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### 1.1 INTRODUCTION TO PLANCK'S QUANTUM THEORY

Planck's Quantum theory was proposed by Max Planck in 1900. This theory explains the nature of black body radiation.

#### *1.1.1 Black Body Radiation*

When solids are heated, they emit radiation over a wider range of wavelengths.

#### *Example*

When an Iron rod is heated in a furnace, it first turns to dull red and then progressively becomes dark red color as the temperature increases. As this is heated further, the radiation emitted becomes blue as the temperature becomes very high. In terms of frequency, it means that the frequency of emitted radiation goes from lower frequency to higher frequency as the temperature increases. The red colour lies in the lower frequency region while blue colour belongs to the higher frequency region of the electromagnetic spectrum.

#### *Definition*

"An ideal body which can emit and absorb radiation of all frequencies is called a *black body*".

The radiation emitted by such bodies is called "*black body radiation*".

## 1.2 ORIGIN OF PLANCK'S QUANTUM THEORY

The variation of frequency for a black body radiation depends on the temperature. At a given temperature, the intensity of radiation is found to increase with an increase in the wavelength of radiation which increases to a maximum value and then decreases with an increase in the wavelength. This phenomenon couldn't be explained with the help of Maxwell's suggestions. Hence, Planck proposed the Planck's quantum theory to explain this phenomenon.

### 1.2.1 Planck's Quantum Theory

When a black body is heated, it emits thermal radiations of different wavelengths (or) frequency. To explain these radiations, Max Planck put forward a theory known as Planck's quantum theory.

The main points of quantum theory are,

- The emission and absorption of the energy by an atom, occurs in the form of radiation, is not a continuous process.
- The emission and absorption of the energy by a body occurs in the form of pockets of energy is called quanta (or) photon.
- The energy of a quantum is directly proportional to the frequency of radiation.

$$E = hv$$

Where,  $v$  is the frequency of radiation and  $h$  is Planck's constant  $= 6.626 \times 10^{-27}$  erg. sec (or)  $6.626 \times 10^{34}$  J.sec.

- A body can radiate (or) absorb energy in whole number multiples of a quantum,  $hv$ ,  $2hv$ ,  $3hv$  ....  $nhv$ . Where ' $v$ ' is the positive integer.

$$E = nhv$$

$$\text{where } v = \frac{c}{\lambda}$$

$$E = nh c/\lambda$$

- Neils Bohr used this theory to explain the structure of atom.

Thus, Planck's quantum theory was able to explain the distribution of intensity of the radiation from black body as a function of frequency (or) wavelength at different temperatures.

## 1.3 DUAL NATURE OF MATTER

In case of light some phenomenon like diffraction and interference can be explained on the basis of its wave character. However, the other phenomenon such as black body radiation and photoelectric effect can be explained only on the basis of its particle nature. Thus, light is said to have a dual character. Such studies on light were made by Einstein in 1905. Louis de Broglie, in 1924 extended the idea of photons to material particles such as electron and he proposed that matter also has a dual character as wave and as particle.

### 1.3.1 Verification of Dual Character

#### 1. Particle character

The particle character of microscopic particles such as electrons can be verified by observing the scintillations produced upon their striking on a fluorescent screen.

#### 2. Wave character

The wave character of microscopic particles such as an electron can be verified by the Davission and Germer experiment. The experiment was originally suggested to verify the wave character of an electron. In this experiment, a beam of electrons obtained from a heated filament is allowed to strike

on a nickel crystal. The nickel crystal operates like a natural grating and a characteristic diffraction pattern is observed on a photographic plate placed behind the crystal. This experiment confirms that the electron is capable of exhibiting diffraction, which is characteristic of a wave. This is how it establishes the wave character of electrons.

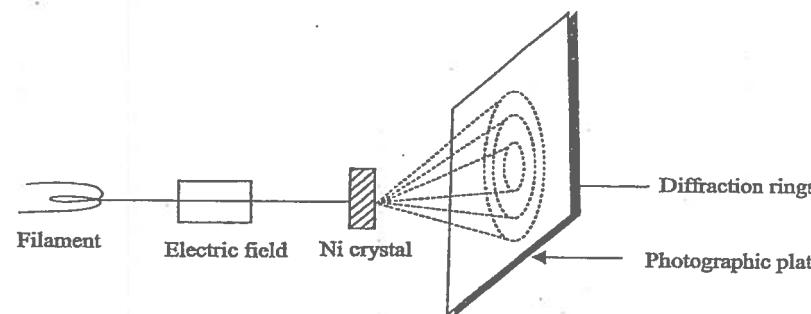


Fig. 1.1 Davission - Germer experimental setup

### 1.3.2 Derivation of de-Broglie Equation

The wavelength of the wave associated with any material particle was calculated by analogy with photon.

According to the Planck's quantum theory, If the photon has wave nature and its energy is given by,

$$E = hv \quad \dots(1)$$

Where,  $v$  is frequency of the wave and ' $h$ ' is Planck's constant

According to Einstein's law of mass energy equivalence, If the photon is supposed to have particle nature, its energy is given by,

$$E = mc^2 \quad \dots(2)$$

Where ' $m$ ' is the mass of photon, ' $c$ ' is the velocity of light.

From equation 1 and 2 we get,

$$hv = mc^2$$

$$\text{But } v = c/\lambda$$

$$h c/\lambda = mc^2$$

$$(\text{or}) \lambda = h/mc$$

The above equation is applicable to material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle.

Thus, for any material particle like electron

$$\lambda = h/mv \quad (\text{or}) \lambda = h/p$$

Where,  $p$  is the momentum of the particle.

### 1.3.3 Applications

#### 1. Application to particle having low mass

Let us consider, an electron having low mass,

$$m = 9.11 \times 10^{-27} \text{ gm}$$

$$v = 3 \times 10^{10} \text{ cm/sec.}$$

$$h = 6.626 \times 10^{-27} \text{ erg.sec}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27}}{9.11 \times 10^{-27} \times 3 \times 10^{10}}$$

$$= 0.24 \times 10^{-9} \text{ cm}$$

#### 2. Application to a particle having high mass

Let us consider, an Iron ball having 100 gm mass and move with velocity 1000 cm/sec.

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27}}{100 \times 1000} = 6.626 \times 10^{-32} \text{ cm}$$

De-Broglie wavelength of an Iron ball is low, which indicates that the Iron ball has maximum particle nature.

From the above discussion we concluded that, De-Broglie wave equation is more significant to particles having low mass.

### 3. Application to Bohr's atomic model

According to Bohr's atomic model, the angular momentum of an electron which revolves around the nucleus in an atom is quantised.

$$mvr = \frac{nh}{2\pi}$$

Where,  $mvr$  = angular momentum of an electron

$n = 1, 2, 3 \dots$  etc

$h$  = Planck's constant

Why the angular momentum of an electron is quantised is not explained the Bohr's atomic model. It is explained on the basis of De-Broglie concepts as follows, According to De-Broglie concept, the electron revolves around the nucleus with wave nature in circular path, the perimeter of the circle is equal to  $n\lambda$

$$2\pi r = n\lambda$$

But we know that  $\lambda = h/mv$

$$\therefore \lambda = \frac{2\pi r}{n}$$

$$2\pi r = nh/mv$$

$$mvr = nh/2$$

Thus, an angular momentum of an electron is quantised.

### 1.4 THE SCHRÖDINGER WAVE EQUATION

Consider an electron in an atom. The total energy of it ( $E$ ) is equal to the sum of kinetic energy and potential energy ( $V$ )

$$\Rightarrow E = \frac{1}{2}mv^2 + V$$

$$E = \frac{(mv)^2}{2m} + V = \frac{P^2}{2m} + V$$

$$= \frac{P_x^2 + P_y^2 + P_z^2}{2m} + V \quad \dots(1)$$

where,  $P = mv$  = momentum

This classical quantity  $E$  can be converted into the corresponding quantum mechanical operator for energy by the following replacements.

The operator corresponding to the energy  $E$  is called the **Hamiltonian operator** and is represented by the symbol  $H_{op}$

$$\therefore E \rightarrow H_{op}$$

$$\text{Similarly, } V \rightarrow V$$

$$P_x \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial x}$$

$$P_y \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial y}$$

$$P_z \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial z}$$

... (2)

From equations (1) and (2), we can get

$$\begin{aligned}
 H_{op} &= \frac{1}{2m} \left\{ \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x} \right)^2 + \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial y} \right)^2 + \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial z} \right)^2 \right\} + V \\
 &= \frac{-\hbar^2}{8\pi^2 m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V
 \end{aligned}$$

$$\boxed{H_{op} = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V}$$
 ... (3)

where,  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is **Laplacian operator**.

For Hamiltonian operator, it can be written as

$$\boxed{H_{op} \Psi = E \Psi} \quad \dots (4)$$

From equations (3) and (4),

$$\left( \frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V \right) \Psi = E \Psi$$

$$\text{(or)} \quad \nabla^2 \Psi + \frac{8\pi^2 m}{\hbar^2} (E - V) \Psi = 0$$

The equation (5) is **Schrödinger equation**.

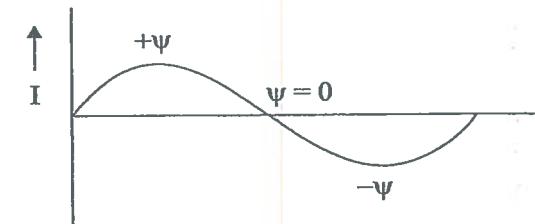
#### 1.4.1 Significance of $\Psi$ and $\Psi^2$

##### 1. Significance of $\Psi$

- (i) It is a solution of Schrödinger equation
- (ii) It represents the amplitude of wave of an electron
- (iii) It describes the variation of amplitude of an electron with direction and distance.
- (iv) Of number of values, only a few are acceptable, which are known as eigen functions.

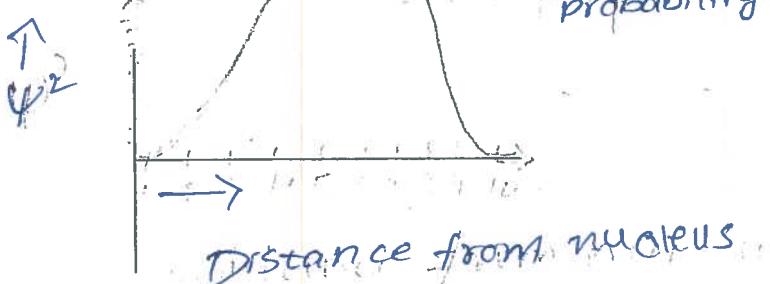
- (v) Each eigen function corresponds to an atomic and molecular orbitals of an atom and a molecule respectively.
- (vi)  $\Psi$  is the wave function. It represents amplitude of intensity of the wave in which electron revolves.

The intensity of the electron cloud is indicated by the formation of crest and trough. They are represented by  $+\Psi$  and  $-\Psi$ . It is zero on the plane at which the wave crosses the axis. But the amplitude must be always +ve and crest be -ve. Therefore the wave function  $\Psi$  is replaced by  $\Psi^2$ .



##### 2. Significance of $\Psi^2$

It represents electron density (or) maximum probability of finding an electron around the nucleus in a three dimensional model. The electron density ( $\Psi^2$ ) around the nucleus is represented in the graph.



From the above diagram, we observe that at nucleus the electron density is minimum. As the distance increases the electron density also increases and reaches a maximum value. It is called **orbital**. After this  $\psi^2$  value is zero. It is called **nodal plane** and again the  $\psi^2$  value increases.)

#### 1.4.2 Applications of Schrödinger Equation to Hydrogen

The hydrogen atom consists of one electron and a proton of charge  $+e$ .

The time-independent form of Schrödinger equation is

$$H_{op} \Psi_{\text{total}} = E_{\text{total}} \Psi_{\text{total}} \quad \dots(1)$$

As the hydrogen atom has two particles viz., proton and electron, the wave function ( $\Psi_{\text{total}}$ ) depends on six co-ordinate variables, three each for proton in nucleus ( $x_n, y_n, z_n$ ) and electron ( $x_e, y_e, z_e$ ). The Hamiltonian operator consists of two terms, viz., the kinetic energy and the potential energy terms. Moreover, the kinetic energy operator has two terms, one for the proton and the other for the electron.

Thus, we have

$$\begin{aligned} H_{op} &= K.E_{op} + V_{op} \\ &= \left( \frac{-h^2}{8\pi^2 m_e} \nabla_e^2 - \frac{-h^2}{8\pi^2 m_n} \nabla_n^2 \right) - \frac{Ze'^2}{r} \quad \dots(2) \end{aligned}$$

Here  $Z=1$  and in S.I. units  $e' = \frac{e}{\sqrt{4\pi\epsilon_0}}$

The Schrödinger equation can be written as

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] \Psi = 0 \quad \dots(3)$$

This equation (3) can be solved by transforming the Cartesian coordinates to spherical coordinates,  $r, \theta, \phi$ .

The Schrödinger equation after transformation into spherical coordinates takes into the following form.

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2} \sin^2 \theta \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2} \sin^2 \theta \frac{\partial^2 \Psi}{\partial \phi^2} \\ + \frac{8\pi^2 m}{h^2} \left( E + \frac{e^2}{r(4\pi\epsilon_0)} \right) = 0 \quad \dots(4) \end{aligned}$$

The wave equation (4) may also be written as a product of three functions. The first one depends on  $r$ , the second on  $\theta$ , and the third on  $\phi$ .

$$\Psi(R\Theta\phi) = R(r)\Theta(\theta)\phi(\phi) \quad \dots(5)$$

Substituting the value of  $\Psi$  from equation (5) in equation (4) and solving it, three ordinary differential equations result. Each differential equation on solving by imposing the boundary conditions leads to the emergence of three quantum numbers, which must be integers.

(a) *The principal quantum number (n)*

It arises from the freedom of electron to vary its distance from the nucleus and have values 1, 2, 3 ...

(b) *The azimuthal quantum number (or) the angular momentum quantum number (l).*

It takes the integral values from 0 to  $(n-1)$ .

The azimuthal quantum number describes the total angular momentum of the electron by the following expression

$$L = \sqrt{l(l+1)} \frac{h}{2\pi}$$

(c) *The magnetic quantum number (m).*

It takes the integral values from  $-l$  to  $+l$ , including zero, giving a total of  $(2l+1)$  values.

The magnetic quantum number describes the  $z$ -component of the angular momentum of the electron by the following equation.

$$L_z = m \left( \frac{h}{2\pi} \right)$$

## 1.5 PARTICLE IN A BOX

Consider the motion of a particle of mass ( $m$ ) along  $x$ -axis and confined between the walls of the container of length  $L$  (figure 1.2). Beyond  $L$ , the potential energy is very high and there will be zero probability of finding the particle.

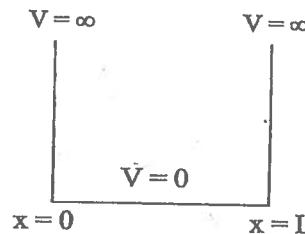


Fig. 1.2 A particle in a one dimensional region

As  $V(x) = \infty$  for  $x < 0$  and  $x > L$

$\therefore \psi^2 = 0$  for  $x < 0$  and  $x > L$

and thus  $\psi = 0$  for  $x \leq 0$  and  $x \geq L$

The potential of it is zero between  $x=0$  and  $x=L$  and rises abruptly to infinity as soon as it touches the walls.

In the region of  $0 < x < L$ , i.e., inside the one dimensional box, the particle is free and the potential energy  $V$  is taken as zero.

$$V(x) = 0 \text{ for } 0 \leq x \leq L$$

$\therefore$  The Schrödinger equation for the motion of the particle is

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots(1)$$

$$\Rightarrow \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \quad [\because V = 0] \quad \dots(2)$$

$$\frac{d^2 \psi}{dx^2} + k^2 \psi = 0 \quad \dots(3)$$

$$\text{Where } k^2 = \frac{8\pi^2 m}{h^2} E$$

Equation (3) is a differential equation whose general solution is

$$\psi = A \cos kx + B \sin kx \quad \dots(4)$$

Hence, the particle inside the box behaves as a free particle.

From equation (4),

$$\psi = A \cos kx + B \sin kx$$

At  $x = 0$ , equation (4) becomes

$$\psi = A \cos 0 + B \sin 0 = A \quad \dots(5)$$

since at  $x = 0$ ,  $\psi = 0$  hence  $\psi = A = 0$

Thus, equation (4) becomes

$$\psi = B \sin kx \quad \dots(6)$$

Imposing second boundary condition,  $\psi \rightarrow 0$  for  $x \rightarrow L$

$$\therefore O = B \sin kL \Rightarrow \sin kL = 0$$

$$\Rightarrow kL = n\pi \Rightarrow k = \frac{n\pi}{L} \quad \dots(7)$$

where,  $n = 1, 2, 3$

From equations (5) and (7), we get

$$E = \frac{k^2 \hbar^2}{2m} = \frac{(n\pi/L)^2 \hbar^2}{2m} = \left( \frac{n^2 \pi^2}{L^2} \frac{\hbar^2}{4\pi^2} \right)$$

$$\Rightarrow E = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, 3, 4 \dots \quad \dots(8)$$

As the constant  $n$  can have only integral values, energy associated with the motion of a particle in a box is *quantized*.

The lowest energy of the particle is, for  $n=1$ , is  $E_1 = \frac{\hbar^2}{8mL^2}$ , it is called as *zero point energy*. If the particle is confined to a region, it is always in motion i.e., have some kinetic energy. As the  $\psi$  is zero at the walls, but smooth, continuous and not zero everywhere, then it must be curved. This curvature in a wave function implies the possession of kinetic energy.

From equation (6) and (7), we get

$$\psi = B \sin \frac{n\pi}{L} x \quad \dots(9)$$

The above wave function contains the undetermined constant  $B$ . Its value can be found out by knowing that total

probability of finding the particle from  $x=0$  to  $x=L$  will be unity.

$$\text{Thus, } \int_0^L \psi \psi^* dx = 1 \quad \dots(10)$$

From equations (9) and (10), we get

$$\int_0^L \left[ B \sin \left( \frac{n\pi}{L} x \right) \right]^2 dx = 1$$

$$\Rightarrow B^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1$$

$$\Rightarrow \frac{B^2}{2} \int_0^L \left[ 1 - \cos \left( \frac{2n\pi x}{L} \right) \right] dx = 1$$

$$\Rightarrow \frac{B^2}{2} \left[ (x)_0^L - \left\{ \frac{\sin \left( \frac{2n\pi x}{L} \right)}{\left( \frac{2n\pi}{L} \right)} \right\}_0^L \right] = 1$$

$$\Rightarrow \frac{B^2}{2} L = 1 \Rightarrow B = \sqrt{\frac{2}{L}} \quad \dots(11)$$

From equations (7) and (10), we have

$$P = \pm k \hbar = \pm \left( \frac{n\pi}{L} \right) \left( \frac{\hbar}{2\pi} \right)$$

$$\Rightarrow P = \pm \frac{nh}{2L} \quad \dots(12)$$

From de-Broglie equation,  $\lambda = \frac{h}{mv} = \frac{h}{P}$

$$\therefore \lambda = \frac{h}{nh/2L} = \frac{2L}{n}$$

$$\Rightarrow L = \frac{n\lambda}{2} \quad \dots(13)$$

Substituting the values of  $B$  from equation (11) in equation (6), we get

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \quad \dots(14)$$

The corresponding energy levels are

$$\Sigma = \frac{n^2 h^2}{8mL^2}$$

S.No.	Wave function ( $\psi$ )	Energy ( $E$ )
1.	$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x$	$E = \frac{h^2}{8mL^2}$ (zero-point energy)
2.	$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x$	$E = \frac{h^2}{2mL^2}$
3.	$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi}{L} x$	$E = \frac{9h^2}{8mL^2}$
4.	$\psi_4 = \sqrt{\frac{2}{L}} \sin \frac{4\pi}{L} x$	$E = \frac{16h^2}{mL^2}$

With the help of above equations we can draw the Fig. 1.3.

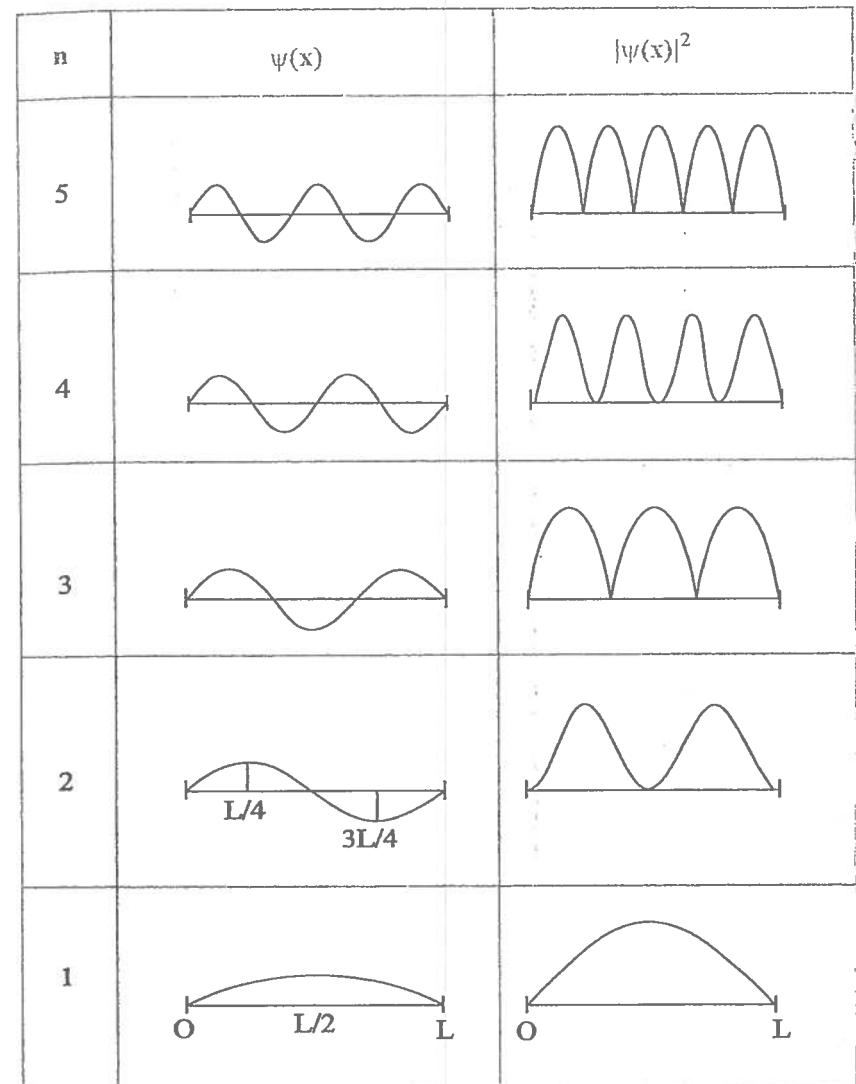


Fig. 1.3 Quantization of Energy Levels in a One-dimensional Box

From the above analysis the following points are concluded.

- (a) Each wave functions goes to zero at the walls of the box and also have zero values at various points within the box. The number of times,  $\psi$  becomes zero is equal to  $(n + 1)$ . The point at which  $\psi = 0$  is known as the *node*.
  - (b) The number of nodes increases with  $n$ .
  - (c) The separation between energy levels with Quantum number 'n' and  $n + 1$  is
- $$E_{n+1} - E_n = (2n + 1) \frac{h^2}{8mL^2}$$
- (d) The probability density is not uniform at all positions. When  $n$  is small, probability density is more, when  $n$  is increased, the distribution becomes more and more uniform. But for very high values of  $n$ , the distribution is completely uniform.

#### 1.5.1 Applications of Particle in a Box for Conjugated Molecules

The particle in a box model can also be applied to electrons moving freely ( $\pi$ - electrons) in a conjugated molecule.

- (a) For example, butadiene has an absorption band at 217 nm for the first  $\pi - \pi^*$  transition.

As a simple approximation, consider butadiene as being a one dimensional box of length  $4 \times 1.4 = 5.6 \text{ \AA}$ . Consider the 4  $\pi$  electrons to occupy the levels calculating using the particle in box model



- (b) The calculated excitation energy is

$$\Delta \epsilon = h\nu = E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$\lambda_{\text{max}} = \frac{hc}{\Delta \epsilon}$$

where,

LUMO = Lowest unoccupied molecular orbital

HOMO = Higher occupied molecular orbital

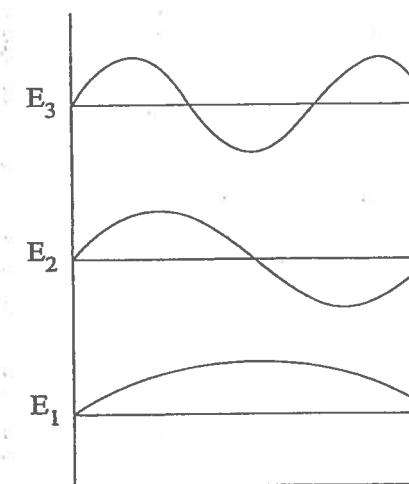


Fig. 1.4 Application of particle in a box for conjugated molecules

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$\Delta E = E_3 - E_2 = (9 - 4) \frac{h^2}{8mL^2} = 5 \frac{h^2}{8mL^2}$$

$$\lambda_{\text{max}} = \frac{hc}{\Delta E}$$

$$\therefore \lambda_{\text{max}} = \frac{8mL^2 hc}{5h^2} = \frac{8mL^2 C}{5h}$$

## 1.6 MOLECULAR ORBITAL THEORY

According to molecular orbital theory, the atomic orbitals of individual atoms combine to form, equivalent number of molecular orbitals. The electrons in molecules are present in the molecular orbitals. These molecular orbitals are filled in the same way as the atomic orbitals in atoms are filled.

### *1.6.1 Bonding and antibonding orbitals*

Two atomic orbitals, one from each bonded atom, overlap to form two molecular orbitals. One of these molecular orbitals is lower in energy than either of the atomic orbitals from which it was formed. This lower energy molecular orbital is called **bonding orbital**. The other molecular orbital is higher in energy and is therefore called **antibonding orbital**. The antibonding orbitals are represented by superscript asterisks (\*).

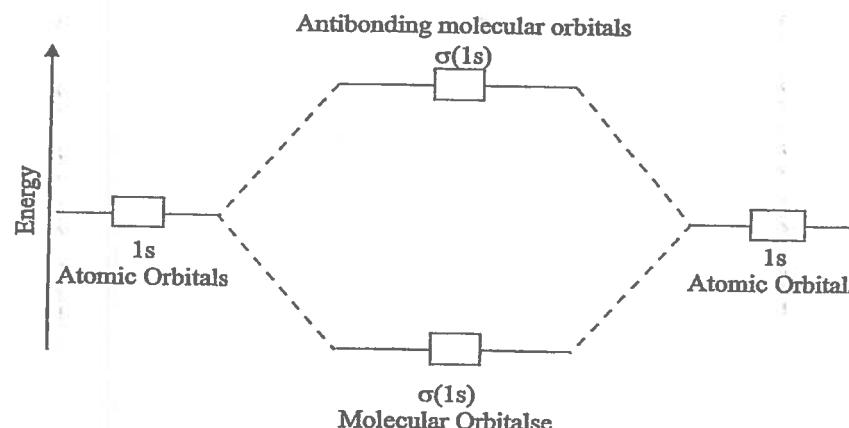


Fig. 1.5 Molecular orbitals arising from 1s atomic orbitals

### Significance of Bonding and Antibonding orbitals

To understand the significance of bonding and antibonding molecular orbitals in terms of wave functions, it

is necessary to know the electronic charge distribution of these orbitals.

The electronic charge distribution can be understood from the derivation of molecular orbitals by the Linear Combination of Atomic Orbitals (LCAO method).

### *1.6.2 Rules for filling electrons in molecular orbitals*

1. Each orbital can hold two electrons. (Pauli's exclusion principle).
2. The electrons enter the various orbitals in the order of increasing energy. (Aufbau principle).

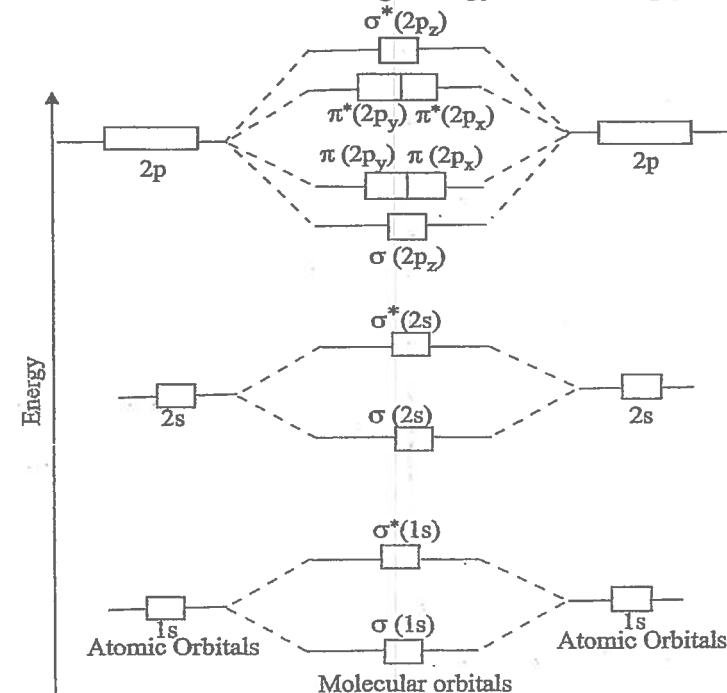


Fig. 1.6 Energy level diagram of MO for simple diatomic molecules

3. It may be noted that  $\pi(2p_y)$  and  $(\pi(2p_x))$  bonding MOs are of equal energy. According to Hund's rule, these orbitals are first singly filled and paring starts only when more electrons are to be accommodated.

## 1.7 BONDING IN HOMONUCLEAR AND HETEROGENUCLEAR DIATOMIC MOLECULES

### 1.7.1 Bonding in Homonuclear Diatomic Molecule

The order of energy levels of the homonuclear MOs is in the order of increasing energy.

$$\begin{aligned}\sigma(1s) &< \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) \\ &< \left\{ \begin{array}{l} \pi(2p_y) \\ \pi(2p_x) \end{array} \right\} < \left\{ \begin{array}{l} \pi^*(2p_y) \\ \pi^*(2p_x) \end{array} \right\} < \sigma^*(2p_z)\end{aligned}$$

### 1.7.2 Bonding in Heteronuclear Diatomic Molecule

The energies of MOs obtained from the mixed atomic orbitals will be somewhat different from the energies of MOs obtained from unmixed AOs. The energy of  $\sigma(2p_z)$  BMO becomes higher, (gets raised) than the energy of  $\pi(2p_x)$  and  $\pi(2p_y)$  BMOs.

