiation in the microwave region.

**Q. Is any dispersing element needed in this technique?**

**Ans.** In microwave spectroscopy, no specific dispersing element is needed. The klystron source produces, at a given applied voltage, a beam of monochromatic microwave radiation.

**Q. What is the physical state of sample in this technique?**

**Ans.** Mostly gaseous samples are used in microwave studies. However, solids or liquid substances which have their vapour pressure above 0.01 mm of Hg can be easily examined by microwave spectroscopy.

**Q. What detector is used in microwave spectroscopy?**

**Ans.** It is possible to use an ordinary superheterodyne radio receiver as detector. However, a simple crystal detector is found to be more sensitive.

**Q. Whatis Stark Effect?**

**Ans.** If the rotational spectrum is recorded in the presence of a strong electric field E, it will be observed that the lines have been shifted and split. This splitting and shifting of lines is known as Stark effect.

**Q. Write some applications of microwave spectroscopy.**

**Ans.** *(i)* This technique is used to determine bond angle and bond length.

(ii) The structures of $XeOF_4$, OCS, $NH_3$, $O_3$ etc. have been confirmed by this technique.

(iii) This technique has been used successfully to determine the abundance of various isotopes in molecule.

(iv) This technique can detect different conformational isomers, provided they have different moment of inertia.

**Q. Could this technique detect the presence of particular molecular groupings in a sample?**

**Ans.** This technique cannot detect the presence of particular molecular groupings in a sample like-OH or $-CH_3$ because it is the whole molecule, by virtue of its moment(s) of inertia, which is examined by microwave spectroscopy.

**Q. What are limitations of microwave spectroscopy?**

**Ans.** (i) Only molecules with permanent dipole moments can be studied.

(ii) Molecule should be in gaseous form.

(iii) This technique is not suitable in the characterization of new compounds.

**Q. Is it possible to locate the position of a particular isotope in the molecule?**

**Ans.** Yes, it is possible to locate the position of a particular isotope in the molecule by using microwave spectroscopy.

**Q. Write some examples of molecules which give no rotational spectrum.**

**Ans.** $CO_2$, $H_2$, $N_2$ etc.

## 8.3 Ultraviolet – Visible Spectroscopy

**Q. What is the region of uv-visible spectroscopy?**

**Ans.** The uv-visible region extends approximately from 200nm to 800nm, below 200nm upto 50nm being vacuum ultraviolet region.

**Q. What is the principle of uv-visible spectroscopy?**

**Ans.** When a molecule is irradiated with ultraviolet or visible light, valence shell electrons of the molecules are excited from ground state to higher energy state. These electronic transitions generally occur from the highest occupied MO to the lowest unoccupied MO. The wavelength of the absorbed radiations depends on the energy difference between these two levels.

**Q. Where does maximum absorption of light radiations occur?**

**Ans.** Maximum absorption of light radiations occurs at points when the energy of light of certain wavelength becomes equal to that required for excitations. These points of maximum absorption are recorded by a spectrophotometer on a graph as a function of wavelength.

**Q. Why uv-visible spectroscopy is known as electronic spectroscopy?**

**Ans.** Since the absorption of uv-visible radiations results in the transitions among the electronic energy levels of the molecules, it is also termed as electronic spectroscopy.

**Q. Why the region below 200nm cannot be studied by conventional uv-spectrophotometer?**

**Ans.** Because oxygen (in the air) absorbs strongly in this region. However, if oxygen is expelled out by flushing the instrument with nitrogen, the range can be extended to 150nm below which nitrogen also absorbs strongly.

**Q. What is the range of normal or quartz uv-region?**

**Ans.** Ordinary uv-region extends from 200 nm to 380 nm. because the atmosphere is transparent in this region.

**Q. What is a spectrophotometer?**

**Ans.** It is a device used to measure the intensity of absorbed or emitted radiations at various wavelengths.

**Q. What are the principal characteristic parameters of an absorption band?**

**Ans.** The principal characteristic parameters of an absorption band are its position and intensity. The position of maximum absorption ($\lambda$ max) corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition. The intensity of absorption is indicated by $\varepsilon_{max}$ called the molar absorptivity.

**Q. Explain Lambert-Beer's law.**

**Ans.** According to this law the intensity of the emitted light decreases exponentially as the thickness and concentration for the absorbing medium increases arithmetically. Mathematically it is expressed as:

$$A = \log \frac{I_o}{I} = \varepsilon.C.l$$

where $A$ = Absorbance or optical density (OD).

$I_o$ = Intensity of incident light.

$I$ = Intensity of transmitted light.

$\varepsilon$ = Molar absorptivity.

$c$ = Concentration in moles per $dm^3$.

$l$ = Path length in centimeters.

**Q. What is molar absorptivity?**

**Ans.** The molar absorptivity $\varepsilon$, formerly known as molar extinction coefficient, is a constant characteristic of the solute at a given wavelength.

$$\varepsilon = \frac{A}{c.l}$$

or $\varepsilon = A$ (if c is 1 mole litre and $l$ is 1 cm).

Thus $\varepsilon$ is the absorbance of a solution whose conc. is 1 mole per litre and the path length is 1cm. When calculated against $\varepsilon$ max, $\varepsilon$ is called $\varepsilon$ max. It has units of 1000 $cm^2$/mole. However it is customary not to mention the units. Since the values for $\varepsilon$ can be very large, the absorption intensity can be alternatively expressed as log $\varepsilon$.

**Q. What is transmittance? How it is related to absorbance?**

**Ans.** The transmittance is defined as

$$T = \frac{I}{I_o}$$

Where T = Transmittance

I = Intensity of transmitted light

$I_o$ = Intensity of incident light

It is related to absorbance as

$$A = \log \frac{1}{T}$$

$$\%T = 100 \times T.$$

**Q. What is the range of commonly recorded absorbance?**

**Ans.** The range of commonly recorded absorbance is 0 – 2.

**Q. Briefly explain various types of electronic transitions associated with uv-visible spectroscopy.**

**Ans.** On the absorption of light energy by the compounds under study, the $\sigma$, $\pi$ and nonbonding (n) electrons are promoted from the ground state to the higher state. These higher energy states are nothing but antibonding orbitals. The electronic transitions involved in the uv-visible regions are of the following types.

$\sigma \longrightarrow \sigma^*$ (As in $CH_3 - CH_3$)

$n \longrightarrow \sigma^*$ (As in $CH_3OH$, $CH_2Cl$)

$\pi \longrightarrow \pi^*$ (As in double or triple bonds)

$n \longrightarrow \pi^*$ (As in $>C=O$, $-C \equiv N$).

**Q. Write the energy order of electronic transitions.**

**Ans.** $\sigma \longrightarrow \sigma^* > n \longrightarrow \sigma^* > \pi \longrightarrow \pi^* > n \longrightarrow \pi^*$

**Q. What is Franck-Condon principle.**

**Ans.** It states that electronic transitions occur so rapidly that the vibrating atoms do not change their internuclear distance appreciably during this period.

**Q. What is the effect of polar solvent on various electronic transitions?**

**Ans.** Polar solvents generally shift $n \longrightarrow \pi^*$ band to shorter wavelength and $\pi \longrightarrow \pi^*$ band to loger wavelength.

**Q. Explain the various important terms involved in electronic spectroscopy.**

**Ans.** The electronic spectroscopy involves the following important terms:

**Chromophore:** Any functional group present in the molecule that is responsible for the absorption of uv-visible radiation and hence for imparting colour to a compound is known as chromophore. Typical examples of chromophore are C=C, C=O, N=N, $-NO_2$ etc.

**Auxochrome:** It is a substituent on a chromophore which causes a shift in the absorption to longer wavelength and increases intensity of the absorption peak. Common auxochromic groups are –OH, SH, $-NH_2$ etc.

**Red Shift or Bathochromic Effect:** It is a shift of an absorption maximum towards longer wavelength. It may be produced by change of medium or by the presence of an auxochrome.

**Blue shift or Hypsochromic effect:** It is a shift towards shorter wavelength. This may be caused by a change of medium and also by such phenomenon as the removal of conjugation.

**Hyperchromic effect:** It is an effect leading to increased absorption intensity.

$\lambda_{max}$: It is the wavelength of an absorption maximum.

$E^{1\%}_{1cm}$: It is an absorption or absorbance (A) of a 1% solution in a cell with path length of 1cm. This is used in place of '$\varepsilon$ (epsilon)' when the molecular weight of a compound is not known, or when a mixture is being studied.

**Isobestic point:** It is a point common to all absorption curves produced in the spectra of a compound taken at several pH values.

**Q. Why does a compound look coloured?**

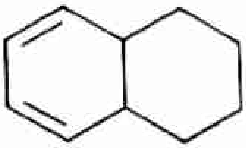
**Ans.** A compound looks coloured because it has absorbed certain electromagnetic radiations or wavelengths from the visible region of the spectrum (400nm – 800nm). The precise colour of a compound depends on which wavelength it subtracts (absorbs) from the white light. It must be remembered that no light is absorbed by colourless substances whereas black substances absorb all the visible light.

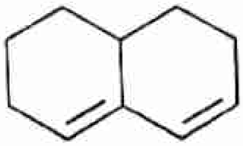
**Q. Which solvents are used in uv-visible spectroscopy?**

**Ans.** The solvents to be used for making solution must be transparent within the wavelength range to be examined. Water, ethanol and n-hexane are generally used.

**Q. Explain the difference between homoannular diene and heteroannular diene.**

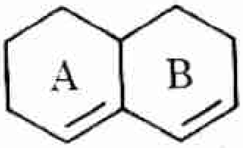
**Ans.** A homoannular diene is a conjugated diene in which both double bonds are present in a single ring, e.g; 1, 3-cyclohexadiene. On the other hand, a heteroannular diene is one in which the two double bonds are not present in a single ring.


Homodiene


Heterodine

**Q. What is exocyclic double band?**

**Ans.** It is a double bond in the conjugated backbone which is outside a ring such that one the double bonded C-atom is a part of the ring, e.g.; the double bond in ring A is exocyclic to ring B.



**Q. What are Woodward-Fieser Rules for conjugated Diene System?**

**Ans.** For the use of uv-visible spectroscopy as an effective tool for structure determination of conjugated dienes and polyens as well as α, β unsaturated carbonyl compounds, certain empirical rules have been developed by R.B. Woodward and L.F. Fieser and are called Woodward-Fieser rules. These rules enable us to calculate $\lambda_{max}$.

**Rules for substituted conjugated Dienes.**

| **Parent diene** | **λmax (nm)** |
|---|---|
| Acyclic | 217 |
| Homonannular | 253 |
| Heteroannular | 214 |
| Extended conjugation (per C=C) | + 30 |
| Alkyl substituent (per group) | + 5 |
| Cl or Br | + 5 |
| Exocyclic double bond | + 5 |

## Rules for α, β-unsaturated carbonyl compounds.

| Parent system | λmax(nm) |
|---|---|
| For cyclic and six membered cyclic ketones | 215 |
| Five membered cyclic ketones | 202 |
| Carboxylic acids and esters | 195 |
| Increment for each |  |
| double bond extending conjugation | + 30 |
| Homodienic component | + 39 |
| Exocyclic double bond | + 5 |

| Substitvents | α | β | γ |
|---|---|---|---|
| Alkyl group | +10 | +12 | +18 |
| –OH | +35 | +35 | +30 |
| –OR | +35 | +30 | +17 |
| –OAC | +6 | +6 | +6 |
| –Cl | +15 | +12 | +12 |

**Q. How many bands are displayed by Benzene?**

**Ans.** Benzene displays three absorption bands, all originating from $\pi \rightarrow \pi$ transitions. It absorbs at 184 nm and at 204 nm and has a fine structure at 254 nm of relatively low intensity. The first two bands (ethylenic) of benzene are designated as $E_1$ and $E_2$ bands, while the fine structure is designated as B-bond.

**Q. What is the source of visible and uv-radiations?**

**Ans.** The source of visible radiation is usually a tungsten filament lamp while a deuterium discharge lamp or hydrogen discharge lamp is used for uv-radiations.

**Q. What are the main components of a uv-visible spectrophotometer?**

**Ans.** A typical uv-visible double beam spectrophotometer consists of the following major components:

(i) Source of radiation
(ii) Monochromater
(iii) Beam splitter
(iv) Sampling area
(v) Light chopper
(iv) Detector
(vii) Amplifier and recorder.

**Q. How light intensity is measured?**

**Ans.** Light intensity is measured with a photocell. It contains a material capable of transforming light energy into electrical energy.

**Q.** **How wavelength selection is achieved?**

**Ans.** A source of light produces a continuos spectra, we need a device for selection of a narrow band, this is achieved by the use of (i) filters and (ii) monochromators.

**Q.** **What are filters?**

**Ans.** Filters are the devices that allow to pass through radiatons of certain wavelengths while absorbing the others wholly or partially. Ordinary filters in the visible region are made up of dyed gelatin. They have a fixed wavelength transmission profile that cannot be altered. Moreover they give broad band of wavelengths.

**Q.** **What do you know about monochromators?**

**Ans.** A monochromator is an optical system that has a spectral transmittance profile that can be adjusted for both peak wavelength and spectral band width. It consists of dispersive (wavelength-selecting) element-a prism or a diffraction grating together with some arrangements like entrance and exit slit and lenses.

Early monochromator used prisms as the dispersive element. However, prisms suffer from the fact that their dispersion is a function of wavelength, temperature, and the exact type of glass used. Automated wavelength selection by rotation of the prism is therefore difficult. Moreover, prisms are suitable for near uv through mid IR regions but are not applicable elsewhere.

**Q.** **What is a diffraction grating? How does it work?**

**Ans.** It is a type of monochromator which uses the optical dispersion properties of a diffraction grating to separate the wavelength components of light into a spectrum.

A grating consists of a large number of parallel lines (grooves) ruled on a highly polished surface such as alumina. The grooves act as scattering centres for light rays impinging upon the grating. The result is equal dispersion of all wavelength of a given order; that is, linear dispersion.

**Q.** **Which monochromator is better?**

**Ans.** Generally the resolving power of grating is better than prisms, moreover, the former can be used in all regions of the spectrum.

**Q.** **Does a monochromater give only one wavelength?**

**Ans.** A monochromator gives only a narrow spectral bandwidth.

**Q.** **What characteristics would be used to define the quality of a monochromater?**

**Ans.** The characteristics required are spectral bandwidth, peak transmittance, wavelength accuracy and precision, stray light and energy through put.

**Q. What is spectral bandwidth?**

**Ans.** It is the range of wavelengths passing through the exit slit.

**Q. How does the spectral bandwidth be reduced or resolution be increased?**

**Ans.** The spectral band width can be reduced by adopting the following measures:

*(i)* decreasing the slit width.

*(ii)* using a monochromator with longer focal length.

*(iii)* using a diffracting grating with more lines per metre.

*(iv)* using a higher order spectrum.

**Q. What is stray light? Where does it come from?**

**Ans.** Stray light is radiation, arriving at the detector, that has either (i) not passed through the sample, or (ii) is of a different wavelength to that being used.

In practice, stray light is mainly light of wrong wavelength emerging from the manochromator, and passing through the sample.

**Q. Could the monochromator be placed between the sample and the detector instead of between the sample and source?**

**Ans.** For the basic operation of the system, it does not matter where the wavelength selection occurs – either before or after the sample. However, for uv systems it is preferable to place the monochromator before the sample in order to reduce the total amount of uv energy which falls on the sample. This reduces the stray light that could be re-emitted due to the fluorescence of the sample (possibly at the measurement wavelength).

**Q. Why do some similar characteristics appear in many different types of instruments?**

**Ans.** The following general characteristics are used to quantify the response to analytical signals in many types of instruments:

**Responsivity:** The ratio of the output signal divided by the input signal.

**Linearity:** The extent to which the responsivity remains constant for different values of the input.

**Offset:** The value of the output signal when the input signal is zero.

**Drift:** The gradual random change of the output signal with time when the input remains constant.

**Noise:** The rapid random change of the output signal with time when the input remains constant.

**Dynamic range:** The ratio of the largest signal that can be measured to the smallest signal.

**Selectivity:** The differential response to the wanted analyte compared to that of an unwanted analyte.

**Q. What is the principle of phototube?**

**Ans.** A phototube (photocell) consists of an evacuated glass envelope, a semi-cylindrical cathode and a central metal wire anode. When the photon strikes the cathode, the photon energy, E, is sufficient to release an electron into the vacuum. This electron is attracted to the anode by the positive voltage and will then pass through the external circuit as an electrical signal current.