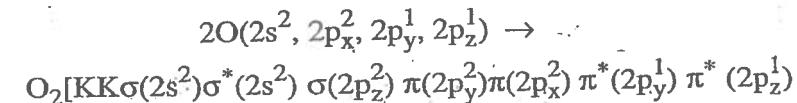
The new sequence of energy levels of the heterogeneous MOs is in the order of increasing energy.

$$\begin{aligned}\sigma(1s) &< \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \left\{ \begin{array}{l} \pi(2p_x) \\ \pi(2p_y) \end{array} \right\} \\ &< \sigma(2p_z) < \left\{ \begin{array}{l} \pi^*(2p_x) \\ \pi^*(2p_y) \end{array} \right\} < \sigma^*(2p_z)\end{aligned}$$

### 1.8 ENERGY LEVEL DIAGRAMS FOR SOME DIATOMIC MOLECULES

#### 1.8.1 Energy Level Diagram of oxygen ( $O_2$ )

Oxygen molecule is formed from the combination of two O-atoms ( $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ ). The outer shell of the O-atom ( $2s^2, 2p_x^2, 2p_y^2, 2p_z^2$ ) contains 6 electrons. Accordingly there are 12 electrons to be accommodated in these two molecular orbitals of  $O_2$ . The electronic configuration of the molecule is represented by the equation.



The molecular orbital energy level diagram for  $O_2$  molecule is shown in fig.1.7

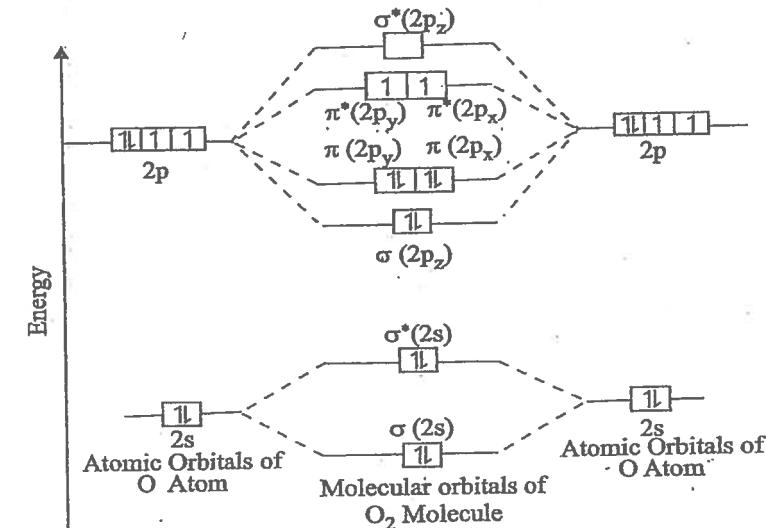


Fig 1.7 Molecular orbital diagram of  $O_2$  molecule

(i) The bond order in  $O_2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8 - 4}{2} = 2$$

Thus, the two oxygen atoms are bonded through two bonds (one  $\sigma$  and other  $\pi$ ). The molecule is stable and exists.

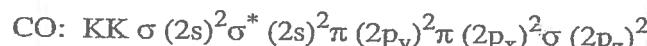
(ii) Magnetic properties

According to Hund's rule, the last two electrons in  $\pi^*(2p_y)$  and  $\pi^*(2p_z)$  orbitals remain unpaired. Therefore the molecule is paramagnetic due to the presence of two unpaired electrons.

### 1.8.2 Energy level diagram of Carbon monoxide (CO)

Carbon monoxide is formed from the combination of one C – atom and one O – atom. The outer shell of the C – atom ( $2s^2, 2p^2$ ) contains 4 electrons and O – atom ( $2s^2, 2p^4$ ) contains 6 electrons in the outer shell. Accordingly there are 10 electrons to be accommodated in the molecular orbitals of CO.

The electronic configuration of CO molecule is represented by the equation.



The molecular orbital energy level diagram for CO molecule is shown in fig. 1.8

(i) The bond order in CO

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8 - 2}{2} = 3$$

Thus, the C – atom and O – atom are bonded through three bonds (one  $\sigma$  and two  $\pi$ ).

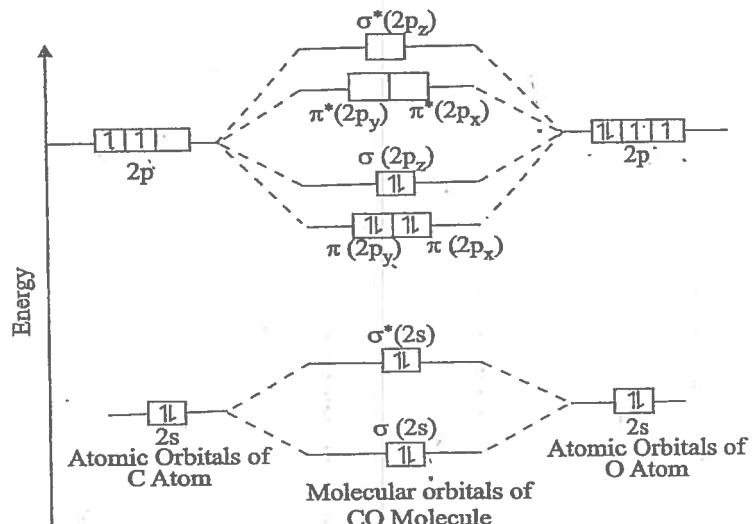


Fig. 1.8 Molecular orbital diagram of CO molecule.

(ii) Bond energy

The bond dissociation energy of CO molecule =  $1067.8 \text{ kJ mol}^{-1}$

(iii) Magnetic properties

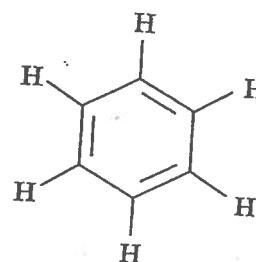
Since no unpaired electron is present in CO molecule. It is diamagnetic.

### 1.9 $\pi$ MOLECULAR ORBITALS OF BENZENE AND BUTADIENE

#### 1.9.1 $\pi$ Molecular Orbitals of Benzene

Benzene ( $C_6H_6$ ) is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached. All carbon-carbon bonds have the same lengths having single and double bonds. There is a delocalized electrons above and below the plane of ring.

1.26 There are six p-orbital electrons that form the stabilizing electron clouds below and above the aromatic ring.



### Molecular orbital description

We know that benzene has a planar hexagonal structure in which all the six carbon atoms are  $sp^2$  hybridized. Of four valence electrons of each carbon atom, three forms covalent bonds with two carbon and one hydrogen atoms. The remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding.

The plus and minus signs, shown in the diagram, do not represent electrostatic charge but refer to phase signs. When the phases, corresponds the orbitals, overlap to generate a common region of like phase, with those orbitals having greatest overlap (e.g.,  $\pi_1$ ) being lowest in energy. The

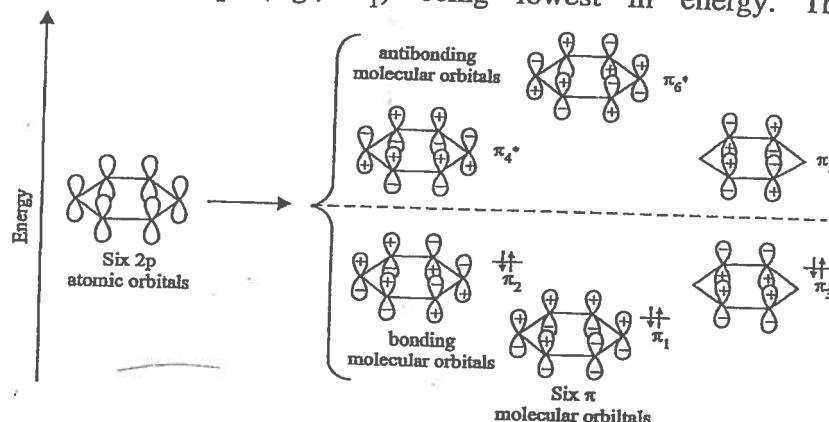


Fig. 1.9  $\pi$  MO of Benzene

remaining carbon valence electrons then occupy these molecular orbitals, in pairs, resulting in a fully occupied set of bonding molecular orbitals.

### 1.9.2 $\pi$ molecular orbitals of butadiene

Butadiene is composed of 4 carbons with two adjacent  $\pi$  bonds. These  $\pi$  bonds are conjugated. All the four P orbitals are aligned with each other and build up into a larger  $\pi$  system. Since butadiene consists of 4 individual p orbitals, the  $\pi$  system of butadiene will contain  $4\pi$  molecular orbitals (containing  $4\pi$  electrons). During filling the lowest energy molecular orbitals get filled first as shown in the diagram.

The molecular orbital diagram of butadiene shows two molecular orbitals.

1. Highest occupied molecular orbital. (HOMO)
2. Lowest unoccupied molecular orbital. (LUMO)

Molecular orbital diagram for Butadiene  $\swarrow \searrow 4\pi$  electrons

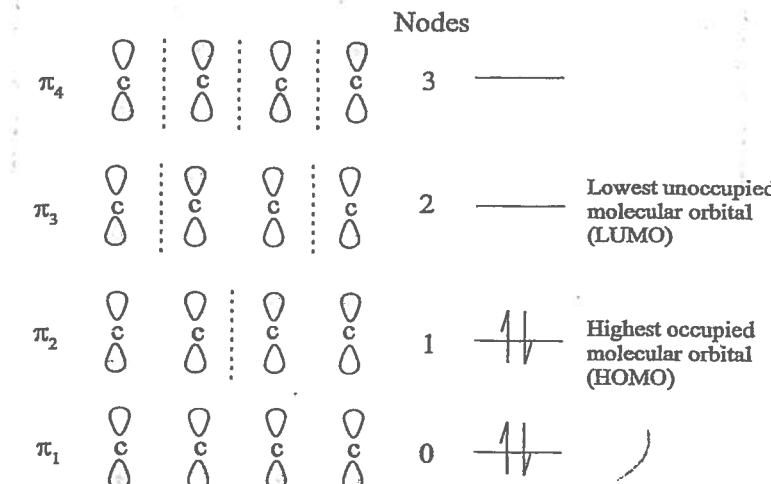


Fig. 1.10  $\pi$  MO of butadiene

### 1. HOMO

HOMO is  $\pi_2$ . It is the valence electrons of the  $\pi$  system. They will be lost readily. If butadiene participates in a reaction, where it is the electron-donor (nucleophile), its electrons are going to come from that orbital.

### 2. LUMO

LUMO is  $\pi_3$ . It is the lowest-energy unoccupied orbital. If butadiene participates in a reaction, where it is the electron acceptor (electrophile), the electrons will be donated to that orbital.

### 1.10 CRYSTAL FIELD THEORY (CFT)

The crystal field theory considers, that the central metal ion is surrounded by an electrical field caused by the ligands. The ligands may be negatively charged (like  $F^-$ ,  $Cl^-$ ,  $CN^-$ , etc.) or neutral molecule (like  $NH_3$ ,  $H_2O$ ) but, must donate a pair of electrons to the metal ion. Thus due to the electrons belonging to the central metal ion and their interaction with the ligand electrons, an electrical field is developed. In the case of transition metals, this electrical field changes the energy of d-orbitals.

#### 1.10.1 Grouping of d-orbitals into two sets

From the shape of d-orbitals, it is clear that, the d-orbitals are grouped into two set of orbitals.

(i)  $e_g$  set of orbitals ( $d_z^2$  and  $d_{x^2-y^2}$ ): It is called doubly degenerate set.

(ii)  $t_{2g}$  set of orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ): It is called triply degenerate set.

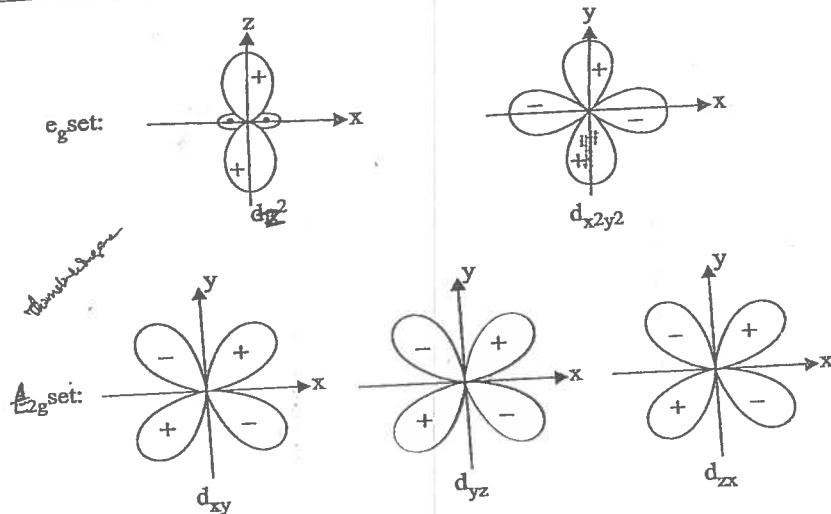


Fig 1.11 Grouping of d-orbitals

#### Explanation

The lobes of  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals are situated somewhat between the axis, whereas the lobes of  $d_{x^2-y^2}$  and  $d_z^2$  orbitals are more concentrated on the axis. Thus when a ligand approaches the central metal ion along the axis,  $d_{x^2-y^2}$  and  $d_z^2$  orbitals will be more affected and suffer larger repulsion than the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals, because of the greater interaction of  $d_{x^2-y^2}$  and  $d_z^2$  orbitals.

#### 1.10.2 Salient features of CFT

1. The metal ion and the ligands act as point charges and the interaction between them is purely electrostatic, i.e., the metal - ligand bonds are 100% ionic.
2. A complex is considered as a combination of central metal ion surrounded by ligands.
3. There is no overlap of metal and ligand orbitals.

4. The d - orbitals of the metal atom which were of the same energy, i.e., degenerate and their degeneracy gets destroyed by ligands when a complex is formed.
5. The ligands in a complex are either negatively charged (or) neutral molecules which have a dipole such that the negative end is closest to the central ion.
6. (The interactions between the electrons of the metal and ligands is purely repulsive) These repulsive forces are responsible for the splitting of the d - orbitals of the metal ion into groups.
7. Different crystal fields will have different effects on the relative energies of the five d - orbitals.

### 1.14 CRYSTAL FIELD SPLITTING OF d-ORBITALS IN OCTAHEDRAL COMPLEXES

In an octahedral complex, the central metal ion is surrounded by six ligands (six lone pairs of electrons) as shown in the figure 1.12.

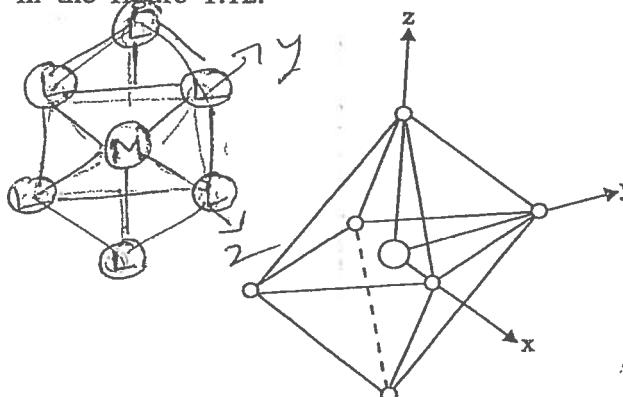


Fig. 1.12 Arrangement of ligands in octahedral complex.

The following two types of electrostatic interaction play an important role in the complex.

#### (i) Attraction

There is an attraction between the positive metal ion and the negative end of a ligand. This force binds the ligands to the central metal ion in the complex.

#### (ii) Repulsion

There is an electrostatic repulsion between the lone pairs of electrons in the ligands and the electrons in the d-orbitals of the metal. The magnitude of this repulsion depends on the particular d-orbitals involved.

(i) We know that the lobes of  $d_{x^2-y^2}$  and  $d_z^2$  orbitals point along the x,y and z axes, where the lone - pair of electrons approach. Thus the electron residing in these orbital will experience a greater repulsion. So the energy of the  $d_{x^2-y^2}$  and  $d_z^2$  orbitals are increased.

(ii) But, the lobes of  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals point in between the axes will experience a lower repulsion. So the energy of  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  are decreased.

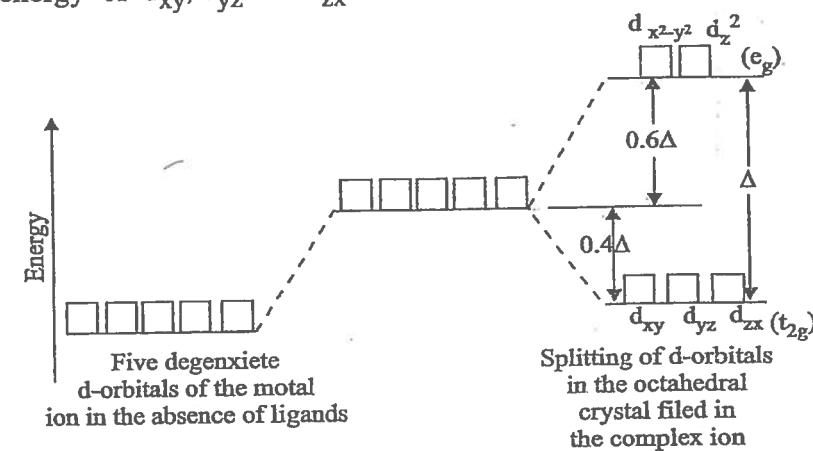


Fig. 1.13. Crystal field splitting of d-orbitals in octahedral complexes.

Thus, the five d-orbitals, which are degenerate (equal energy) in the absence of any ligands, split into two sets of degenerate orbitals,  $t_{2g}$  and  $e_g$  orbitals, as shown in fig. 1.14.

The difference in energy between these two sets of d-orbitals is called the **crystal field splitting** ( $\Delta$  (or)  $10D_q$ ) its magnitude depends on the metal and the nature of the ligands.

The gain in energy by preferential filling up of orbitals by electrons is known as **Crystal Field Stabilization Energy** (CFSE). Greater the amount of CFSE of the complex, greater is its stability.

#### 1.11.1 Filling up of electrons in the orbitals

When more than one d electron is present in octahedral complex, first the electrons tend to enter the more stable  $t_{2g}$  orbitals of lower energy in accordance with Hund's rule of maximum multiplicity, i.e., they enter into different orbitals with their spins parallel before pairing up.

If the metal ion contains more than 3 electrons, it has two options to follow:

(i) It may pair up with the electrons in the  $t_{2g}$  orbitals,  
(or)

(ii) It may enter the higher  $e_g$  orbitals in accordance with Hund's rule of maximum multiplicity.

The chosen path is dependent upon the strength of the ligand.

**Strong and Weak ligand fields (low spin and High spin complexes)**

##### 1. Strong ligand field (low spin)

In a strong ligand field, the electrons pair up, since  $\Delta$  is large enough to force them to do so and fill the  $t_{2g}$  orbitals

(Table 1.1). Thus in the presence of strong ligand field, the complex will be low spin. e.g.,  $[\text{Fe}(\text{CN})_6]^{4-}$

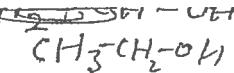
Table 1.1 Arrangement of electrons in octahedral complexes in strong ligand field

$d^x$ ions	Distribution of d-electrons			n
	$t_{2g}$ set	$e_g$ set		
$d^1$	1	—	—	1
$d^2$	1	1	—	2
$d^3$	1	1	1	3
$d^4$	1/1	1	1	2
$d^5$	1/1	1/1	1	1
$d^6$	1/1	1/1	1/1	0
$d^7$	1/1	1/1	1/1	1
$d^8$	1/1	1/1	1/1	2
$d^9$	1/1	1/1	1/1	1
$d^{10}$	1/1	1/1	1/1	0

Where, n = Number of unpaired electrons

##### 2. Weak ligand field (high spin)

In a weak ligand field, since  $\Delta$  is small, it can't force the electrons to pair up and hence the electrons will enter the  $e_g$  orbitals. (Table 1.2) Thus in the presence of weak ligand field, the complex will be high spin. e.g.,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



ate

 $\text{N}_3^-$ 

### Spectrochemical Series

When different ligands are arranged in increasing order of  $\Delta_0$ , we get the spectrochemical series.

(Weak ligand field)  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{EtOH} < (\text{COO})_2^- < \text{H}_2 < \text{EDTA} < \text{NH}_3 < \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2 < \text{NO}_2^- < \text{CN}^- < \text{CO}$  (Strong ligand field).

Table 1.2 Arrangement of electrons in octahedral complexes in weak ligand field.

$d^x$ ions	Distribution of d-electrons					n
	$t_{2g}$ set	$e_g$ set				
$d^1$	1	—	—	—	—	1
$d^2$	1	1	—	—	—	2
$d^3$	1	1	1	—	—	3
$d^4$	1	1	1	1	—	4
$d^5$	1	1	1	1	1	5
$d^6$	1	1	1	1	1	4
$d^7$	1	1	1	1	1	3
$d^8$	1	1	1	1	1	2
$d^9$	1	1	1	1	1	1
$d^{10}$	1	1	1	1	1	0

Where, n = Number of unpaired electrons

Example: Crystal field splitting of  $[\text{Fe}(\text{CN})_6]^{3-}$

In an octahedral complex of  $[\text{Fe}(\text{CN})_6]^{3-}$ , the central metal ion,  $\text{Fe}^{3+}$ , has the electronic configuration of  $3d^5$ . Since the cyanide ion ( $\text{CN}^-$ ) is a strong field ligand, pairing of electrons takes place in the lower d-orbitals ( $t_{2g}$ ) and so a low-spin complex is formed as shown in the figure 1.14.

	3d	4s	4p
Fe (At. No. 26)	1 1 1 1 1	1	
$\text{Fe}^{3+}$	1 1 1 1 1		
But, $\text{Fe}^{3+}$ in $[\text{Fe}(\text{CN})_6]^{3-}$	1 1 1 1 1		

(Strong field)

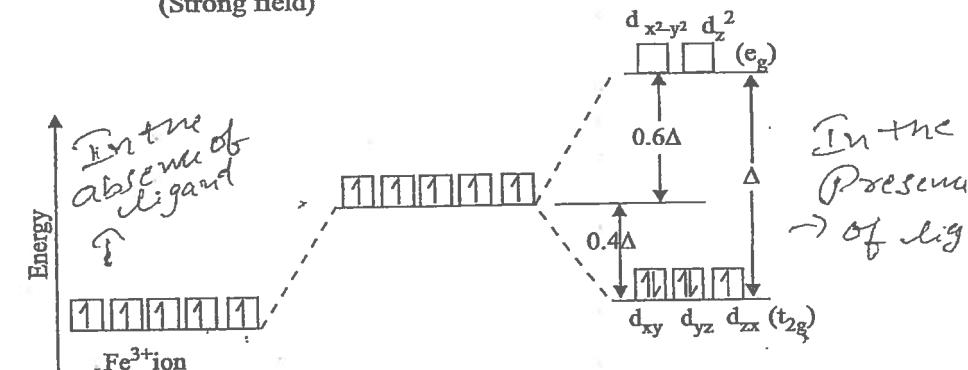


Fig. 1.14 Crystal field splitting of  $[\text{Fe}(\text{CN})_6]^{3-}$  complex

### Magnetic properties

Since the complex has one unpaired electron in the  $t_{2g}$  orbital, this complex is paramagnetic.

### 1.12 CRYSTAL FIELD SPLITTING OF d-ORBITALS IN TETRAHEDRAL COMPLEXES

In the tetrahedral complex, the metal ion is not in the centre of cube and the four alternate corners of the cube are occupied by four ligands as shown in fig 1.15. The directions

of x,y and z axes point to the centres of the faces of the cube.

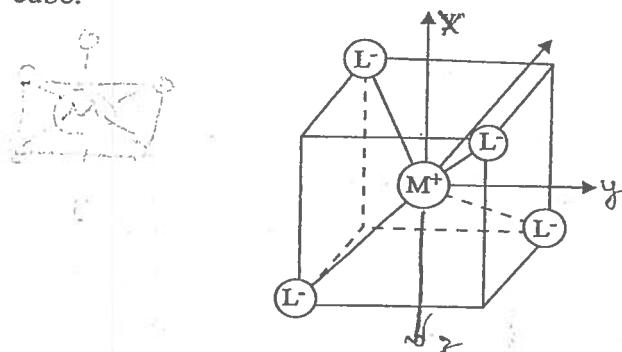


Fig. 1.15 Arrangement of ligands in tetrahedral complex

We know that the lobes of  $e_g$  orbitals point along x, y and z axes (ie., towards the centres of the faces), while the lobes of  $t_{2g}$  orbitals point between x,y and z axes (ie., towards the centres of the edges of the cube).

But, the direction of approach of the four ligands does not coincide exactly with either the  $e_g$  or  $t_{2g}$  orbitals. Any how, the  $t_{2g}$  orbitals are nearer to the direction of the ligands than the  $e_g$  orbitals, so the energy of  $t_{2g}$  orbitals is raised

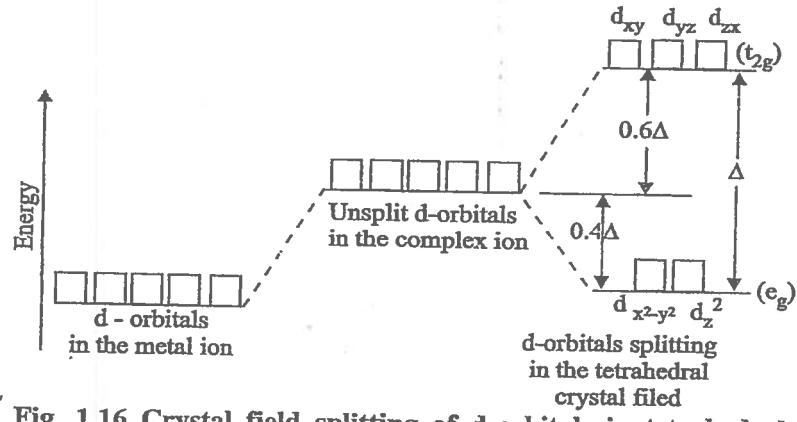


Fig. 1.16 Crystal field splitting of d-orbitals in tetrahedral complexes

maximum. Consequently, crystal field splitting is opposite to that in octahedral complexes takes place. (Fig. 1.17)

Crystal field splitting ( $\Delta_t$ ) of tetrahedral complex is lesser than that in octahedral complex why?

This is due to the following reason

- There are only 4 ligands, so the ligand field is small.
- The direction of the orbitals does not coincide with that of ligands.

Thus, the tetrahedral splitting ( $\Delta_t$ ) is always much smaller than the octahedral splitting ( $\Delta_o$ ). (Tetrahedral complex (iii))

*Example:* Crystal field splitting of  $[\text{CoCl}_4]^{2-}$

In a tetrahedral complex of  $[\text{CoCl}_4]^{2-}$ , the central metal ion,  $\text{Co}^{2+}$ , has the electronic configuration of  $3d^7$

	3d	4s	4p
Co (At. No. 27)	1 1 1 1 1	1	
$\text{Co}^{2+}$	1 1 1 1 1		
But, $\text{Co}^{2+}$ in $[\text{CoCl}_4]^{2-}$	1 1 1 1 1		

(Weak field)

Since chloride ion ( $\text{Cl}^-$ ) is a weak field ligand, it can't force the electrons to pair up in the lower d-orbitals ( $e_g$ ) and so **high spin complex** is formed as shown in the fig.1.17.

#### Magnetic properties

Since the complex has three unpaired electron in the  $t_{2g}$  orbital, this complex is **paramagnetic**.

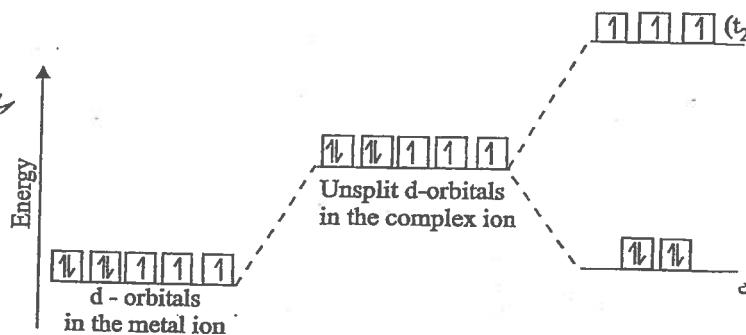


Fig 1.17 Crystal field splitting of  $[\text{CoCl}_4]^{2-}$  complex

### 1.13 MAGNETIC PROPERTIES AND COLOUR OF COMPLEXES BASED ON CFT

#### 1. Colour of transition metal complexes

Most of the complexes of transition metals give absorption bands in the visible region. It means that they are coloured. According to CFT, the colour is due to d - d transition between  $t_{2g}$  and  $e_g$  orbitals. The colour intensity depends upon the magnitude of  $\Delta_o$ .

#### 2. Magnetic properties

##### (a) Diamagnetic

The complexes having paired electrons (i.e., having no unpaired electrons) are said to be diamagnetic.

##### (b) Paramagnetic

The complexes having one or more unpaired electrons are said to be paramagnetic.

CFT is successful in calculating the number of unpaired electrons in high spin and low spin complexes. With the help of number of unpaired electrons, the value of magnetic moment can be calculated using spin only formula,

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

From a knowledge of  $\mu$  value and the unpaired electrons

- (i) the valence state of the central metal ion in octahedral complex
- (ii) the nature of bonding (i.e., whether the complex is high spin (or) low spin) can be known.

### 1.14 BAND THEORY OF SOLIDS

According to the molecular orbital theory, molecular orbitals are formed by the combination of atomic orbitals. The number of molecular orbitals formed are equal to the number of atomic orbitals taking part in molecular orbital formation.

Example: Formation of crystal of Li metal.

In order to understand the band theory of solids, let us imagine the construction of a crystal lithium metal by adding Li-atoms like  $\text{Li}_2$ ,  $\text{Li}_3$ ,  $\text{Li}_4$ , ....  $\text{Li}_N$ .

#### Explanation

The electronic configuration of each Li-atom is  $1s^2, 2s^1, 2p^0$ . The 2s-atomic orbitals overlap in  $\text{Li}_2$  to form two molecular orbitals.

In  $\text{Li}_3$  the 3s - atomic orbitals overlap to form 3 molecular orbitals.

Similarly in  $\text{Li}_N$  the Ns - atomic orbitals overlap to form a band of N closely spaced MO as shown in figure 1.18.

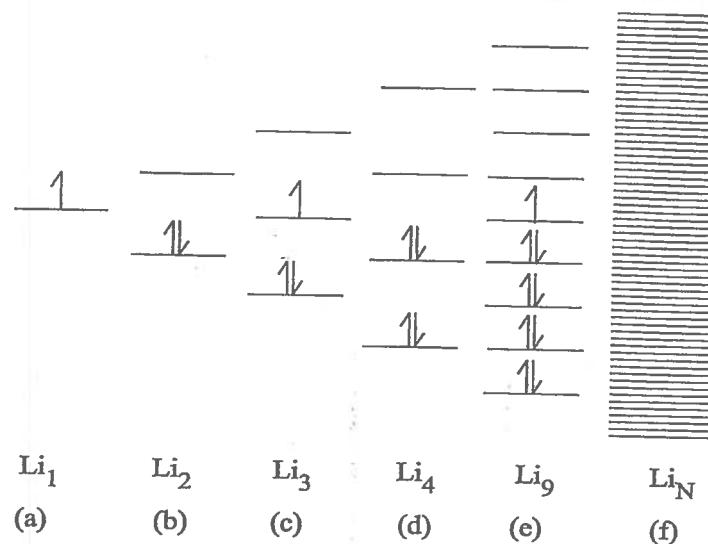


Fig. 1.18 Illustration of band theory of solids

#### 1.14.1 Formation of Various Bands in Solids

##### Example-1

Formation of various bands, can be explained with the example of lithium crystal.

##### 1s band

This is called **non conduction band**. It is formed by the combination of completely filled orbitals.