**Q. What is photomultiplier tube? How does it work?**

**Ans.** It is also used as a detector in uv-visible spectrophotometer to detect the feeble radiant power. This is based on secondary emission. When radiant energy hits a cathode (as in phototube) electrons are ejected. When these electrons strike on a second sensitive surface – a dynode, at more positive potential, several secondary electrons are emitted. These are in turn accelerated and strike another dynode whereby the no. of electrons is again increased due to the same reason. With such a system, it is quite normal to obtain gain factors as high as a million.

**Q. What types of cells are used in uv-visible spectrophotometer?**

**Ans.** The cells generally used, are made of quartz or fused silica. A cell made of glass can be used in the visible region but it cannot be used in the uv-region because glass absorbs the uv-radiations. Quartz is transparent in both uv and visible region.

**Q. What is single beam instrument? What are its disadvantages?**

**Ans.** A single beam instrument uses only one beam of radiation that is passed through single sell. The reference and the sample cells may be slid into the radiation beam in turn. The reference cell is used to set the absorbance scale at zero for each wavelength examined. It is then replaced by sample cell to determine the absorbance of the sample solution. When the sample cell is in the radiation beam, the response of the detector is less than when the reference cell is in the beam; and the resulting difference in emf is balanced by a potentiometer connected to the absorbance scale.

Although the ratio of the values of the two powers was obtained on the read out scale, the two values were obtained at separate times. Any current irregularities or fluctuations in the source lamp or detector unit in this time interval could result in an error in the sample reading. Moreover, single beam instrument is used for studies at single wavelength, it cannot be used to automatically scan a range of wavelengths.

**Q. What is a double-beam instrument? Write some of its advantages.**

**Ans.** A double-beam instrument divides the radiation into two beams of equal intensity that are passed through two separate cells. One of the cell is filled with sample solution, while the other, called the reference cell, is filled with either pure solvent or a blank solution. Sine the read out from the instrument is the difference between the amount of radiation that is absorbed in the two cells, the absorption in the sample is automatically corrected for absorption occurring in the solvent, and for changes in the intensity of incident radiation. It has a following advantages.

(i) It is not necessary to continually replace the blank with sample.

(ii) Any error due to changes in the intensity of the source and fluctuation in the detector is minimized.

(iii) It can be used at a fixed wavelength or to scan a region of wavelengths.

**Q. Write some applications of uv-visible spectroscopy.**

**Ans.** There are numerous applications of uv-visible spectroscopy. Some important applications are given below.

(i) This technique is used to determine the nature of a chromophoric group present in a compound.

(ii) The number of conjugation can be determined.

(iii) Geometric isomers can be identified.

(iv) It is a powerful tool for the determination of rates of many reactions which involve a change in an absorbing group.

(v) The ionization constant of an acid (or a base) can be determined from the absorbance measurement if the acid or its anion absorbs radiation.

(vi) This technique can be used for quantitative analysis, using Lambert-Beer's law. Therefore the concentration of an unknown compound can be determined.

(vii) Quantitative mixture analysis can be done.

(viii) Molecular mass of a chromophoric substance can be determined.

(ix) It is possible to make some generalization about structure of a compound from uv-visible data.

(x) Tautomeric equilibria and molecular complex formation can be studied.

**Q. What is the maximum value of absorbance and transmittance?**

**Ans.** The maximum value of absorbance is 2 while that of transmittance is 100.

Absorbance: 0 —— 2

Transmittance: 0 —— 100

## 8.4. Infra-Red Spectroscopy

**Q. What is the range of IR spectroscopy?**

**Ans.** Electromagnetic radiations lower in energy than visible radiations are called infra-red radiations. The ordinary IR region extends from 2.5 μm (wavelength) to 15 μm (wavelength) or 4000 to 625 $cm^{-1}$ (wave number).

**Q. What is the principle of IR spectroscopy?**

**Ans.** When IR radiations are passed through an organic molecule, the energy absorbed by the molecule is sufficient to produce vibrations in the molecule. The energy which is not absorbed is transmitted through the sample.

**Q. Why IR spectroscopy is called vibrational spectroscopy?**

**Ans.** The absorption of IR radiation is associated with the excitation of the molecules from the ground state to a higher vibrational energy state. It is the amplitude of vibration that is increased. Due to this reason it is also known as vibrational spectroscopy.

**Q. How IR spectrum is usually recorded?**

**Ans.** A plot of absorbance (A) or percent transmittance (100T) as ordinate against the wavelength or wavenumber as abscissa, results in IR spectrum. It is an important record which gives sufficient information about the structure of a compound.

**Q. What are fundamental vibration?**

**Ans.** Those vibrations which are associated with the vibrations of individual bonds or functional groups, are called fundamental vibrations.

**Q. What are different modes of fundamental vibration?**

**Ans.** There are two main modes of fundamental vibrations, i.e., stretching vibrations and bending vibrations.

**Q. How does stretching vibration differ from bending vibration?**

**Ans.** A stretching vibration is one in which the internuclear distance of two atoms increases or decreases, but the atoms remain in the same bond axis. This vibration can be either symmetric or antisymmetric.

In the bending vibration the position of the atoms changes relative to original bond axis. Bending vibrations can be classified as rocking, scissoring, twisting or wagging.

**Q. What is the necessary condition for absorption of IR radiations by a molecule?**

**Ans.** A molecule must involve a net change in dipole moment during its vibrational motion in order to absorb IR radiations.

**Q.** **Which of the following molecules do not absorb in the IR region? $H_2$, HCl, $O_2$, $N_2$, $H_2O$, $CO_2$.**

**Ans.** $H_2$, $O_2$ and $N_2$ do not absorb in the IR region.

**Q.** **Define degree of freedom. Explain its various types?**

**Ans.** Degree of freedom is defined as the number of co-ordinate axis required to locate the position of an atom in three dimensional system. A molecule consisting of *n*-atoms has a total of 3*n* degrees of freedom. Out of these, three degrees of freedom describe the translational motion, three rotational motion (two in case of linear molecule) and 3*n*-6 degrees of freedom are for vibrational motion (3*n*-5 in case of linear molecule).

**Q.** **Determine the total number of possible vibrational modes for $H_2O$ and $CO_2$.**

**Ans.** For $H_2O$, (a nonlinear molecule) the number of vibrational modes = $3n-6 = (3 \times 3) - 6 = 3$.

For $CO_2$, (a linear molecule), the number of possible vibrational modes = $3n-5 = (3 \times 3) - 5 = 4$.

**Q.** **Theoretical number of fundamental bands are seldom obtained, why?**

**Ans.** It has been observed that the theoretical number of fundamental vibrations are seldom obtained. It is because of the following reasons that

(i) the fundamental vibrations fall outside the region under investigation.

(ii) Fundamental vibrations are too weak to be observed as bands.

(iii) Fundamental vibrations that are so close that they overlap.

(iv) Certain vibrational bands do not appear for want of the required change in dipole moment.

**Q.** **Why some additional bands are observed in IR spectrum?**

**Ans.** There may appear some additional bands called combination bands, difference bands and overtones. Thus, due to these, a large number of bands will be observed as compared to the theoretical number. Let there are two fundamental bands at *x* and y, then the additional bands can be expected at:

*(i)* $2x$, $2y$ (overtones).

*(ii)* $x + y$, $2x + y$, $x + 2y$ etc. (combination bands).

*(iii)* $(x - y)$, $(x - 2y)$, $(2x - y)$ etc. (difference bands).

**Q.** **What is the selection rule of IR spectroscopy?**

**Ans.** Only those vibrations which cause dipole moment to fluctuate and thus produce a fluctuating electric field, will interact with IR radiation and hence will cause absorption. Such vibrations are said to be IR active vibrations.

**Q.** **Where do stretching vibrations generally occur?**

**Ans.** The stretching vibrations generally occur in the following regions:

| | |
|---|---|
| C–H, O–H and N–H | 3700–2700 $cm^{-1}$ |
| C ≡ C and C ≡ N | 2300 – 2000 $cm^{-1}$ |
| C = C, C=O, C=N and N=O | 1900 – 1500 $cm^{-1}$ |
| C–C, C–O and C–N | 1300 – 800 $cm^{-1}$ |

**Q.** **What is the region of bending vibrations?**

**Ans.** All types of bending vibrations occur below 1600 $cm^{-1}$.

**Q.** **What is functional group region?**

**Ans.** The region from 4000 to 1600 $cm^{-1}$ is known as functional group region.

**Q.** **What is finger print region? Discuss its significance.**

**Ans.** We know that absorptions due to bending vibrations occur at frequencies below 1600 $cm^{-1}$. These are not very useful for structural information as confusion of one with other may occur. Moreover bands are observed due to overtones and combination bands. The region from 1600 to 625 $cm^{-1}$ is called fingerprint region.

This region is important for comparing the identity of two compounds and also for the detection of certain functional groups like esters, ethers etc.

**Q.** **What are the various factors which influence the absorption frequencies?**

**Ans.** *(i)* Hydrogen bonding

*(ii)* Conjugation.

*(iii)* Ring strain.

*(iv)* Coupling.

**Q.** **What is Fermi resonance?**

**Ans.** It is a common phenomena in IR spectroscopy and involves the coupling between a fundamental vibration and an overtone or a combination band. One example of this phenomenon is provided by the absorption pattern of $CO_2$.

**Q.** **What are the requirements of Fermi resonance?**

**Ans.** *(i)* The coupling vibrations must be of the same symmetry.

*(ii)* They must originate from groups close to each other.

**Q.** **What is the effect of ring strain on vibrational frequency?**

**Ans.** The ring strain raises the frequency of vibrational motion.

**Q.** **What are the main components of a double beam IR spectrophotometer?**

**Ans.** *(i)* Radiation source.

*(ii)* Sample compartment.

*(iii)* Monochromator.

*(iv)* Detector.

*(v)* Amplifier.

*(vi)* Readout device.

**Q. What is the common source of IR radiation?**

**Ans.** The common source of IR radiation is either Nerst filament or a Globar. The Nerst filament or glower is composed of a mixture of oxides of zirconium, yttrium and thorium. While Globar is a bonded silicon carbide. Radiations are produced by electrically heating the source to 1000 – 1800°C.

**Q. What is a detector? Which types of detectors are used in IR-Spectroscopy?**

**Ans.** It is a device which measures radiant energy falling on it by means of its heating effect. Two common types of detectors are used in IR spectroscopy.

*(i)* Thermocouple.

*(ii)* Bolometer.

**Q. What is the principle of thermocouple detector ?**

**Ans.** The thermocouple detector works on the thermopile principle. When two ends of the metal wire are attached with the two ends of another metal wire, then a difference in temperature between the two ends causes a current to flow in the wires. In the thermocouple detector, the radiant energy heats one of the two metal junctions and an emf is produced between the two junctions proportional to the degree of heating.

**Q. What is the principle of Bolometer?**

**Ans.** It is a metal conductor whose temperature changes as IR radiations fall on it. This change in temperature of the conductor brings about a change in the resistance of this conductor and the degree of change in resistance corresponds to the amount of IR radiation falling on it.

**Q. What is the nature of sample for IR spectra?**

**Ans.** IR spectra may be obtained for gases, liquids or solids.

**Q. How gaseous sample is examined?**

**Ans.** Gases and boiling liquids are examined in evacuated gas cells which are available in lengths ranging from a few centimeter to some meters.

**Q. How liquid sample is examined?**

**Ans.** Liquids may be examined neat as a thin film between NaCl plates.

**Q. How solid samples are examined ?**

**Ans.** Solid samples are usually examined either as a mull (a two phase mixture) or as a KBr disc.

**Q. Why alkali metal halides (usually NaCl or KBr) are used?**

**Ans.** Solids for the IR spectrum are examined as alkali metal halides (usually NaCl or KBr), because they are transparent throughout the IR region and hence do not absorb in this region.

**Q. What are commonly used mulling agents?**

**Ans.** Some commonly used mulling agents are:

(i) Nujol.

(ii) Hexachlorobutadiene.

(iii) Chlorofluoro carbon oil etc.

**Q. What is Nujol? How mulls are prepared?**

**Ans.** The most commonly used mulling agent is nujol which is a mixture of liquid paraffinic hydrocarbons with high molecular weights. Mulls are prepared by grinding about 2 to 5 mg of the solid with a drop of mulling agent, with a mortar and pestle. The mull is examined as a thin film between NaCl plates.

**Q. What happens when nujol is used?**

**Ans.** When nujol is used as mulling agent, absorption due to C–H stetching at 3030–2860 $cm^{-1}$ and those for C–H bending at about 1460 $cm^{-1}$ and 1374 $cm^{-1}$ are not observed. Clearly, no observation about the sample can be recorded from these regions.

**Q. How KBr discs are prepared?**

**Ans.** KBr discs or pallets are prepared by grinding and mixing intimately about 1.0 mg of solid sample with 100 mg of dry, powdered KBr in a smooth agate mortar. Pressing is usually carried out in commercially available die under pressures of about 20,000 psi.

**Q. What are the commonly used solvents for IR spectroscopy?**

**Ans.** The solvents commonly used in IR technique are:

*(i)* $CHCl_3$

*(ii)* $CCl_4$

*(iii)* $CS_2$

Water and ethanol are not commonly used because they dissolve the NaCl used for plates, causing fogging on their surface. Moreover they also absorbs strongly in the IR region.

**Q. Write some applications of IR spectroscopy.**

**Ans.** Some important applications of IR spectroscopy are as under:

*(i)* It is mainly used for the determination of structure of organic compounds.

*(ii)* It is used to establish the identity of a compound by comparison of its IR spectrum with that of an authentic sample.

*(iii)* Presence of impurities can be detected.

*(iv)* Force constant and vibrational frequencies can be calculated.

(v) Symmetry of a molecule can be determined.

(vi) It is used to study reaction kinetics.

(vii) It finds uses in coordination chemistry.

(viii) It finds applications in polymers to detect their end groups.

(ix) It is also possible to make a quantitative determination of a compound making use of its IR spectra, if Beer's law is obeyed.

**Q. Write some limitations of IR spectroscopy.**

**Ans.** Some of the limitations of IR spectroscopy are as under:

(i) This cannot be used to find molecular weight of a compound.

(ii) No information can be obtained regarding the relative position of various groups present in the compound.

(iii) It is not possible to find whether the given compound is pure or is a mixture of compounds by taking single IR spectrum.

**Q. What do you know about FTIR spectrophotometer?**

**Ans.** An infrared spectrophotometer records the trasmittance, T (or absorbance), of a test sample for wavelengths within the mid-infrared region of electromagnetic spectrum (625 to 4000 $cm^{-1}$).

Until about 1990, IR spectrophotometers used wavelength dispersive systems with a scanning monochromater. However, the performance of these scanning IR systems was severely limited by the performance capabilities of the thermal IR detectors available at the time, which were slow in comparison to photon detectors and had poor signal to noise (S/N) characteristics. The development of faster IR detectors, plus the use of Fourier-Transform (FT) system has permitted the use of a totally different method of collecting the data.

A typical FTIR-spectrophotometer uses a Michelson interferometer instead of monochromater. A monochromater only transmits a very narrow band of wave numbers at any given setting of diffraction grating. In contrast, the interferometer has a sinusoidal transmittance pattern, which is spread across the full spectral range.

**Q. What are the advantages of FTIR spectrophotometry ?**

**Ans.** In the normal spectrophotometer, the different wavelengths within the spectrum are recorded sequentially. However, this 'scanning' process takes time. As there is no monochromater in an FTIR spectrophotometer, all wavelengths in the input spectrum fall on the detector simultaneously, and so are recorded simultaneously. The time taken to record the spectrum is therefore only a matter of seconds.

**Q. What are non-dispersive IR photometers?**

**Ans.** Non-dispersive IR photometers differ from the usual IR photometers in that no grating or prism is used – all IR radiations pass through the sample and the reference cell alternatively. The radiations are absorbed by the detector, raising its temp, in proportion to intensity. These instruments do not record a spectrum but instead are designed to quantify one or many compounds. For example, measurement of CO and $CO_2$ from car exhaust is done by NDIR photometer.

**Q. What is Raman spectroscopy?**

**Ans.** Raman spectroscopy is based on the Raman effect and gives the same kind of molecular information as the IR spectroscopy.

**Q. What is Raman Effect?**

**Ans.** When monochromatic radiation is allowed to pass through a substance, the direction of the motion of incident radiation is changed. This phenomenon is known as scattering of radiation. This arises as a result of the interaction of radiation with the atoms or molecules of the medium.

Raman discovered that when monochromatic radiation is scattered by molecules of a transparent substance of any kind, the scattered radiation is found to have different frequencies from that of the incident radiation. This phenomenon of change in frequency of incident and scattered radiation is known as Raman scattering or Raman effect.