##### 2s band

This is called **valence band** as it is half filled. The upper half of this band is empty, while the lower half is completely filled. Since the energy difference between these two halves is very small, the electrons can move from lower half to upper half.

##### 2p band

This is called **vacant band (or) overlapping band**. Since 2s and 2p energy levels are close to each other, these two

orbitals can overlap, so that the electrons from 2s orbitals can move to 2p orbitals. Thus it is also called **Conduction band**.

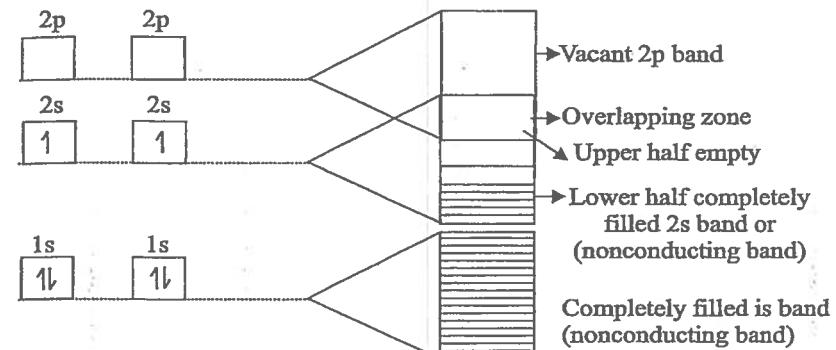


Fig. 1.19 1s band, 2s band and 2p bands in Li crystal

Thus, a band that is either partially filled (or) completely vacant is called **Conduction band**. When an electric field is applied across a lithium crystal, the electrons start moving in one direction and so lithium is a good conductor of electricity.

From the above diagram it is clear that when the number of Li-atoms increase, the spacing between the MO decreases.

##### Example-2

The bands in sodium (Na) metal is shown in the figure 1.22. The sodium crystal possesses the completely filled  $1s^2, 2s^2, 2p^6$  bands. The 3s valence band and 3p vacant band (overlapping band) overlap to form conduction bands.

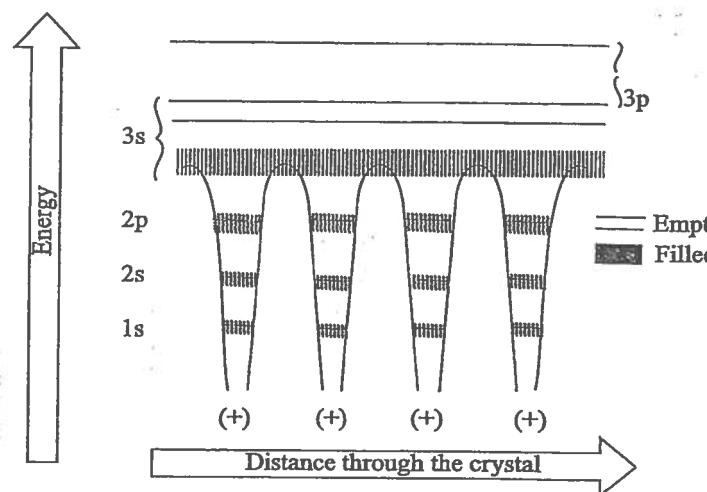


Fig 1.20 Bands in metallic sodium

#### 1.14.2 Classification of materials (solids) based on band gap

The materials are classified into the following 3 categories depending upon the energy gap between the valence and conduction bands.

- (a) Insulators
- (b) Conductors
- (c) Semiconductors

##### 1. Insulators

In insulators (non-metals) there is a large band gap between the filled valence bands and empty conduction bands. Therefore electrons cannot be promoted from the V.B to C.B, where they can't move freely.

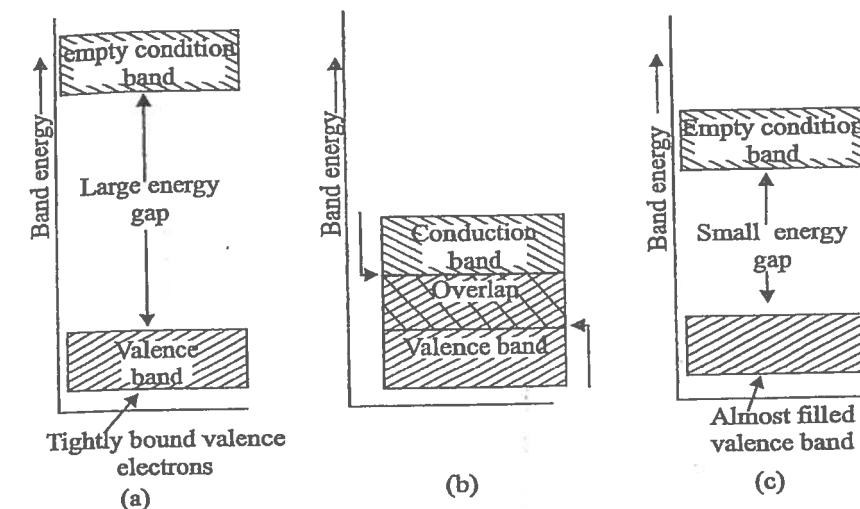


Fig 1.21 Energy band in (a) Insulators (b) Conductors (c) Semiconductors

##### 2. Conductors

In conductors (metals), the valence bands and conduction bands overlap, so there is no band gap. Therefore electrons can freely move.

##### 3. Semiconductors

In semiconductors, there is a small band gap between the filled V.B and empty C.B. Therefore electrons can be promoted from V.B to C.B with rise in temperature (or) by adding dopants.)

#### 1.15 EFFECTS OF DOPING ON CONDUCTANCE

The conductivity of semiconductors is very low at room temperature. Therefore, their conductivity is increased by adding an appropriate amount of suitable impurity. This process is known as doping.

### Doping

The process by which impurity is introduced in semiconductors to enhance their conductivity is called doping. It can be done with an impurity which is electron rich (or) electron deficient. Such impurities introduce electronic defects in them.

#### 1.15.1 Types of Doping

On the basis of impurities, added for doping, semiconductors are of two types:

##### 1. n - Type Semiconductor

###### (Electron-Rich Impurities)

Silicon and germanium belong to group 14 and have four valence electrons each. In their crystals, each atom forms four covalent bonds with its neighbours. (Fig. 1.22)

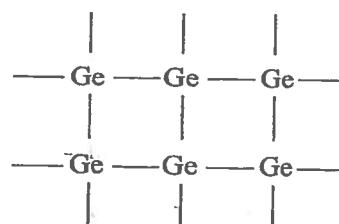


Fig. 1.22 Perfect Ge crystal

When silicon (or) germanium crystal is doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon (or) germanium crystal (Fig. 1.23). Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is not used in bonding thus, it is considered as extra and hence, becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or) germanium. Here, the increase in conductivity is due to negatively charged electrons, hence doped germanium with electron rich impurity is called n-type semiconductor.

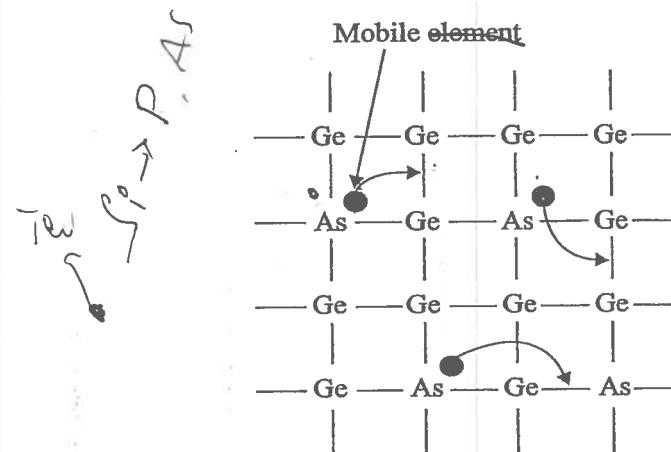


Fig. 1.23 n - type semiconductor

##### 2. p - Type Semiconductor

###### (Electron-Deficit Impurities)

When silicon (or) germanium is doped with a group 13 element like B (or) Al, which contains only 3 valence electrons. In the place of fourth electron, a hole is created. This is called electron hole (or) electron vacancy. (Fig. 1.24)

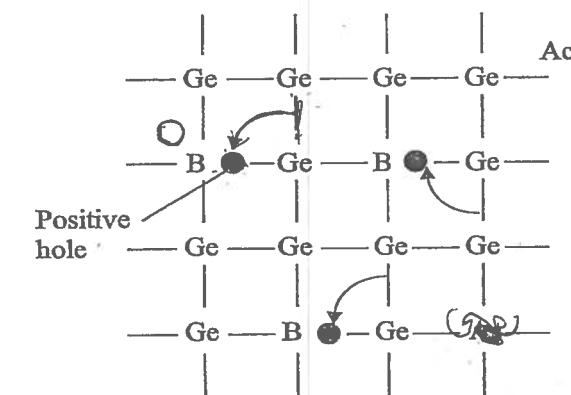


Fig. 1.24 p - type semiconductor

An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position.

In this way, this hole moves through the crystal like positive charge giving rise to electrical conductivity.

When an electric field is applied, the electrons move towards positively charged plate and electron holes move towards the negatively charged plate. Hence, silicon and germanium doped with electron deficit impurities are called p-type semiconductors.

### 1.16 DESCRIPTIVE TYPE QUESTIONS

1. Give Schrödinger wave equation.
2. Explain particle in one dimensional box.
3. Draw and explain MO of  $O_2$ .
4. With a neat diagram explain  $\pi$  molecular orbital of benzene.
5. Explain the features of CFT.
6. Explain with an example crystal field splitting of  $d$ -orbitals in octahedral complexes.
7. Write notes on band theory of solids.
8. Based on the band gap explain conductors, semiconductors and insulators.
9. Explain with neat diagram n-Type and P-Type semiconductors.

## Electrochemistry and Applications

### 2.1 ELECTRODES - CONCEPTS

An electrode is a solid electric conductor that carries electric current into non-metallic solids (or) liquids (or) gases. They are typically good electric conductors.

#### Types of electrodes

1. Anode: Anode is an electrode at which oxidation occurs.
2. Cathode: Cathode is an electrode at which reduction occurs.

#### 2.1.1 Origin of Electrode Potential

A metal (M) consists of metal ions ( $M^{n+}$ ) with valence electrons. When the metal (M) is placed in a solution of its own salt, any one of the following reactions will occur.

- (i) Positive metal ions may pass into the solution.  

$$M \longrightarrow M^{n+} + ne^- \text{ (oxidation)}$$
- (ii) Positive metal ions from the solution may deposit over the metal.  

$$M^{n+} + ne^- \longrightarrow M \text{ (reduction)}$$

The above reactions indicate that the electrodes of a galvanic cell are at different potentials. So, it is necessary to know how potential arises in an electrode.

### 2.1.2 Illustration of Electrode Potential

In order to understand the origin of electrode potential, the following two examples are considered.

#### Example-1 Zn electrode dipped in $ZnSO_4$ solution

When Zn electrode is dipped in  $ZnSO_4$  solution, Zn goes into the solution as  $Zn^{2+}$  ions due to oxidation.



Now, the Zn electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative charges developed on the electrode attract the positive ions from solution. Due to this attraction the positive ions remain close to the metal. (Fig. 2.1.a)

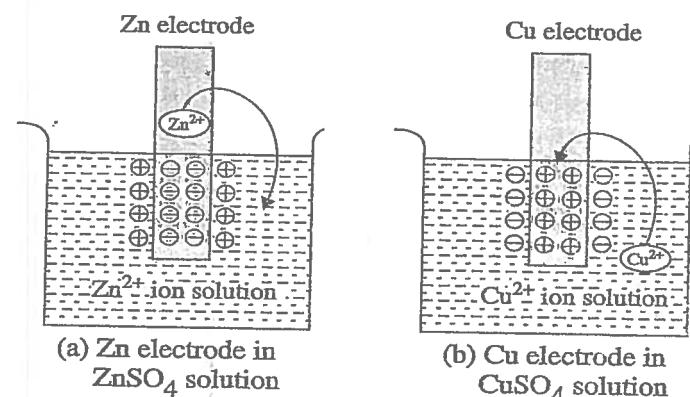


Fig. 2.1 Electrode potential

#### Example -2 Cu electrode dipped in $CuSO_4$ solution

When Cu electrode is dipped in  $CuSO_4$  solution,  $Cu^{2+}$  ions from the solution deposit over the metal due to reduction.



Now, the Cu electrode attains a positive charge, due to the accumulation of  $Cu^{2+}$  ions on the metal. The positive charges developed on the electrode attract the negative ions from solution. Due to this attraction, the negative ions remain close to the metal. (Fig. 2.1.b)

Thus, a sort of layer (positive (or) negative ions) is formed all around the metal. This layer is called **Helmholtz electrical double layer**. This layer prevents further passing of the positive ions from or to the metal. A difference of potential is consequently set up between the metal and the solution. At equilibrium, the potential difference becomes a constant value, which is known as the electrode potential of a metal.

#### Factors affecting electrode potential

The rate of the above reactions depend on

- (i) The nature of the metal.
- (ii) The temperature.
- (iii) The concentration of metal ions in solution.

#### Single electrode potential ( $E$ )

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

#### Standard electrode potential ( $E^\circ$ )

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at  $25^\circ\text{C}$ .

### 2.1.3 Oxidation and Reduction Potentials

#### 1. Oxidation potential

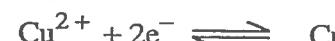
If oxidation occurs at the electrode, at equilibrium, the potential of the electrode is oxidation potential.



Thus, the tendency of an electrode to lose electrons is called the oxidation potential.

## 2. Reduction potential

If reduction occurs at the electrode, at equilibrium, the potential of the electrode is reduction potential.



Thus, the tendency of an electrode to gain electrons is called the reduction potential.

## 2.2 NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following redox reaction



For such a redox reversible reaction, the free energy change ( $\Delta G$ ) and its equilibrium constant ( $K$ ) are interrelated as

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \dots \dots (1)\end{aligned}$$

where,  $\Delta G^\circ$  = Standard free energy change:  $\Delta G^\circ = -RT \ln K$

The above equation (1) is known as Van't Hoff isotherm.

The decrease in free energy ( $-\Delta G$ ) in the above reaction will produce electrical energy. In the cell, if the reaction involves the transfer of ' $n$ ' number of electrons, then ' $n$ ' faraday of electricity will flow. If  $E$  is the emf of the cell, then the total electrical energy ( $nEF$ ) produced in the cell is

$$\begin{aligned}-\Delta G &= nEF \\ (\text{or}) \\ -\Delta G^\circ &= nE^\circ F \quad \dots \dots (2)\end{aligned}$$

where,

- $\Delta G$  = decrease in free energy change
- (or) -  $\Delta G^\circ$  = decrease in standard free energy change

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[\text{M}]}{[\text{M}^{n+}]} \quad \dots \dots (3)$$

Dividing the above equation (3) by  $-nF$

[ ∵ the activity of solid metal  $[\text{M}] = 1$  ]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

$$\text{In general, } E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [\text{M}^{n+}]$$

(or)

$$E = E^\circ + \frac{2.303 RT}{nF} \log [\text{M}^{n+}] \quad \dots \dots (4)$$

When,  $R = 8.314 \text{ J/K/mole}$ ;  $F = 96500 \text{ coulombs}$ ;  $T = 298 \text{ K (25°C)}$ , the above equation becomes

$$E = E_{\text{red}}^\circ + \frac{0.0591}{n} \log [\text{M}^{n+}] \quad \dots \dots (5)$$

In general,  $E = E_{\text{red}}^\circ + \frac{0.0591}{n} \log C$

Similarly for oxidation potential

$$E = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log [M^{n+}] \quad \dots\dots \quad (6)$$

The above equation 5&6 are known as "Nernst equation for single electrode potential".

#### Applications of Nernst equations

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metals can be predicted.

#### 2.2.1 Problems based on Nernst equation

##### Problem 1

What is the potential of a lead electrode that is in contact with a solution of 0.015 M in  $\text{Pb}^{2+}$  ions. Standard electrode potential ( $E^{\circ}$ ) for  $\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$  is 0.13 volt.

##### Solution

Std. oxidation potential is given as



Given

Concentration of  $(\text{Pb}^{2+}) = 0.015 \text{ M}$

$$E^{\circ} = + 0.13 \text{ V}$$

$\therefore$  The Nernst equation for oxidation potential of  $\text{Pb}^{2+}$  is

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log [ \text{Pb}^{2+} ]$$

$$E = E^{\circ} - \frac{0.0591}{n} \log [ \text{Pb}^{2+} ]$$

$$= 0.13 - \frac{0.0591}{2} \log [ 0.015 ]$$

$$= 0.13 - 0.02955 (- 1.824) = 0.13 + 0.0539$$

Oxidation potential of Pb = 0.184 volt.

##### Problem 2

Calculate the electrode potential of zinc electrode dipped in 0.1 M  $\text{ZnSO}_4$  solution at  $25^{\circ}\text{C}$ .

##### Solution

Given

Concentration of  $\text{ZnSO}_4 = 0.1 \text{ M} ; n = 2$

$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = - 0.763 \text{ V} \text{ (Known std. value)} ; E = ?$$

$\therefore$  The nernst equation for reduction potential of  $\text{Zn}^{2+}$  is

$$E = E^{\circ} + \frac{0.0591}{n} \log [ \text{Zn}^{2+} ] \text{ at } 25^{\circ}\text{C}$$

$$= - 0.763 + \frac{0.0591}{2} \log [ 0.1 ]$$

$$= - 0.763 + (- 0.02955)$$

Reduction potential of Zn =  $- 0.79255 \text{ V}$ .

##### Problem 3

Calculate the single electrode potential of zinc in 0.05 M  $\text{ZnSO}_4$  solution at  $25^{\circ}\text{C}$ .  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = 0.763 \text{ V}$ .

**Solution**

Given

Concentration of  $\text{ZnSO}_4 = 0.05 \text{ M}$

$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.763 \text{ V}$$

$$n = 2$$

$\therefore$  Nernst equation for oxidation potential of  $\text{Zn}^{2+}$  is

$$E = E^\circ - \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

$$= 0.763 - \frac{0.0591}{2} \log [0.05]$$

$$= 0.763 - 0.02955(-1.301) = 0.763 + 0.0384$$

Oxidation potential of Zn = 0.8014 V.

**Problem 4**

Calculate the reduction potential of  $\text{Cu}^{2+}/\text{Cu} = 0.5 \text{ M}$  at  $25^\circ\text{C}$ .  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337 \text{ V}$

**Solution**

Given

Concentration of  $[\text{Cu}^{2+}] = 0.5 \text{ M}$

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337 \text{ V}; n = 2$$

$\therefore$  The Nernst equation for reduction potential of  $\text{Cu}^{2+}$  is

$$\therefore E = E^\circ + \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

$$= 0.337 + \frac{0.0591}{2} \log [0.5]$$

$$= 0.337 + 0.02955(-0.3010)$$

$$= 0.337 - 0.0089$$

Reduction potential of Cu = 0.328 V.

**Problem 5**

Find the oxidation potential of  $\text{Zn}/\text{Zn}^{2+} = 0.2 \text{ M}$  electrode at  $25^\circ\text{C}$ . Standard oxidation potential of  $\text{Zn}/\text{Zn}^{2+}$  is 0.763 V.

**Solution**

Given

Concentration of  $[\text{Zn}^{2+}] = 0.2 \text{ M}$

$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.763 \text{ V}$$

$\therefore$  The Nernst equation for oxidation potential of  $\text{Zn}^{2+}$  is

$$E = E^\circ - \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

$$= 0.763 - \frac{0.0591}{2} \log [0.2]$$

$$= 0.763 - 0.02955(-0.69897)$$

$$= 0.763 + 0.02065$$

Oxidation potential of Zn = 0.78365 V.

**Problem 6**

The emf of weston cadmium cell is 0.683 volt at  $25^\circ\text{C}$ . If the reduction potential of mercury electrode is 0.280 V. What would be the oxidation potential at the cadmium electrode?

**Solution**

The Weston Cadmium cell is represented as



$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Hg}^{2+}/\text{Hg}} - E^\circ_{\text{Cd}^{2+}/\text{Cd}}$$

Given

$$E^\circ = 0.683 \text{ V}$$

$$E^\circ_{\text{calomel (right)}} = 0.283 \text{ V}$$

$$E^\circ_{\text{Cd}^{2+}/\text{Cd} \text{ (left)}} = ?$$

$$\therefore 0.683 = 0.283 - E^\circ_{\text{Cd}^{2+}/\text{Cd}}$$

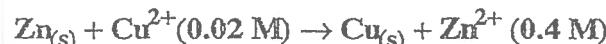
$$E^\circ_{\text{Cd}^{2+}/\text{Cd}} = 0.283 - 0.683 = -0.4 \text{ volt}$$

Reduction potential of cadmium electrode = -0.4 V

But, oxidation potential of cadmium  
(sign must be changed) } = +0.4 V

**Problem 7**

Find the potential of the cell in which the following reactions take place at 25°C.



Given:  $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ ;  $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$

**Solution**

The electrode reaction and the net cell reaction of the above cell is



We know that 2 electrons are involved in the reaction  
i.e.,  $n = 2$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_R - E^\circ_L = E^\circ_{(\text{Cu}^{2+}/\text{Cu})} - E^\circ_{(\text{Zn}^{2+}/\text{Zn})} \\ &= 0.34 - (-0.76) \text{ V} = 1.10 \text{ V} \end{aligned}$$

∴ According to Nernst equation,  $E_{\text{cell}}$  for the given cell

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{2.303 \text{ RT}}{\text{nF}} \log \frac{\text{Zn}^{2+} \text{ (product)}}{\text{Cu}^{2+} \text{ (reactant)}} \\ &= 1.10 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{0.4}{0.02} \\ &= 1.10 - 0.0296 (1.30) \\ &= 1.10 - 0.03848 \end{aligned}$$

Potential of the cell = 1.06 V.

**Problem 8**

Calculate the half cell potential at 298 K for the reaction  $\text{Zn}^{2+} \text{ (aq)} + 2e^- \longrightarrow \text{Zn} \text{ (s)}$  if  $[\text{Zn}^{2+}]$  is 5.0 M and  $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

**Solution**

Given

Concentration of  $[\text{Zn}^{2+}] = 5.0 \text{ M}$

$n = 2$

$$E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

$$E = ?$$

The Nernst equation for reduction potential of  $Zn^{2+}$  is

$$E = E^\circ + \frac{0.0591}{n} \log [Zn^{2+}] \text{ at } 298 \text{ K.}$$

$$= -0.76 + \frac{0.0591}{2} \log [5.0]$$

$$= -0.76 + 0.02955 \times 0.699$$

$$= -0.76 + 0.02066$$

$$= -0.74 \text{ V.}$$

Half cell potential of the cell = -0.74 V

### 2.3 REFERENCE ELECTRODES (OR) STANDARD ELECTRODES

Reference electrode is the electrode the potential of which is known or arbitrarily fixed as zero. The important primary reference electrode used is a standard hydrogen electrode, standard electrode potential of which is taken as zero.

It is very difficult to set up a hydrogen electrode. So other electrodes called secondary reference electrodes like calomel electrodes are used.

#### ~~2.3.1 Saturated calomel electrode (Secondary reference electrode)~~

Construction

Calomel electrode consists of a glass tube containing mercury at the bottom over which mercurous chloride is placed. The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a

platinum wire (Fig. 2.2). The side tube is used for making electrical contact with a salt bridge. The electrode potential of the calomel electrode is +0.2422 V.

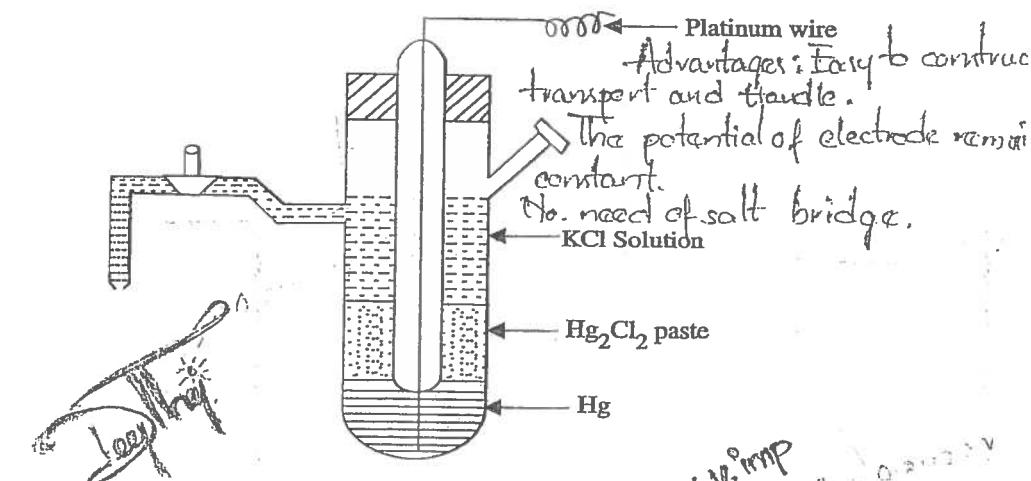


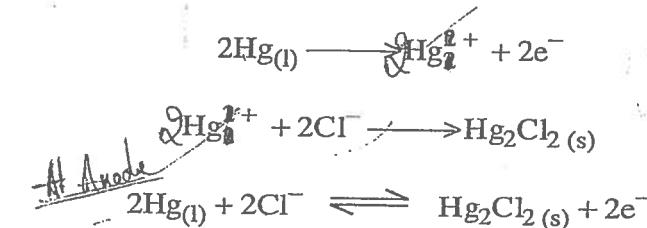
Fig. 2.2 Calomel Electrode *V.N.V. IITP*  
*Hg, Hg<sub>2</sub>Cl<sub>2</sub>(s), KCl (sat.solution); E° = 0.2422 V*

It is represented as,



Anode reaction

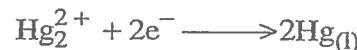
If the electrode acts as anode the reaction is



Cathode reaction

If the electrode acts as cathode the reaction is





The electrode potential is given by (for example cathode)

$$E_{(\text{calomel})} = E^\circ_{(\text{calomel})} - \frac{RT}{2F} \ln a_{\text{Cl}^-}$$

The electrode potential depends on the activity of the chloride ions and it decreases as the activity of the chloride ions increases.

The single electrode potential of the three calomel electrodes on the hydrogen scale at 298 K are given as

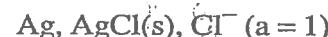
$$0.1 \text{ N KCl} = 0.3338 \text{ V}$$

$$1.0 \text{ N KCl} = 0.2800 \text{ V}$$

$$\text{Saturated KCl} = 0.2422 \text{ V.}$$

### 2.3.2 Silver-Silver Chloride Electrode (Secondary Reference Electrode)

This electrode consists of a silver wire coated with a layer of silver chloride dipping into a solution of a chloride (e.g. KCl or HCl) of unit activity. This is represented as



The electrode reaction is



The electrode potential is given by

$$E_{\text{Ag/AgCl}} = E^\circ_{\text{AgCl}} - \frac{RT}{1 \times F} \ln \frac{1}{a_{\text{Cl}^-}}$$

(Or)

$$E_{\text{Ag/AgCl}} = E^\circ_{\text{Ag/AgCl}} - \frac{RT}{F} \ln \frac{1}{[\text{Cl}^-]}$$

The standard electrode potential with respect to SHE is 0.2224 V at 298 K.

#### Merits of Ag/AgCl Electrode

It is used to measure the pH of the solution.

### 2.3.3 Glass membrane electrodes (Internal Reference Electrode)

#### Construction

A glass membrane electrode is constructed in a similar way to that of pH electrode. consists of thin-walled glass bulb (the glass is a special type having low melting point and high electrical conductivity) containing a Pt wire in 0.1M HCl (Fig. 2.3). The glass electrode is represented as

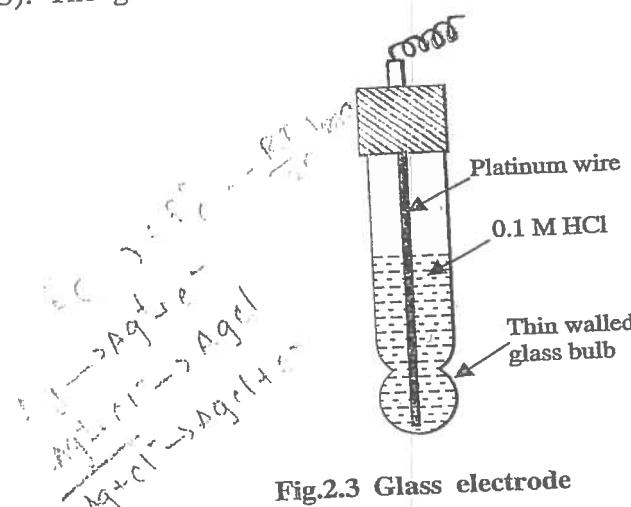


Fig.2.3 Glass electrode

Pt, 0.1 M HCl / Glass

HCl in the bulb furnishes a constant  $\text{H}^+$  ion concentration.

Glass electrode is used as the "internal reference electrode". The pH of the solutions, especially coloured solutions containing oxidizing or reducing agents can be determined. The thin walled glass bulb called glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the  $\text{Na}^+$  ions of glass and  $\text{H}^+$  ions in solution. The potential difference varies with the  $\text{H}^+$  ion concentration, and is given by the expression.

$$\text{E}_G = \text{E}^\circ_G + 0.0592 \text{ V pH.}$$

#### Determination of pH of a Solution using Glass Electrode

The glass electrode is placed in the solution under test and is coupled with saturated calomel electrode as shown in the figure 2.4.

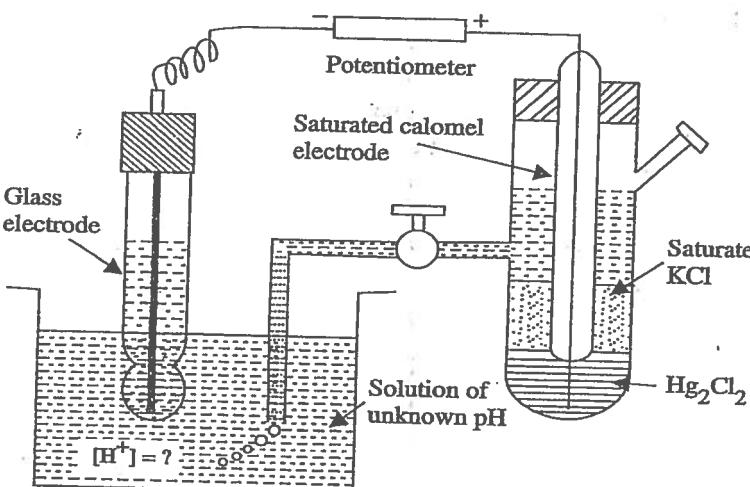


Fig. 2.4 Determination of pH of a solution

The emf of the cell is measured. From the emf, the pH of the solution is calculated as follows.

$$\text{E}_{\text{cell}} = \text{E}_{\text{right}} - \text{E}_{\text{left}}$$

$$\text{E}_{\text{cell}} = \text{E}_{\text{cal}} - \text{E}_{\text{glass}}$$

$$\text{E}_{\text{cell}} = 0.2422 \text{ V} - [\text{E}^\circ_G + 0.0592 \text{ V pH}]$$

$$\text{E}_{\text{cell}} = 0.2422 \text{ V} - \text{E}^\circ_G - 0.0592 \text{ V pH}$$

$$\therefore \text{pH} = \frac{0.2422 \text{ V} - \text{E}^\circ_G - \text{E}_{\text{cell}}}{0.0592 \text{ V}}$$

#### Advantages of Glass Electrode

- (i) It can be easily constructed and readily used.
- (ii) The results are accurate.
- (iii) It is not easily poisoned.
- (iv) Equilibrium is rapidly achieved.

#### Limitations

- (i) Since the resistance is quite high, special electronic potentiometers are employed for measurement.
- (ii) The glass electrode can be used in solutions only with pH range of 0 to 10. However above the pH 12 (high alkalinity), cations of the solution affect the glass and make the electrode useless.

#### 2.4 ELECTROCHEMICAL CELLS OR GALVANIC CELLS

Electrochemical cells are Galvanic cells in which the electrons, transferred due to redox reaction, are converted to electrical energy.

*Example:* Daniel cell (Fig. 2.5)

#### Cell device (*Construction*)

Daniel cell consists of a zinc electrode dipped in 1 M  $\text{ZnSO}_4$  solution and a copper electrode dipped in 1 M  $\text{CuSO}_4$  solution. Each electrode is known as a half cell. The

two solutions are inter connected by a salt bridge and the two electrodes are connected by a wire through the voltmeter.

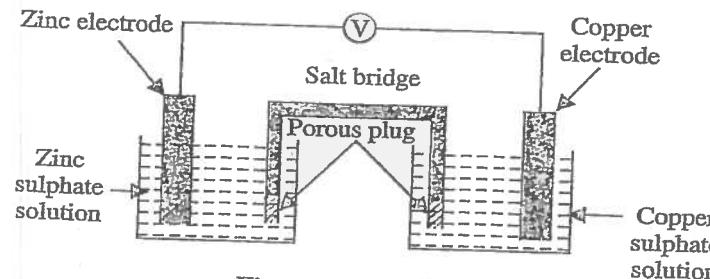
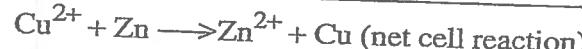
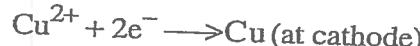
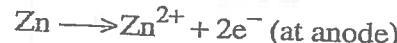


Fig. 2.5 Daniel cell

#### Reactions occurring in the cell

**At anode:** Oxidation takes place in the zinc electrode by the liberation of electrons, so this electrode is called negative electrode or anode.

**At cathode:** Reduction takes place in the copper electrode by the acceptance of electrons, so this electrode is called the positive electrode or cathode.



The electrons liberated by the oxidation reaction flow through the external wire and are consumed by the copper ions at the cathode.

#### Salt bridge

It consists of a U - tube containing saturated solution of  $\text{KCl}$  or  $\text{NH}_4\text{NO}_3$  in agar-agar gel. It connects the two half cells of the galvanic cells.

#### Functions of salt bridge

- (i) It eliminates liquid junction potential.
- (ii) It provides the electrical continuity between the two half cells.

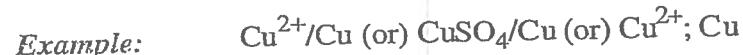
#### 2.4.1 Representation of a galvanic cell (or) Cell diagram

- (i) A galvanic cell consists of two electrodes anode and cathode.
- (ii) The anode is written on the left hand side while the cathode is written on the right hand side.
- (iii) The anode must be written by writing electrode metal first and then electrolyte. These two are separated by a vertical line or a semicolon. The electrolyte may be written by the formula of the compound (or) by ionic species.

#### Examples



- (iv) The cathode must be written by writing electrolyte first and then the electrode metal. These two are separated by a vertical line or a semicolon.



- (v) The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

Using the above representation, the galvanic cell is represented as follows



## 2.5 EMF OF A ELECTROCHEMICAL CELL

### Definition

*Electromotive force is defined as, "the difference of potential which causes flow of electrons from one electrode of higher potential to the other electrode of lower potential.*

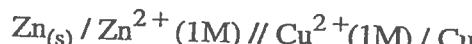
Thus, the emf of a galvanic cell can be calculated by using the following relationship.

$$\text{EMF} = \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of right} \\ \text{hand side electrode} \end{array} \right\} - \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of left} \\ \text{hand side electrode} \end{array} \right\}$$

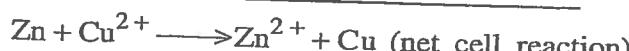
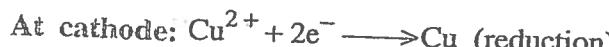
$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

### 2.5.1 Example: Nernst equation for emf of a electrochemical cell

The daniel cell can be represented as



The cell reaction is



The Emf of the cell is given as

$$E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Zn}} \quad \dots (1)$$

We know that

The Nernst equation for reduction potential of Cu

$$E_{\text{Cu}} = E_{\text{Cu}}^\circ + \frac{0.0591}{2} \log [\text{Cu}^{2+}] \quad \dots (2)$$

Similarly, the Nernst equation for reduction potential of Zn

$$E_{\text{Zn}} = E_{\text{Zn}}^\circ + \frac{0.0591}{2} \log [\text{Zn}^{2+}] \quad \dots (3)$$

Substituting equation 2 & 3 in 1, we get,

$$E_{\text{cell}} = (E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ) + \frac{0.0591 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

This is the Nernst equation for emf of a electro chemicial cell (daniel cell).

### 2.5.2 Measurement of emf of a cell

The potential difference or emf of a cell can be measured on the basis of poggendorff's compensation principle. Here the emf of the cell is just opposed or balanced by an (emf standard cell) external emf, so that no current flows in the circuit.

The potentiometer consists of a uniform wire AB (Fig. 2.6). A storage battery (K) is connected to the ends A and B of the wire through a rheostat (R). The cell of unknown emf ( $x$ ) is connected in the circuit by connecting its positive pole to A and the negative pole is connected to a sliding contact (D) through a galvanometer (G). The sliding contact is freely moved along the wire AB till no current flows through the galvanometer. Then the distance AD is measured. The emf of unknown cell is directly proportional to the distance AD.

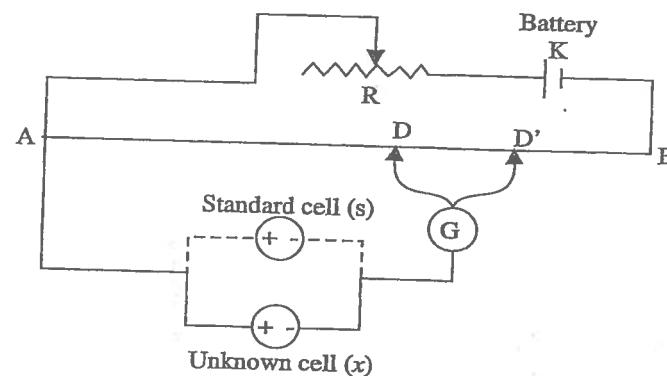


Fig. 2.6 Potentiometer for the measurement of emf

$$E_x \propto AD$$

Then the unknown cell ( $x$ ) is replaced by a standard cell ( $s$ ) in the circuit. The sliding contact is again moved till there is null deflection in the galvanometer. Then the distance  $AD'$  is measured.

The emf of standard cell  $E_s$  is directly proportional to the distance  $AD'$ .

$$E_s \propto AD'$$

Then, the emf of the unknown cell can be calculated from the following equation.

$$\frac{\text{Emf of the unknown cell } x}{\text{Emf of the standard cell } s} = \frac{\text{Length } AD}{\text{Length } AD'}$$

$$\frac{E_x}{E_s} = \frac{AD}{AD'}$$

$$\therefore \text{Emf of the unknown cell } = E_x = \frac{AD}{AD'} \times E_s$$

### 2.5.3 Factors affecting emf of a cell

1. Nature of the electrolytes and electrodes.
2. Concentration and composition of the electrolytes.
3. pH and temperature of the solution.

### 2.5.4 Applications of emf measurements

1. The valency of an ion can be determined
2. Solubility of a sparingly soluble salt can be determined
3. Potentiometric titrations can be carried out.
4. Hydrolysis constant can be determined.
5. Determination of standard free energy change and equilibrium constant
  - (i) The standard free energy change of a reaction can be calculated as follows  $-\Delta G^\circ = nFE^\circ$

where,

$n$  = Number of electrons involved;  $F = 96,500$  coulombs  
 $E^\circ$  = Standard emf of the cell.

- (ii) The equilibrium constant of a reaction can be calculated as follows.

$$E^\circ = \frac{0.0591}{n} \log K$$

$E^\circ$  = Standard emf of the cell;  $K$  = Equilibrium constant

6. Determination of pH by using a standard hydrogen electrode

A hydrogen electrode is introduced into the solution, pH of which is to be determined. It is then coupled with a standard hydrogen electrode through the salt bridge and the emf of the cell is measured. If  $E$  is the emf of the cell.

$$E = \frac{-2.303 RT}{nF} \log [H^+]$$

From the above equation the hydrogen ion concentration or the pH of the solution can be calculated.

### 2.5.5 Problems based on emf (or) Cell potential

#### Problem 1

Calculate the standard emf of the following cell  $Zn/ZnSO_4//CuSO_4/Cu$ . The standard reduction potential of zinc and copper are  $-0.763$  volt and  $+0.34$  volt respectively.

#### Solution

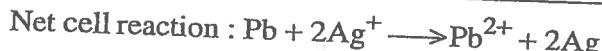
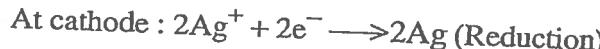
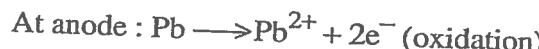
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{right}} - E^\circ_{\text{left}} \\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} \\ &= +0.34 - (-0.763) = 1.103 \text{ volt.} \end{aligned}$$

#### Problem 2

The standard electrode potentials of lead and silver are  $-0.18$  V and  $+0.80$  V respectively. Write down the cell reaction and calculate the emf of the cell.

#### Solution

##### (i) Cell reaction



#### (ii) Emf of the cell

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= +0.80 - (-0.18) = +0.98 \text{ V.} \end{aligned}$$

#### Problem 3

Calculate the emf of iron-copper voltaic cell given the standard electrode potential of copper and iron as  $+0.34$  and  $-0.44$  volt respectively.

#### Solution



Given:  $E^\circ_{\text{right}} = 0.34 \text{ V}$

$E^\circ_{\text{left}} = -0.44 \text{ V}$

$$\begin{aligned} \therefore E^\circ_{\text{cell}} &= E^\circ_{\text{right}} - E^\circ_{\text{left}} = 0.34 - (-0.44) \\ &= 0.34 + 0.44 \\ &= 0.78 \text{ volt} \end{aligned}$$

#### Problem 4

Calculate the emf of the following cell  $Zn/ZnSO_4(1 \text{ M})//CdSO_4(1 \text{ M})/Cd$ .

$E^\circ_{\text{Zn}} = -0.76 \text{ V}; E^\circ_{\text{Cd}} = -0.4 \text{ V}$

#### Solution

$$\begin{aligned} EMF &= E^\circ_{\text{right}} - E^\circ_{\text{left}} \\ &= -0.4 - (-0.76) \\ &= -0.4 + 0.76 \\ EMF &= +0.36 \text{ V.} \end{aligned}$$

## 2.6 POTENTIOMETRIC TITRATIONS

### Principle

Emf of a cell depends on the concentration of the electrolytes with which the electrodes are in contact. Therefore, the electrode reaction is,



As the concentration of  $M^{n+}$  changes, the emf of the cell also changes correspondingly.

Thus, the potentiometric titrations involve the measurement of emf between reference electrode and an indicator electrode, with the addition of the titrant.

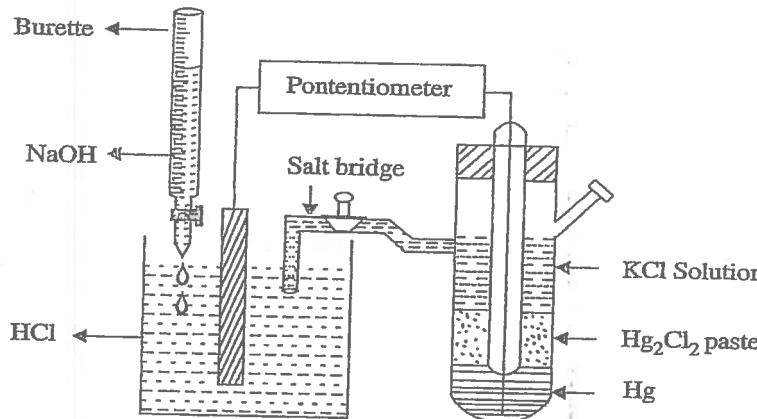
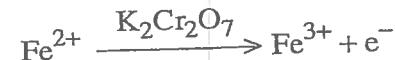


Fig. 2.7 Potentiometric titration

### 2.6.1 Redox titration ( $FeSO_4$ Vs $K_2Cr_2O_7$ )

Known amount of  $FeSO_4$  solution is taken in a beaker and the indicator electrode (platinum electrode) is inserted in it. It is then connected to a reference electrode (calomel electrode), to form a galvanic cell. The cell is then connected to the potentiometer and its  $E_{cell}$  is determined.

When it is titrated against the standard  $K_2Cr_2O_7$  solution, taken in the burette, the emf is going on increasing as the concentration of  $Fe^{3+}$  increases due to the following reaction.



At the end point the emf is suddenly increases. After the end point there is no change in the potential.

When the emf is plotted against the volume of  $K_2Cr_2O_7$  added, a curve of the type shown in figure 2.8 is obtained. The end point is the point, where the slope of the curve is maximum.

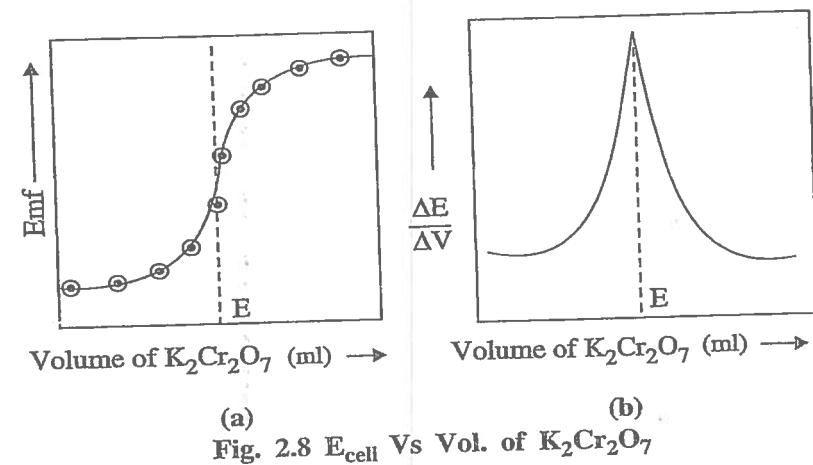


Fig. 2.8  $E_{cell}$  Vs Vol. of  $K_2Cr_2O_7$

A more sensitive and satisfactory method of detecting the end point will be the graph of  $\frac{\Delta E}{\Delta V}$  against volume of  $K_2Cr_2O_7$ . The resulting curve rises to a maximum at the equivalent point, which is the end point.

### 2.6.2 Advantages of potentiometric titrations

1. The necessary apparatus required is cheap and easily available.
2. This method can be used for coloured solution.
3. Fixing up end point is easier when compared to the titrations in which indicators are used to fix up end points.
4. Very dilute solutions can be titrated with accuracy.
5. Several components may be titrated in the same solution.

## 2.7 CONDUCTIVITY (OR) CONDUCTANCE

We know that the electrolyte solutions conduct electrical current through them by the movement of ions to the electrodes. Thus, conductivity (or) conductance of an electrolyte solution is a measure of its ability to conduct electricity. Like metallic conductors electrolytes also obey ohm's law.

### 2.7.1 Concept of conductivity

Electrons play an important role when an electric current passes through a solid material. Similarly ions (cation and anion) also play an important role when a current passes through a liquid such as an aqueous solution. Since conductivity is an indicator of how easily current passes through a solution. The conductivity mainly depends on quantity of ions and their mobility in that solution. Ohm's law provides the fundamental rules for all types of conductivity.

#### 1. Ohm's law

The resistance of a conductor is directly proportional to its length and inversely proportional to its cross sectional area

$$R \propto l \quad \dots (1)$$

$$R \propto \frac{1}{a} \quad \dots (2)$$

### Combining (1) & (2)

$$R \propto \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

Where,  $R$  = Resistance in ohms;  $\rho$  = specific resistance;  $l$  = length in centimeter;  $a$  = area of cross-section in  $\text{cm}^2$

Thus, if  $l = 1 \text{ cm}$  and  $a = 1 \text{ cm}^2$

$$R = \rho$$

#### 2. Conductance (c)

The conductance of an electrolyte is the reciprocal of its resistance

$$c = \frac{1}{R}$$

#### Unit of conductance:

$$c = \frac{1}{\text{ohm}} = \text{ohm}^{-1} \text{ (or) mho.}$$

#### 3. Specific resistance ( $\rho$ )

According to ohm's law  $R \propto l/a$

$$R = \rho l/a \text{ (or) } \rho = R \times a/l$$

Where,  $\rho$  = specific resistance

If  $l = 1 \text{ cm}$  and  $a = 1 \text{ cm}^2$ , then  $\rho = R$

Thus, specific resistance is defined as the resistance of a conductor, if its length is 1 cm and area is  $1 \text{ cm}^2$ .

#### Unit of specific resistance:

$$\rho = \frac{\text{ohm} \times \text{cm}^2}{\text{cm}} = \text{ohm.cm}$$

#### 4. Specific Conductance ( $\kappa$ )

The reciprocal of specific resistance is called specific conductance. (or) It is the conductance of  $1\text{ cm}^3$  of a material.

$$\kappa = \frac{1}{\rho}$$

$$= \frac{1}{R \times \frac{a}{l}}$$

$$= \frac{1}{R} \times \frac{l}{a}$$

$$(or) \quad \kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = c \times \frac{l}{a}$$

$$\text{Where, } \frac{1}{R} = c$$

#### Unit of Specific Conductance

$$\kappa = \frac{\text{cm}}{\text{ohm} \times \text{cm}^2}$$

$$= \frac{1}{\text{ohm} \times \text{cm}} = \text{ohm}^{-1} \text{ cm}^{-1} \text{ or mho} \cdot \text{cm}^{-1}$$

#### 5. Equivalent conductance ( $\Lambda_{eq}$ )

It is defined as the conducting power of all the ions produced by dissolving 1 gram equivalent of an electrolyte in the solution.

$$\Lambda_{eq} = \frac{1000 \kappa}{C}$$

Where, C = concentration of the solution in gm equivalent weight.

#### Unit of equivalent conductance

$$\begin{aligned}\Lambda &= \frac{\text{cm}^3}{\text{gm. equivalent}} \times \text{mho} \cdot \text{cm}^{-1} \\ &= \text{mho} \cdot \text{cm}^2 \cdot \text{gm} \cdot \text{equ}^{-1}\end{aligned}$$

#### 6. Molar conductance ( $\Lambda_m$ )

It is defined as "the conducting power of all the ions produced by dissolving 1 mole of an electrolyte in a given solution."

$$\Lambda_m = \frac{1000 \kappa}{C}$$

Where, C = molar concentration

#### Unit of molar concentration

$$\Lambda_m = \frac{\text{cm}^3}{\text{mole}} \times \text{mho} \cdot \text{cm}^{-1} = \text{mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$$

#### 7. Cell constant (x):

It is the ratio of distance between two electrodes (l) and area of the electrodes (a).

$$x = \frac{l}{a}$$

Where, l = length in cm; a = area in  $\text{cm}^2$

This cell constant is multiplied with observed conductance (c) or  $\left(\frac{1}{R}\right)$  to get specific conductance ( $\kappa$ )

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

#### Unit of cell constant

$$x = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$$

### 2.7.2 Conductivity cell

The solution whose conductivity is to be determined is placed in a special type of cell "known as the conductivity cell". Thus, conductivity cell is a cell used to measure the conductivity of the solution.

#### Construction

A conductivity cell consists two electrodes, fitted in the cell, made of platinum plates coated with platinum black. These are welded to platinum wires fused in two thin glass tubes and are connected to copper wires.

An AC voltage is applied between the cell and the resulting current is measured. Conductive ions, produced from the salts, produce a path for current to flow. Therefore high conductivity indicates high ionic concentration.

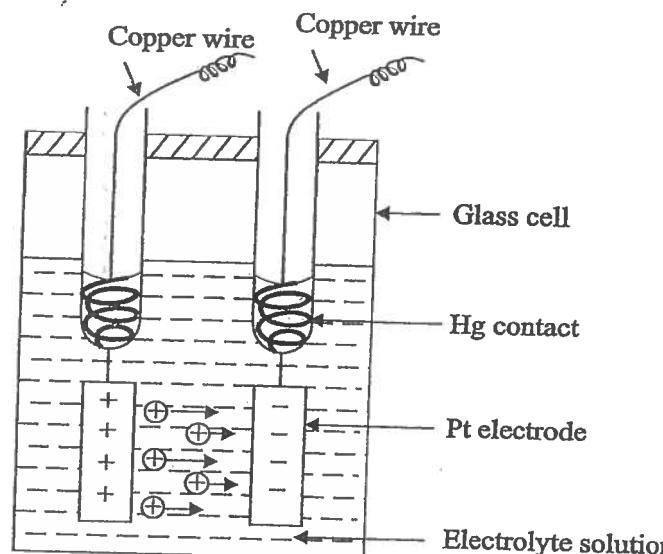


Fig. 2.9 Conductivity cell

### 2.7.3 Conductometric Titration

#### Principle

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.

The conductance of a solution depends on

- (i) the number and charge on the free ions, and
- (ii) the mobility of the ions.

#### Acid-Base titrations

##### 1. Strong acid Vs Strong base (HCl Vs NaOH)

Known amount of acid (HCl) is taken in the conductivity cell and the alkali (NaOH) in the burette. Initially the conductivity of the HCl is high, this is due to the presence of fast moving  $\text{H}^+$  ions (Point A in the graph). As the NaOH is added gradually, conductance will be going on decreasing until the acid has been completely neutralized (indicated by the line AB). This is due to the replacement of fast moving  $\text{H}^+$  ions by slow moving  $\text{Na}^+$  ions. The point 'B' indicates complete neutralization of all  $\text{H}^+$  ions.

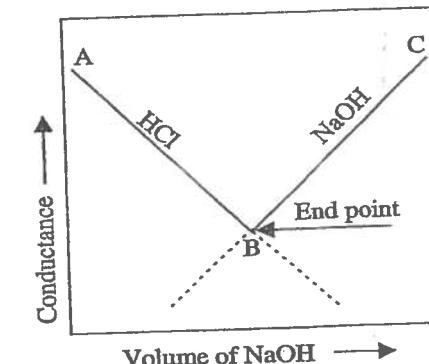
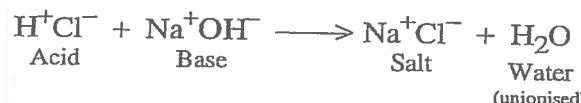


Fig. 2.10 Strong acid Vs strong base



Further addition of NaOH will introduce the fast moving  $\text{OH}^-$  ions. Therefore the conductance, after reaching a certain minimum value, will begin to increase (indicated by the line BC).

On plotting the conductance against the volume of alkali added, the two lines intersect at a point 'B' gives the end point. This corresponds to the volume of NaOH required for neutralization.

## 2. Weak acid Vs Strong base ( $\text{CH}_3\text{COOH}$ Vs $\text{NaOH}$ )

Known amount of weak acid ( $\text{CH}_3\text{COOH}$ ) is taken in the conductivity cell and the alkali ( $\text{NaOH}$ ) in the burette. Initially the conductivity of  $\text{CH}_3\text{COOH}$  is low, this is due to the poor dissociation of  $\text{CH}_3\text{COOH}$ . (point A in the graph). As  $\text{NaOH}$  is added gradually, conductance will be going on slowly increasing (indicated by the line AB). This is due to the formation of highly ionised  $\text{CH}_3\text{COONa}$ .

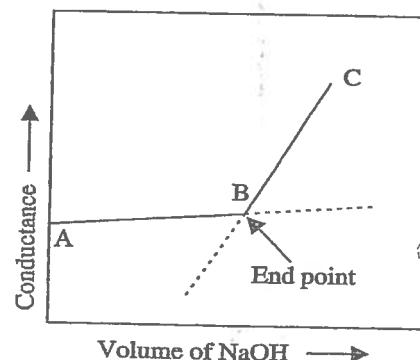
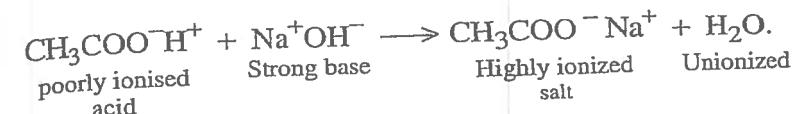


Fig. 2.11 Weak acid Vs. Strong base



The point 'B' indicates complete neutralization of  $\text{CH}_3\text{COOH}$ .

Further addition of NaOH introduces excess of fast moving  $\text{OH}^-$  ions. Therefore the conductance of the solution begins to increase even more sharply than before (line BC).

On plotting the conductance against the volume of alkali added, the two lines intersect at point 'B' gives the end point.

## 3. Strong acid Vs weak base ( $\text{HCl}$ Vs $\text{NH}_4\text{OH}$ )

Known amount of HCl is taken in the conductivity cell and  $\text{NH}_4\text{OH}$  is added gradually from the burette. Initially the conductivity of HCl is high (Point A in the graph). As the  $\text{NH}_4\text{OH}$  is added gradually the conductance will be going on decreasing until all the acids been completely neutralised (line AB). This is due to the replacement of  $\text{H}^+$  ions by slow moving  $\text{NH}_4^+$  ions.

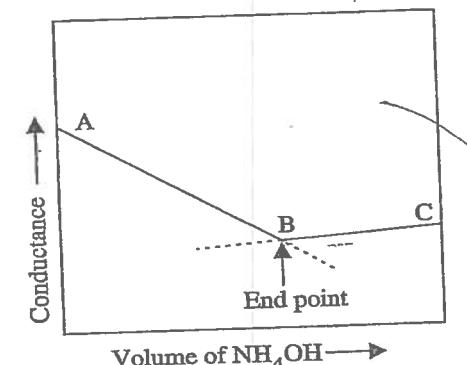
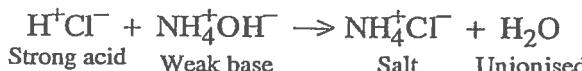


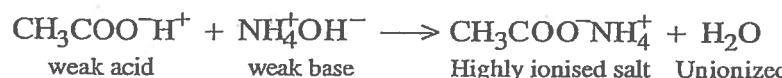
Fig. 2.12 Strong acid Vs Weak base



Further addition of poorly ionized  $\text{NH}_4\text{OH}$  does not cause any appreciable change in the conductance (slow increase) (line BC). The point of intersection 'B' is the end point.

#### 4. Weak acid Vs weak base ( $\text{CH}_3\text{COOH}$ Vs $\text{NH}_4\text{OH}$ )

When  $\text{CH}_3\text{COOH}$  is titrated against  $\text{NH}_4\text{OH}$ , conductivity is going on increasing (indicated by the line AB). This is due to the formation of highly ionised salt  $\text{CH}_3\text{COO}^-\text{NH}_4^+$ .



After the neutralisation of  $\text{CH}_3\text{COOH}$ , further addition of poorly ionized  $\text{NH}_4\text{OH}$  does not cause any appreciable change in the conductance (slow increase) (line BC). The point of intersection 'B' is the end point.

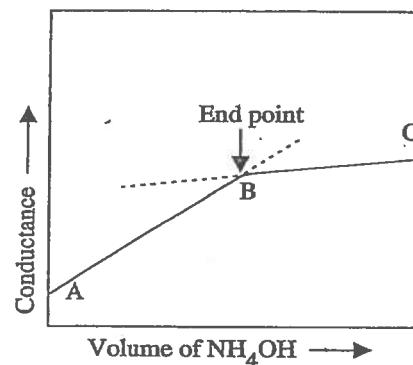


Fig. 2.13 Weak acid Vs Weak base

#### 2.13 PHOTOVOLTAIC CELL (OR) SOLAR CELL

##### Definition

**Photovoltaic cell** is the one, which converts the solar energy (energy obtained from the sun) directly into electrical energy.

##### Principle

The basic principle involved in the solar cells is based on the photovoltaic (PV) effect. When the solar rays fall on a two layer of semi-conductor devices, a potential difference between the two layer is produced. This potential difference causes flow of electrons and produces electricity.

##### Construction

Solar cells consist of a p-type semiconductor (such as Si doped with B) and n-type semiconductor (such as Si doped with P). They are in close contact with each other.

##### Working

When the solar rays fall on the top layer of p-type semiconductor, the electrons from the valence band get promoted to the conduction band and cross the p-n junction into n-type semiconductor. There by potential difference between two layers is created, which causes flow of electrons (i.e., an electric current). The potential difference and hence

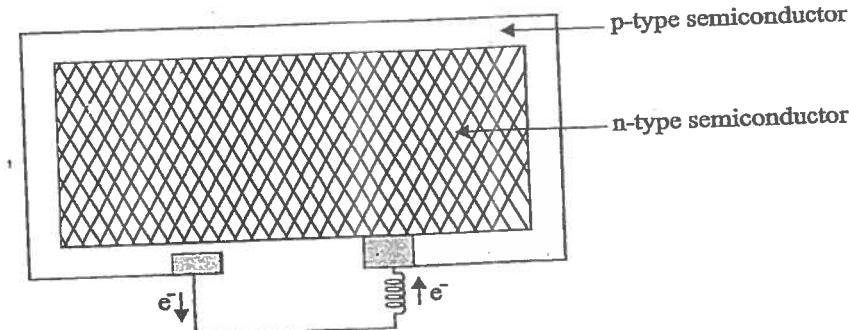


Fig. 2.14 Solar cell

current increases as more solar rays falls on the surface of the top layer.

Thus when this p and n layers are connected to an external circuit, electrons flow from n-layer to p-layer, and hence current is generated.

### 2.8.1 Applications of solar cells

#### 1. Lighting purpose

Solar cells can be used for lighting purpose. Now a days electrical street lights are replaced by solar street lights.

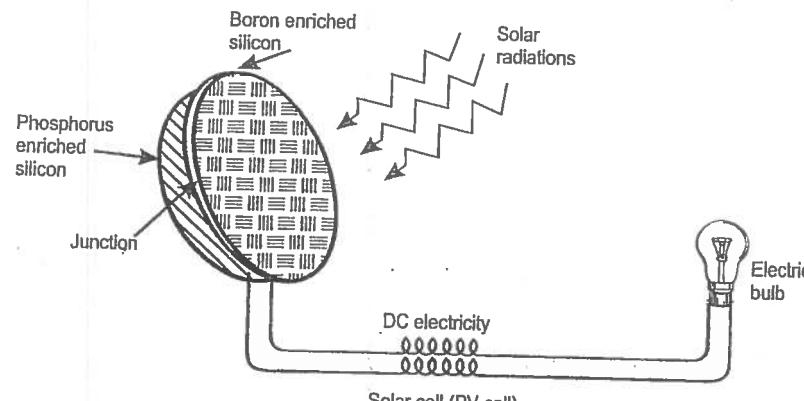


Fig. 2.15 Solar light

#### 2. Solar pumps run by solar battery

When a large number of solar cells are connected in series it form a solar battery. Solar battery produces more electricity which is enough to run, water pump, street-light, etc., They are also used in remote areas where conventional electricity supply is a problem.