The differences in frequencies between incident radiation and the scattered radiation are characteristic of the scattering molecules.

**Q. Write some applications of Raman spectroscopy.**

**Ans.** *(i)* It find applications in qualitative and quantitative analysis.

*(ii)* Determination of constitution of organic molecules.

*(iii)* Determination of molecular structure and symmetry.

*(iv)* Study of non-polar substances such as nitrogen, oxygen etc.

## 8.5. Nuclear Magnetic Resonance Spectroscopy

**Q. What is NMR spectroscopy?**

**Ans.** As the name implies, this form of spectroscopy depends upon the magnetic property of an element, thus it deals with the transitions between magnetic energy levels of nuclei of a molecule. Like uv-visible and IR spectroscopy, nuclear magnetic resonance depends upon the absorption of certain wavelengths of radiation. The radiation is in the radio frequency range.

**Q. How are magnetic energy levels created?**

**Ans.** To create magnetic energy levels, the nuclei are kept in a magnetic field. Without the magnetic field, the spin state of the nuclei are degenerate and so no energy level transitions are possible.

**Q. What is spin quantum number of nucleus?**

**Ans.** The spin of a nucleus is usually given by the symbol I, called the spin quantum number. It is related to atomic number and mass number of the nucleus.

*(i)* Nuclei with both P and N even have zero spin (e.g. $^{4}He$, $^{12}C$).

*(ii)* Nuclei with both P and N odd have integral spin (e.g. $^{14}N$ spin = 1).

*(iii)* Nuclei with odd mass have half-integral spins (e.g. $^{15}N$, spin = $^{1}/_{2}$)

**Q. What is the basic requirement for NMR studies?**

**Ans.** NMR studies are done with nuclei having I = $^{1}/_{2}$, e.g. $^{1}H$, $^{13}C$, etc. No spectra is obtained for I = O.

**Q. What is the principle of NMR spectroscopy?**

**Ans.** Nuclei with an odd atomic number or odd mass number have a nuclear spin. Spinning nuclei have spin angular momentum and are influenced by external magnetic field. Thus a spinning charge (positive or negative) like a proton (or $^{1}H$ nucleus) generates a magnetic field along the spin axis called its magnetic moment. Such a nucleus behaves as a tiny bar magnet. When an external magnetic field is applied, the tiny bar magnet can take up different orientations with respect to applied magnetic field.

**Q. What is PMR-Spectroscopy?**

**Ans.** The case where NMR studies are limited to protons, the name proton magnetic resonance (PMR) spectroscopy is also used.

**Q. How number of possible orientations are determined?**

**Ans.** According to the quantum mechanics, the number of possible orientations of a nuclear magnet in an applied magnetic field is determined by the spin quantum number of the nucleus, and is given by (2I + 1).

**Q. Calculate the possible orientations for the nuclei with spin quantum number of 1/2.**

**Ans.** Possible orientations = 2I + 1

$$= 2 \times \tfrac{1}{2} + 1$$

$$= 2$$

Thus only two orientations are allowed with spin quantum number of ½ ($^{1}_{1}H$, $^{13}_{6}C$, $^{15}_{7}N$), one along the applied magnetic field and other against the field.

**Q. How many orientations are possible for the nuclei with spin quantum number of 1 ?**

**Ans.** Possible orientations = 2I + 1

$$= 2 \times 1 + 1$$

$$= 3$$

Thus nuclear with spin quantum number of ($^{2}_{1}D$, $^{14}_{7}N$) can take up three orientations, one along the applied field, another against the field, and the third orientation is perpendicular to the field.

**Q. Which nuclei are magnetically inactive ?**

**Ans.** The nuclei having zero spin ($_2^4He$, $_8^{12}C$, $_8^{16}O$ etc) are magnetically inactive.

**Q. How many spin states are possible for proton?**

**Ans.** A proton with a spin quantum number of $^1/_2$ has two spin states, one with the spin value of + ½ and designated as α-spin and the other with the spin value of – ½ and designated as β-spin.

**Q. Are these two sates are degenerate? If so then how degeneracy is removed.**

**Ans.** Ordinarily, there is no difference in the energy of these two states, i.e., the two spin states are degenerate. However, the degeneracy can be removed, by placing the proton in a strong magnetic field. Thus when protons are placed in a magnetic field, the magnetic dipoles, associated with the spinning protons, tend to align either along the field (α-spin) or against the field (β-spin).

**Q. What is spin-flipping?**

**Ans.** The transition of a proton from lower energy α-spin state to higher energy β-spin state is called spin flipping. The energy for this transition is provided by electromagnetic radiations of radio wave region.

**Q. Why the term nuclear magnetic resonance is used ?**

**Ans.** The absorption of energy by the proton to induce spin flipping takes place when the frequency of electromagnetic radiation is exactly equal to the precessional frequency of the spinning proton, i.e.; the two frequencies are in resonance, hence the term nuclear magnetic resonance (NMR).

**Q. What is precession?**

**Ans.** A proton like any magnetic nucleus would spin around an imaginary axis. In a magnetic field, unless the axis of the nuclear magnet is exactly parallel with applied magnetic field, there will be a certain force by the external magnetic field to orientate the axis along its direction. The effect of the force is that its rotational axis draws out a circle perpendicular to the applied field. This motion of the axis is called precession.

**Q. What is spin relaxation? How does it occur?**

**Ans.** It is a radiationless transition by which a nucleus in an upper spin state returns to a lower spin state. There are two ways in which radiationless relaxation can occur:

(*i*) spin-spin relaxation.

(*ii*) spin-lattice relaxation.

**Q. What are different modes of inducing spin-flipping?**

**Ans.** There are two modes of inducing spin-flipping:

(i) **Frequency sweep:** In this mode the strength of applied magnetic field is kept constant and the frequency of electromagnetic radiation is varied gradually.

(ii) **Field Sweep:** In the mode of field sweep, the frequency of electromagnetic radiation is kept constant and the strength of applied magnetic field is varied gradually.

For purely technical reasons, it is more convenient t use the mode of field sweep.

**Q. What do you mean by shielding and deshielding of protons?**

**Ans.** A proton in a molecule is surrounded by a could of electronic charge. The applied magnetic field induces circulation of electrons around the proton in a plane perpendicular to itself. this produces a magnetic field which opposes the external field and thus electrons are said to shield the proton from the effect of the external field. Thus the strength of the magnetic field has to be increased accordingly to cause spin flipping.

The extent of shielding depends on the density of the electron could around the nucleus, and the density of the electron around the nucleus depends a the electronegativity of the group attached to the nucleus. As the electronegativity of the attached groups increases, electrons are drawn away from the nucleus and the amount of shielding decreases; the nucleus in this case is said to be deshielded.

**Q. What is the behaviour of shielded and deshielded proton towards the applied magnetic field?**

**Ans.** Compared with a naked proton, a shielded proton requires a high applied field strength and a deshielded proton requires a lower applied field.

**Q. What are equivalent protons?**

**Ans.** In a given molecule, protons with the same environment absorb at the same applied field strength, protons with different environments absorb at different applied field strengths. A set of protons with the same environment are said to be equivalent.

**Q. What is NMR spectrum?**

**Ans.** An NMR spectrum is a plot of the induced voltage versus the sweep of the magnetic field. The area under the peak depends on the total number of nuclei which are flipping.

**Q. What does the number of signals in NMR spectrum tell us?**

**Ans.** The number of signals in an NMR spectrum tells us different sets of equivalent protons.

**Q. How many signals are given by the following compounds:**

**(i) Ethyl chloride**

**(ii) Isopropyl chloride**

**(iii) n-propyl chloride**

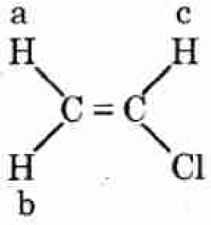
**(iv) 2-Bromopropene.**

**Ans.** (i) $\underset{a}{CH_3} - \underset{b}{CH_2} - Cl$ 2 NMR signals

(ii) $\underset{a}{CH_3} - \underset{b}{CHCl} - \underset{a}{CH_3}$ 2 NMR signals

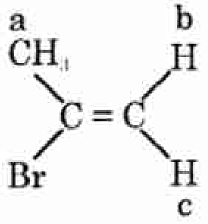
(iii) $\underset{a}{CH_3} - \underset{b}{CH_2} - \underset{c}{CH_2} - Cl$ 3 NMR signals

(iv)



3 NMR signals

(v)



3 NMR signals

Equivalent protons are designated with the same letter in the formula.

**Q. What are magnetically equivalent protons?**

**Ans.** Magnetically equivalent protons are simply chemically equivalent protons. To be chemically equivalent, protons must also be stereo-chemically equivalent.

**Q. What does the position of the signal tell us?**

**Ans.** The position of the NMR signals help to tell us what kinds of protons they are: aromatic, aliphatic, primary secondary, tertiary, benzylic, vinylic, adjacent to halogens etc. These different kinds of protons have different electronic environments, and it is the electronic environment that determines just where in the spectrum a proton absorbs.

**Q. What is chemical shift? How is it measured?**

**Ans.** The separation of the absorption position of a particular proton from the absorption position of some arbitrarily chosen standard is called the chemical shift.

Chemical shifts are measured with reference to the absorption of protons of a reference compound. The reference compound most often used is tetramethyl silane (TMS).A 1% solution of TMS in $CCl_4$ or $CDCl_3$ is used to make the solutions of compounds.

**Q. Why TMS is used as a standard compound?**

**Ans.** Tetramethylsilane, $(CH_3)_4$ Si, is used as a standard or reference compound for several reasons:

*(i)* It is relatively inert.

*(ii)* It has 12 hydrogen atoms, which are magnetically equivalent, and therefore, give rise to an intense single signal even at very low concentration.

*(iii)* It is miscible with most organic liquids and therefore, can be used as internal reference compound.

*(iv)* Since silicon is less electronegative than carbon, the protons of TMS are in region of high electron density. They are, as a result, highly shielded, and signals from TMS occur in region where other protons do not absorb.

*(v)* Finally, it is volatile; its boiling point is 27°C. After the spectrum has been determined, TMS can be removed easily by evaporation.

**Q. How is chemical shift expressed?**

**Ans.** Chemical shift is generally expressed as the frequency difference ($\Delta\nu$) in CPS between the absorption frequencies of the sample and the reference compound.

The chemical shift of a proton, when expressed in hertz, is proportional to the strength of the external magnetic field. Since spectrometer with different magnetic field strengths are commonly used, it is desirable to express the chemical shifts in a form that is independent of the strength of the external field. This can be done by dividing the chemical shift by the frequency of the spectrometer.

**Q. What are two scales of chemical shift?**

**Ans.** Two scales employed to express chemical shifts in terms of ppm are:

*(i)* The $\delta$ (delta) scale, where in

$$\delta = \frac{\Delta\nu \text{ (in Hertz)}}{\text{Frequency of Spectrometer}} \times 10^6 \text{ ppm}$$

*(ii)* . The $\tau$ scale, wherein

$$\tau = 10 - \delta$$

**Q. Calculate the chemical shift for an NMR signal which comes at 100 Hz low field with reference to TMS in a spectrophoto meter using 60 MHz.**

**Ans.** $\delta \text{ (ppm)} = \frac{100}{60 \times 10^6} \times 10^6 = 1.66$

**Q. What does a small or large value of δ and τ indicate?**

**Ans.** On the δ scale, the position of TMS signal is taken as 0.00 ppm whereas on the τ scale it is assigned the value of 10.00 ppm. A small value of δ means a small downfield whereas a large value means a large down field.

On the τ scale, a small value of τ means a low field absorption and a high value means a high field absorption.

**Q. What is the cause of chemical shift?**

**Ans.** The bands in NMR spectrum are observed at different chemical shifts δ or τ values. The cause of this difference is the different magnetic field experienced by different nuclei as a result of secondary magnetic fields associated with the molecules. These secondary magnetic fields are produced by the circulating electrons in the molecule which oppose the applied field.

**Q. Why do the NMR spectra of alkylbenzenes show two signals?**

**Ans.** The NMR spectra of alkylbenzenes – toluene, p-xylene and mesitylene show two signals – one for the side chain protons and one for the ring protons.

**Q. What does the peak area tell us?**

**Ans.** It is general quality of all NMR spectra that area under an NMR signal is directly proportional to the number of protons giving rise to the signal. It can be found by integration method.

**Q. Calculate the areas ratio of protons in the following compounds:**

**(i)** $CH_3OH$

**(ii)** $CH_3CH_2OH$

**Ans.** (i) $CH_3OH$

a b

a:b = 3:1

(ii) $CH_3CH_2OH$

a b c

a:b:c = 3:2:1

**Q. What solvents are used in NMR spectroscopy?**

**Ans.** Commonly used solvents are:

*(i)* Carbon tetrachloride and carbon disulphide (no solvent peak).

*(ii)* Deuterated chloroform, benzene, acetone and water (no solvent peak)

*(iii)* Benzene, cyclohexane, acetone, chloroform and water (one solvent peak)

**Q. What is a diamagnetic effect?**

**Ans.** The effect of circulating electrons to shield a proton is called a diamagnetic effect.

**Q. What is ring current? How does it produce?**

**Ans.** In the molecule of benzene and other aromatic compounds, the circular motion of the π electrons produces a substantial electric current called the ring current. The ring current induces a circular magnetic field around the edges of benzene ring such that in the plane of the ring it opposes the applied field inside the ring and reinforces it outside the ring. This effect is called the ring current effect. It accounts for the large shielding of the ring protons.

**Q. What is paramagnetic effect?**

**Ans.** The effect of circulating electrons to deshield a proton is known as paramagnetic effect.

**Q. What is spin-spin coupling? How it is produced?**

**Ans.** We have studied earlier that an NMR spectrum indicates a pignal for each type of proton in a molecule, i.e., the number of signals is equal to the number of kinds of protons present in the molecule. But in actual practice most spectra appear to be much more complicated. Two, three or more peaks are observed when on the same atom or on adjacent atoms, magnetically different proton or protons are present. This is called splitting of NMR signals. This is because the spin of the neighbouring proton affects the net field felt by a proton generally through the bonding electrons, and causes the proton to experience different net field. So this interaction between neighbouring protons to cause the spin-spin splitting as known as spin-spin coupling.

**Q. What is the significance of spin-spin coupling?**

**Ans.** Although, it complicates the spectrum and makes interpretation much more difficult, yet it provides may valuable information about the number and types of protons on carbon atom adjacent to one bearing the proton under observations.

**Q. What are the general rules for the splitting of proton signals?**

**Ans.** The following rules are used to predict which protons in a molecule are expected to couple.

*(i)* The spin-spin splitting is expected to be observed only between non-equivalent protons.

*(ii)* Splitting of one proton by another proton on the same carbon is quite uncommon.

*(iii)* Mutual splitting of protons separated by more than two atoms is also very rare.

*(iv)* The number of peaks into which a proton signal is split equals one more than the number of vicinal protons.

**Q.** **Define coupling constant and discuss its significance.**

**Ans.** The distance between peaks in a multiplet is known as coupling constant. It is denoted by symbol J. Its value is independent of the applied field. It is a measure of the effectiveness of spin-spin coupling.

**Q.** **Write some applications of NMR-Spectroscopy.**

**Ans.** Important applications of NMR technique are as follows:

*(i)* Identification of an organic compound.

*(ii)* Determination of molecular structure.

*(iii)* Rates of reactions can be studied.

*(iv)* Presence or absence of a particular functional group can be detected.

*(v)* Quantitative analysis can be done.

*(vi)* Surfactant chain length can be determined.

*(vii)* The % of hydrogen in an unknown sample may be determined.

*(viii)* It is possible to make a study of H-bonding in organic compounds and metal chelates using this technique.

*(ix)* The moisture content of a sample can be determined.

*(x)* Structure of some complexes such as $WF_6$, $SOF_4$, $ClF_3$ can be determined.

*(xi)* Keto-enol tautomerism can be studied.

**Q.** **What other nuclei (in addition to proton) have been studied by NMR spectroscopy?**

**Ans.** In addition to proton a few nuclei which have magnetic moments have been studied by NMR spectroscopy. Some of these an $^{13}C$, $^{19}F$, $^{31}P$ etc.

**Q.** **Write some limitations of NMR spectroscopy.**

**Ans.** The various limitations of NMR technique are listed below:

*(i)* It is limited to a few nuclei.

*(ii)* In most of the cases only liquids can be studied.

*(iii)* In some compounds, overlap of spectra results due to similar resonance frequencies.