3. Solar cells are used in calculators, electronic watches, radios and TVs.

4. Solar cells are superior to other type of cells, because these are nonpolluting and eco-friendly.

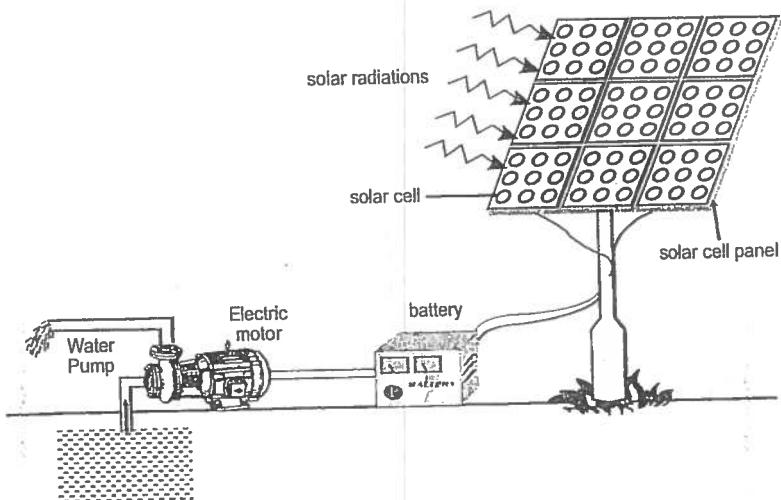


Fig. 2.16 Solar pump run by solar cells (Battery)

5. Solar energy can be stored in Ni-Cd batteries and lead-acid batteries.

6. Solar cells can be used to drive vehicles.

7. Solar cells, made of silicon, are used as a source of electricity in space craft and satellites.

## 2.9 PHOTOGALVANIC CELLS

Photogalvanic cell consists of a semiconductor, forming one electrode in a water solution and is connected to another metal electrode placed in the other side. This is very similar to a battery.

When light falls on the semiconductor, electron and hole are formed. The electron then flows across the wire to the other metal electrode combine with water ( $H_2O$ ) to make  $OH^-$  and  $H_2$ .

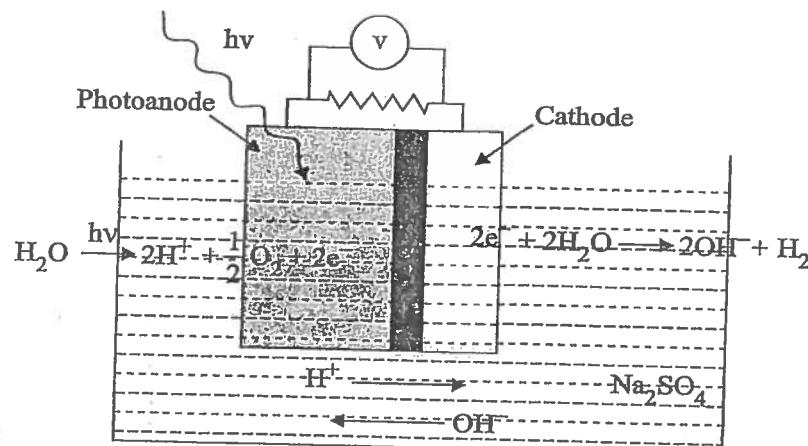
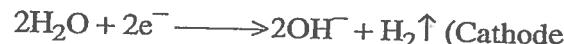
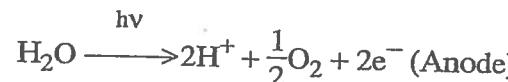


Fig. 2.17 Photogalvanic Cells



Then the  $OH^-$  flows through the solution back to the semiconductor to join up with the hole left behind to become neutral again. An ion flowing through a solution competing the circuit is once again very much like a battery.

## 2.10 SENSORS AND THEIR TYPES

Sensors are devices which convert one form of energy into another.

There are so many sensors of which the followings are some important sensors.

1. Potentiometric sensors
2. Amperometric sensors
3. Electrochemical sensors

### 2.10.1 Potentiometric Sensors

Potentiometry deals with the electromotive force (emf) generated in a galvanic cell, where spontaneous chemical reaction is taking place. Analytical potentiometry deals with the use of the emf response of a potentiometric cell to determine concentrations of analytes in samples.

Solid state, gas-sensing electrodes, or Liquid and polymer membrane electrodes are sensors that may be based, or incorporate an ion-selective electrode (ISE).

The glass membrane electrode was the 1<sup>st</sup> ISE to be discovered and characterised and used for pH measurements.

#### Types of ISEs

ISEs are potentiometric devices selective for ionic species, exist that combine some characteristics from different sensor types.

1. Glass electrodes
2. Solid - membranes electrodes
3. Liquid - membrane electrodes
4. Gas - sensing electrodes
5. Neutral - carrier based ion selective electrodes.

#### Characteristics of ISE

An ISE can be considered a suitable sensor for quantitative ion analysis. Of these slope, selectivity, limit of detection and electrode working life are the most important.

#### Applications of ISEs

1. The ISEs are used for the detection of commonly occurring inorganic cations and anions with membrane based potentiometric sensors.
2. It is also used to detect the species like organic ions, proteins and enzymes, vitamins, medicines and other

- species of complex molecular composition that can also be detected.
3. ISE is commonly used as detectors in autotitrations, where the electrode is used to detect the end point of titrations.

### 2.10.2 Amperometric Sensors

Amperometric sensors are based on the principle that, when a species is oxidised or reduced at an electrode, the current produced is directly related to the concentration of a species.

Information is obtained with this type of electrochemical sensors from the current-concentration relationship alone.

Amperometric measurements are made by recording a current flow in a cell at a single applied potential.

### 2.10.3 Electrochemical Sensors

A number of electrochemical systems are produced commercially for the determination of specific species. These devices are sometimes called electrodes (or) detectors but are, infact, complete electrochemical cells and are better referred to as sensors.

#### Examples for Electrochemical Sensors

Two of these devices are

- (i) Oxygen sensors
- (ii) Enzyme - based sensors.

#### *1. Oxygen Sensors*

The dissolved oxygen in a variety of aqueous environments, such as seawater, blood, sewage and soils can be determined by using clark oxygen sensor.

#### Clark Oxygen Sensor

The cell consists of a platinum disk cathodic working electrode <sup>biased</sup> imbedded in a centrally located cylindrical insulator. Surrounding the lower end of this insulator is a ring-shaped silver anode. The tubular insulator and electrodes are mounted inside a second cylinder that contains a buffered solution of potassium chloride. A thin ( $\approx 20 \mu\text{m}$ ) replaceable, oxygen permeable membrane of teflon (or) polyethylene is held in place at the bottom end of the tube by an O - ring. The thickness of the electrolyte solution between the cathode and the membrane is approximately  $10 \mu\text{m}$ .

When the oxygen sensor is immersed in a flowing (or) stirred solution of the analyte; oxygen diffuses through the membrane into the thin layer of electrolyte immediately

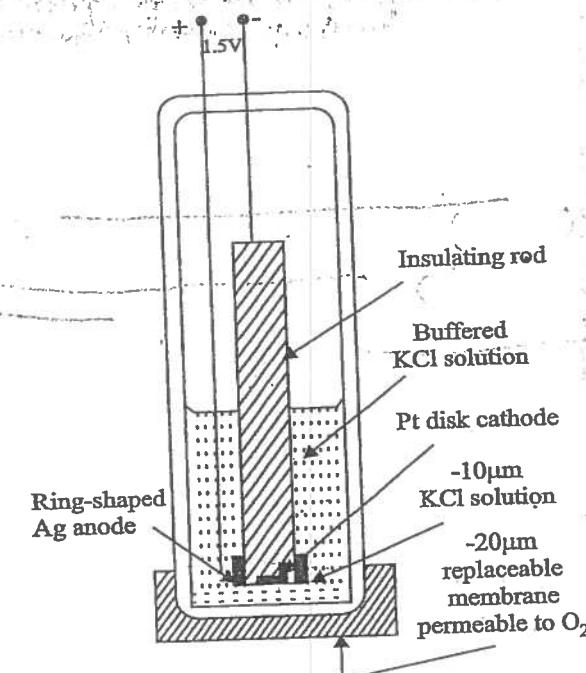
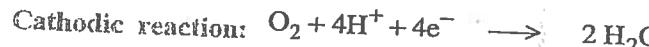


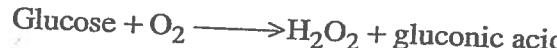
Fig. 2.18 Clark Electrochemical Oxygen Sensor

adjacent to the disk cathode, where it diffuses to the electrode and is immediately reduced to water. Two diffusion process are involved, one is through the membrane and the other through the solution between the membrane and the electrode surface. In order for a steady-state condition to be reached in a reasonable period (10 to 20 S), the thickness of the membrane and the electrolyte film must be 20  $\mu\text{m}$  or less. Under these conditions, it is the rate of equilibration of the transfer of oxygen across the membrane that determines the rate at which steady-state currents are achieved.



2. Enzyme-Based Sensors Membranes - 3 layers  
 Inner layer - cellulose acetate (permeable to  $\text{H}_2\text{O}$ , to give out)  
 Outer layer - polycarbonate (glucose not filter)  
 Example: Glucose Sensor Middle layer - Immobilized Glucose Oxidase

The glucose sensor is widely used in clinical laboratories for the determination of glucose in blood. This device is similar in construction to oxygen sensor shown in the above figure. The membrane in this case is more complex and consists of three layers. The outer layer is a polycarbonate film that is permeable to (glucose) but impermeable to proteins and other constituents of blood. The middle layer is an immobilized enzyme, (glucose oxidase) in this instance. The inner layer is a cellulose acetate membrane, which is permeable to small molecules, such as hydrogen peroxide. When this device is immersed in a glucose-containing solution, glucose diffuses through the outer membrane into the immobilized enzyme, where the following catalytic reaction occurs.



The hydrogen peroxide then diffuses through the inner layer of membrane and to the electrode surface, where it is oxidised to give oxygen.



The resulting current is directly proportional to the glucose concentration of the analyte solution.

### ~~TYPES~~ BATTERY (WELL) CELLS

A battery is an arrangement of several electrochemical cells connected in series, that can be used as a source of direct electric current.

Thus,

A Cell: Contains only one anode and cathode.

A Battery: Contains several anodes and cathodes.

#### 2.11.1 Requirements of a battery

A useful battery should fulfil the following requirements

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. The voltage of the battery should not vary appreciably during its use.

#### 2.11.2 Types of Battery

##### 1. Primary Battery (or) Primary cells

In these cells, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy. The reactions occur only once and after use they become dead. Therefore, they are not chargeable.

Examples: Dry cell, mercury cell.

##### 2. Secondary Battery (or) Secondary cells

In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing electric current and used again and again. These are also called Storage cells (or) Accumulators.

Examples: Lead acid storage cell, Nickel-cadmium cell.

### 3. Flow battery (or) Fuel cell

In these cells, the reactants, products and electrolytes are continuously passing through the cell. In this chemical energy gets converted into electrical energy. (without combustion)

*Example:* Hydrogen-oxygen fuel cell.

## 2.12 IMPORTANT PRIMARY BATTERY

### 2.12.1 Zinc-Air battery

Zinc-air batteries work by the oxidation of Zn with oxygen from the air.

#### Construction

A mass of loose granulated zinc particles mixed with an electrolyte such as KOH to form a ~~porous~~-anode. The ~~anode~~ <sup>carbon</sup> plate, in the other side, acts as cathode.

#### Working

Oxygen, from the air, at the cathode forms hydroxide ions which migrate into the zinc paste and form zincate i.e.,  $[Zn(OH)_4]^{2-}$  releasing electrons to travel to the cathode. This zincate decays into zinc oxide and water.

The water and hydroxide ions from the electrodes are recycled, so the water is not consumed. This battery produces 1.65V

#### Factors affecting rate of reaction

1. The rate of reaction can be controlled by varying the oxygen flow.
2. The rate of reaction can be increased by replacing oxidized Zinc/electrolyte paste by fresh paste.

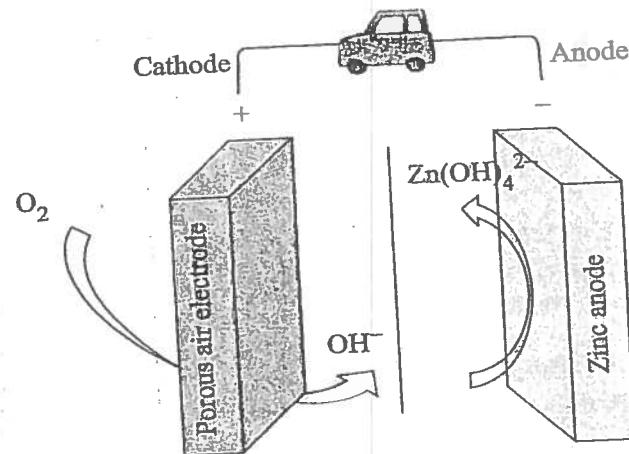


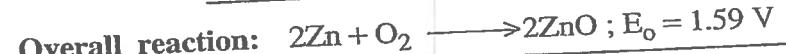
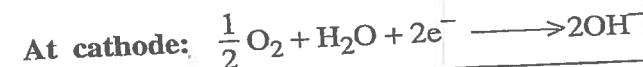
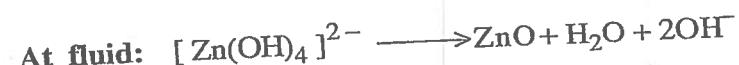
Fig. 2.19 Zinc-Air battery

#### Cell Representation



#### Chemical reactions

The various chemical reactions occurring in the cell are



### 2.12.2 Fuel Cells

#### Definition

Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity without combustion. It converts the energy of the fuel directly into electricity. In

these cells, the reactants, products and electrolytes pass through the cell.



### Examples

*Hydrogen-oxygen fuel cell; Methyl alcohol-oxygen fuel cell.*

### Fuel Battery

When a large number of fuel cells are connected in series, it form fuel battery.

### I. Hydrogen-Oxygen fuel cell

Hydrogen-oxygen fuel cell is the simplest and most successful fuel cell, in which the fuel-hydrogen and the oxidiser-oxygen and the liquid electrolyte are continuously passed through the cell.

#### Description

It consists of two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag). In between the two electrodes an electrolytic solution such as 25% KOH or NaOH is filled. The two electrodes are connected through the volt meter.

#### Working

Hydrogen (the fuel) is passed through the anode compartment, where it is oxidised. The oxygen (oxidiser) is passed through the cathode compartment, where it is reduced.

#### Various reactions

##### At Anode

Hydrogen gas, passed through the anode, is oxidised with the liberation of electrons which then combine with hydroxide ions to form water.

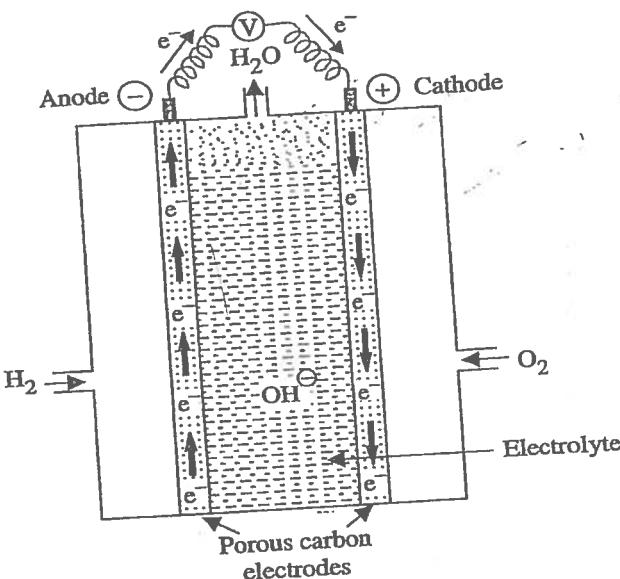
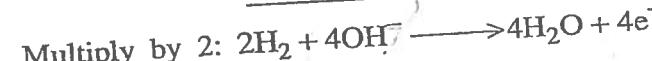
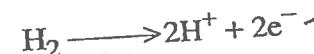
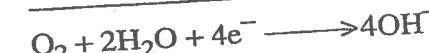
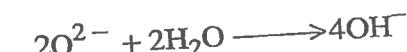


Fig. 2.20  $\text{H}_2\text{-O}_2$  Fuel cell



##### At cathode

The electrons, produced at the anode, pass through the external wire to the cathode where it is absorbed by oxygen and water to produce hydroxide ions.

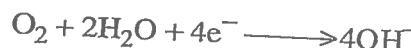


### Overall cell reaction

At anode:



At cathode:



→ The emf of the cell = 0.8 to 1.0 V

### Applications

1.  $\text{H}_2-\text{O}_2$  fuel cells are used as auxiliary energy source in space vehicles, submarines and military-vehicles.
2. In case of  $\text{H}_2-\text{O}_2$  fuel cells, the product of water is proved to be a valuable source of fresh water by the astronauts.

## 2. Methanol Oxygen fuel cell

### Description

Methanol oxygen fuel cell is made of two fuel electrodes. One consists of porous nickel plate coated with a catalyst platinum black and the other is the similar porous nickel plate coated with a silver catalyst. In between these electrodes 25% NaOH or KOH is taken.

### Working

Now air is allowed to bubble on the surface of the silver catalyst. Now 35 cc of pure  $\text{CH}_3\text{OH}$  vapour is added and the fuel cell is activated. When the cell operates the water vapour and the carbon dioxide are liberated at around the electrodes.

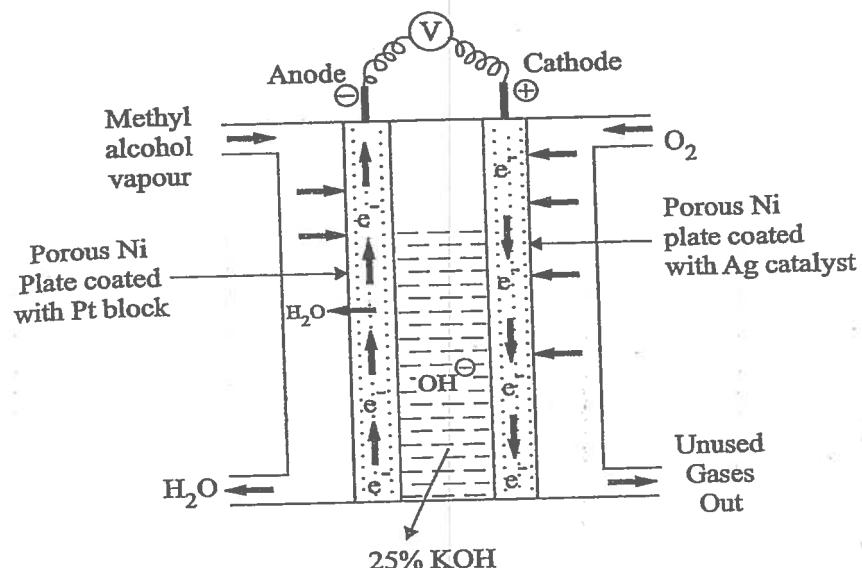
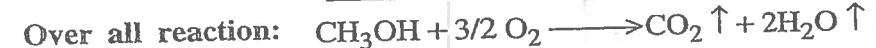
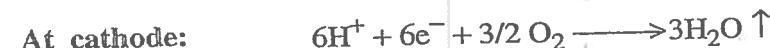


Fig. 2.21 Methanol-Oxygen fuel cell

### Cell reaction

The following reactions occur at each electrode



### Applications

The power produced in methanol oxygen fuel cell is enough to run a simple transistorised radio even without bubbling of air.

### 2.13 IMPORTANT SECONDARY BATTERY

*Syllabus Not in RBSE*

#### 2.13.1 Lead Storage Cell (or) Lead accumulator (or) Acid Storage Cell

A lead acid storage cell is a secondary battery, which can operate both as a voltaic cell and as an electrolytic cell. When it acts as a voltaic cell, it supplies electrical energy and becomes "run down". When it is recharged, the cell operates as an electrolytic cell.

#### Description

A lead-acid storage battery consists of a number of (3 to 6) voltaic cells connected in series to get 6 to 12 V battery. In each cell, the anode is made of lead. The cathode is made of lead dioxide  $\text{PbO}_2$  or a grid made of lead, packed with  $\text{PbO}_2$ . A number of lead plates (anodes) are connected in parallel and a number of  $\text{PbO}_2$  plates (cathodes) are also connected in parallel. Various plates are separated from the adjacent one by insulators like rubber or glass fibre. The entire combination is then immersed in dil.  $\text{H}_2\text{SO}_4$  (38% by mass) having a density of 1.30 gm/ml.

The cell may be represented as;



#### Working (Discharging)

When the lead-acid storage battery operates, the following reaction occurs.

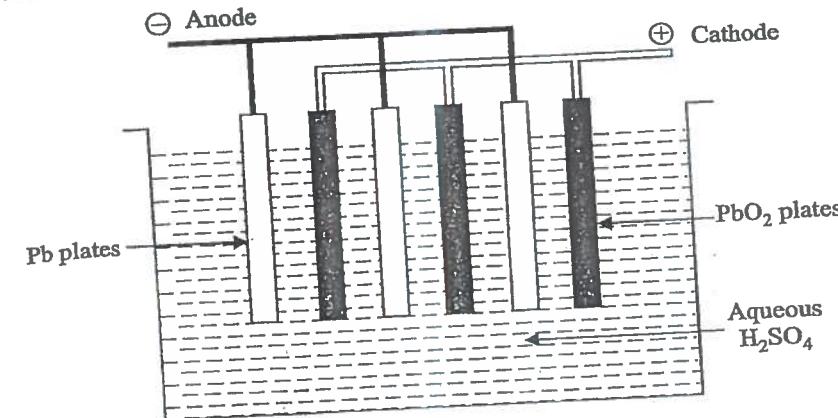
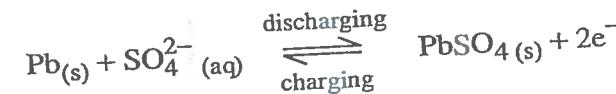
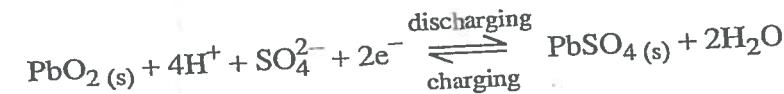


Fig. 2.22 Lead storage cell

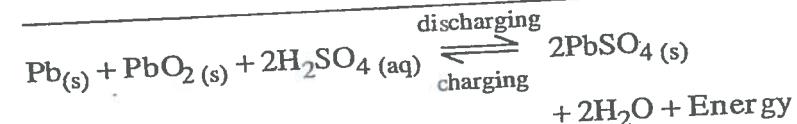
At anode: Lead is oxidized to  $\text{Pb}^{2+}$  ions, which further combines with  $\text{SO}_4^{2-}$  forms insoluble  $\text{PbSO}_4$ .



At cathode:  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  ions, which further combines with  $\text{SO}_4^{2-}$  forms insoluble  $\text{PbSO}_4$ .



Overall cell reaction during use (discharging):



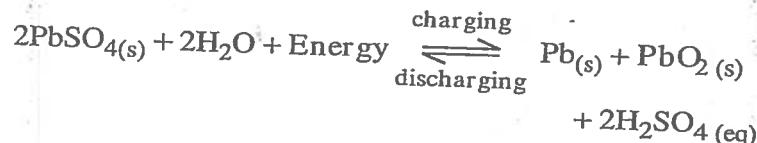
From the above cell reactions it is clear that,  $\text{PbSO}_4$  is precipitated at both the electrodes and  $\text{H}_2\text{SO}_4$  is used up. As a result, the concentration of  $\text{H}_2\text{SO}_4$  decreases and hence the

density of  $\text{H}_2\text{SO}_4$  falls below 1.2 gm/ml. So the battery needs recharging.

### Recharging the Battery

The cell can be charged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a result, Pb is deposited at anode and  $\text{PbO}_2$  at the cathode. The density of  $\text{H}_2\text{SO}_4$  also increases.

The net reaction during charging is



### Advantages of lead-acid batteries

- (i) It is made easily.
- (ii) It produces very high current.
- (iii) The self-discharging rate is low when compared to other rechargeable batteries.
- (iv) It also acts effectively at low temperature.

### Disadvantages of lead-acid batteries

- (i) Recycling of this battery causes environmental hazards.
- (ii) Mechanical strain and normal bumping reduces battery capacity.

### Uses

1. Lead storage cell is used to supply current mainly in automobiles such as cars, buses, trucks, etc.,
2. It is also used in gas engine ignition, telephone exchanges, hospitals, power stations, etc.,

### 2.13.2 Lithium-ion batteries (or) Lithium-ion cells

Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode. As the name suggests, the movement of lithium ions are responsible for charging & discharging. Lithium-ion cell has the following three components.

- A positive electrode (Layers of lithium-metal oxide) (cathode)
- A negative electrode (Layers of porous carbon) (anode)
- An electrolyte (Polymer gel) (separator)

### Construction

The positive electrode is typically made from a layers of chemical compound called lithium-cobalt oxide ( $\text{LiCoO}_2$ ).

The negative electrode is made from layers of porous carbon (C) (graphite).

Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the  $\text{Li}^+$  ions to pass through.

### Working

### Charging

During charging,  $\text{Li}^+$  ions flow from the positive electrode ( $\text{LiCoO}_2$ ) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and  $\text{Li}^+$  ions combine at the negative electrode and deposit there as Li.



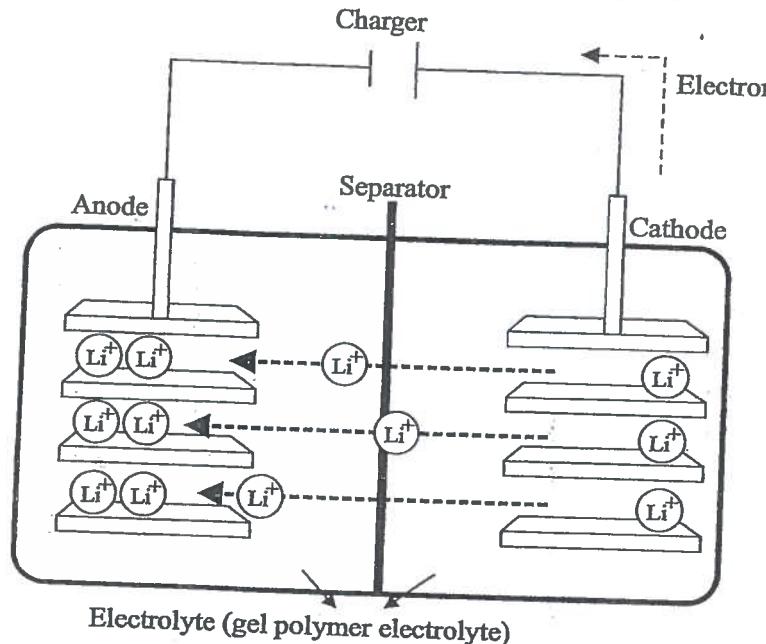


Fig. 2.23 Lithium-ion cell during charging

#### Discharging

During discharging, the  $\text{Li}^+$  ions flow back through the electrolyte from positive electrode to the negative electrode. Electrons flow from the positive electrode to the negative electrode. The  $\text{Li}^+$  ions and electrons combine at the negative electrode and deposit there as Li.

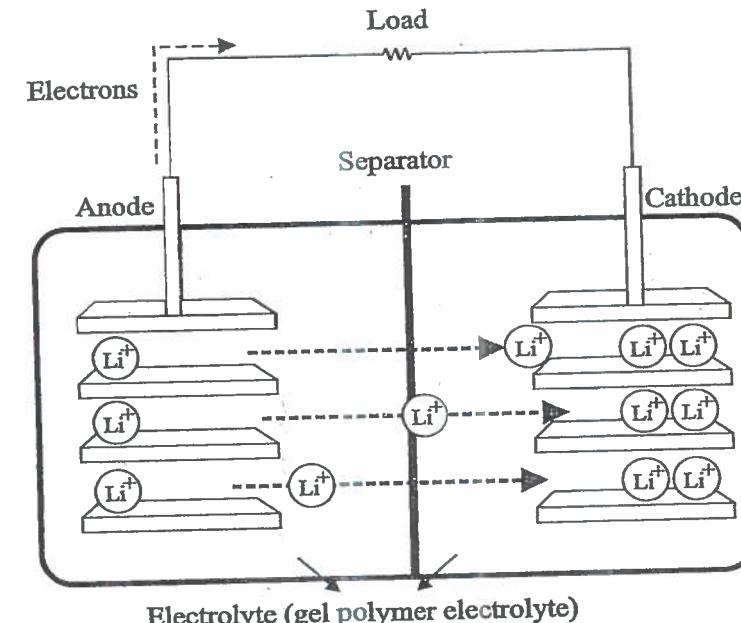


Fig. 2.24 Lithium-ion cell during discharging

#### Advantages (or) Characteristics

1. Lithium-ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three time the voltage of Ni-Cd batteries.
4. It has none of the memory effect seen in Ni-Cd batteries.

#### Uses

It is used in cell phone, note PC, portable LCD TV, semiconductor driven audio, etc.,

Uses:- calculator, watches, TV, laptop.

## 2.14 DESCRIPTIVE TYPE QUESTIONS

- Write notes on the followings
  - Calomel electrode
  - Silver-silver chloride electrodes
- Derive nernst equation for emf of a galvanic cell.
- Explain the various steps involved in redox titration.
- Explain construction, working and applications of photovoltaic cell.
- Explain electrochemical sensors with an example.
- Draw and explain the functions of zinc-air battery
- Explain the working and applications of methanol-oxygen fuel cell with neat diagram.
- Explain the charging and discharging reactions of lithium-ion cell.
- Write notes on
  - Amperometric sensors
  - Conductivity cell

Addition polymerisation  
mechanism  
Bakelite  
Brea  
Formaldehyde

# Polymer Chemistry

## 3.1 INTRODUCTION TO POLYMERS

The word polymer is derived from Greek words "poly" means "many" and "mer" means "unit" or "part".

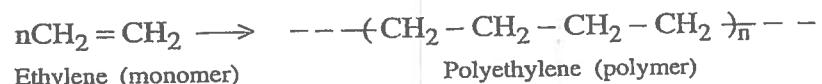
Polymers are generally macromolecules formed by the repeated linking of large number of small molecules. Polymers are widely used in automobiles, defence, electrical goods and computer components etc.

### 3.1.1 Polymers

Polymers are macro molecules (giant molecules of higher molecular weight) formed by the repeated linking of large number of small molecules called monomers.