*(iv)* One of the serious problem is the lack of sensitivity.

**Q.** **What do you known about $^{13}C$ NMR spectroscopy?**

**Ans.** Carbon–NMR is possible. However, there is complication. The most abundant isotope of carbon, carbon–12 is not detected by NMR. Fortunately another isotope, carbon–13, is present in nature at a level of 1.11%. Its behavior in the presence of magnetic field is same as that of hydrogen ($^1H$). Hence the case where NMR studies are limited to carbon–13, the name $^{13}C$–NMR spectroscopy is used.

**Q. What are the limitations of $^{13}C$ NMR spectroscopy?**

**Ans.** The NMR signals given by $^{13}C$ nucleus is inherently much weaker than proton signals and in addition only 1.11% of all C-atoms in the sample are $^{13}C$. Thus, even with an NMR spectrometer properly tuned for $^{13}C$ magnetic resonance (15MHZ at 14, 100 G), the peaks are too weak to be detected and are lost in the background noise. This hampered the development of $^{13}C$ NMR (CMR) spectroscopy as a routine technique for organic structure determination.

**Q. What is FT–NMR spectroscopy?**

**Ans.** NMR–Spectroscopy which is based on the mathematical technique Fourier transform (FT), is known as FT-NMR spectroscopy. As a technique for sensitivity enhancement, FT-NMR is practically essential for $^{13}C$ NMR. It is also used for $^{1}H$ NMR spectra.

**Q. What is the principle of FT-NMR spectroscopy?**

**Ans.** This technique involves irradiating the sample with a brief but intense pulse of radio-frequency region, exciting all the nuclei in the sample to the high spin state. The excited nuclei then relax to their lower energy state, and it is this process that is monitored and the data are converted to spectrum by Fousier transform technique.

**Q. What are the advantages of FT-NMR technique?**

**Ans.** The major advantages are:

*(i)* Much faster spectral accumulation (seconds instead of minutes).

*(ii)* Enhancement of sensitivity

*(iii)* Improvement in signal to noise ratio

**Q. What is the advantage of low abundance of $^{13}C$?**

**Ans.** One advantage of low abundance of $^{13}C$ is the absence of carbon carbon coupling. Just like hydrogen, two adjacent carbons, if magnetically non-equivalent, split each other. In practice such splitting is not observed. Why ? Because coupling can occur only if two $^{13}C$ isotopes come to lie next to each other. With the abundance of $^{13}C$ in the molecule at 1.11% this event has very low probability. This feature simplifies the $^{13}C$ NMR spectra appreciably, reducing the problem of their analysis to a determination of coupling patterns to any attached hydrogens.

**Q. What is the range of chemical shift in $^{13}C$ NMR technique?**

**Ans.** The chemical shift $\delta$ is defined as in $^{1}H$ NMR and is determined relative to an internal standard, normally the carbon absorption in $(CH_3)_4Si$. The chemical shift range of carbon is much longer than that of hydrogen. For most organic compounds, it covers a distance of about 200 ppm, in contrast with very narrow spectral 'window' (10 ppm) of hydrogen.

**Q. Write some applications of $^{13}C$ NMR spectroscopy.**

**Ans.** Structure elucidation is the most common application of $^{13}C$ NMR spectroscopy. PMR and CMR are often employed as complementary techniques. CMR is particularly useful in the investigation of structures of complex natural products and biopolymers. Other applications include:

*(i)* Study of dynamic properties of the molecules.

*(ii)* Study of molecular geometry.

*(iii)* Investigation of biosynthetic pathways, particularly in microorganisms.

*(iv)* Detection and identification of labelled sites.

**Q. What is magnetic resonance imaging (MRI)?**

**Ans.** Magnetic resonance imaging is a technique based n proton NMR which can be used to obtain images of objects containing hydrogen atoms. This important development of three-dimensional NMR, allows observation of the inside of the living organisms without any penetration.

**Q. How MRI is studied?**

**Ans.** In biomedical science, the total volume under observation is placed in a magnetic field which requires the fabrication of a very large superconducting magnets for total body. The signal due to the protons of water is the most easily observed in the biological tissues. In the body, the hydrogen of water attached to the surface of the biological molecules have been found to relax faster than those in the free fluid. In addition, there are also slight differences depending on the nature of the tissue or the structure to which the water is bound. These differences can be used to image the inside of the human body by MRI.

**Q. Write some applications of MRI.**

**Ans.** Following are some important applications of MRI:

*(i)* Malignant tissues in the body can be located.

*(ii)* Blood flow can be observed.

*(iii)* Kidney secretions can be observed.

*(iv)* It is particularly helpful in detecting abnormalities not readily found by CAT scans and conventional X-rays.

**Q. What are the advantages of MRI over CAT scan and X-rays?**

**Ans.** Unlike other imaging methods, the technique is noninvasive, requiring neither ionizing radiation nor the injection of a radioactive isotopes for visualization.

**Q. What are the main components of an NMR spectrophotometer?**

**Ans.** The main components of a typical NMR spectrophotometer are:

*(i)* Powerful magnet

*(ii)* Field sweep generator

*(iii)* Sample tube

(iv) Radio frequency transmitter
(v) Radio frequency receiver
(vi) Amplifier
(vii) Readout device and integrator.

## 8.6 Electron Spin Spectroscopy

**Q. What is electron spin resonance spectroscopy?**

**Ans.** It is a branch of spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electrons with unpaired spins. This phenomenon is known by different names:

"electron paramagnetic resonance" (EPR)

"electron spin resonance" (ESR), and

"electron magnetic resonance" (EMR)

These names are equivalent and merely emphasize different aspects of the same phenomenon.

**Q. What is the principle of ESR-spectroscopy?**

**Ans.** When chemical species (e.g. atoms, molecules or ions) with unpaired spins of an electron are exposed to electromagnetic readiations of appropriate wavelength in the presence of an applied magnetic field, absorption of electromagnetic radiation takes place resulting in the splitting of magnetic energy levels of electrons with unpaired spins. This forms the basis of ESR. The basic principles of ESR are closely related to those of NMR spectroscopy, but the applications as well as instrumentation are quite different.

**Q. How does an electron differ from a proton in respect of magnetic properties?**

**Ans.** Like a proton, an electron also possesses a spin. By virtue of its spin and charge, a free electron is a far more powerful magnet than is the proton.

**Q. Which types of substances are usually studied by ESR spectroscopy?**

**Ans.** Substances with unpaired electrons are studied by ESR technique. The magnetic movement of an electron is nearly 1,000 times greater than that of a proton.

**Q. How does an electron behave in an applied magnetic field?**

**Ans.** We know that the spin quantum number of an electron is $\pm\ ^1/_2$. In the absence of magnetic field, the quantum numbers will give a two-fold degenerate spin energy state, one corresponding to $+\ ^1/_2$ and the other to $-^1/_2$.

When a magnetic field is applied, the two fold degeneracy is removed and two non-degenerate states appear. This is due to the fact that a spinning electron under the influence of an applied magnetic field will assume only two orentation either parallel or antiparallel to the direction of magnetic field.

**Q. How many kinds of multiplet structures are observed in ESR spectrum?**

**Ans.** The magnetic properties of the unpaired electrons are modified by other electrons and by nuclei in their vicinity. Two kinds f multiplet structures are observed in ESR spectrum. These;

(i) Fine structure.

(ii) Hyperfine structure.

**Q. How does fine structure differ from hyperfine structure?**

**Ans.** A fine structure is a multiplet structure which occurs only in crystals that contains more than one unpaired electronic spin. While hyperfine structure arises because of the interactions between the spinning electrons and the adjacent spinning magnetic nuclei.

**Q. Where do transitions occur in ESR-spectroscopy?**

**Ans.** In ESR, transitions of the electron from spin state $m_s = {}^{-1}/_2$ to the spin state $m_s = {}^{+1}/_2$ occur at frequencies in the microwave region, whereas in NMR transitions occur in radio frequency region.

**Q. Write the main components of an ESR-spectrometer.**

**Ans.** The main components of an ESR-spectrometer are:

*(i)* Source

*(ii)* Circulator or magic-T

*(iii)* Sample cavity

*(iv)* Magnet

*(v)* Crystal detector

*(vi)* Recording unit

**Q. What is the concentration of sample for ESR–studies?**

**Ans.** For structure determination and quantitative analysis, the concentration should be in the range of $10^{-6} — 10^{-7}$M.

**Q. What is the physical state of sample for ESR–studies?**

**Ans.** ESR–spectra can be obtained for gases, solutions, powder, single crystal and frozen solutions.

**Q. What types of solvents are used in ESR-studies?**

**Ans.** Solvents having high dielectric constants, such as water, alcohol etc. are not used in ESR studies, because they strongly absorb microwave radiations. The solvents which freeze to form glasses are used in ESR-studies. Methylcyclohexane, toluene, iso-octane, nujol and sulphuric acid are some of the important solvents which form good glasses.

**Q. What are the requirements of a standard used in ESR-studies?**

**Ans.** *(i)* It should be stable

*(ii)* It should have line widths close to that of the sample

(*iii*) It should have the number of unpaired spins close to that of the sample.

**Q. What types of standards are used in ESR–studies?**

**Ans.** The type of paramagnetic substance used as the standard could be

(*i*) a salt like $CuSO_4 .5H_2O$

(*ii*) a free radical in the solid form like biphenyl picrylhydrazyl.

(*iii*) a solution of $K_2(SO_3)_2NO$, or

(*iv*) a transition metal ion highly diluted in a convenient host lattice like $Cr^{3+}$ in $Al_2O_3$ or MgO

**Q. What is the most widely used standard?**

**Ans.** The most widely used standard is 1, 1-diphenyl 1-2, picryl hydrazyl free radical. It is chemically stable substance having the splitting factor, g= 2.0039.

**Q. How ESR-spectrum is represented.**

**Ans.** As in NMR, the ESR spectrum can be represented by plotting intensity against the strength of the applied field, but ESR-spectrum is commonly represented as derivative curves, i.e., the first derivative (the slope) of the absorption curves is plotted against the strength of magnetic field.

**Q. What is the prominent feature of ESR-spectrum?**

**Ans.** The most prominent and revealing feature of ESR-spectrum is the splitting caused in the transition between two electron orientation states. This splitting arises due to the interaction of magnetic movement of the spinning electron with the magnetic moments of nuclei in the molecule.

**Q. How is the position of an ESR-signal determined?**

**Ans.** The position of an ESR-signal is determined by the "g" value. The "g" value for a free electron is 2.0023. But, this is slightly modified for electrons in molecules. "g" is called spectroscopic splitting factor or Lande splitting factor.

**Q. Write some applications of ESR-spectroscopy.**

**Ans.** As stated earlier, to yield an ESR-spectrum, a substance must have one or more unpaired electrons. Some important applications of ESR-technique are:

(*i*) The radicals which are formed as intermediates in chemical reactions can be studied.

(*ii*) Odd electrn molecules such as $NO_2$, NO, $ClO_2$ etc. can be identified in gas phase by ESR-study.

(*iii*) The presence of free radicals in healthy and diseased tissues has been studied by ESR.

(*iv*) Many enzyme catalyzed biological redox reactions proceed via electron step, which involve the formation of enzyme bound free radical, are studied by this technique.

*(v)* Organo-metallic compounds and transition metal complexes can be studied.

*(vi)* Rate of reaction can be studied.

*(vii)* The traces of V in petroleum products and Mn in aqueous solutions can be analysed.

*(viii)* It is used to estimate polynuclear hydrocarbons by converting them into radical cation and analysing the free radicals.

*(ix)* It is also useful in the study of N-type semiconduction.

*(x)* Moreover, the effect of ionizing radiations on the matter such as polyethylene can be studied by ESR-technique.

## 8.7 Fluorimetry

**Q. What is fluorimetry?**

**Ans.** Fluorimetry is a very selective and sensitive analytical technique which is based on the phenomenon of luminescence. The corresponding measurements are made with fluorimeters or spectrofluorimeters and, for chromatographic applications, with fluorescence detectors.

**Q. What is luminescence? Explain the difference between fluorescence and phosphorescence.**

**Ans.** Certain compounds, whether present in solution or in solid state (as molecular or ionic crystals) emit light when they are excited by photons in the visible or near uv domain of spectrum. This phenomenon is called luminescence.

Certain compounds, when excited in solution by visible or near uv radiation, re-emit all or part of this energy as radiation. After excitation, the intensity of the emitted light decreases exponentially. The emission can be classified as fluorescence which has a very rapid decrease in intensity, or phosphoresecnce, where emission decay is much slower. Phosphorescence is basically a delayed fluorescence.

**Q. What is the origin of fluorescence?**

**Ans.** Molecules initially in the ground electronic state So are instantaneously excited by absorption to a vibrational level Vi of the excited electronic state $S_1$. Molecules relax down to the Vo vibrational level of this electronic state $S_1$ very rapidly (in $10^{-12}$ s) by internal conversion without the emission of photons. It is from this energy level the fluorescence occurs. (in $10^{-9}$ to $10^{-7}$s) causing molecules to return to a vibrational level of the ground electronic state So.

**Q. What is the origin of phosphorescence?**

**Ans.** Phosphorescence corresponds to a different relaxation process. After the absorption phase, corresponding to the transfer of one electron into $S_1$ level (singlet state),a spin inversion can occur leading the electron to a $T_1$ state (triplet state) that is slightly more stable. From this $T_1$ state, the electron returns to the

So state with the emission of energy as light. This is slower process because it involves another spin inversion.

**Q. Can a compound show the phenomenon of fluorescence and phosphorescence?**

**Ans.** Yes, a compound can both fluoresce and phosphoresce.

**Q. What factors affect the fluorescence?**

**Ans.** Fluorescence, which often occurs in cyclic, rigid molecules that contain $\pi$ electrons, is enhanced by the presence of electron donating groups and decreased by electron-withdrawing groups. It also depends on pH and solvent.

**Q. Give same examples of fluorescent compounds.**

**Ans.** Aniline, fluorene, biphenyl, naphthalene, fluoresceine.

**Q. Compare the sensitivity of fluorimetry with uv-visible spectrometry?**

**Ans.** Spectrofluorimetry is a very sensitive technique. The detection limit of a compound in solution that fluoresces is detection often 1000 times lower than the detection limit in the uv-visible technique.

**Q. Solutions must be dilute to obtain good results in fluorimety, why ?**

**Ans.** To obtain good results in fluorimetry, solutions must be dilute. Above a given limit, fluorescence is no longer proportional to concentration because of the non-linearity of Beer-Lambert's law. Excitation is weaker and association complexes are formed between excited and ground state molecules.

**Q. What types of instruments are available for this technique?**

**Ans.** Two categories of fluorescence instruments are available from manufactures.

- *(i)* Fluorescence ratio fluorimeters.
- *(ii)* Spectrofluorimeters

**Q. What are the main components of a fluorimeter?**

**Ans.** The main components of a fluorimeter are:

- *(i)* Source
- *(ii)* Excitation monochromator
- *(iii)* Sample
- *(iv)* Emission monochromator
- *(v)* Detector.

**Q. What is the source of radiation in fluorimetry?**

**Ans.** Xenon arc lamp is used as soure of radiation in fluorimetry.

**Q. What types of detectors are used in fluorimetry?**

**Ans.** The measurement of light intensity is carried out using a photomultiplier tube or a photodiode.

**Q. Define chemiluminescence?**

**Ans.** It is the emission of light during a chemical reaction. This phenomenon is also involved in some analytical applications.

**Q. What do you mean by fluorescence derivatisation?**

**Ans.** Only 5 to 8% of all existing molecules possess natural fluorescence, others can be made to fluoresce by chemical modification. By chemical reaction, a fluorophore reagent can be incorporated into analyte. This is called fluorescence derivatisation.

**Q. Write some applications of fluorimetry?**

**Ans.** *(i)* HPLC analysis of polycyclic aromatic hydrocarbons (PAII) in drinking water.

*(ii)* Determination of aflatoxins in certain batches of grain cereals.

*(iii)* Determination of steroids, vitamins, quinine etc.

*(iv)* Determination of metal cations through chelation complexes.

*(v)* Determination of NO and $NO_2$ in polluted atmosphere.

**Q. What is X-ray fluorescence spectrometry?**

**Ans.** X-ray fluorescence is a spectroscopic technique of analysis, based on the fluorescence of atoms in the X-ray domain, to provide qualitative and quantitative information on the elemental composition of a sample.