#### Example

*Polyethylene is a polymer formed by the repeated linking of large number of ethylene molecule.*



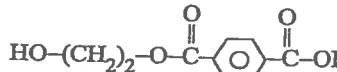
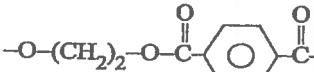
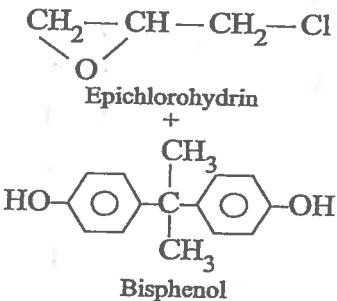
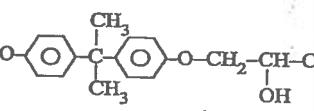
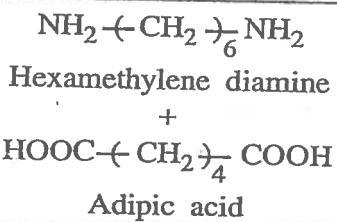
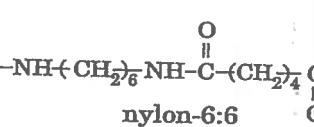
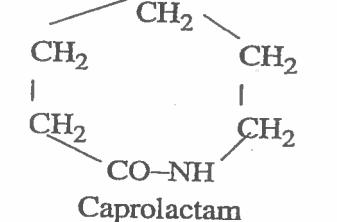
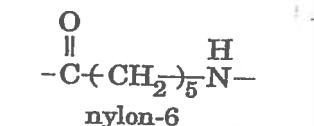
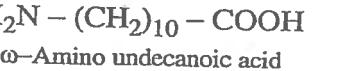
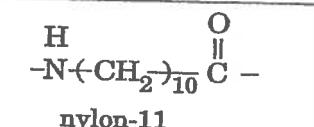
### 3.1.2 Monomer

Monomer is a micro molecule (small molecule) which combines with each other to form a polymer.

Some monomers and repeating unit of the polymers are given below.

S. No.	Monomer	Repeating unit of the polymer.
1.	$\text{CH}_2 = \text{CH}_2$ Ethylene	$-\text{CH}_2 - \text{CH}_2 -$ polyethylene (P.E)
2.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{CH}_3 \end{array}$ Propylene	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_3$ polypropylene (pp)
3.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{Cl} \end{array}$ Vinyl chloride	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{Cl}$ polyvinyl chloride (PVC)
4.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{C}_6\text{H}_5 \end{array}$ Styrene	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{C}_6\text{H}_5$ polystyrene (PS)
5.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{CN} \end{array}$ Acrylonitrile	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{CN}$ polyacrylonitrile (PAN)
6.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{OCOCH}_3 \end{array}$ Vinyl acetate	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{OCOCH}_3$ polyvinyl acetate (PVAc)
7.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{COOH} \end{array}$ Acrylic acid	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{COOH}$ polyacrylic acid

S. No.	Monomer	Repeating unit of the polymer.
8.	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{COOCH}_3 \end{array}$ Methyl acrylate	$-\text{CH}_2 - \text{CH} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{COOCH}_3$ polymethyl acrylate (PMA)
9.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 = \text{C} \\   \\ \text{COOCH}_3 \end{array}$ Methyl methacrylate	$-\text{CH}_2 - \text{C} -$ $\quad \quad \quad  $ $\quad \quad \quad \text{COOCH}_3$ polymethyl methacrylate (PMMA)
10.	$\text{CF}_2 = \text{CF}_2$ Tetrafluoro ethylene	$-\text{CF}_2 - \text{CF}_2 -$ polytetrafluoro ethylene (PTFE)(TEFLON) (FLUON)
11.	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ Butadiene	$-\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 -$ polybutadiene
12.	$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$ Isoprene	$-\text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 -$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_3$ polyisoprene
13.	$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \\   \\ \text{Cl} \end{array}$ Chloroprene	$-\text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 -$ $\quad \quad \quad  $ $\quad \quad \quad \text{Cl}$ polychloroprene

S. No.	Monomer	Repeating unit of the polymer.
14.	 Ethylene terephthalate	 polyethylene terephthalate (PET)
15.	 Epichlorohydrin + Bisphenol A	 epoxy resin
16.	 Hexamethylene diamine + Adipic acid	 nylon-6:6
17.	 Caprolactam	 nylon-6
18.	 omega-Amino undecanoic acid	 nylon-11

### 3.2 FUNCTIONALITY OF MONOMERS AND THEIR SIGNIFICANCE

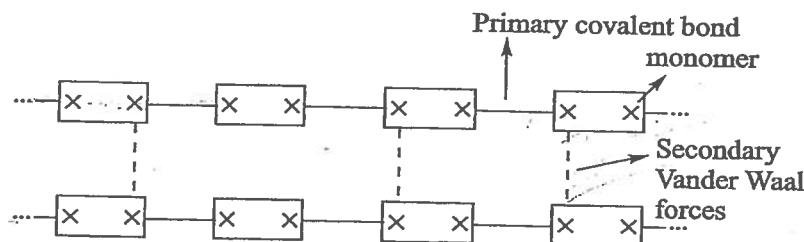
The number of bonding sites or reactive sites or functional groups, present in a monomer, is known as its **functionality**.

S. No.	Example	Functionality
1.	$\text{CH}_2 = \text{CH}_2$ (Ethylene)	-2 (Two bonding sites are due to the presence of one double bond in the monomer. Therefore ethylene is a bifunctional monomer).
2.	$\text{H}_2\text{N} \leftarrow \text{CH}_2 \rightarrow \text{NH}_2$ (Hexa methylene diamine)	-2 (This monomer contains two functional groups, hence it is a bifunctional monomer).
3.	$\begin{array}{c} \text{CH}_2 - \text{OH} \\   \\ \text{CH} - \text{OH} \\   \\ \text{CH}_2 - \text{OH} \end{array}$ (Glycerol)	-3 (This monomer contains three functional groups, hence it is a trifunctional monomer).

#### 3.2.1 Significance

##### 1. Bifunctional monomers

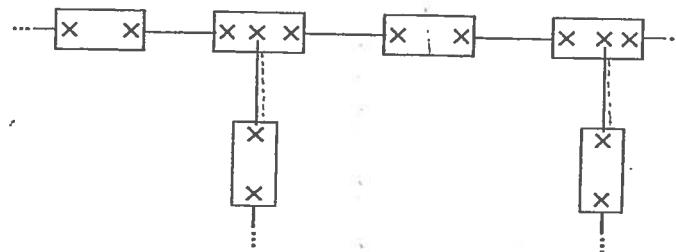
Bifunctional monomers (i.e., functionality of the monomer is 2) mainly form linear (or) straight chain polymer. Each monomeric unit in the linear chain is linked by strong covalent bonds (primary bonds), but the different chains are held together by weak Vander Waal's forces of attraction (secondary bonds). Therefore, there is no restriction to movement of one chain over another. This type of polymers are soft and flexible, and possess less strength, low heat resistance. These are soluble in organic solvents.



## 2. Mixed functional monomers

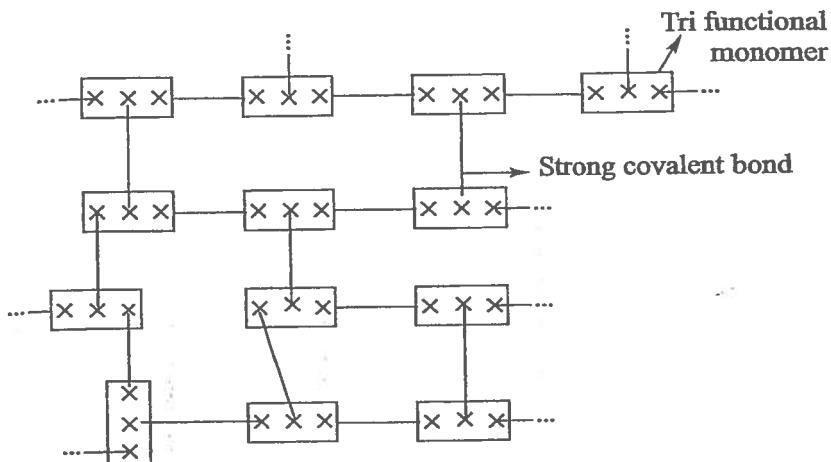
When a trifunctional monomer (i.e., functionality of the monomer is 3) is mixed in small amounts with a bifunctional monomer, they form branched chain polymer.

The movement of polymer chain in branched polymer is more restricted than that of straight chain polymers.



## 3. Polyfunctional monomers

Polyfunctional monomers form cross-linked polymer (three-dimensional network polymer). All the monomers in the polymer are connected to each other by strong covalent bonds. Therefore the movement of polymer chain is totally restricted. This type of polymers are hard and brittle and possess very high strength and heat resistance. They are insoluble in almost all organic solvents.



## 3.3 POLYMERISATION

Polymerisation is a process in which large number of small molecules (called monomers) combine to give a big molecule (called a polymer) with or without elimination of small molecules like water.

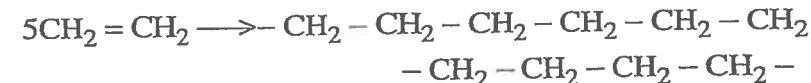
### 3.3.1 Degree of Polymerisation (DP)

The number of repeating units ( $n$ ) in a polymer chain is known as degree of polymerisation. It is represented by the following relationship.

**Degree of polymerisation (n) (DP)**

$$= \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$

**Example**



*In this example, five repeating units are present in the polymer chain. So, the degree of polymerisation is 5.*

## Oligomers

Polymers with low degree of polymerisation are known as Oligomers, their molecular weight ranges from 500 – 5000.

## High polymers

Polymers with high degree of polymerisation are known as High polymers, their molecular weight ranges from 10,000 – 2,00,000.

## 3.4 TYPES OF POLYMERISATION

Polymerisation reactions may be carried out by any one of the following methods.

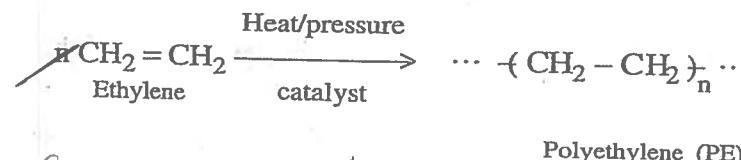
1. Addition (or) chain growth polymerisation
2. Condensation (or) step-wise polymerisation
3. Co-ordination polymerisation
4. Co-polymerisation

### 3.4.1 Addition (or) chain growth polymerisation

It is a reaction that yields a polymer, which is an exact multiple of the original monomeric molecule. The original monomeric molecule, usually, contains one or more double bonds. In this addition polymerisation there is no elimination of any molecule.

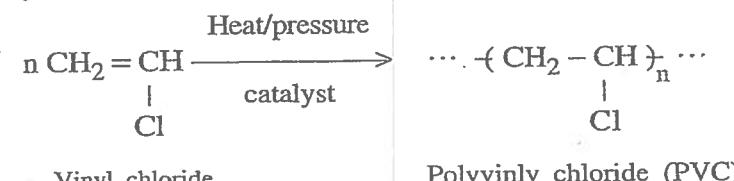
#### Examples

##### *1. Polyethylene is produced from ethylene.*

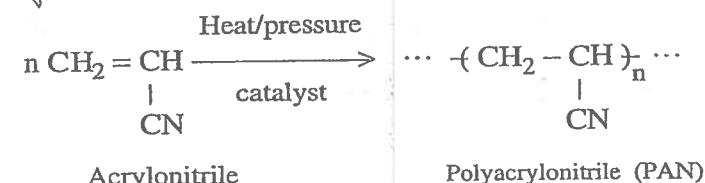


The organic monomers containing  $\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$  undergo polymerisation in the presence of Lewis acids or Lewis bases or peroxides to form a polymer that polymer is called addition polymer & the process is known as Addition (A) polymerisation.

PVC is produced from vinyl chloride.



PAN is produced from acrylonitrile.



### Mechanism of Addition Polymerisation

Mechanism of addition polymerisation can be explained by any one of the following types.

1. Free radical mechanism
2. Ionic mechanism

#### 1. Free radical mechanism (or) free radical polymerisation

Free radical polymerisation occurs in three major steps.

- (i) Initiation
- (ii) Propagation
- (iii) Termination

##### (i) Initiation

Initiation involves two reactions.

##### (a) First reaction

First reaction involves production of free radicals by homolytic dissociation of an initiator (or catalyst) to yield a pair of free radicals ( $\text{R}^\bullet$ )

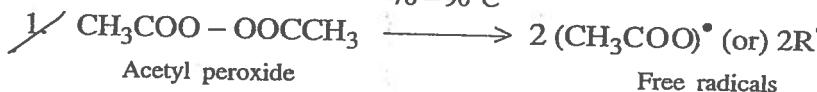


### Initiators

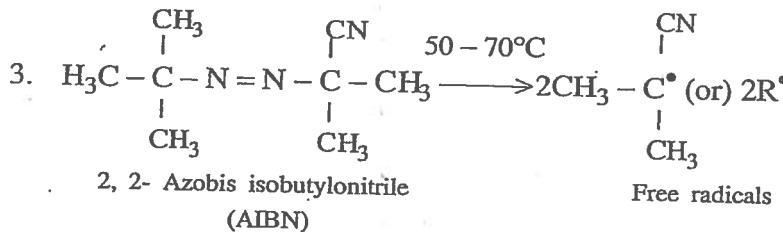
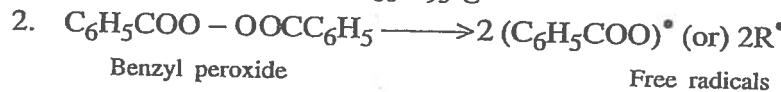
Initiators are compounds which produce free radicals by the homolytic dissociation. If the homolytic dissociation is carried out at high temperature they are called thermal initiators.

### Examples of some commonly used initiators

70–90°C

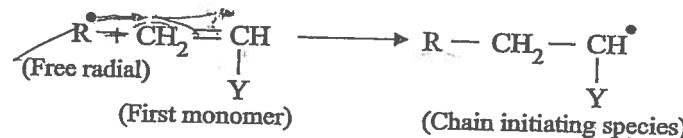


80–95°C



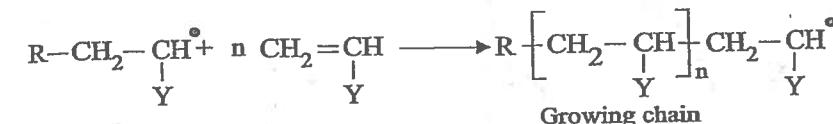
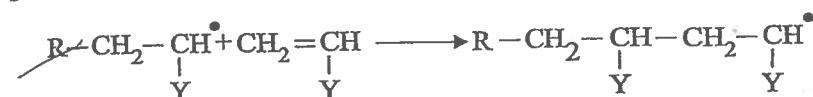
### (b) Second reaction

Second reaction involves addition of this free radical to the first monomer to produce chain initiating species



### (ii) Propagation

It involves the growth of chain initiating species by the successive addition of large number of monomers.

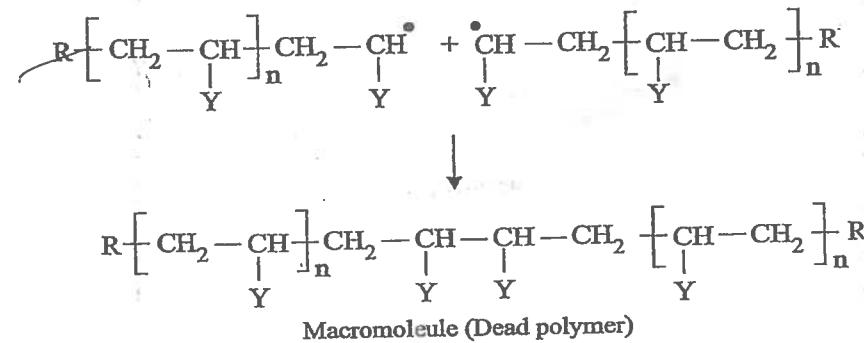


### (iii) Termination

Termination of the growing chain of the polymer occurs either by coupling reaction or disproportionation.

#### (a) Coupling (or) combination

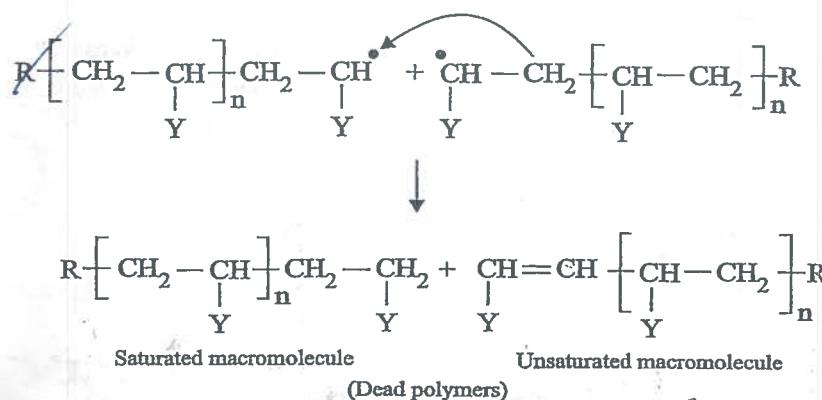
It involves coupling of free radical of one chain end to another free radical to form macromolecule (dead polymer)



#### (b) Disproportionation

It involves transfer of a hydrogen atom of one radical centre to another radical centre forming two macromolecules, one saturated and another unsaturated.

The products of addition polymerisation is known as Dead polymers.

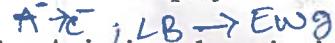


## 2. Ionic mechanism (or) Ionic polymerisation

Ionic polymerisation is faster than the free radical polymerisation. Ionic polymerisation is initiated by either a positive ion (cation) or a negative ion (cation). Depending upon the nature of ions (initiators) the ionic polymerisation takes place in two ways.



A. Cationic polymerisation (or) carbonium ion mechanism



B. Anionic polymerisation (or) carbanion mechanism

### IMP A. Cationic polymerisation

Cationic polymerisation occurs in three major steps

- (i) Initiation
- (ii) Propagation
- (iii) Termination

This polymerisation takes place when electron donating groups like  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  are present in a monomer. These groups stabilise the carbonium ion formation. It is carried out at low temperature and in a non polar solvent.

### Examples

Monomers: Styrene, Isobutylene, Isoprene

Catalysts: The catalysts (initiators) used to initiate the reaction are Lewis acids like  $\text{AlCl}_3$ ,  $\text{BF}_3$  with a co-catalyst like  $\text{HCl}$ ,  $\text{H}_2\text{O}$ .

#### (i) Initiation

The catalyst initiates polymerisation by the addition of  $\text{H}^+$  ion to the monomer to form chain initiating species.



Catalyst      Co-catalyst



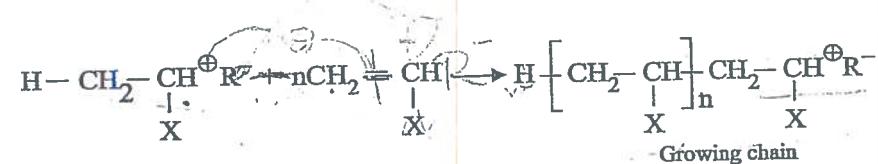
X                                    X

[Chain initiating species]

Where, X = electron donating groups

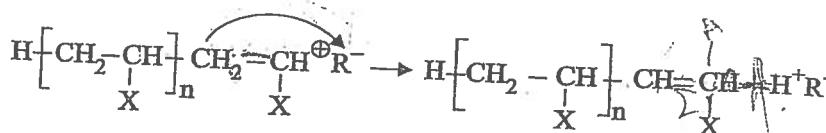
#### (ii) Propagation

It involves the growth of chain initiating species by the successive addition of large number of monomers and the positive charge simultaneously shifts to the newly added monomer.



## (iii) Termination

Termination of the growing chain involves removal of proton from the polymer chain.



## B. Anionic polymerisation

Anionic polymerisation occurs in three steps

- (i) Initiation
- (ii) Propagation
- (iii) Termination

This polymerisation takes place when electron withdrawing groups like  $\text{Cl}^-$ ,  $\text{CN}^-$  are present in a monomer. These groups stabilise the carbanion formation.

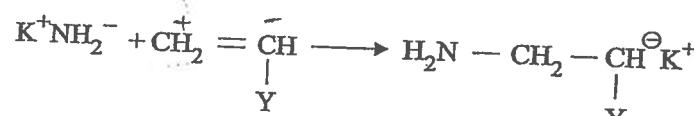
Examples

Monomers: Vinyl chloride, Styrene, Acrylonitrile

Catalysts: The catalysts (initiators) used to initiate the reaction are Lewis base like,  $\text{KNH}_2$ ,  $\text{NaNH}_2$ ,  $\text{LiNH}_2$ .

## (i) Initiation

The catalyst initiates polymerisation by the addition of  $\text{NH}_2^-$  ion to the monomer to form chain initiating species.

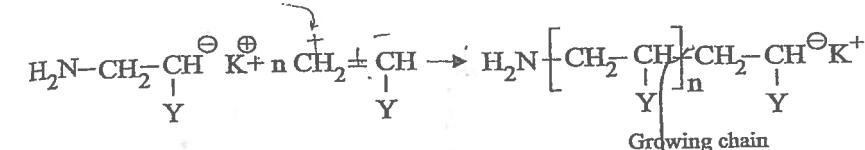


Chain initiating species

Where,  $\text{Y}$  = electron withdrawing group

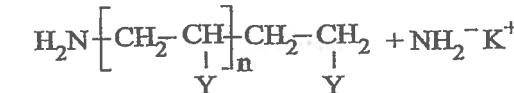
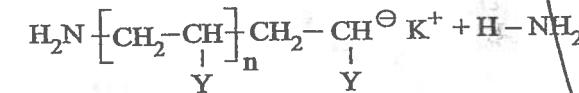
## (ii) Propagation

It involves the growth of chain initiating species by the successive addition of large number of monomers. The negative charge simultaneously shifts to the newly added monomer.



## (iii) Termination

Termination of the growing chain occurs by the addition of suitable terminating agents.



Saturated dead polymer

## Living polymer

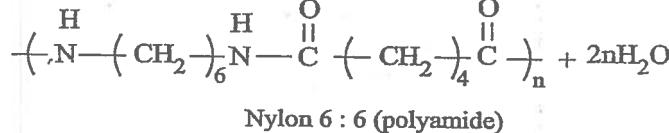
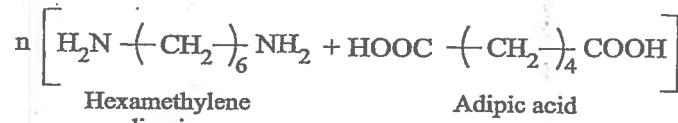
When anionic polymerisation is carried out using a catalyst in an inert solvent, chain termination does not take place and the polymer formed contains terminal ion pair. When these polymer samples are again mixed with fresh monomer the polymer sample grows. These polymers are referred to as living polymers.

### 3.4.2 Condensation (or) Step-growth polymerisation

It is a reaction between simple polar groups containing monomers with the formation of polymer and elimination of small molecules like  $\text{H}_2\text{O}$ ,  $\text{HCl}$ , etc.,

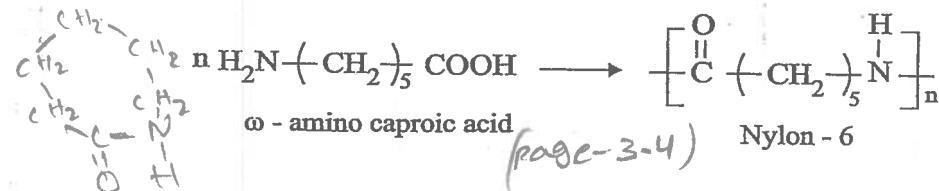
**Example**

1. Hexamethylene diamine and adipic acid condense to form a polymer, Nylon 6:6 (polyamide).



**Example**

2. Polymerisation of  $\omega$ - amino caproic acid to form Nylon - 6



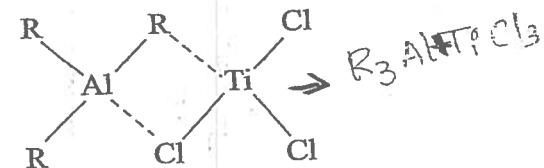
In some cases condensation polymerisation takes place without the elimination of small molecules like  $\text{H}_2\text{O}$ ,  $\text{HCl}$  etc., but by just the opening of cyclic compounds.

The organic monomers containing bi or tri functional group undergoes polymerisation to form the polymer with the elimination of small molecules like  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{NH}_3$  etc.

This polymer is known as condensation polymerisation.

### 3.4.3 Co-ordination Covalent (or) Zeigler - Natta Polymerization

Zeigler and Natta are scientists, they prepared a co-ordination complex, called Zeigler - Natta catalyst, by reacting transition metal halide (like  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiCl}_2$ ,  $\text{ZrBr}_3$ , etc.,) with an organo metallic compounds (like triethyl aluminium, trimethyl aluminium). Using Zeigler - Natta catalyst stereo specific polymerisation can be carried out.



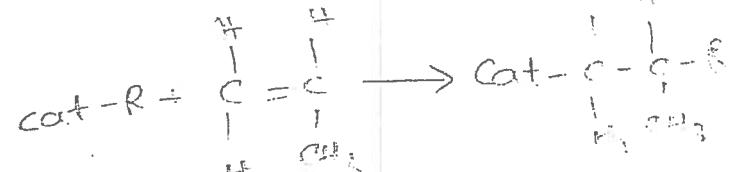
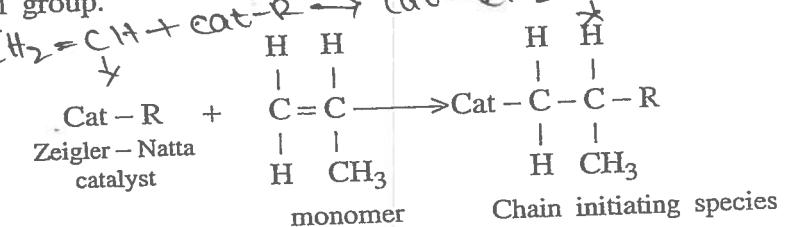
Structure of a typical Zeigler - Natta catalyst is given below.

In order to explain the mechanism of Zeigler - Natta polymerisation, the catalyst is generally represented as Cat-R.  
Mechanism

The monomers like propylene, isoprene, etc., follow this mechanism.

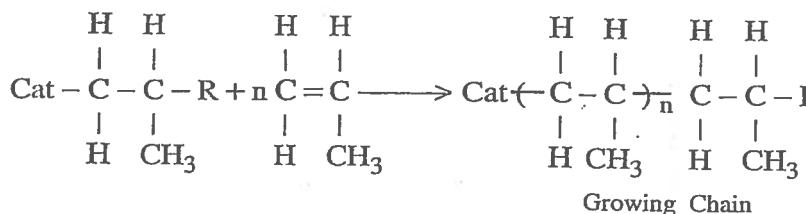
#### (i) Initiation

It involves the formation of chain initiating species, where monomer is inserted in between transition metal and alkyl group.



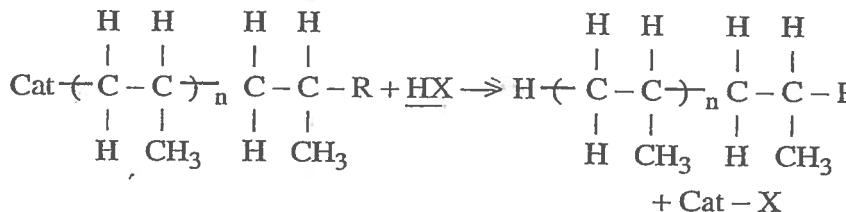
## (i) Propagation

It involves the growth of chain initiating species by successive insertion of large number of monomers between metal and alkyl group.



## (ii) Termination

Termination of the growing chain occurs by adding active hydrogen compound (HX).

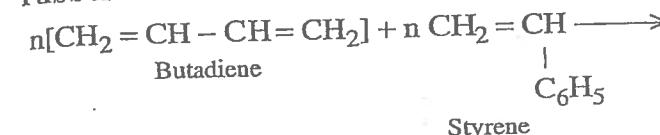


## 3.4.4 Copolymerisation (Stereospecific polymerisation)

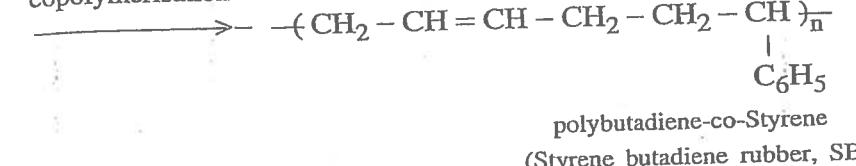
It is the joint polymerisation in which two (or) more different monomers combine to give a polymer. High molecular weight polymers, obtained by copolymerisation, are called copolymers. Copolymerisation is mainly carried out to vary the properties of polymers such as hardness, strength, rigidity, heat resistance etc.

## Examples

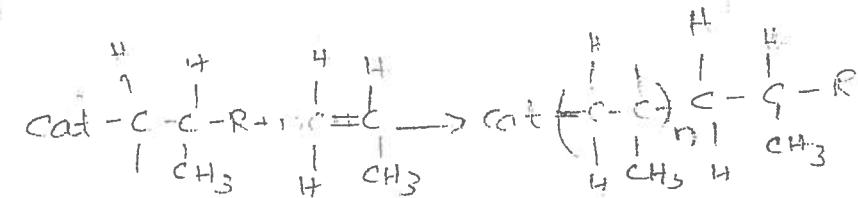
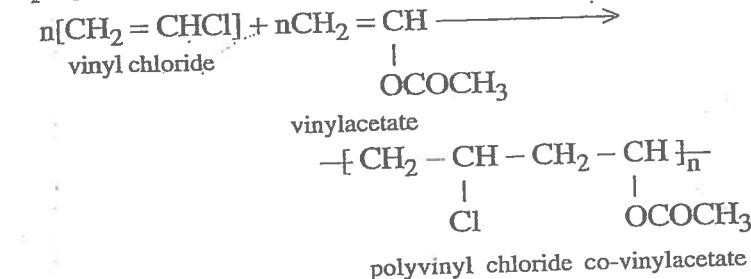
1. Butadiene and styrene copolymerise to give GR-S rubber



copolymerisation



2. Vinyl chloride and vinyl acetate copolymerise to give polyvinyl chloride-co-vinyl acetate



*Imp*

### 3.4.5 Differences between addition (chain) polymerisation and condensation (step) polymerisation

S.No.	Addition/chain polymerisation	Condensation/step polymerisation
1.	The monomer must have atleast one multiple bond  <b>Example:</b> (i) Acetylene: $\text{CH} \equiv \text{CH}$	The monomer must have atleast two different functional groups.  <b>Example:</b> $\text{N}(\text{H}_2)_5\text{N}_2$
2.	Monomers add on to give a polymer and no other by product is formed.	Monomers condense to give a polymer and by-products such as $\text{H}_2\text{O}$ , $\text{CH}_3\text{OH}$ are formed.
3.	Number of monomeric units decreases steadily throughout the reaction.	Monomers disappear at the early stage of reaction.
4.	Molecular weight of the polymer is an integral multiple of molecular weight of monomer.	Molecular weight of the polymer need not be an integral multiple of monomer.
5.	High molecular weight polymer is formed at once.	Molecular weight of the polymer rises steadily throughout the reaction.
6.	Longer reaction times give higher yield, but have a little effect on molecular weight.	Longer reaction times are essential to obtain high molecular weight.

S.No.	Addition/chain polymerisation	Condensation/step polymerisation
7.	Thermoplastics are produced. <b>Example:</b> polyethylene, PVC, etc.,	Thermosetting plastics (or) thermoplastics are produced. <b>Example:</b> Bakelite, Nylon - 6.
8.	Homo-chain polymer is obtained.	Hetero-chain polymer is obtained.

### 3.5 PLASTICS

*Plastics are high molecular weight organic materials, that can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst.*

Originally, plastics were discovered and then developed based on trial and error method. The present time is sometime referred as plastic age, because the use of polymeric material is percolated in large variety of applications. This rapid growth has taken place only in the last 50 years. It was man's desire to develop plastics for engineering applications to replace, glass, metal, ceramic, wood and other materials of constructions. Since plastics possess the following advantages, they have wider applications.

#### 3.5.1 Advantages and disadvantages of plastics

##### Advantages of plastics over other materials

1. They are light in weight.
2. They possess low melting point.
3. They can be easily moulded and have excellent finishing.
4. They possess very good strength and toughness.
5. They possess good shock absorption capacity.

6. They are corrosion resistant and chemically inert.
7. They have low co-efficient of thermal expansion and possess good thermal and electrical insulating property.
8. They are very good water-resistant and possess good adhesiveness.

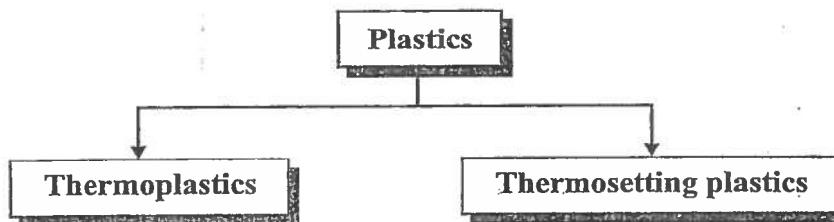
#### Disadvantages of plastics

1. They have high softness.
2. They undergo embrittlement at low temperature.
3. They undergo deformation under load.
4. They possess low heat-resistant and poor ductility.
5. Combustibility is high.
6. They undergo degradation upon exposure to heat and UV- radiation.
7. They are Non bio-degradable.

#### 3.5.2 Classification of Plastics

Based on the structure and type of resin used for the manufacture of plastics, plastics are classified into two main types.

1. Thermoplastics.
2. Thermosetting plastics.



#### Examples

- (i) Polyethylene
- (ii) Polyvinyl chloride
- (iii) Polystyrene
- (iv) PAN

#### Examples

- (i) Bakelite
- (ii) Polyester
- (iii) Urea-formaldehyde
- (iv) Epoxy-resin

#### Resin

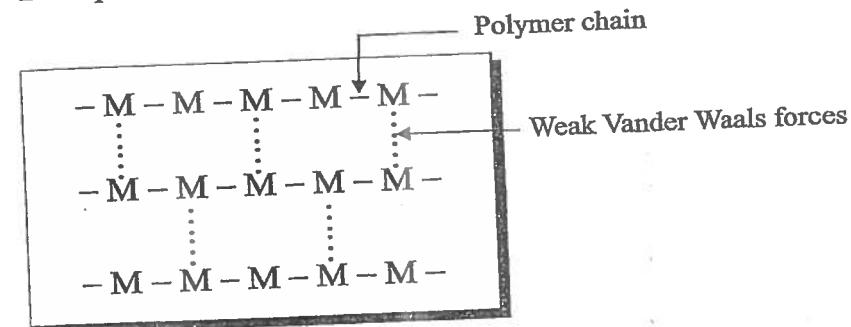
Resin is a basic binding material, present in plastics, which undergoes polymerization reaction during moulding.

#### 1. Thermoplastic resins

Thermoplastics are prepared by addition polymerisation. They are straight chain (or) slightly branched polymers and various chains are held together by weak Vander Waal's forces of attraction.

Thermoplastics can be softened on heating and hardened on cooling. They are generally soluble in organic solvents.

**Examples** Polyethylene, Polyvinyl chloride.



#### 2. Thermosetting resins (or) Thermosets

Thermosetting plastics are prepared by condensation polymerisation. Various polymer chains are held together by strong covalent bonds (called crosslinks).

Thermosetting plastics get harden on heating and once harden, they cannot be softened again. They are almost insoluble in organic solvents.

Examples: Bakelite, Polyester.

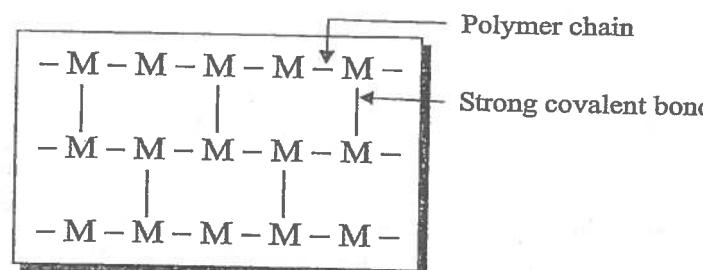


Table 3.1 Difference between thermoplastic and thermosetting resins

S. No.	Thermoplastic resins	Thermosetting resins
1.	They are formed by addition polymerisation.	They are formed by condensation polymerisation.
2.	They consist of linear long chain polymers.	They consist of three dimensional network structure.
3.	All the polymer chains are held together by weak VanderWaals forces.	All the polymer chains are linked by strong covalent bonds.
4.	They are weak, soft and less brittle.	They are strong, hard and more brittle.
5.	They soften on heating and harden on cooling.	They do not soften on heating.
6.	They can be remoulded.	They cannot be remoulded.

S. No.	Thermoplastic resins	Thermosetting resins
7.	They have low molecular weights.	They have high molecular weights.
8.	They are soluble in organic solvents.	They are insoluble in organic solvents.
9.	The resin is synonymous with plastics.	Resin is not synonymous with plastics.
10.	<b>Example:</b> Polyethelene, PVC, etc.,	<b>Example:</b> Bakelite, Ureaformaldehyde resin, etc.,

### 3.6 SOME IMPORTANT POLYMERS

#### 3.6.1 Bakelite (or) Phenolic resin

It is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of acid or alkali catalyst.

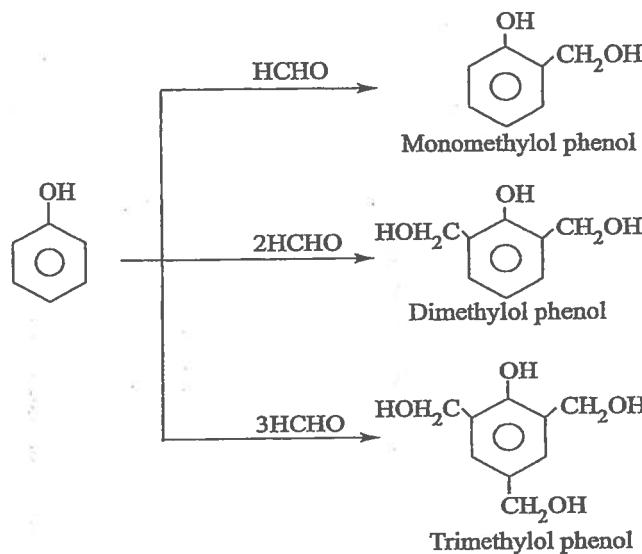
##### Preparation

The reaction involves the following 3 steps.

##### I Step

##### Methylation

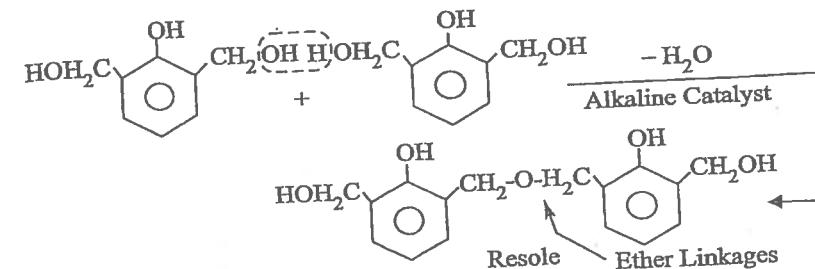
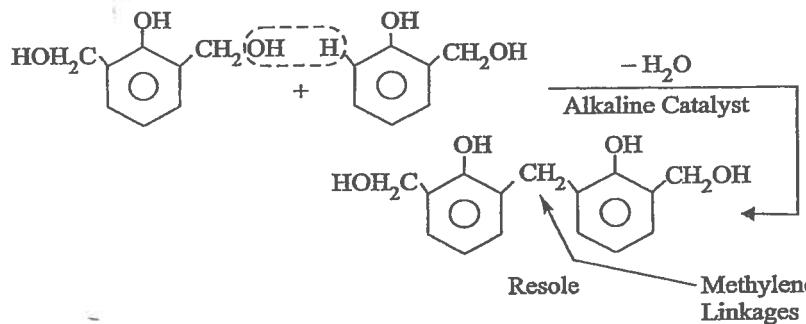
The first step is the reaction between phenol and formaldehyde, forms mono, di and tri-methylol phenols.

**II Step**

## (i) Formation of A - stage resin (Resole)

When methylol phenols are heated with excess of formaldehyde in presence of alkaline catalyst. The methylol phenols condense either through methylene linkages or through ether linkages to form resoles.

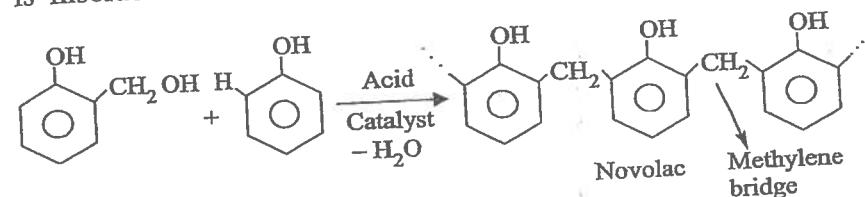
Resole is a low molecular weight linear polymer. It is completely soluble in alkaline solution.



## (ii) Formation of B - stage resin (Novolac or Resitol)

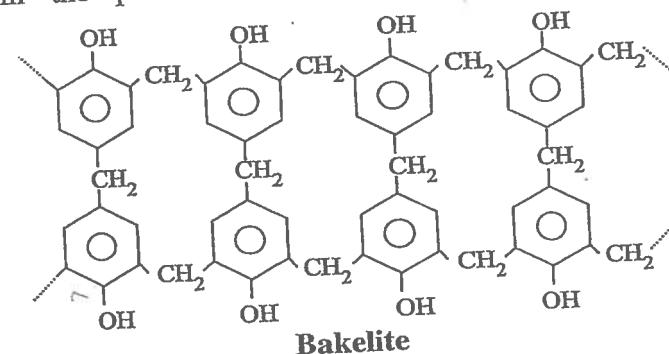
When methylol phenols are heated with excess of phenol in presence of acid catalyst, the methylol phenols condense with phenol through methylene linkages to form novolacs.

Novolac is a high molecular weight linear polymer. It is insoluble in alkaline solutions.

**III Step**

## Production of C - stage resin (Bakelite)

Further heating of A - stage resin or B - stage resin or both in the presence of a curing agent (hexamethylene



tetramine) produces hard, rigid, infusible, cross-linked polymer called bakelite.

#### Properties

- Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalis because of the presence of  $-OH$  groups.
- It possesses excellent electrical insulating property.

#### Uses

- Bakelite is used as an adhesive in plywood laminations & in grinding wheels, etc.
- It is also widely used in paints, varnishes.
- It is used for making electrical insulator parts like plugs, switches, heater handles, etc.,

### 3.6.2 Amino Resins (or) Urea-formaldehyde

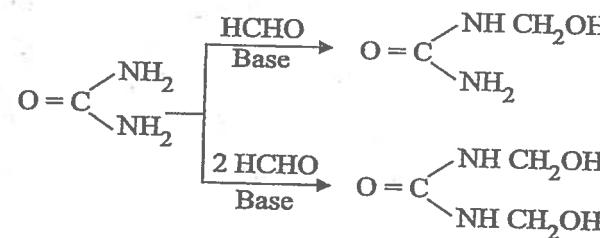
Urea formaldehyde is obtained by the condensation polymerisation of urea and formaldehyde in the presence of base catalyst.

#### Preparation

The reaction involves the following 2 steps

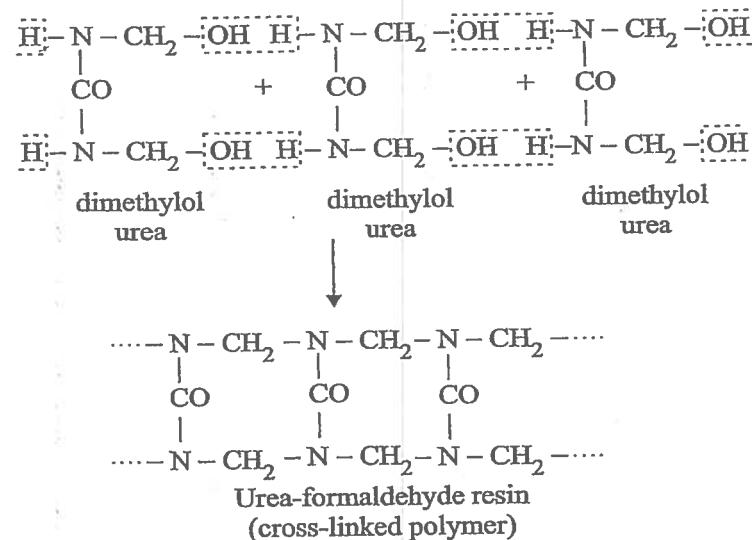
#### I Step Methyolation

The first step is the reaction between urea and formaldehyde, forms mono or dimethylol urea.



#### II Step Condensation of methylol urea

When the methylol ureas are heated with fillers, plasticizers, pigments and catalyst and cured (by applying heat and pressure), a three dimensional network cross linked polymer will be obtained.



#### Properties

- Urea-formaldehyde resins give white-water soluble products.
- It has good tensile strength, good electrical insulation, good chemical-resistance, and great hardness.

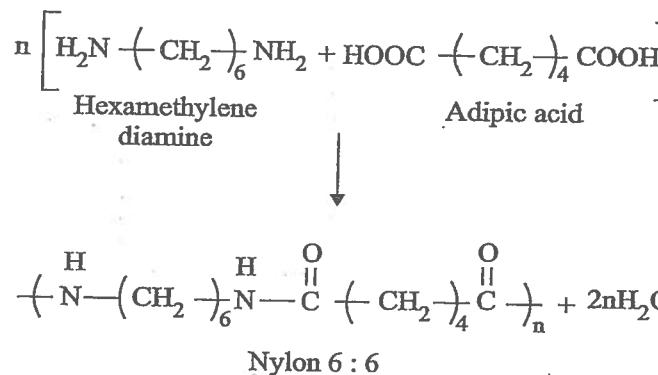
#### Uses

- It is used in bonding of grinding wheels, plywoods.
- It is used as a binder of glass fibres, rock wool and foundry cores.
- It is used as decorative articles like plates, drinking glasses, dishes, electrical insulators.
- It is used as lacquers and surface adhesives.

### 3.6.3 Nylon-6:6

#### Preparation

It is obtained by the polymerization of adipic acid with hexamethylenediamine.



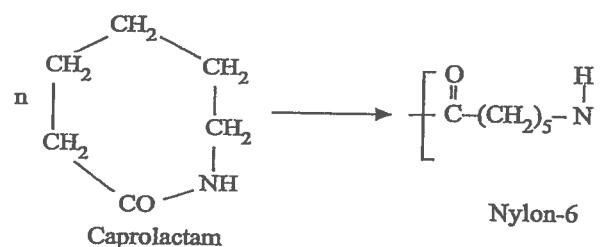
#### Properties of Nylon 6:6

- (i) Nylon 6:6 is a less soft and stiff material when compared to nylon 6.
- (ii) Its melting point is 264°C.

### 3.6.4 Nylon-6 (Kapron)

#### Preparation

It is produced by the self-condensation of E-aminocaproic acid ( $\epsilon$ -caprolactam).



#### Properties of Nylon-6

- (i) Nylon 6 is a light weight, soft and less stiff material.
- (ii) Its melting point is 225°C.

#### General properties of nylons

- (i) They behave as plastic as well as fiber.
- (ii) They are translucent, white, horny and high melting polymers.
- (iii) They are insoluble in common organic solvents but soluble in phenol and formic acid.
- (iv) They possess good mechanical properties and fairly resistant to moisture.
- (v) They are characterised by combination of high strength, elasticity, toughness and abrasion resistance.

#### Uses of Nylons

- (i) Nylon 6:6 is used for fibers, which are used in making socks, ladies shoes, dresses, carpets, etc.,
- (ii) Nylon 6 is mainly used for moulding purposes for gears, bearings, electrical mountings, etc., Nylon bearings work without any lubrication.
- (iii) Nylons are used for making filaments for ropes, bristles for tooth-brushes, films and tyre-cords.

### 3.6.5 Carbon fibers

Carbon fibers are obtained as a continuous filament, by the pyrolysis of organic fibers such as cellulose, polyacrylonitrile (PAN) in an inert atmosphere. The monofilaments of these fibers have diameters of about 5 – 10  $\mu$ .

#### Properties of carbon fibres

1. Carbon fibre has high strength to weight ratio.

2. It is very rigid.
3. It is corrosion resistant and chemically stable.
4. It is electrically conductive.
5. It possesses very good tensile strength.
6. It is non flammable and fire resistant.
7. It has low coefficient of thermal expansion.
8. It is non poisonous, biologically inert and X - ray permeable.
9. It is expensive and brittle.

#### Advantages

These are used as very good reinforcing materials due to

- (i) ~~high~~ high modulus, specific strength and stiffness even at elevated temperatures.
- (ii) resistant to acids, bases, number of solvents and moisture.

#### Uses

1. They are used as reinforcing material with polyester resins (or) epoxy resins to form composites, which have higher specific strength than metals.
2. They are high performance fibers, used for highly complicated works.

### 3.7 RUBBERS (OR) ELASTOMERS

*Rubbers (or) elastomers are non-crystalline high polymers (linear polymers), having elastic and other rubber-like properties.*

#### 3.7.1 Types of Rubbers

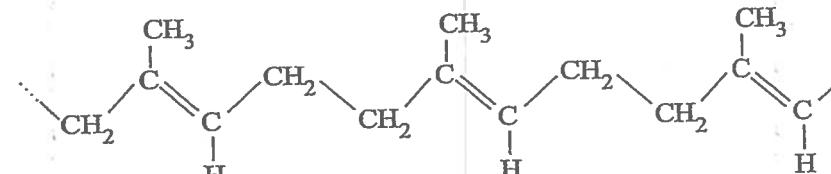
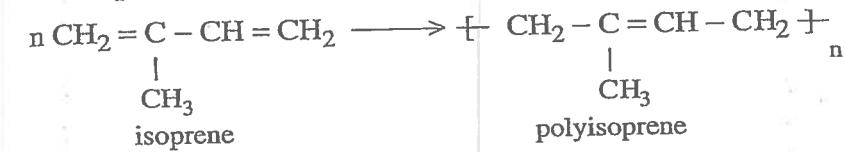
Rubbers can be obtained from two sources, which may be natural or artificial. Thus, we have:

1. Natural rubber, and
2. Synthetic rubber (elastomers)

#### 1. Natural rubber

Natural rubber is obtained from the tree as a latex, which is a dispersion of isoprene. During the treatment of latex, these isoprene molecules undergo polymerisation to form long coiled chain of polyisoprene.

Example : *Cis Polyisoprene*



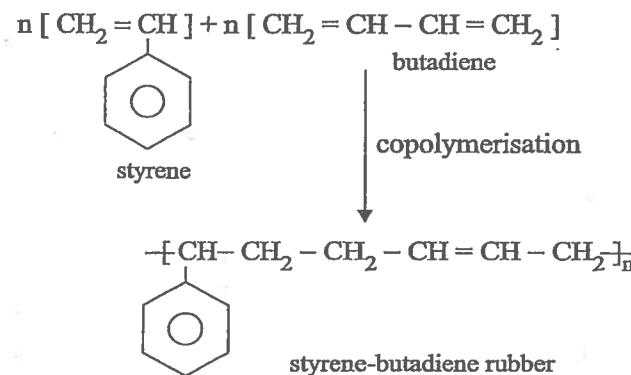
Cis form of polyisoprene

#### 2. Synthetic rubber

An elastomer (synthetic rubber) is any vulcanisable man made rubber like polymer, which is superior to natural rubber in certain properties.

Example: *Styrene rubber (Buna-S)*

Buna-S rubber is produced by copolymerization of butadiene and styrene.

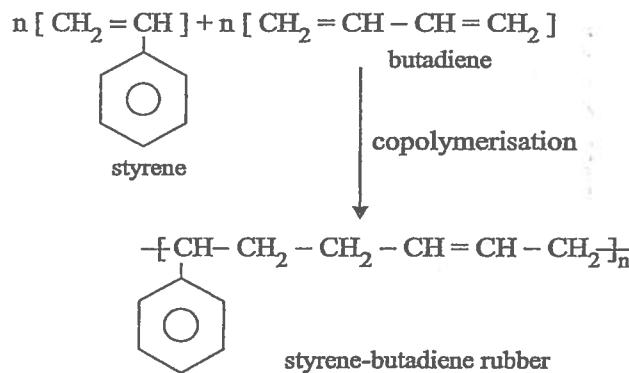


### 3.7.2 SBR (Styrene-butadiene rubber) (GR-S (or) Buna-S (or) ameripol rubber (or) cold rubber)

SBR is the polymer of about 75% butadiene and 25% styrene.

#### Preparation

SBR is obtained by copolymerizing an aqueous emulsion of the mixture containing 75% butadiene, 25% styrene and an emulsifying agent (cumene hydroperoxide).



#### Properties

1. SBR is resistant to abrasion and possess high load bearing capacity.

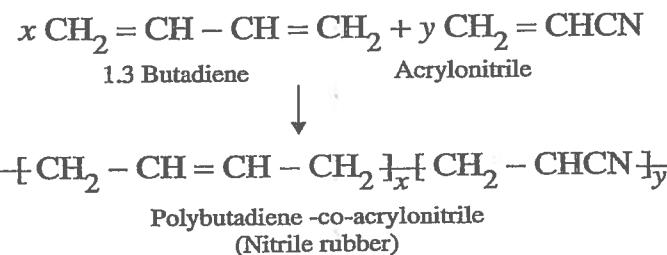
2. It undergoes oxidation readily, when traces of ozone is present in the atmosphere.
3. It requires less sulfur for vulcanization when compared to natural rubber.
4. Tensile strength and flexibility of SRB are inferior to those of natural rubber.

#### Uses

1. SRB is used for making light duty tyres, belts hoses and gaskets.
2. It is also used in footwear industry.
3. It is used as an adhesives and in electrical insulation.

### 3.7.3 Buna-N (or) Nitrile rubber (or) GR-A Rubber

Buna-N is a copolymer of butadiene and acrylonitrile. It is obtained by copolymerizing butadiene with acrylonitrile.



#### Properties

1. It has excellent resistance to heat and sunlight.
2. It is easily affected by alkali.
3. It can be vulcanised in the same way as natural rubber.
4. It is resistant to oils, acids and salt.

#### Uses

1. It is used in making conveyor belts and tank linings.
2. It is used in the production of hoses and gaskets.
3. It is also used in the production of resistant foams and automobile parts.

### 3.8 CONDUCTING POLYMERS

Generally polymers like plastics, elastomers are regarded as insulators because of the presence of strong C - C covalent bond. But, under certain circumstance, these can be made to behave like a metal (conductor).

Thus, those polymers, which conduct electricity are called conducting polymers. The conduction in the polymers is mainly due to the following reasons.

#### Reason for the conduction in the polymer

- (a) Presence of unsaturated conjugated double bonds in the polymer.
- (b) Addition or removal of electrons (doping) in to the polymer.

#### Examples

Two important examples for conducting polymers are Polyaniline, polyacetylene, etc.,

#### 3.8.1 Preparation of conducting polymers

Conducting polymers are mainly prepared by doping the polymers.

#### Doping

To becoming electrically conductive, the electrons of the polymer need to be free to move. The polymers having conjugated double bond has to be disturbed either by removing electron from or inserting the electron into the polymer by oxidation or reduction. This process is known as doping.

#### Types of doping

1. p - doping: Oxidation with Lewis acids (or) halogens.
2. n - doping: Reduction with Lewis acids (or) alkali metals.

base<sup>b</sup>

#### 1. p - doping

In p - doping an intrinsically conducting polymer or the polymer having conjugated C = C bonds are treated with Lewis acids or halogens, which oxidises the polymers and creates positively charged sites on polymer back bone.

Due to the positive charge on the polymer backbone, they are acting as good conductors of electricity like metal.

#### Examples

Examples for p-dopant: I<sub>2</sub>, Br<sub>2</sub>, AlCl<sub>3</sub>, AsF<sub>5</sub>, FeCl<sub>3</sub>

#### 2. n - doping

In n - doping an intrinsically conducting polymers or the polymers having conjugated C = C bonds are treated with Lewis bases or alkali metals, which reduces the polymers are creates negatively charged sites on polymer back bone.

Due to the negative charge on the polymer back bone, they are acting as good conductor of electricity like metal.

#### Examples

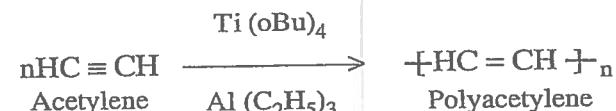
Examples for n-dopant: Na, K, Lithiumnaphthalides, etc.,

### 3.9 IMPORTANT CONDUCTING POLYMERS

#### 3.9.1 Polyacetylene

##### Preparation

Polyacetylene is prepared by the addition polymerisation of acetylene. Acetylene gas is passed over the Ziegler - Natta catalyst to get polyacetylene.



Polyacetylene is a infusible, insoluble and becomes brittle on exposure to air.

### Mechanism of conduction (or) Synthesis of conducting polyacetylene

The conductivity of cis - polyacetylene is less when compare to trans polyethylene.

The conductivity of polyacetylene can be improved by either p - doping (or) n - doping.

#### 1. p - doping

It involves, the following two steps.

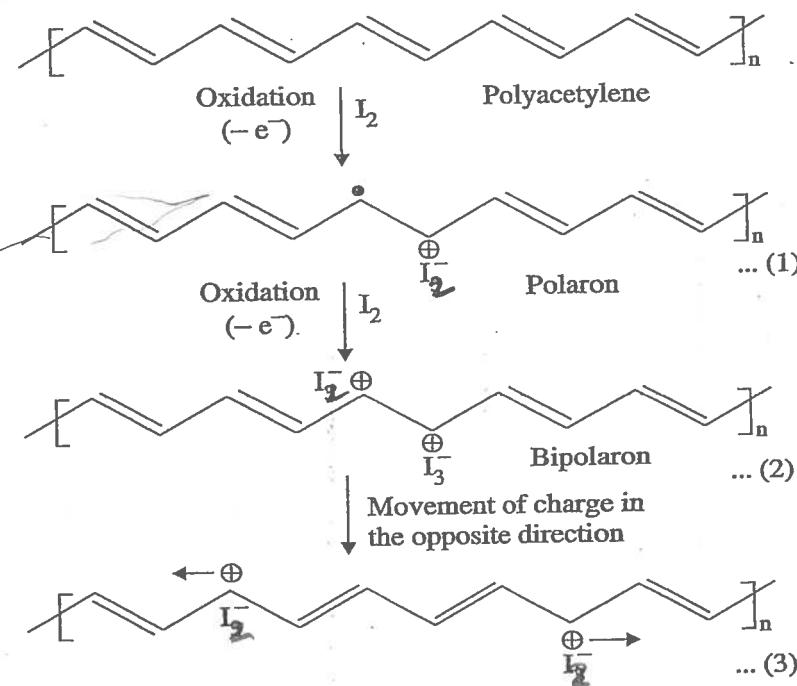
##### Step 1

1 step involves the oxidation of a polyacetylene with iodine vapour (Lewis acid).

During oxidation, (as shown in reaction 1) the iodine molecules remove an electron from polyacetylene chain and becomes  $I_2^-$ . Now the polyacetylene chain carrying the +ve charges is called polaron.

##### Step 2

The second oxidation of polaron (as shown in reaction 2) produces two +ve charges on the chain called bipolaron. This +ve charges are mobile because of delocalisation and responsible for electrical conductance (as shown in reaction 3).



#### 2. n - doping

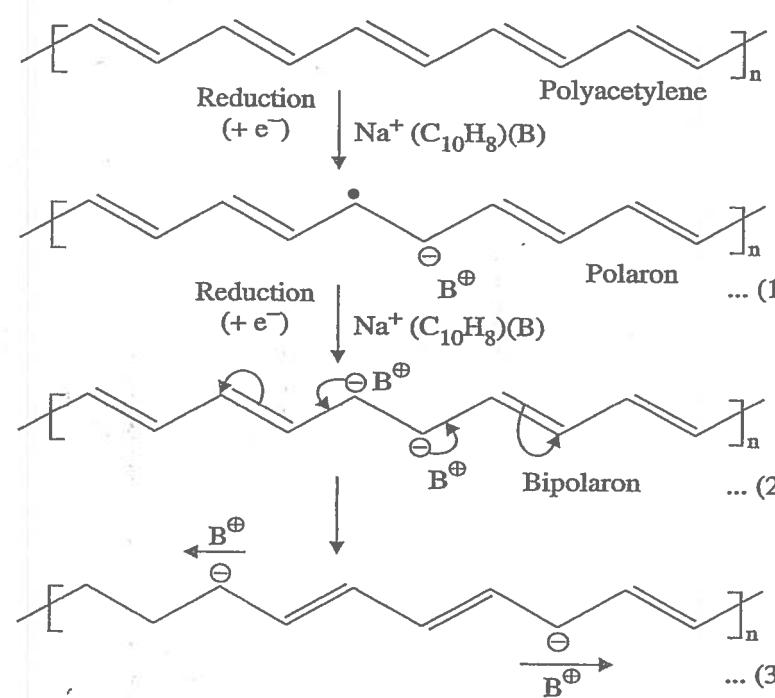
n - doping also involves two steps

##### Step 1

Step 1 involves reduction of polyacetylene with sodium naphthalide  $Na^+(C_{10}H_8)^-$ . During the reduction (as shown in reaction 1) sodium naphthalide donates an electron to polyacetylene chain. Now the polyacetylene carrying the (-)ve charge is called polaron.

##### Step 2

Step 2 involves second reduction of polaron (as shown in reaction 2) to produce two (-)ve changes on the chain called bipolaron. This (-)ve charges are mobile because of delocalisation and responsible for electrical conductance (as shown in reaction 3).



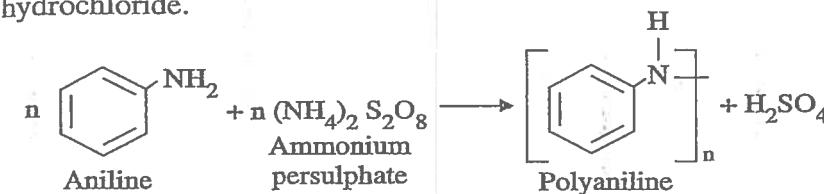
#### Applications of Polyacetylene

1. It is used in various electronic devices as active and passive electrodes.
2. The main areas of its application are batteries, nonlinear optics and microelectronics.
3. PA with various conductivities are used for the formation of schottky barriers, p-n transitions, heterojunctions.
4. It is used in the development of photovoltaic devices.
5. It is also used as an electrode material in solid-state batteries operating at room temperature.

#### 3.9.2 Polyaniline

##### Preparation

Polyaniline is prepared by the slow addition of aqueous solution of ammonium per sulphate to a solution of aniline in aqueous HCl at lower temperature (0 – 5°C). The precipitate formed is separated by filtration, which is emeraldine hydrochloride.



Polyaniline is a transparent and stable material. It shows green colour in conducting state. It turns to red under reducing condition and blue under oxidising condition.