**Q. Write some applications of X-ray fluorescence technique.**

**Ans.** X-ray fluorescence can be used to analyse all types of samples. Its applications are numerous in research and development and in quality control. It finds applications in metal and mineral industry, ceramic and glass industry, cement industry, petroleum industry, paper mills, toxicology and environmental application. (such as dust, fumes from combustion) heavy metals and dangerous materials in wastes such as Pb, As, Cd, Cr etc.

## 8.8 Atomic Spectroscopy

**Q. What is atomic spectroscopy?**

**Ans.** Atomic spectroscopy is the study of interaction of light radiation with the matter in atomic form. In this technique, samples are vaporized at very high temperature (2000–3000°C) and the concentration of the selected atoms are determined by measuring absorption or emission at their characteristic wavelengths.

**Q. What are different types of atomic spectroscopy?**

**Ans.** There are four types of atomic spectroscopy. These are:

*(i)* Atomic absorption spectroscopy (AAS)

*(ii)* Flame emission spectroscopy (FES)

*(iii)* Atomic emission spectroscopy (AES)

*(iv)* Fluorescence spectroscopy.

**Q. What is atomic absorption spectroscopy?**

**Ans.** In atomic absorption spectroscopy (AAS), the optical absorption of atoms in their ground state is measured when the sample is irradiated with the appropriate source. It is a method for detecting and measuring elements, particularly metallic elements.

**Q. How does atomic absorption differ from atomic emission?**

**Ans.** The mechanism of atomic absorption is the inverse of that for emission technique. In emission, the excited atoms emit radiation of characteristic wavelength; in atomic absorption, those same atoms in the non-excited, non-ionized state are capable of absorbing light of a characteristic wavelength.

**Q. Write the name of device used for atomic absorption spectroscopy.**

**Ans.** Atomic absorption spectrophotomter is used for the study of atomic absorption phenomenon.

**Q. What is the principle of atomic absorption spectrophotometer?**

**Ans.** When a solution of the test element is sprayed into a flame, neutral gaseous atoms of the metals are formed . A large proportion of the gaseous metal atoms without getting excited remains in the ground state. Thus, when a light of suitable wavelength is passed through the flame containing these atoms, a part of the light would be absorbed by the ground state atoms. The measured absorbance is directly proportional to the concentration of the ground state atoms of the test metal.

**Q. What is the other name for atomic absorption spectroscopy?**

**Ans.** Absorption flame photometry.

**Q. What is the source of radiation in AAS?**

**Ans.** Hallow cathode lamp is used as a source of radiation in AAS. It is used to produce light of required wavelength. It is made up of same element which is being analysed.

**Q. Why cathode lamp is used as a source of radiation in AAS instead of a continuous source?**

**Ans.** In atomic absorption spectroscopy, each element absorbs at a particular wavelength known as a resonance wavelength. It is not practically possible to isolate a particular resonance wavelength from a continuous source using a monochromator. This is because resonance line is so narrow that its absorption could not be accurately measured. This problem is overcome by using hollow cathode lamp that produces monochromatic radiation characteristic of the element being analysed.

**Q. Is the same hollow cathode lamp used for all elements?**

**Ans.** No, a separate lamp is used for each element. Sometimes to save time multielement lamps are used. The main disadvantage is that the most volatile metal settles out and coats the other metals thus affecting its efficiency badly.

**Q. What are the main components of AAS?**

**Ans.** The main components of AAS are:

*(i)* Source
*(ii)* Chopper
*(iii)* Burner
*(iv)* Monochromator
*(v)* Detector
*(vi)* Amplifier and readout system

**Q. How does HCL emit radiation?**

**Ans.** The cathode of the hollow cathode lamp comprises an element identical to that under investigation in the flame. Upon excitation by an electric current the metal atoms are sputtered off. Collision of these atoms with an inert gas (argon or neon) induces excitation of these metal atoms and subsequent emission of characteristic radiation.

**Q. What elements are usually determined by AAS?**

**Ans.** All the metallic elements can be determined by AAS. This technique has been widely applied to biological, agricultural, metallurgical, geological and pollution samples.

**Q. What is the role of flame in AAS?**

**Ans.** Flame causes the atomization of analyte species from the solution.

**Q. What types of flames are used in AAS?**

**Ans.** The flames generally used are acetylene and compressed air or acetylene and nitrous oxide. Acetylene is the fuel and air or nitrous oxide is used as support. Oxygen is never used as support as it may cause explosion.

**Q. What is the function of monochromator in AAS?**

**Ans.** It passes the resonance line and filters out others.

**Q. Write some advantages of AAS?**

**Ans.** Following are the important advantages of AAS:

*(i)* It is highly specific for the element of interest.
*(ii)* Spectral interferences are almost non-existent.
*(iii)* Interferences are few and can be easily removed.
*(iv)* Detection limits can be improved.

**Q. What is flame emission spectroscopy (FES)?**

**Ans.** Flame emission spectroscopy or flame photometry is a technique whereby the radiation intensity emitted by a small fraction of the atoms that have passed into the excited state by the elevated temperature is measured.

**Q. Briefly explain the principle of flame photometry.**

**Ans.** When a solution of the metal salt is introduced into a flame as the exciting source, a vapour containing the metal atoms is formed. Some of these gaseous neutral atoms are excited to a higher energy level by the thermal energy of the flame. The excited atoms being unstable emit radiation and return to lower energy state. The emitted radiation is characteristic of the metal, and is proportional to the number of atoms in the flame and hence in the solution.

**Q. Briefly discuss the various processes involved in FES?**

**Ans.** *(i)* Vaporization of the solvent leaving the solid residue.

*(ii)* Vaporization of the solid residue to gaseous state.

*(iii)* Dissociation of the gaseous atoms to form neutral molecules.

*(iv)* Thermal excitation of the gaseous neutral atoms.

*(v)* De-excitation of the atoms.

*(vi)* Measurement of emitted radiation.

**Q. What are different methods of excitation?**

**Ans.** Basically, there are two methods of excitation.

*(i)* Electrical excitation.

*(ii)* Thermal excitation.

**Q. Write the name of device used to study emission spectra.**

**Ans.** Flame photometer is the device used to study the emission spectra of the element.

**Q. Write the main components of a flame photometor.**

**Ans.** The main components of flame photometer are:

*(i)* The Cell (atomizer and burner)

*(ii)* Monochromator

*(iii)* Detector

*(iv)* Amplifier

*(v)* Readout system

**Q. How does the total consumption burner differ from the premix burner?**

**Ans.** In a total consumption burner, the sample solution, the fuel, and the oxidizing gas are carried through separate passages and meet at an opening at the base of the flame.

In a premix burner, the sample is aspirated into a large chamber by a stream of oxidant, here, the fine mist of the sample, the oxidant and fuel supply are mixed and then forced to the burner opening.

**Q. What is the function of an atomizer?**

**Ans.** An atomizer is used to produce a fine, uniform spray or aerosol of the solution containing the sample.

**Q. Write some fuels used in flame phitometry.**

**Ans.** Commonly used fuel are:

*(i)* Hydrogen with air or oxygen (2100 — 2700°C)

*(ii)* Acetylene with air or oxgen (2200 — 3100°C)

(iii) Natural gas with air or oxygen (1000 — 2800°C)

**Q. What should be the characteristics of the flame?**

**Ans.** *(i)* The flame should be steady and quiet.

*(ii)* The flame should be colourless.

*(iii)* The emission from the flame should be constant for any particular concentration.

**Q. How does flame photometer differ from an ordinary spectrophotometer.**

**Ans.** A flame photometer differs from an ordinary photometer or spectrophotometer only in the matter of light source. In ordinary photometer, one uses a light source, while in flame photometer light source is replaced by an atomizer and burner. The optical systems and photodetectors are almost identical.

**Q. Could you convert photometer into flame photometer?**

**Ans.** Conversion of an instrument from one application to the other is a relatively simple matter and involves the replacement of light source of photometer or spectrophotometer with an atomizer or burner.

**Q. Write source advantages of FES.**

**Ans.** *(i)* No light source, other than flame is required.

*(ii)* The instrument is less costly and needs less space.

*(iii)* Analysis is often faster.

*(iv)* Flame spectra have comparatively few lines. Consequently it is easier to resolve and identify the element.

*(v)* Sometimes non-metals can be determined.

**Q. How would you prepare a 100 ppm solution of Na?**

**Ans.** Dry about one gram of NaCl at 120°C for an hour and cool for 30 minutes. Weigh and dissolve 0.254 g of NaCl in water and dilute to one liter.

**Q. How would you prepare further dilution from the above standard solution ?**

**Ans.** The various dilution from the standard solution can be prepared by using the following formula:

$$\underset{\text{(Stock)}}{C_1V_1} = \underset{\text{(Required)}}{C_2V_2}$$

**Q. Is there any need to calibrate the instrument?**

**Ans.** Yes, the instrument should be properly calibrated using standards of high purity, otherwise results would not be reliable.

**Q. There are many metallic elements in the samples, could you determine all these simultaneously or only specific one.**

**Ans.** All the metallic elements could not be determined simultaneously. There are separate filters for each element. This particular filter allows only those radiations which are emitted from the corresponding atoms, rest of all would be blocked. This means that there are separate filters for Na, K, Li, Ca etc.

**Q. Write some applications of flame photometry.**

**Ans.** Flame photometry has proved to be an accurate and rapid technique for estimating a range of metallic elements such as Li, Na, K, Ca, Mg, Cu, Fe, Mn, Ni etc. as well as non-metallic elements such as P and S. These elements can be determined at low concentrations as low as 0.1 ppm.

Currently, this technique is mainly used for the determination of Na, K, Ca in soil, plant, water samples, and biological fluids such as blood, urine.

**Q. Write some limitations of flame photometry.**

**Ans.**

*(i)* This technique has low energy of exciting source.

*(ii)* Liquids samples are generally used.

*(iii)* There is limitation on the number of atoms that can be determined.

*(iv)* Halides or inert gases cannot be determined.

*(v)* It does not give information about the molecular form of the metal.

**Q. Write the number of elements that can be determined by atomic spectroscopy.**

**Ans.** Atomic spectroscopy (both absorption and emission) is a method of quantitative analysis that can be used to measure approximately 70 elements (metals and non-metals). The concentration in ppm region or lower can be estimated.

**Q. What is atomic or optical emission spectroscopy (OES)?**

**Ans.** Atomic or optical emission spectroscopy is based on the study of radiation emitted by atoms in their excited states ionized by the effect of high temperature. Elemental analysis from atomic emission spectra is thus a versatile analytical method when high temperature are obtained by sparks, electrical arcs or inert gas plasma.

**Q. How does optical emission differ from flame emission?**

**Ans.** *(i)* In flame emission, excitation is achieved through flame, while in optical emission excitation is achieved through sparks, electrical arcs or plasma.

*(ii)* In flame emission, only limited number of elements are analysed, while in optical emission all elements can be analysed.

*(iii)* Optical emission spectra is more complex than the flame emission spectra.

**Q. What are the main components of optical emission spectrophotometer?**

**Ans.** Optical emission spectrophotometer contains three principal compartments.

*(i)* Device responsible for bringing the sample to a sufficient temperature.

*(ii)* Optics, including a mono-or polychromator

*(iii)* Microcomputer that cantrols instrument.

**Q. What is inductively coupled plasma-atomic emission spectroscopy?**

**Ans.** It is a type of atomic emission spectroscopy in which inductively coupled plasma torch is used as an exciting source. The plasma torch is a simple device that can reach temperatures of upto 8000 K. Any element introduced into the torch will start to emit.

**Q. What is a plasma?**

**Ans.** Plasma is a neutral environment formed by atoms in equilibrium between their neutral and ionised (1 to 2%) state and by electrons. It is considered as the fourth state of matter.

**Q. What are the advantages and disadvantages of ICP-AES?**

**Ans.** Its main advantages are high temperature and stability which eliminate many of the interferences and sources of error encountered with conventional–AES. Present ICP–atomic emission spectrophotometers allow multi-element analysis to be performed either simultaneously or sequentially. Another advantage is its linearity of response over a large range of concentrations. The main disadvantage is their high price. These instruments constitute a major investment for any analytical laboratory.

**Q. What is your opinion about the performance and detection limits of ICP–AES?**

**Ans.** Its rapidity and detection limits, which are in the order of a few ppt ($10^{-12}$) for many elements, make this technique as one of the best technique currently available for elemental analysis.

**Q. Write some applications of atomic emission spectroscopy.**

**Ans.** *(i)* It finds analytical applications in industry–for example, monitoring the wear of car and aircraft motors by measuring the metals in the oils.

*(ii)* Environmental analysis is probably the area when best advantage of this method can be taken.

*(iii)* Samples for analysis can come from products of vegetable or animal origin (milk, meat), water, air, (ashes emitted by incinerator) or soils in which elements are present over a wide range of concentrations.

*(iv)* This technique also has applications in the area of forensic sciences and clinical medicine (tissue analysis or biological fluid).

## 8.9 Mass Spectrometry

**Q. What is mass spectrometry?**

**Ans.** Mass spectrometry (MS) is an analytical method based on the determination of atomic or molecular masses of individual species in a sample. It is concerned with the interaction of chemical species with the applied magnetic field, and their separation according to mass to charge ratio.

**Q. Define mass spectrometer.**

**Ans.** Mass spectrometer is the instrument which sorts out the ions and separate the individual atoms or molecules on the basis of the difference in their masses.

**Q. What is the principle of mass spectrometry?**

**Ans.** When a minute quantity of the sample in the gas phase (or suitable form) is bombarded with a beam of electrons (high energy), the electrons ionize the neutral gas molecules by knocking out one or more of the orbital electrons. The resulting positive ions under the influence of an electric field will more towards the cathode. Since ions of different masses are present, their velocities will be different. As a result, the ions are separated on the basis of mass to charge ratio. The masses of the ions are recorded in the mass spectrometer. The spectrum produced known as mass spectrum gives information about various masses produced and their relative abundance.

**Q. What are different areas for the uses of this technique?**

**Ans.** This technique is used in several diverse areas: organic and inorganic chemistry, biochemistry, clinical chemistry, environmental sciences, agriculture, geochemistry as well as many industrial control processes and for regulation compliance.

**Q. How does molecular ion differ from fragment ion?**

**Ans.** When the molecule is bombarded with a beam of electron of energy about 10eV, molecular ion is produced by the removal of an electron from the original molecule.

If the molecule of the sample is bombarded with an electron beam of energy 70 eV, the molecular ion formed by the loss of an electron breaks into smaller ions called the fragment ions or daughter ions.

**Q. Could negative ions be produced by bombardment process?**

**Ans.** Bombardment of the sample molecule with electron also produces negative ions, but their number is very small as compared to that of the +ve ions.

**Q. Briefly describe the various processes occurring in mass spectrometer.**

**Ans.** The various processes occurring in mass spectrometer are:

- *(i)* Formation of the ions by the electron bombardment of the substance
- *(ii)* Acceleration and separation of ions under the combined action of electric and magnetic fields in vacuo, and
- *(iii)* Detection of the ions and recording of mass spectrum.

**Q. What is the difference between mass spectrograph and mass spectrometer?**

**Ans.** Instrument which uses photographic plates for recording the mass spectrum is called mass spectrograph and that which makes use of collecting and measuring ion-currents is called the mass spectrometer.

**Q. Write the main components of a typical mass spectrometer?**

**Ans.** All mass spectrometer generally consist of the following components:

- *(i)* The inlet system
- *(ii)* The ion source
- *(iii)* The accelerating electrostatic system.
- *(iv)* The ion separator
- *(v)* The detector and readout system.

**Q. What is the physical state of the sample for analysis?**

**Ans.** A sample is usually analysed in gaseous form. The solid or the liquid sample under analysis is converted into the gaseous state in the inlet system by heating.

**Q. How much sample is required for analysis in mass spectrometry?**

**Ans.** About one micromole of the sample is used for analysis in this technique.

**Q. Why it is essential to maintain a high vacuum in spectrometer?**

**Ans.** As the ions in the mass spectrometer are separated and detected in accordance with their masses, it is essential to maintain a high vacuum in the spectrometer, otherwise there will be loss of ions from the sample because of collision with other molecules (molecules of atmospheric gases).

**Q. Can we use the term mass spectrophotometer?**

**Ans.** We cannot use the term mass spectrophotometer. This term is used only when some electromagnetic radiation interacts with matter. Here the source is beam of electron, so the term spectrometer is only used.

**Q. What are metastable ions?**

**Ans.** Ions produced from the molecule by electron bombardment are first accelerated and then separated. The life time of an ion may be so small that it decomposes after nearly complete acceleration but before compete separation. The ions so formed on decomposition are called metastable ions.

**Q. How will you define molecular ion peak?**

**Ans.** When a molecule of the sample is bombarded with an electron beam of energy 10–15 eV, an ion called the molecular on or parent ion is produced by the removal of a single electron from the original molecule. All these ions will appear in a single peak called the molecular ion peak or parent peak in the mass spectrum.

**Q. What is base beak? Discuss its significance.**

**Ans.** Base peak is the one which corresponds to the most stable ion and is assigned 100% intensity.

The intensities (or heights) of the other peaks are measured relative to that of the base peak. The base peak may be either a fragment ion peak or the parent ion peak depending on the nature of the compound.

**Q. Could you observe isotopic peaks in mass spectrum?**

**Ans.** In organic compounds there appears a small peak one mass unit higher than the parent peak designated by M + 1 peak which corresponds to $^{13}C$ or $^{2}H$ isotope. Molecules containing O, S, Cl or Br give M+2 peaks. These peaks are also called satellite peaks.

**Q. What is nitrogen rule? Discuss its significance.**

**Ans.** It states that "if a molecule contains an odd number of nitrogen atoms, it will have an odd numerical value for its molecular weight, whereas if it contains zero or even number of nitrogen atoms, it will have an even numbered molecular weight.

This rule is used to determine whether a particular peak is the molecular ion peak or not.

**Q. What is ion-current?**

**Ans.** The current generated due to ions in the mass spectrometer is called ion-current.

**Q. Write some applications of mass spectrometry.**

**Ans.** Following are the important applications of mass spectrometry.

*(i)* Determination of molecular mass.

*(ii)* Determination of molecular formula.

*(iii)* Determination of molecular structure.

*(iv)* Determination of masses of isotopes.

*(v)* Studies involving reaction mechanisms.

*(vi)* Distinction between cis-trans-isomers.

*(vii)* Study of bio-chemical reactions.

*(ix)* Quantitative analysis of mixture.

*(x)* Identification of an unknown compound.

*(xi)* Characterization of polymers.

*(xii)* Amino acid sequence analysis in peptides.

*(xiii)* Detection of impurities.

*(xiv)* Drug metabolism.

*(xv)* Clinical and forensic studies.

**Q. What are the advantages of mass spectrometry over uv-visible, IR and NMR spectroscopy?**

**Ans.** The main advantages of mass spectrometry over other physical methods are:

*(i)* Small quantity of the sample is needed.

*(ii)* It is a specific and sensitive technique.

*(iii)* It is possible to determine the exact molecular formula, and molecular mass and also the molecular structure of the compound with the help of this technique.

*(iv)* Ionization potential and bond strength can be estimated.

*(v)* Qualitative and quantitative analysis can be carried out.

*(vi)* The masses of isotopes can be determined very precisely and their relative abundance can be determined.

*(vii)* Information about the fragmentation pattern of a molecule can be obtained.

*(viii)* Study of fast reaction can be done.

*(ix)* The mass spectrum of each component in a complex mixture can be determined by coupling an appropriate GLC column or capillary electrophoresis column to mass spectrometer.

# *Part Nine*

# BIOTECHNOLOGY

## 9.1 Introduction

**Q. What is Biotechnology?**

**Ans.** Industrial exploitation of biological systems or use of living organisms (microbes) often but not always in industrial processes is called biotechnology. It may involve algae, bacteria, fungi, and yeast, cells of higher plants & animals or subsystems of any of these or isolated components from living matter.

According to European Federation of Biotechnology; it is integrated use of biochemistry; microbiology and engineering sciences in order to achieve technological applications of the capabilities of microorganisms, cultured tissue, cells and parts their off.

**Q. What is Biotechnology by IUPAC?**

**Ans.** The application of biochemistry; biology. microbiology and chemical engineering to industrial processes and products and on environment.

**Q. How the term Biotechnology is derived?**

**Ans.** The term biotechnology is derived from a fusion of biology & technology.

**Q. What is old biotechnology?**

**Ans.** Processes, based on the natural capabilities of micro-organisms are commonly termed as old Biotechnology.

Long before the term "biotechnology" was coined for the process of using living organisms to produce improved commodities, people were utilizing living micro-organisms to produce valuable products. A list of early biotechnology applications follows below.

| | |
|---|---|
| Proving bread with leaven | prehistoric period |
| Fermentation of juices to alcoholic beverages | prehistoric period |
| Knowledge of vinegar formation from fermented juices | prehistoric period |
| Cultivation of vine | before 2000 BC |
| Manufacture of beer in Babylonia and Egypt | 3rd century BC |
| Wine growing promoted by Roman Emperor Marcus Aurelius Probus | 3rd century AD |
| Production of spirits of wine (ethanol) | 1150 |
| Vinegar manufacturing industry | 14th century |

| | |
|---|---|
| Discovery of the fermentation properties of yeast by Erxleben | 1818 |
| Description of lactic acid fermentation by Pasteur | 1857 |
| Detection of fermentation enzymes in yeast by Buchner | 1897 |
| Discovery of penicillin by Fleming | 1928/29 |
| Discovery of many other antibiotics | from about 1945 |

**Q. What is new biotechnology?**

**Ans.** The development of recombinant DNA technology which allows man to modify micro- organisms and other organisms to create in them highly valuable, novel and naturally nonexistent capabilities is called new biotechnology. "Protein engineering, Transgenics, and mass production of protein are results of rDNA

**Q. What is protein engineering?**

**Ans.** Protein engineering involve (a) various types of mutagenesis (to cause changes in specific locations or regions of a gene to produce a new gene product), (b) expression of the new gene to form a stable protein, (c) characterization of the structure and function of the protein produced, and (d) selection of new locations or regions to modify as a result of this characterization.

**Q. What are the commercial implications of biotechnology?**

**Ans.** The commercial implications are that a large number of proteins, existing only in tiny quantities in nature, can now be mass-produced if needed.

**Q. What are transgenic?"**

**Ans.** It has become possible to transform (genetically modify) plants and animals that are important for food production

**Q. Briefly describe the scope & importance of biotechnology in promoting human welfare?**

**Ans.** Biotechnology has a Potential Impact on virtually all domains of human welfare. In recent years revolution in biology has occurred due to potential of biotechnology. Techniques have been developed to produce rare and medicinally valuable molecules; to change hereditary traits of plants and Animals; to diagnose diseases; to produce useful chemicals and; to clean up and restore the environment.

In this way biotechnology has great impact in the fields of health, food; agriculture and environmental protection.

**Q. What is microbial mining?**

**Ans.** Microbes are being employed for the extraction of metals from low grade ores is called microbial mining

**Q. What is bioleaching?**

**Ans.** The mobilization of metal cations from insoluble ores by biological oxidation and Complexation processes is referred to as bioleaching. Metals for which these techniques mainly employed include copper cobalt, nickel, zinc and uranium.

**Q. What is biomining?**

**Ans.** A general term covering both bio-oxidation and bio-leaching techniques can be biomining.

**Q. What is industrial biotechnology?**

**Ans.** The micro- organisms are being employed for the production of a variety of biochemical ranging from alcohol to? and processing of foods and feeds. This type of biotechnology is called Industrial biotechnology.

**Q. What is Bio- Control?**

**Ans.** Control of pathogens with the help of microorganisms is called biocontrol. Several biological agents such as viruses, fungi, amoebae, bacteria etc, are being exploited for the control of plant diseases and insect pests. These are called biopesticides and bioinsecticides.

**Q. What is biosensor?**

**Ans.** BIOSENSOR is an analytical device that brings together an immobilized biological sensing material (e.g. enzyme, antibody, antigen, microbial cell) and a transducer to produce an electronic signal that is proportional to the concentration of a target chemical substance. The signal from the biological material to the transducer may take the form of a charge in parameters such as charge, potential current, heat, light and mass.

**Q. What is sensor?**

**Ans.** Sensor is defined as a measuring device exhibiting a characteristic of an electrical nature (charge, voltage, or current) when it is subjected to some analyses.

**Q. What is transducer?**

**Ans.** A transducer is a physical system that transforms one physical quantity into another, which is function of the first.

**Q. What is bioreceptor?**

**Ans.** In a biosensor the phenomenon is recognized by a biological system called as bioreceptor which is in direct contact with the sample and forms the sensitive component of the biosensor.

**Q. What is biosensor by IUPAC?**

**Ans.** A biosensor is a self contained integrated device that is capable of providing specific quantitative or semi quantitative analytical information using a biological recognition element which is indirect spatial contact with a transduction element.

**Q. What are key factors for the development of biosensor?**

**Ans.** Selectivity and compatibility.

Sensitivity and resolution

Dynamic range

Speed of response

Amenable to testing and calibration

Physical robustness

Insensitivity to interferences like temp environment

Price and reusability

**Q. Write applications of biosensor?**

**Ans.** Clinical diagnosis e.g. blood glucose monitoring

Bioprocess e.g. fermentation control

Microbiology e.g. bacterial and viral analysis

Pharmaceutical and drug analysis

Pollution control and monitoring

Mining industrial and toxic gases

Military application e.g. biological warfare

## 9.2. Recombinant DNA Technology

**Q. Define gene? How it works?**

**Ans.** In modern sense an inherited factor that determines a biological character of an organism .Gene is a part of chromosome and made up of DNA. This is functional unit of hereditary material. It determines the intrinsic capabilities of the cells which forms the basis of Biotechnological processes.

**Q. How does the variation arise in living organisms?**

**Ans.** A low frequency of changes occur in genes naturally (mutations), these mutations are ultimate source of all the heritable variation in living organisms. The second source of variation is recombination b/w genes which occur during the meiotic cell division, during gamete formation.

**Q. What is recombinant DNA? How it is formed?**

**Ans.** A DNA molecule that is created in test tube by ligating together pieces of DNA that is not normally. Contiguous is recombinant molecule.

Restriction enzymes are used for cutting and then joining different DNA fragments.

**Q. What are the objectives of formation of recombinant DNA?**

**Ans.** They are produced with one of the following three objectives,

(1) To obtain a large no. of copies of specific DNA fragment.

(2) To recover large quantities of proteins produced by the concerned gene.

(3) To integrate the gene into the chromosome, where it express itself.

**Q. What is meant by gene cloning?**

**Ans.** Insertion of a fragment of DNA carrying a gene, into a cloning vector, and subsequent propagation of the recombinant DNA molecule in a host organism. Also used to describe those techniques that achieve the same result without the use of cloning vector mean direct gene transfer.

**Q. What is meant by cloning?**

**Ans.** A population of identical cells, generally those containing recombinant DNA molecules is clone, their Production is termed as cloning.

**Q. Define recombinant DNA technology?**

**Ans.** All of the techniques involved in the construction, study and use of recombinant DNA molecules is recombinant DNA technology. It is also termed as gene cloning or genetic engineering.

**Q. Explain the function of restriction endonucleases?**

**Ans.** Endonucleases are the enzymes which produce internal cuts in DNA molecule. A class of endonucleases that cleave DNA only within or near those sites which have specific base sequence; such endonucleases are restriction endonucleases and the sites recognized by them are called recognition sites.

**Q. Explain restriction analysis?**

**Ans.** Determination of the number and sizes of DNA fragments produced when a particular DNA molecule is cut with a restriction endonuclease.

**Q. What is vector?**

**Ans.** A vector is a DNA molecule capable of replication in a host organism, into which a gene is inserted to construct a recombinant DNA molecule.

**Q. What is complementary DNA cloning?**

**Ans.** A cDNA cloning is a cloning technique involving conversion of purified mRNA to DNA Before insertion into a vector.

**Q. What is plasmid?**

**Ans.** A usually circular piece of DNA , primarily independent of the host chromosome often found in bacteria and some other types of cell.

**Q. What Is complimentary DNA library?**

**Ans.** A complimentary DNA library is a population of bacterial transformants in which each mRNA isolated from an organism or tissue is represented as its cDNA in a plasmid or a phage vector.

**Q. Differentiate b/w cloning and Expression vector?**

**Ans.** All vectors used for the propagation of DNA inserted in a suitable host are called cloning vectors. But when a vector is designed for expression i.e. production of the protein specified by the DNA insert , it is termed as expression vector.

## 9.3. Animal Tissue Culture & Hybridoma Technology

**Q. What is tissue culture technology?**

**Ans.** Animal cells can be grown indefinitely in *vitro* like protozoa and other microorganism if we provide suitable nutrient medium. The term tissue culture refers to the culture of whole organs, tissue fragments as well as dispersed cells. It can be divided into (1) Organ culture (2) Cell culture.

**Q. Explain briefly organ culture and cell culture?**

**Ans.** In organ cultures whole embryonic organs or small tissue fragments are cultured in *vitro* in such a manner that they retain their tissue architecture. In contrast, cell culture are obtained by either enzymatic or individual cells or by spontaneous migration of cells from an explant. They are maintained as monolayer or cell suspensions.

**Q. What are research areas in biotechnology depending mostly on cell culture?**

**Ans.** These areas are:

Genetic manipulation which is possible in cells or organs in culture.

Chromosomal analysis of cells derived from womb.

Cell fusion techniques.

Monoclonal antibodies whose production requires cell line culture.

Production of antiviral vaccines.

Cancer research which required the study of uncontrolled cell division in culture.

Study of the effects of toxins and pollutants using cell lines.

**Q. What are primary cultures?**

**Ans.** Freshly isolated cell cultures are called cell culture; they are usually heterogeneous and slow growing, but are more representative of the tissue of their origin both in cell type and properties.

**Q. What are cell lines? Differentiate b/w finite and infinite cell lines?**

**Ans.** Once a freshly isolated cell culture is sub cultured, it gives rise to cell lines, which may die. After several subcultures, these are termed as finite cell lines. Some may continue to grow indefinitely, such lines are called infinite cell lines.

**Q. Write only the name of techniques employed for organ culture?**

**Ans.** Following five types of techniques employed for organ culture,

(1) Plasma clot or watch glass technique.

(2) Raft method.

(3) Agar gel.

(4) Grid method.

(5) Cyclic exposure to medium and gas phase.

**Q. What is meant by living skin equivalent?**

**Ans.** The improvements in the technology have permitted the reconstitution of virtual complete skin i.e. both dermis & epidermis, called living skin equivalent.

**Q. How many types of cells are involved in cell culture?**

**Ans.** The cultured cell may be of three types

(i) Stem cells or Precursor cells.

(ii) Undifferentiated cells.

(iii) Mature differentiated cells.

**Q. What are differentiated cells?**

**Ans.** The cell formed by maturation of precursor cell and they do not have the capacity of division.

**Q. Explain anchorage dependent growth?**

**Ans.** Cells in a culture need a surface to adhere so they can proliferate cells that are unable to adhere to a substrate and unable to divided i.e. their growth is dependent the surface so their growth is anchorage dependent.

**Q. What is hybridoma technology?**

**Ans.** The term hybridoma is applied to fuse cells resulting due to fusion of two types of cells. A hybrid cell obtained by fusing a β- lymphocyte with usually a tumor cell of the antibody forming system. The hybrid cells thus possess the ability to produce antibody due to β- Lymphocyte genome and the capacity for indefinite growth in *vitro* due to tumor cell involved in the fusion. This technology of producing antibodies is called hybridoma technology.

**Q. Define clonal selection?**

**Ans.** When antigen reacts to the cell surface receptor of β-lymphocytes, it proliferates rapidly to yield a population of β-cells all of which produce antibodies of the same specificity, it is called clonal selection.

## 9.4. Animal Biotechnology

**Q. Describe the main products of cell culture?**

**Ans.** Virus, vaccines, high mol.wt proteins like enzymes, hormones, cellular biochemical like interferon & monoclonal antibodies are the main products of animal cell culture.

**Q. What is an antigen?**

**Ans.** Any molecule that includes the production of antibody specific to itself, when it is introduced in the body of animal is called antigen.

**Q. How immunization is produced in an animal? Or describe the basic phenomenon of immunization?**

**Ans.** When an antigen enters in the body of an animal, its antigen determinant ultimately binds to the surface of β- lymphocytes which produce specific antibody. This binding stimulates a rapid proliferation of these lymphocytes, so that their no increases drastically. As a consequence in the blood serum of antibodies specific to concerned antigen increases dramatically. This phenomenon is basis of immunization.

**Q. Define and describe the function of interferon?**

**Ans.** Interferon is protein produced by a cell infected by a virus, and provide protection to other healthy cells from viruses.

**Q. What are recombinant proteins?**

**Ans.** Proteins produced by genes transferred into selected host cell by genetic engineering are called recombinant proteins since they are based on recombinant DNA technology.

**Q. What are hybrid antibodies?**

**Ans.** Antibodies are the protein molecules which provide immunity against the attack of viruses. When antibody molecules are modified or designed using recombinant DNA technology such antibodies are termed as recombinant or hybrid antibody.

**Q. Differentiate b/w immunogenicity and antigenicity?**

**Ans.** Production of antibody in response to antigen, by animal is called immune response and this activity of the antigen is called immunogenicity. In contrast the ability of antigens to interact with antibodies is referred as antigenicity.

**Q.** **Describe the objectives of DNA finger printing?**

**Ans.** DNA finger printing is generally used for the identification of criminals from blood stains, semen etc. and for establishing percentage in cases of dispute.

**Q.** **Define genome map?**

**Ans.** Genome map is defined as a detailed schematic description of the structural and functional organization of all the chromosomes in the genome of an organism. At present we have two types of maps;

(1) Genetic or linkage maps.

(2) Physical maps.

## 9.5. Transgenic Animals

**Q.** **What are transgenic animals?**

**Ans.** Those animals which contains in their genome, a gene or genes introduced by one or the other techquine of transfection, are called transgenic animals.

**Q.** **What is surrogate genetics?**

**Ans.** An approach to carryout genetic analysis using an organism or cell different from whose gene are being studied has been termed as surrogate genetics.

**Q.** **Differentiate b/w a promoter sequence and an enhancer sequence?**

**Ans.** A promoter is the site to which RNA polymerase first binds during the initiation of transcription; the affinity of RNA polymerase to the promoter sequence is several orders of magnitude higher than other DNA sequence. In essence the presence of a promoter sequence is absolutely essence for the transcription of DNA segment, the promoter must be locate at that end of the gene which has the initiation codon AUG. In contrast an enhancer sequence is itself not the site of RNA polymerase binding, but it enhance the activity of promoter located in its neighborhood often up to several kilo bases away.

**Q.** **What is Lipofection?**

**Ans.** The delivery of DNA into cell using liposome is called lipofection.

**Q.** **What is meant by homologous recombination?**

Ans. Homologous recombination is the exchange of identical segments b/w two DNA molecules that have identical or almost identical sequences.

**Q.** **Define co-transfection?**

**Ans.** When two different genes constitutes are mixed and used for transfection, they tend to be integrate together at the same site, this is known as co-transfection.

**Q. What is insertional mutagenesis?**

**Ans.** When integration of a transgene leads to the loss of function of a host gene, it is called insertional mutagenesis.

**Q. What is meant by insert – sensitive speciesism?**

**Ans.** Use of animals in biotechnological research causes greater suffering to the animals , but most people seem to accept some animal suffering to serve the basic insert and welfare of mankind ; this attitude is has been termed as insert sensitive speciesism.

## 9.6. Plant Tissue Culture

**Q. What is organ culture?**

**Ans.** When organized structures like root tips , shoot tips , embryos etc; are cultured invitro to obtain their development as organized structures , it is called organ cultures.

**Q. What is meant by surface sterilization?**

**Ans.** All plant materials to be used for culture are treated with an appropriate sterilizing agent to inactivate the microbes present on their surface, this is called surface sterilization.

**Q. What is meant by dedifferentiation?**

**Ans.** When explants are cultured on a suitable GR (growth regulator) combination, many of its cells undergo division. Even mature and certain differentiated cell undergo changes to become meristematic, this is called dedifferentiation.

**Q. What are suspension cultures?**

**Ans.** Tissues and cells cultured in a liquid medium produce a suspension of single cells and cells clumped of few to many cells, these are called suspension cultures.

**Q. What is meant by cloning?**

**Ans.** A clone of cell consists of all the cells derived through mitosis from a single cell, and the process of obtaining a clone is called cloning.

**Q. What is meant by conditioned medium?**

**Ans.** A medium in which plant cells have been grown for about 48 hrs.

**Q. What is somatic embryogenesis?**

**Ans.** A somatic embryo is an embryo derived from a somatic cell, other than zygote, usually on culture in vitro, and the process is known as somatic embryogenesis.

**Q. What is somatic hybridization?**

**Ans.** Production of hybrid plants through the fusion of protoplast of two different plant species/varieties is called somatic hybridization, and such hybrids are known as somatic hybrids.

**Q. Describe embryo-nurse endosperm technique?**

**Ans.** The young embryos are ordinarily excised and cultured directly on the medium. But often young embryos may prove difficult to culture directly on the medium. In such cases, embryos may be placed on to or implanted into developing endosperms that are cultured in vitro; this techquine is known as embryo-nurse endosperm.

## 9.7. Plant Biotechnology

**Q. What is plant biotechnology? And why plant tissue culture form integral parts of plant biotechnology?**

**Ans.** Plant biotechnology is the generation of useful products or services from plant cells, tissues and often, organs. Such cell, tissues and organs are either continuously maintained in vitro or they pass through a variable phase to enable regeneration from them of complete plants which are ultimately transferred to the field. Therefore plant tissue culture forms an integral part of any plant biotechnology.

**Q. What are advantages of immobilized cell reactions?**

**Ans.** Immobilized cell reactions have following advantages,

(1) No risks of cell wash out.

(2) Low contamination.

(3) Protection of cells from liquid shear.

(4) Better control on cell aggregate size. etc

**Q. What is meant by micro propagation?**

**Ans.** Tissue culture enables rapid clonal propagation of plants. This is usually called micro propagation.

**Q. What is meant by adventitious shoot bud?**

**Ans.** A shoot bud arising anywhere other than a leaf axial or the shoot tip is called adventitious shoot bud.

**Q. Describe the process of thermotherapy.**

**Ans.** Conventially viruses are eliminated by thermotherapy of whole plants in which plants are exposed to temperature b/w 35-40 °C for a few minutes to several weeks depending on the host – viruses combination. Thermotherapy is based on the fact that most viruses are killed at temperature much below those which kill host plants only a small proportion of plants become susceptible to other diseases possibly due to inactivation of their defense mechanisms.

**Q. What is chemotherapy?**

**Ans.** Some chemicals e.g. virazole , cycloheximide etc which interfere with virus multiplication may be added into the culture medium for curing the shoot-tips of viruses , this is known as chemotherapy.

**Q. What are doubled haploid plants?**

**Ans.** The chromosome number of haploid plants is readily doubled by using colchicines, the plant so obtained are called doubled haploids plants.

**Q. How DNA finger print of an individual is prepared?**

**Ans.** A DNA finger print of an individual is prepared by digesting its DNA with a restriction enzyme subjecting the DNA digest to electrophoresis and southern hybridization with a probe specific for highly variable region so that a large amount of polymorphism is generated.

**Q. What is molecular map?**

**Ans.** A linear map of different chromosomes of a species depicting the location of various molecular markers is known as molecular map.

**Q. What are biofertilizers?**

**Ans.** Biofertilizers are organisms that enrich the nutrient quality of soil. The main sources of biofertilizers are bacteria, fungi, and cyanobacteria (blue-green algae). The most striking relationship that these have with plants is symbiosis, in which the partners derive benefits from each other.

**Q. What type of relations plant have with microorganisms.**

**Ans.** Plants have a number of relationships with fungi, bacteria, and algae, the most common of which are with mycorrhiza, rhizobium, and cyanohypheae. These are known to deliver a number of benefits including plant nutrition, disease resistance, and tolerance to adverse soil and climatic conditions. These techniques have proved to be successful biofertilizers that form a health relationship with the roots.

**Q. What is importance of biofertilizers with respect to soil?**

**Ans.** Biofertilizers will help solve such problems as increased salinity of the soil and chemical run-offs from the agricultural fields. Thus, biofertilizers are important if we are to ensure a healthy future for the generations to come.

**Q. What is importance of nitrogen as a plant nutrient?**

**Ans.** Nitrogen is an essential plant nutrient. It is the nutrient that is most commonly deficient, contributing to reduced agricultural yields throughout the world. Molecular nitrogen or dinitrogen ($N_2$) makes up four-fifths of the atmosphere but is metabolically unavailable directly to higher plants or animals.

**Q. What is Biological Nitrogen Fixation (BNF)?**

**Ans.** Nitrogen is available to some species of microorganism through Biological Nitrogen Fixation (BNF) in which atmospheric nitrogen is converted to ammonia by the enzyme nitrogenase.

**Q. What are diazotrophs?**

**Ans.** Microorganisms that fix nitrogen are called diazotrophs.

**Q. What is energy requirement of BNF?**

**Ans.** BNF requires energy. Those microbes that fix nitrogen independent of other organisms are called free living. The free-living diazotrophs require a chemical energy source if non photosynthetic, whereas the photosynthetic diazotrophs utilize light energy. The free-living diazotrophs contribute little fixed nitrogen to agricultural crops.

**Q. What is Associative nitrogen-fixation?**

**Ans.** Associative nitrogen-fixing microorganisms are those diazotrophs that live in close proximity to plant roots (that is, in the rhizosphere or within plants) and can obtain energy materials from the plants. They may make a modest contribution of fixed nitrogen to agriculture and forestry, but quantification of their potential has not been established.

**Q. How symbiotic relationships provide large amounts of nitrogen?**

**Ans.** The symbiotic relationship between diazotrophs called rhizobia and legumes (for example, clover and soybean) can provide large amounts of nitrogen to the plant and can have a significant impact on agriculture.

**Q. Where symbiosis between legumes and the nitrogen-fixing rhizobia occurs?**

**Ans.** The symbiosis between legumes and the nitrogen-fixing rhizobia occurs within nodules mainly on the root and in a few cases on the stem. A similar symbiosis occurs between a number of woody plant species and the diazotrophic actinomycete Frankia.

**Q. How atmospheric nitrogen is reduced to ammonia?**

**Ans.** The plant supplies energy materials to the diazotrophs, which in turn reduce atmospheric nitrogen to ammonia. This ammonia is transferred from the bacteria to the plant to meet the plant's nutritional nitrogen needs for the synthesis of proteins, enzymes, nucleic acids, chlorophyll, and so forth.

## 9.8. Transgenic Plants

**Q. What are transgenic plants?**

**Ans.** The plants obtained through genetic engineering contain a gene or genes through genetic engineering contain a gene or genes are called transgene and plant containing transgene are known as transgenic plants.

**Q. What is meant by electroporation?**

**Ans.** The introduction of DNA into cells by exposing them for very brief periods to high voltage electrical pulses which is thought to induce transient pores in the plasma lemma is called electroporation.

**Q. What is meant by Direct – gene transfers?**

**Ans.** The introduction of DNA into plant cell without the involvement of a biological agent and leading to stable transformation is known as direct-gene transfer.

**Q. Define probes.**

**Ans.** Probes are small (15-30 bases long) nucleotide (DNA/RNA) sequence used to detect the presence of complementary sequence in nucleic acid samples. Both DNA and RNA are used as probes.

**Q. Describe briefly co- suppression of genes.**

**Ans.** Many endogenous plant genes, an over expression of the sense RNA or mRNA surprisingly leads to a drastic reduction in the level of expression of the genes concerned this is called co-suppression.

**Q. What is downstream processing? And why down stream processing from plant is costlier than from micro-organisms?**

**Ans.** Purification of the desired biochemical from the biomass or the culture medium is called downstream processing. It is generally assumed that down stream processing from plant is more difficult and costlier than that from micro-organisms mainly due to the low concentration of recombinant protein in the total biomass.

**Q. What is meant by recombinant vaccines?**

**Ans.** Conventional vaccines consist of attenuated or inactivated pathogens. Increase of many pathogens the gene encoding a critical antigen has been isolated and expressed in bacterial animals, and the recombinant protein so produced is used as a vaccine, such vaccines are called recombinant vaccines.

**Q. Define disarming.**

**Ans.** The detection of genes governing auxin and cytokinin production from t-DNA of a Ti plasmid is known as disarming.

**Q. Describe briefly the slow ripening Tomato.**

**Ans.** In tomato, enzyme polygalacturonase (PG) degrades pectin which is the major component of fruit cell wall. This leads to the softening of fruits and deterioration in fruit quality, transgenic tomatoes have been produced which contain antisense construct of the gene encoding PG. These transgenics show a drastically reduced expression of PG and markedly slower ripening and softening.

**Q. What is micro array?**

**Ans.** An array is an orderly arrangement of samples. A micro array is a tool for analyzing genes expression that consist of a small membrane or glass slide containing samples of genes arranged in a regular pattern.

**Q. What is basic principle of micro array?**

**Ans.** Base pairing and hybridization is the underlying principle.

**Q. What are advantages of micro array?**

**Ans.**
a) miniaturization
b) increased throughput
c) two color comparison
d) more reliable ratios
e) higher density spotting
f) higher sensitivity

**Q. What are applications of micro array?**

**Ans.**
a) Gene discovery
b) determination of gene expression level
c) disease diagnosis
d) drug discovery
e) toxicological research
f) transcriptional array
g) sequence analysis
h) microbial identification
i) biosensors in microbiology

## 9.9. Biotechnology and Health Care

**Q. Define vaccines.**

**Ans.** The prevention of diseases is the most desirable most convenient and highly effective approach to health; this is achieved by vaccination or immunization using biological preparation called vaccines.

**Q. Write the name of some types of vaccines.**

**Ans.**
(1) Conventional vaccines.
(2) Purified antigen vaccines.
(3) Recombinant vaccines.

**Q. Write the important characteristics of an ideal vaccine.**

**Ans.** Following;

(1) It should not be tumerogenic.
(2) It should have very low levels of side effects in normal individuals.
(3) It should not be contaminate the environment.
(4) The technique of vaccination should be simple.

**Q. Write few applications of DNA fingerprinting.**

**Ans.** DNA fingerprinting has application in the clear and precise identification of biological entities . In case of human beings , it can be applied for identification of

(1) Criminals

(2) Victims of murder or accidents

(3) Parents of a child

(4) Genetic disorders etc.

**Q. Write the application of monoclonal antibodies.**

**Ans.** Monoclonal antibody has several therapeutic applications;

(1) To provide passive immunity against diseases

(2) In treatment of diseases like leprosy

(3) To deliver toxin molecules specifically to cancer cell

**Q. Describe some limitations of conventional vaccines or live vaccines.**

**Ans.** These are followings;

(1) In many cases, live vaccines have to be used since killed pathogen vaccines are ineffective.

(2) Live vaccines are generally based on cultured animal cells hence expression tissue culture setup is essential.

(3) Live vaccines are heat labile due to the pathogen inactivation by heat.

**Q. What is antisense oligonucleotide?**

**Ans.** A very effective and specific approach for the treatment of a variety diseases is to design and use oligonucleotides complementary to the $5'$ end of the parasite mRNA; such oligonucleotides are called antisense oligonucleotides.

**Q. What is gene therapy?**

**Ans.** The introduction of normal function gene into cells which contain the defective allele of concerned genetic disorder or an acquired disorder.

**Q. Write application of gene therapy.**

**Ans.** These are following;

(1) Identification of the gene that plays the key role in the development of a genetic disorder

(2) Isolation and cloning of gene

(3) Development of an approach for gene therapy.

**Q. What is PCR?**

**Ans.** PCR stands for Polymerase Chain Reaction. It is a technique used to amplify the number of copies of specific region of DNA.

**Q. What is sequence motif?**

**Ans.** A well conserved easily identified sequence pattern that is characteristic to a particular gene is called signature sequence or sequence motif.

**Q. What is use of signature sequence?**

**Ans.** This signature sequence is used as a mark of identification of a particular DNA.

**Q. What are primers?**

**Ans.** Primer is a short oligonucleotide, synthetic piece of a single stranded DNA that is exactly matched and flanks the stretch of DNA to be amplified.

**Q. What is thermocycler?**

**Ans.** A thermocycler is device that quickly changes temperature from a low one to a high one for the process to move on and is designed to repeat the temperature changes as programmed.

**Q. What is the composition of master mix in PCR reaction?**

**Ans.** Buffer, deoxynucleotide triphosphate NTPs, primers and Taq polymerase that is an enzyme obtained from a bacterium and template DNA that is DNA to be amplified in PCR reaction

**Q. Why Taq Polymerase is used in PCR kinetics?**

**Ans.** Taq Polymerase obtained from, Thermus aquatics is a heat stable enzyme that adds deoxynucleotide to the DNA template.

**Q. What are steps involved in PCR reaction and their corresponding temperatures?**

**Ans.** There is three steps involved in the reaction

Denaturation at 95°C

Annealing at 40-65°C

Extension at 72°C

**Q. What are the PCR additives?**

**Ans.** These include DMSO (dimethyl sulfoxide) betaine, formamide, BSA, and nonionic detergents e.g. Triton X _100, Tween 20, Nonidet p_40 (NP_40)

**Q. What are applications of PCR?**

**Ans.** PCR quickly becomes an essential tool for improving human health and human life, medical research and clinical medicine are profiting from PCR mainly in two areas; detection of infectious disease organisms and detection of variation and mutations in genes, especially human genes. other applications are oncology and forensic medicine.

**Q. What is real time PCR?**

**Ans.** In real time PCR system is based on the detection and quantification of a fluorescent reporter. This signal increases in direct proportion to the amount of PCR product in reaction.

**Q. What are advantages of real time PCR?**

**Ans.** Better precision higher sensitivity higher resolution automated results and different products of similar size can be identified. Numerical results so quantification possible

**Q. What are applications of real time PCR?**

**Ans.** Quantification of gene expression

Array verification

Drug therapy, efficiency or drug monitoring

Viral quantification

Pathogen detection

DNA damage in vitro imaging of cellular processes

Methylation detection

Genotyping

And parental diagnosis or sex determination using single cell isolated from maternal blood or fetal DNA in maternal circumvention

## 9.10. General & Industrial Microbiology

**Q. What is industrial microbiology?**

**Ans.** The use of microbes to obtain a product or service of economic value constitutes or called industrial microbiology.

**Q. What is meant by fermentation?**

**Ans.** Any process mediated by or involving micro-organism in which a product of economic value is obtained is called fermentation.

**Q. What is Pasteur effect?**

**Ans.** In 1861 Pasteur showed that growth and physiology of yeast differs depending on the presence or absence of $O_2$ This phenomenon is known as Pasteur effect.

**Q. Define assay culture.**

**Ans.** The micro-organisms used for assay of the biological activities of microbial products as well as for various screening techniques are known as assay culture.

**Q. What is meant by inoculum development?**

**Ans.** The preparation of a population of micro-organism from a dormant stock culture to active sites of growth that is suitable for inoculum in the final production stage is called inoculum development.

**Q. Define sterilization.**

**Ans.** Sterilization is the process of inactivating or removing all living organisms from a substrate or surface.

**Q. What is biotransformation?**

**Ans.** When an organic compound is modified by simple chemically defined pex, catalyzed by enzymes presence in cells , into a product that is recoverable , it is called biotransformation.

**Q. Write some applications of industrial microbiology?**

**Ans.** These are following,

(1) Metabolite production
(2) Biotransformation
(3) Anaerobic digestion
(4) Recovery of metals etc.

**Q. Write name of different chromatographic procedure?**

**Ans.** These are following,

(1) Adsorption
(2) Ion-exchange
(3) Gel-filtration
(4) Hydrophobic
(5) Affinity
(6) Partition chromatography

**Q. What is mutation and its origin?**

**Ans.** A mutatation is constant hereditary change in the genome that can be induced by chemical agents. Mutations may arise by misreplication i.e. A mistakes at DNA replication b. mispair i.e. mistakes during the DNA damage.

**Q. What is mutatant selection?**

**Ans.** This is the simplest and oldest method and has been used since beginning of human technology more or less unconsciously, and particular in breeding of plants and cereals. That best producing mutant is selected for further propagation.

**Q. What is strain improvement?**

**Ans.** In biotechnology as soon as you have a microorganism available that forms a certain useful product, the aim exists to increase its yield. When from among production strains the best producing are continuously selected out. The procedure involved is strain improvement.

## 9.11. Enzymes Technology

**Q. Define enzymes.**

**Ans.** Enzymes are proteins that catalyzed the chemical reaction.

**Q. What is enzyme technology?**

**Ans.** The use of purified enzymes for generating a useful product or service is called enzymes technology.

**Q. What is co-enzyme?**

**Ans.** Some enzyme possess low molecular weight organic molecule called co-enzyme.

**Q. What is apoenzyme?**

**Ans.** Cofactor and co-enzyme may be covalently or non-covalently attached to the protein molecule called apoenzyme.

**Q. How many classes of enzymes? Write only their names.**

**Ans.** Enzymes have been classified into 6 classes;

(1) Oxidoreductase

(2) Transferase

(3) Hydrolases

(4) Lyases

(5) Isomerases

(6) Ligasesor Synthetases

**Q. How enzymes work?**

**Ans.** An enzyme (E) molecule has highly specific binding site or active site to which its substrate (S)

Bind to produce enzyme-substrate complex (ES). The pex proceeds at the binding cite to produce the products (P), which remain associated with the enzyme. The product is then liberated and the enzyme molecule is an active state to initiate another round of catalysis as depicted in this equation;

$$E + S \longleftrightarrow ES \longleftrightarrow EP \longleftrightarrow E + P$$

Enzymes reduce the overall level of activation energy.

**Q.** **Differentiate b/w enzymes and abzymes.**

**Ans.** Abzymes are antibodies that catalyze specific chemical reactions. Antibodies, by definition have evolved to recognize and bind to the ground state of the molecule they are specific to in contrast enzymes have binding sites that preferentially bind to the transition state of their substrates molecules.

**Q.** **What are extremozymes?**

**Ans.** The enzymes which function optimally under extreme conditions of temperature, ph etc. They are called extremozymes.

**Q.** **Write some applications of enzymes.**

**Ans.** Enzymes are use in industry, medicine, research but important use of enzymes is as follow;

(1) Uses of enzymes in soln
(2) Use of bi-phasic systems
(3) Uses of immobilized enzymes
(4) Biosensors.

**Q.** **What is the chief objective of enzyme engineering?**

**Ans.** The chief objective of enzyme engineering is to produce an enzyme that is more useful for industrial and other applications.

## 9.12. Food & Beverages

**Q.** **What are the advantages of fermented food?**

**Ans.** The advantages of fermented food are following;

(1) Improved flavor
(2) Elimination of undesirable flavor
(3) Improvement in the texture of food
(4) Enhanced nutritional value etc.

**Q.** **What are the three main steps of cheese production?**

**Ans.** The three main steps of cheese production are following;

(1) Coagulum formation
(2) Separation of curd from whey and
(3) Ripening of cheese.

**Q. What is whey?**

**Ans.** The coagulum is heated to 37 °C and cooled. This eliminates the remaining rennet activity and separates, to some extent the watery fluid called whey.

**Q. Why enzymes are used in fruit juice and Brewing industries?**

**Ans.** Enzymes are used in fruit juice and Brewing industries to achieve specific objectives which can not be otherwise achieved.

**Q. Define Beer.**

**Ans.** Beer is an undistilled alcoholic bewerage produced from fermentation of barley malt by yeast especially *S. cerevisiae* or *S. carisbergensis.*

**Q. What is mashing?**

**Ans.** For beer preparation the malt is powered, mixed with warm water at 70 °C and pH 5.0. This is called mashing.

**Q. What are mushrooms?**

**Ans.** Mushrooms are fruiting bodies of certain basidiomycetous. Mushrooms have pleasant flavor and are rich in protein and other nutrients.

**Q. What is single cell protein?**

**Ans.** Biomass produced by unicellular and multicellular organism like Bacteria, Yeast etc is processed and used as human food or animal feed supplement. This biomass is called single cell protein.

**Q. Write some advantages of mushrooms.**

**Ans.** (1) They are delicious to eat & have good flavor

(2) They are rich in protein

(3) They are rich in vitamins etc.

**Q. What is spawn?**

**Ans.** Mushrooms are propagated using spores and for small pieces of the fruiting body, these inoculums are generally called spawn.

**Q. What are applications of biotechnology in food industry?**

**Ans.** Dairy industry use of starter culture in yogurt and cheese production

PCR based diagnosis of food pathogens

Improvement in diacetyl production

Use of whey for ethanol, methane production

Lactic acid gum amino acid, enzymes vitamins oils, single cell protein, and rennin production.

b. production of amino acid for food and feed supplements

c. production of edible for use in confectionary, jams, jellies, canned food, beverages, sauces, ice creams.

d. production of nucleotides as taste and flavor enhancers

e. enzymes in food industry Amylase invertase glucose isomerase and pectnases

f. Intense sweaters aspartame

g. polysaccharides

## 9.13. Fuel Biotechnology

**Q. What is fuel Biotechnology?**

**Ans.** The use of biological agents to convert relatively diffuse and inconvenient to use sources of energy e.g. biomass and sunlight, into more energy dense and convenient to use fuels e.g. methane, ethane, butanol, biodiesel and hydrogen called fuel biotechnology.

**Q. What is meant by biofuels?**

**Ans.** Biologically produced fuels are usually called biofuels.

**Q. What is bio-gas and write its composition?**

**Ans.** Biogas is the mixture of gases produced by anaerobic bacterial digestion of organic matter. Biogas consists of methane and $CO_2$ plus traces of hydrogen and several other gases.

**Q. What is meant by bioethanol?**

**Ans.** Ethanol produced by micro-organisms, is called bioethanol.

**Q. Write only two advantages of ethanol over petrol.**

**Ans:** (1) Ethanol is burnt more completely so hydrocarbon omission is drastically lower then of petrol.

(2) Ethanol has much higher flash point (45 $^0$C) than petrol (130 $^0$C).

**Q. What is meant by flash point?**

**Ans.** Flash point is the temperature at which a substrate catches fire.

**Q. Write three routes for the production of Bioethanol.**

**Ans.**

(1) From starch or sugar crops

(2) From cellulose following enzymatic hydrolysis

(3) From cellulose following chemical hydrolysis.

**Q. What is meant by bio-diesel?**

**Ans.** Diesel like liquid obtained from materials of biological origin is called biodiesel.

**Q. Why is biodesulferization of coal?**

**Ans.** Coal contains sulfur as contamination.biodesulferization of coal by microorganisms improves the quality of coal and oil.

## 9.14. Environmental Biotechnology

**Q. Define environment.**

**Ans.** Environment consists of the sum of all the factors out side an organism. It consists of both Biotic as well as a biotic factor.

**Q. What is pollutant?**

**Ans.** Any product, by – product or residue that cannot be used profitably is known as waste and a waste product is regarded as pollutant.

**Q. What are the objectives of waste treatment?**

**Ans:**

(1) To reduce the amount of organic material remaining in soln phase

(2) To inactivate pathogenic organisms that may be present in the waste.

**Q. What are biotechnological solutions to industrial effluents?**

**Ans.** Biosorption and biodegradation

Electrolytic and biological treatment

Bioremediation

Genotoxicity testing of industrial effluents

**Q. What is bioremediation?**

**Ans.** A process that uses naturally occurring or genetically engineered microorganisms such as yeast , fungi, and bacteria to transfer harmful substances into less toxic or non toxic compounds

**Q. What is biodegradation?**

**Ans.** Microbial degradation or breakdown of a variety of organic compounds by utilizing the contaminants as carbon and energy source.

**Q. What are characteristics of oil degrading bacteria?**

**Ans.**

a. ability to adhere to hydrocarbons (insoluble in water)

b. emulsifier producing potential

c. mechanism of desorption

**Q.** **What is desorption?**

**Ans.** It is moving of bacteria from depleted oil droplet to another one.

**Q.** **What is eutrophication?**

**Ans.** Waste water contributes organic materials and inorganic nutrients to river water. This is called eutrophication.

**Q.** **What is the principle of microbial inflallibility?**

**Ans.** Micro-organisms have the capability of degrading all naturally occurring compounds. This is known as principle of inflallibility.

**Q.** **What are recalcitrant?**

**Ans.** The compounds that resist biodegradation and thereby persist in the environment are called recalcitrant.

**Q.** **What is meant by gratuitous metabolism?**

**Ans.** Several xenophobic compounds are degraded by an existing pathway and are used by microbes as source of energy and reducing equivalents, this is known as gratuitous metabolism.

## 9.15. Nanobiotechnology

**Q.** **What is meant by Nano science?**

**Ans.** Nano science and nanotechnology involve studying and working with matter on an ultra-small scale. One nanometre is one-millionth of a millimeter and a single human hair is around 80,000 nanometers in width.

**Q.** **What is stretch of the technology?**

The technology stretches across the whole spectrum of science, touching medicine, physics, engineering and chemistry. Nanoscale science and technology enables controlled component design and fabrication on atomic and molecular scales. Nano-related research and development unites findings and processes from biotechnology and genetic engineering with chemistry, physics, electronics and materials science with the aim of manufacturing cost-effective innovative products. Nanotechnology has been recognized by leading industrialized countries to be of potential key economic significance in the 21st century.

**Q.** **What is meant by Nanobiotechnology?**

**Ans.** Nanobiotechnology is an emerging area of great scientific and technological opportunity. It is widely recognized as one of the most beneficial areas of nanotechnology to industry and society. Nanobiotechnology applies the tools and measurement techniques of micro and nanoscale physics and chemistry to study biosystems. Nanobiotechnology is beginning to generate remarkable new insights into how biological systems function, essentially on the scale of molecules as machines. Conversely it engenders new classes of micro-and nano-measurement requirements and solutions. Nanobiotechnology is characterized by its highly interdisciplinary nature.

**Q. How nanobiotechnology is characterized by its highly interdisciplinary nature?**

**Ans.** Nano-biotechnology is to a considerable degree an interdisciplinary science: It combines physical laws, chemical procedures and biological principles on the nano-scale.

**Q. What is the Motivation of nanobiotechnology?**

**Ans.** The trend in manufacturing industry toward increasing miniaturization, improving dimensional precision and controlling surface finish is well recognized. Chemical, biological and drug sensors are being developed which combine single molecule sensitivity, monolayer thickness biological sensors with on-chip fluid handling and electronic read-out.

**Q. What is the structure widths of new leading-edge microelectronic devices?**

**Ans.** Structure widths of 0.25 microns are now common in leading-edge microelectronic devices. Lithography lenses used for the manufacture of such devices now approach nanometre-scale form precision and sub-nanometre roughness. Microelectronic and integrated mechanical/ electronic devices (microelectromechanical systems or MEMS) contain thin functional films only a few atom layers in thickness.

**Q. What is important ace of detection and characterization of chemical and biological entities on the nanoscale in analytical science?**

**Ans.** The detection and characterisation of chemical and biological entities on the nanoscale is becoming increasingly important in analytical science. The ultimate challenge in this field is the detection, identification and characterisation of single molecules. The detection of single molecules has several advantages, most notably

a. removal of ensemble averaging phenomena to provide detail about the environment and properties of individual molecules

b. observation of the innate variability of, in particular, biological molecules.

Single Molecule Detection (SMD) is currently the most exciting, challenging and wide-ranging area of physico-chemical study available to researchers.

**Q. What is ongoing work on single molecule scale?**

**Ans.** There are several on-going projects performing scientific study on the single molecule scale in the nanotech, biotech and spectroscopy areas. A new project in the Quantum Metrology Programme is aimed at exploring current capability in at least one measurement technique, to the single molecule detection regime, with a particular emphasis on bio-molecule measurement. A review of candidate techniques has been prepared and experimental work is now in progress at NPL.

**Q. What are techniques involved in single molecule scale in the nanotechnology?**

**Ans.** In particular this has involved the development and use of surface enhanced Raman spectroscopy (SERS) and scanning tunnelling microscopy (STM) to detect biological molecules down to trace, and eventually single molecule, levels. This work has included the production of novel SERS substrates based on colloidal materials

**Q. What are applications of Nano-biotechnology?**

**Ans.** On this field there are already various applications: For example, nano-particles can be used as tools in

a. medical diagnostics

b. therapeutic

c. development of new materials with multi-functional characteristics

d. health products and drug delivery'

e. fabrics

f. automobiles

g. electronics

h. cosmetics

Its high degree of interdisciplinarity on the one hand and the various fields of application on the other hand, make it inevitable for scientists and engineers to acquire additional knowledge in nano-pattern technology and biotechnology.

**Q. What is on chip electronic control of biological and chemical processes?**

**Ans.** Scientists are seeking to achieve electronic control of biological and chemical processes in "lab-on-a-chip" type applications. This is termed as on chip electronic control of biological and chemical processes

**Q. What is the methodology of process?**

**Ans.** The method currently studied is dielectrophoresis. This physical effect allows voltages on micro fabricated electrodes to manipulate living cells in a solution through electric fields, without ever coming into contact with the cells themselves. This effect may be useful for on-chip preparation of biological and chemical specimens before further chemical, electric, and optical analysis occurs, presumably on the same chip.

**Q. What is the effect of these integrations on a single chip?**

**Ans.** Integration of all these functions onto a single chip will ultimately allow cost effective mass production of a new generation of diagnostic and analytical tools.

**Q. What are "bio-bots"?**

**Ans.** Biological cells become attached to silicon or plastic fine structures that mechanically have hinges that allow them to move and bend. Muscles like these could be used in a host of microscopic devices - even to drive miniature electrical generators to power computer chips. These biobots are mini live devices that moves on its own when the cells contract.