##### Mechanism of conduction (or) Synthesis of conducting polyaniline

The conductivity of polyaniline can be improved by either p-doping or n-doping.

##### 1. p-doping

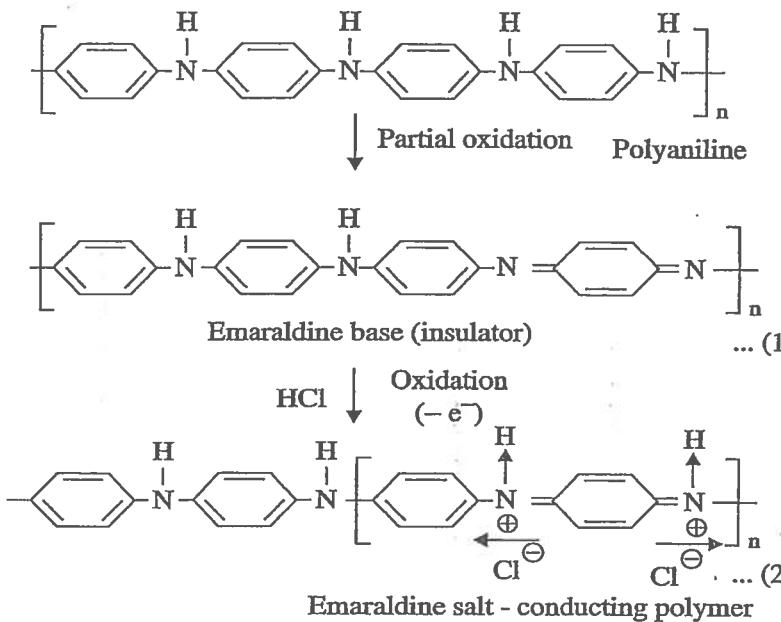
It involves the following two steps.

##### Step 1

Step 1 involves partial oxidation of polyaniline to emeraldine base, which is non conductive (as shown in reaction 1).

##### Step 2

Step 2 involves oxidation of emeraldine base (as shown in reaction 2) using Lewis acid like HCl to emeraldine salt, which is a conducting polymer. During oxidation HCl removes electron from polyaniline chain and creates (+) ve hole in the polymer back bone, which is responsible for conduction.



#### Applications of polyaniline

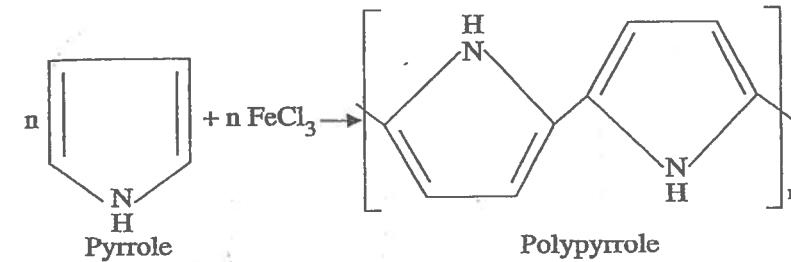
1. Polyaniline is used in sensors, PCB (Printed Circuit Boards), conductive fabrics, smart windows.
2. It is used as a corrosion resistant.
3. It is used as a coating for films and semi-finished articles.
4. In rechargeable batteries, polyaniline is used as a secondary electrode.

#### 3.9.3 Polypyrrole

Polypyrrole is a type of organic polymer formed by the polymerisation of pyrrole. Polymerisation of pyrrole may be carried out chemically (or) electrochemically. It is a very good conducting polymers with conjugated double bonds. Conducting polypyrrole consists of number of connected pyrrole ring structure.

#### Preparation

Polypyrrole is prepared by oxidation (p-doping) of pyrrole using ferric chloride in methanol.



The polymerisation and p-doping can also be carried out electrochemically.

#### Applications

1. Polypyrrole is used as biosensors, gas sensors, antielectrostatic coatings, light weight rechargeable batteries, etc.
2. It is used in carbon composites due to its excellent thermal stability.
3. It is used for manufacturing containers for protein, so it can be used for drug delivery.
4. The blend of polypyrrole based polymer, protects corrosion of metals.
5. It acts as a support for the catalyst used in fuel cells.
6. It is used as a counter electrode in dye-sensitised solar cells.

#### 3.9.4 General applications of conducting Polymers

1. Conducting polymers are used in solar cells.
2. It is used in telecommunication systems.
3. It is also used as a very good electrode material for rechargeable batteries.

4. Conducting polymers are used in antistatic coatings for clothing.
5. It is used as a membrane film for gas separations.
6. Conducting polymers are used as electrocatalytic materials in fuel cells.
7. It is used for making analytical sensors.
8. It is used for making ion exchangers.

### 3.10 DESCRIPTIVE TYPE QUESTIONS

1. Explain the functionality and significance of monomers.
2. Explain the free-radical mechanism of chain growth polymerisation.
3. Write notes on the followings
  - (i) Co-ordination polymerization
  - (ii) Co-polymerisation.
4. Explain thermoplastics and thermosetting plastics.
5. Explain preparation, properties and applications of bakelite.
6. Explain the followings
  - (i) Urea-formaldehyde resin
  - (ii) Nylon 6:6.
7. Explain preparation, properties and uses of SBR rubber
8. What are conducting polymers. Explain the conduction mechanism of polyacetylene.
9. Write notes on conducting polypyrrole.

*-types of polymerisation & conducting polymers*

## Instrumental Methods and Applications

### 4.1 INTRODUCTION

Instrumental methods (or) Analytical technique (or) Spectroscopy is one of the most powerful tool available for the study of atomic and molecular structure, and is used in the analysis of a most of the samples.

Spectroscopy deals with the study of interaction of electromagnetic radiation with the matter. During the interaction, the energy is absorbed (or) emitted by the matter. The measurement of this radiation frequency (absorbed (or) emitted) are made using spectroscopy.

### 4.2 TYPES OF SPECTROSCOPY

The study of spectroscopy can be carried out under the following headings

1. Atomic spectroscopy.
2. Molecular spectroscopy.

#### 1. Atomic spectroscopy

It deals with the interaction of the electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

## 2. Molecular spectroscopy

It deals with the interaction of electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

**Table 4.1 Differences between molecular spectra and atomic spectra**

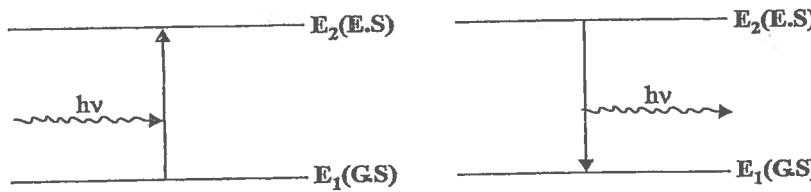
Sl. No.	Atomic spectra	Molecular spectra
1.	It occurs from the interaction of atoms + electromagnetic radiation:	It occurs from the interaction of molecules + electromagnetic radiation.
2.	Atomic spectra is a line spectra.	Molecular spectra is a complicated spectra.
3.	It is due to electronic transition in an element.	It is due to vibrational, rotational and electronic transition in a molecule.

## 4.3 SPECTRUM

How does a Spectrum arise?

### 1. Absorption spectrum

Consider a molecule having only two energy levels  $E_1$  and  $E_2$  as shown in the figure. 4.1.



(a) Absorption spectrum

(b) Emission spectrum

Fig 4.1 Spectrum

When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule absorbs photon of energy  $h\nu$  and undergoes a transition from the lower energy level to the higher energy level. The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy. The spectrum thus obtained is called the **absorption spectrum**. (Fig 4.1. a)

### 2. Emission spectrum

If the molecule comes down from the excited state to the ground state with the emission of photons of energy  $h\nu$ , the spectrum obtained is called **emission spectrum**, (Fig. 4.1.b).

## 4.4 ABSORPTION OF RADIATION

When electromagnetic radiation is passed through a matter, the following changes occur.

- As the photons of electromagnetic radiations are absorbed by the matter, electronic transition, vibrational changes (or) rotational changes may occur. After absorption, molecules get excited from the ground state to excited state. Then they liberate energy quickly in the form of heat (or) re-emit electromagnetic radiation.
- But in some cases, the portion of electromagnetic radiation, which passes into the matter, instead of being absorbed may be scattered (or) reflected (or) re-emitted.
- When the electromagnetic radiation is absorbed (or) scattered, it may undergo changes in polarisation (or) orientation.
- In some cases the molecules absorbs radiation and get excited.

### (a) Fluorescence

If the excited molecules re-emits the radiation almost instantaneously (within  $10^{-8}$  seconds), it is called fluorescence.

(b) **Phosphorescence**

If the excited molecules re-emits the radiation after sometime (slowly), it is called phosphorescence.

#### 4.4.1 Factors affecting absorbance

The fractions of photons being absorbed by the matter depends on,

1. **The nature of the absorbing molecules.**

2. **The concentration of the molecules.**

If the concentration of the molecules are more, the absorbed photons will be more.

3. **The length of the path of the radiation through the matter.**

If the length of the path is long, the larger number of molecules are exposed and hence greater the photons will be absorbed.

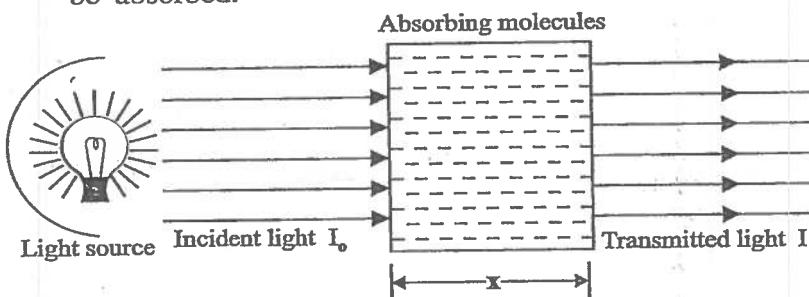


Fig. 4.2 Absorbance of photons by the matter

## 4.5 ELECTROMAGNETIC SPECTRUM

The entire range over which electromagnetic radiation exists is known as electromagnetic spectrum. The electromagnetic spectrum covers larger range of wavelength.

Fig. 4.3 shows a diagrammatic representation of the electromagnetic spectrum. A logarithmic scale is used in this representation. The divisions between the different spectral

regions indicate the origin of radiation. The limits indicated in fig. 4.3 are arbitrary.

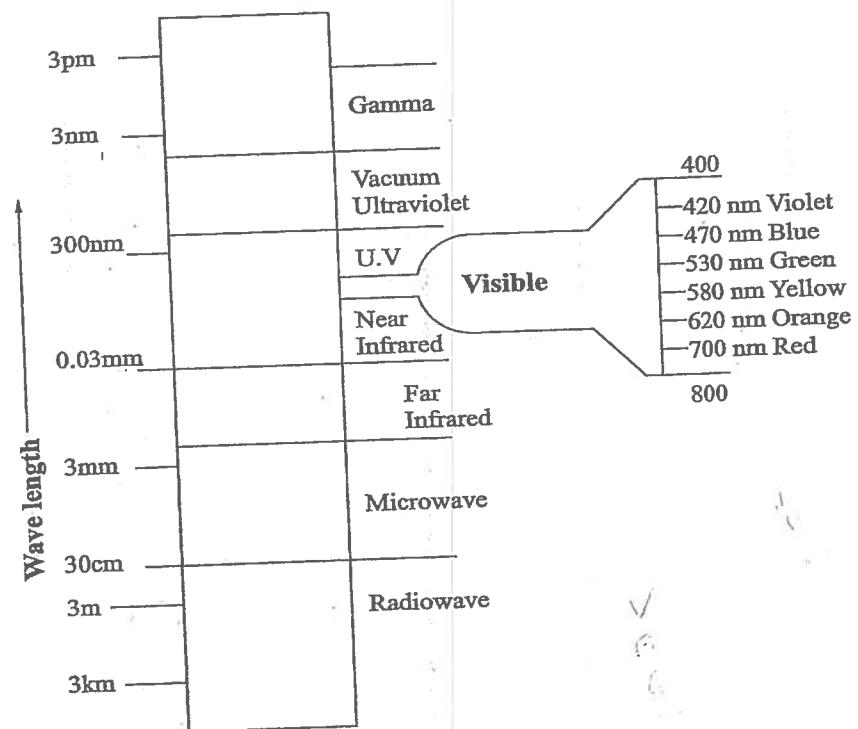


Fig. 4.3 Electromagnetic spectrum

#### 4.5.1 Characteristics of Electromagnetic spectrum

The major characteristics of various spectral regions are described as follows:

Spectral region & Sources	Wave length range	Energy change involved	Characteristics
Gamma rays	100 to 1 pm <i>(picometre)</i>	$10^9$ to $10^{11}$ J/mole (Nuclear level)	Shortest wave length emitted by atomic nuclei.
X-rays	10 nm to 100 nm	$10^7$ to $10^9$ J/mole (K and L shell electrons)	Emitted (or) absorbed by movement of electrons close to nuclei.
Ultraviolet	100 to 400 nm	$10^7$ to $10^6$ J/mole (middle and valance shell electrons)	Since air starts absorbing below 180 nm, above 180 nm is used for chemical analysis.
Visible	400 to 750 nm	$10^6$ to $10^5$ J/mole (valency electrons)	Within the visible region, a person with normal colour vision is able to sense the colour.
Infrared	0.75 to 1000 $\mu\text{m}$ <i>(micrometre)</i>	$10^3$ to $10^5$ J/mole (molecular vibration and rotation)	This region corresponds to change in the vibration of the molecules.

Spectral region & Sources	Wave length range	Energy change involved	Characteristics
Microwave	0.1 to 50 cm	$10^1$ to $10^3$ J/mole (molecular rotation spin orientation)	It corresponds to change in the rotation of molecule.
Radiowave	1 to 30 m	less than $10^1$ J/mole	It corresponds to change the spin of the electron.

#### 4.6 BEER'S LAW (OR) BEER-LAMBERT'S LAW

According to this law, "when a beam of monochromatic radiation is passed through a *solution of an absorbing substance*, the rate of decrease of intensity of radiation ' $dI$ ' with thickness of the absorbing solution ' $dx$ ' is proportional to the *intensity of incident radiation* ' $I$ ' as well as the concentration of the solution ' $C$ '."

It is mathematically represented as

$$\frac{-dI}{dx} = kIC \quad \dots\dots\dots (1)$$

where,  $k$  = molar absorption coefficient.

On integrating the equation (1) between limits  $I = I_0$  at  $x = 0$  and  $I = I$  at  $x = x$ , we get

$$\int_{I_0}^I \frac{dI}{I} = - \int_0^x kCdxdx$$

$$\ln \frac{I}{I_0} = -kCx \quad (\text{or}) \quad 2.303 \log \frac{I}{I_0} = -kCx$$

$$\text{(or)} \log \frac{I_0}{I} = \frac{k}{2.303} Cx$$

$$\text{(or)} A = \epsilon Cx \quad \dots \dots \dots \quad (2)$$

where,  $\epsilon = \frac{k}{2.303}$  = molar absorptivity coefficient

$$\log \frac{I_0}{I} = A = \text{Absorbance (or) Optical density}$$

The equation (2) is called Beer-Lambert's law.

*Thus, the absorbance (A) is directly proportional to molar concentration (C) and thickness (or) path length (x).*

#### 4.6.1 Application of Beer-Lambert's law

##### Determination of unknown concentration

First absorbance ' $A_s$ ' of a standard solution of known concentration ' $C_s$ ' is measured, then according to Beer-Lambert's law

$$A_s = \epsilon C_s x$$

$$\frac{A_s}{C_s} = \epsilon x \quad \dots \dots \dots \quad (3)$$

Now, absorbance ' $A_u$ ' of a solution of unknown concentration  $C_u$  is measured. Now we have

$$A_u = \epsilon C_u x$$

$$\frac{A_u}{C_u} = \epsilon x \quad \dots \dots \dots \quad (4)$$

From equation (5) and (6), we get.

$$\frac{A_s}{C_s} = \frac{A_u}{C_u}$$

$$\therefore C_u = \frac{A_u}{A_s} \times C_s \quad \dots \dots \dots \quad (5)$$

since the values of  $A_u$  and  $A_s$  are experimentally determined and  $C_s$  is known. The value  $C_u$  (unknown concentration) can be calculated from the equation (5).

#### 4.6.2 Limitations of Beer-Lambert's law

1. Beer-Lambert's law is not obeyed if the radiation used is not monochromatic.
2. It is applicable only for dilute solutions.
3. The temperature of the system should not be allowed to vary to a large extent.
4. It is not applied to suspensions.
5. Deviation may occur, if the solution contains impurities.
6. Deviation also occurs if the solution undergoes polymerization (or) dissociation.

#### 4.6.3 Problems Related to Beer-Lambert's law

##### Problem 1

Find out the absorbance (or) optical density of a solution, if the transmittance of a solution is 18.5%.

##### Solution

Given: Percentage of transmittance ( $\%T$ ) = 18.5% (or) Transmittance ( $T$ ) = 0.185.

$\therefore$  Absorbance (or) optical density

$$A = \log \frac{1}{T} \text{ (or)} - \log T$$

$$= -\log 0.185$$

$$(A = \epsilon Cx)$$

Absorbance = 0.733

### Problem 2

The percentage transmittance of  $5 \times 10^{-4} M$  solution of disodium fumarate in a 1 cm cell is 19.2%. Calculate (i) the absorbance ( $A$ ), (ii) the molar absorption coefficient ( $\epsilon$ ).

#### Solution

Given: % T = 19.2% (or)  $T = 0.192$ ;  $C = 5 \times 10^{-4} M$

$$x = 1$$

#### (i) Absorbance

$$A = -\log T$$

$$A = -\log 0.192$$

$$A = 0.717$$

#### (ii) The molar absorption coefficient

$$\epsilon = \frac{A}{Cx}$$

$$= \frac{0.717}{5 \times 10^{-4} \times 1}$$

$$= 1.434 \times 10^3 \text{ mol dm}^{-3}$$

### Problem 3

A solution shows a transmittance of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption coefficient is  $12,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

#### Solution

Given: %T = 20%;  $T = 0.20$ ;  $x = 2.5$ ;  $\epsilon = 12,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

$$\begin{aligned} A &= -\log T = -\log 0.20 \\ &= 0.699 \end{aligned}$$

We know that

$$A = \epsilon Cx$$

$$\therefore C = \frac{A}{\epsilon x} = \frac{0.699}{12,000 \times 2.5}$$

$$= 2.33 \times 10^{-5} \text{ mol dm}^{-3}$$

### Problem 4

Calculate the molar absorption of a solution  $1 \times 10^{-4} M$ . The absorbance of which is 0.20, when the path length is 2.5 cm.

#### Solution

Given:  $A = 0.20$ ;  $C = 1 \times 10^{-4}$ ;  $x = 2.5 \text{ cm}$

We know that,  $A = \epsilon Cx$

$$\therefore \text{Molar absorptivity, } \epsilon = \frac{A}{Cx} = \frac{0.20}{1 \times 10^{-4} \times 2.5}$$

$$\text{Molar absorption} = 800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

### Problem 5

A monochromatic radiation is incident on a solution of  $0.05 M$  concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction co-efficient of the substance.

**Solution**

According to Beer-Lambert law,  $\log \frac{I}{I_0} = -\epsilon Cx$

Given:  $C = 0.05 \text{ M}$ ;  $x = 10 \text{ cm}$ ;  $I = 1/4$ ;  $I_0 = 1$ ;  $\epsilon = ?$

The above equation may be written as

$$\epsilon = \frac{-\log (I/I_0)}{Cx} = \frac{-\log \left[ \frac{\frac{1}{4}}{1} \right]}{0.05 \times 10} = \frac{-(-0.6020)}{0.5}$$

Molar extinction co-efficient  $\epsilon = 1.204 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**Problem 6**

A solution of thickness 2cm transmits 40% incident light. Calculate the concentration of the solution, given that  $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**Solution**

Given: %  $T = 40\%$ ;  $T = 0.40$ ;  $x = 2.0 \text{ cm}$ ;

$$\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$A = -\log T$$

$$= -\log 0.40$$

$$= 0.3980$$

We know that

$$A = \epsilon Cx$$

$$C = \frac{A}{\epsilon x} = \frac{0.3980}{6000 \times 2}$$

$$\text{Concentration} = 3.316 \times 10^{-5} \text{ mol dm}^{-3}$$

**pH - METRY**

pH - metry is a scientific method used to measure the hydrogen ion concentration in water based solutions, indicating its acidity (or) alkalinity expressed as pH. The pH metry is usually carried out by pH meter.

**Principle**

The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode, so the pH meter is also referred to as a potentiometric pH meter. These electrodes are inserted into the solution to be tested.

Since the pH of the solution is related to the  $\text{H}^+$  ion concentration by the following formula,

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

measurement of pH gives the concentration of  $\text{H}^+$  ions in the solution. When NaOH is added slowly from the burette to the solution of HCl, the fast moving  $\text{H}^+$  ions are progressively replaced by slow moving  $\text{Na}^+$  ions. As a result pH of the solution increases.



The increase in pH takes place until all the  $\text{H}^+$  ions are completely neutralised (upto the end point). After the end point, further addition of NaOH increases the pH sharply as there is an excess of fast moving  $\text{OH}^-$  ions.

**Applications of pH metry**

1. The rate of chemical reactions, taking place in water, depends on the acidity of water and is therefore useful to know the acidity of water. It is done by using pH meter.

blood pH  
(1-14)

(1-3) - More acidity  
and less basicity

2. It is useful to monitor the pH in agriculture, water quality, swimming pool, environmental remediation.
3. It is useful in healthcare and clinical applications such as blood chemistry
4. It is also useful in direct measurement of pH inside of living cells.
5. Specially designed electrodes are available to measure the pH of semi-solid substances such as foods.

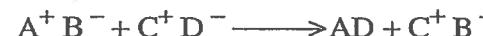
### ~~4.8~~ CONDUCTOMETRY

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry where conductometric titration is a standard technique.

Conductometry is used to describe non-titrative applications. It is applied to determine the total conductance of a solution (or) to analyze the end point of titrations that include ions.

#### Principle

The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of ions mainly depends on the concentration of ions.



where,  $A^+ B^-$  is the solution of strong electrolyte

$C^+ D^-$  is the solution of the reagent

The ionic concentration of  $A^+$  is determined by reacting the electrolyte solution with the reagent solution so that the  $A^+$  ions are replaced by the  $C^+$  ions. This replacement of the ions with the other ions shows the conductance increase (or)

decrease. This is done mainly by the replacement of the hydrogen ion with other cation.

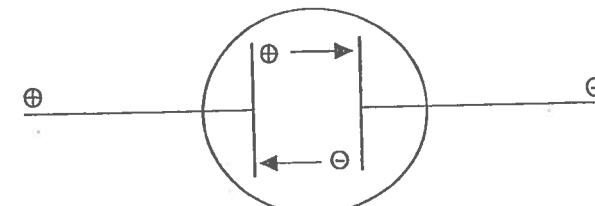


Fig. 4.4 Ionic movement

#### Applications of conductometry

Conductometry is used in the determination of

- (a) solubility of sparingly soluble salts
- (b) ionic product of water
- (c) basicity of organic acids
- (d) salinity of sea water
- (e) chemical equilibrium in ionic reactions
- (f) water purity can be monitored in water purification system
- (g) conductometric titrations

#### Conductometric Titration

Conductometric titration is a volumetric method used to measure conductance of the solution during the titration.

The conductance of a solution depends on

- (i) the number and charge on the free ions, and
- (ii) the mobility of the ions.

## ~~4.9~~ POTENTIOMETRY

### Principle

The principle involved in the potentiometry is when the pair of electrodes is placed in the sample solution, it shows the potential difference by the addition of titrant (or) by the change in concentration of ions.

Emf of a cell depends on the concentration of the electrolytes with which the electrodes are in contact. Therefore, the electrode reaction is,



As the concentration of  $M^{n+}$  changes, the emf of the cell also changes correspondingly.

Thus, the potentiometry titrations involves the measurement of emf between reference electrode and an indicator electrode, with the addition of the titrant.

### Theory

When the electrode of known potential is immersed in the sample solution, then the potential is given by nernst equation  $E = E_0 + (0.592/n) \log C$ . Mainly two electrodes are used in the potentiometry is (i) Reference electrode (ii) Indicator electrode. Reference electrode is used mainly for the determination of the analyte by maintaining the fixed potential.

### Applications of Potentiometry

1. Clinical chemistry: Ion selective electrodes are present sensors for clinical samples because of their selectivity for analyte in complex matrices. The common analytes are electrolytes such as Na, K, Ca, H and Cl and dissolved gases such as  $CO_2$ .

2. Environmental chemistry: For analysis of  $CN^-$ ,  $NH_3$ ,  $NO_3^-$ , F in water and waste water.

3. Agriculture:  $NO_3^-$ ,  $NH_4^+$ , I, Ca, K, CN, Cl in soils, plant materials, fertilizers are analysed.
4. Detergent manufacturing: For analysing Ca, Ba, F and their effects in water quality.
5. Salt content of meat, fish, dairy products, fruit juices are analysed
6. Corrosive effects of  $NO_3^-$  in canned foods.
7. Assay of bisacodyl suppositories and assay of sulpha drugs can be estimated potentiometrically.

## 4.10 UV-VISIBLE SPECTROSCOPY

### 4.10.1 Principle

Ultraviolet (UV) Visible-spectra arises from the transition of valency electrons within a molecule (or) ion from a lower electronic energy level (ground state  $E_0$ ) to higher electronic energy level (excited state  $E_1$ ). This transition occurs due to the absorption of UV (wavelength 100-400 nm) (or) visible (wavelength 400-750 nm) region of the electronic spectrum by a molecule (or) ion.

### 4.10.2 Origin of UV-visible spectroscopy

The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons.

$$\Delta E = E_1 - E_0 = h\nu.$$

Electronic transition depends on the electronic structure of the absorbing medium (sample). The absorption of UV-visible radiation in organic molecule, is mainly due to presence of certain functional groups.

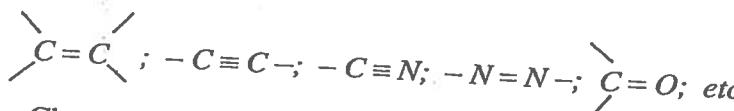
The two important groups, responsible for absorption and position of absorption in UV - visible spectra are

1. Chromophores
2. Auxochromes

### 1. Chromophores

The presence of one (or) more unsaturated linkages ( $\pi$ -electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores.

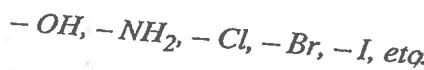
Examples



Chromophores undergo  $\pi \rightarrow \pi^*$  transitions in the short wavelength regions of UV-radiations.

2. Auxochrome *A substituent on a chromophore that leads to red shift*  
It refers to an atom (or) a group of atoms which does not give rise to absorption band on its own, but when conjugate to chromophore will cause a red shift.

Examples:



3. Some important definitions related to change in wavelength and intensity

1.	Bathochromic shift. (red shift)	Shift to higher wave length (lower frequencies).
2.	Hypsochromic shift.(blue shift)	Shift to lower wavelength (higher frequencies).
3.	Hyperchromic effect.	An increase in intensity.
4.	Hypochromic effect.	A decrease in intensity.

### Illustration

In chloroethylene,  $\text{CH}_2=\text{CHCl}$ ,

C = C is a chromophore.

Cl is an auxochrome.

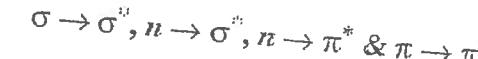
Substitution of a hydrogen atom in ethylene by a halogen atom causes a bathochromic shift and a hyperchromic effect.

Table 4.1: Difference between Chromophore and auxochrome

Sl No.	Chromophore	Auxochrome
1.	This group is responsible for the colour of the compound.	It does not impact colour, but when conjugate to chromophore produce colour.
2.	It does not form salt.	But it forms salt.
3.	It contains at least one multiple bond.	It contains lone pair of electrons.
	<i>Example:</i> $-\text{NO}_2, -\text{NO}, -\text{N}=\text{N}-$	<i>Example:</i> $-\ddot{\text{O}}\text{H}, -\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{R}_2$

### 4.10.3 Types of transitions involved in organic molecules

Energy absorbed in the visible and UV region by a molecule causes transitions of valence electrons in the molecule. These transition are



The energy level diagram for a molecule is shown in the fig 4.5. The energy values for different transitions are in the following order.

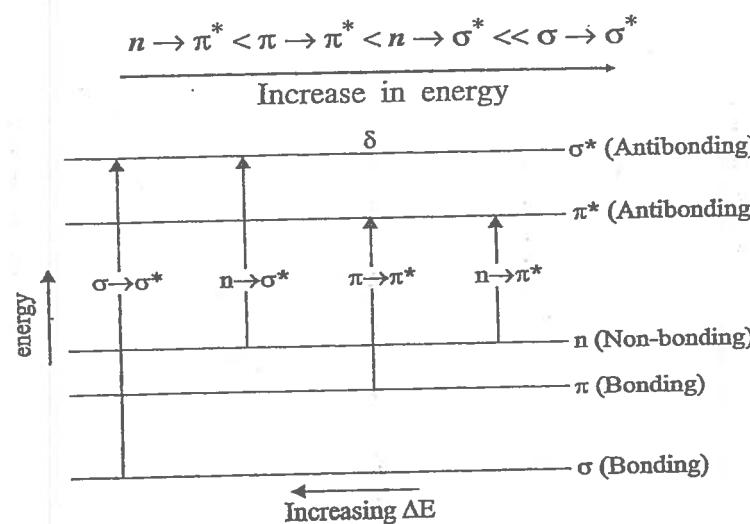


Fig. 4.5 Types of transition

### 1. $n \rightarrow \pi^*$ transitions

$n \rightarrow \pi^*$  transitions are shown by unsaturated molecule containing hetero atoms like N, O & S. It occurs due to the transition of non-bonding lone pair of electrons to the antibonding orbitals. This transition shows a weak band, and occurs in longer wavelength with low intensity.

### 2. $\sigma \rightarrow \sigma^*$ transitions

$\sigma \rightarrow \sigma^*$  transitions occur in the compounds, in which all the electrons are involved in single bonds and there are no lone pair of electrons.

The energy required for  $\sigma \rightarrow \sigma^*$  transition is very large. The absorption band occurs in the far UV region (120-136 nm).

### 3. $n \rightarrow \sigma^*$ transitions

$n \rightarrow \sigma^*$  transitions occur in the saturated compounds containing lone pair (non-bonding) of electrons in addition to  $\sigma \rightarrow \sigma^*$  transitions. The energy required for an  $n \rightarrow \sigma^*$  transition is less than that required for a  $\sigma \rightarrow \sigma^*$  transition. This absorption band occurs at longer wave length in the near UV region (180-200 nm).

### 4. $\pi \rightarrow \pi^*$ transitions

$\pi - \pi^*$  transitions occur due to the transition of an electron from a bonding  $\pi$  orbital to an antibonding  $\pi^*$  orbital. These transition can occur in any molecule having a  $\pi$  electron system. Selection rule determines whether transitions to a particular  $\pi^*$  orbital is allowed (or) forbidden.

### 4.10.4 Applications

#### 1. Predicting relationship between different groups

UV spectroscopy is not useful in the detection of individual functional groups, but it is used in predicting the relationship between different groups.

- i.e., (i) between two (or) more C-C multiple bonds ( $=$  (or)  $\equiv$  bonds).
- (ii) between C - C & C - O double bonds.
- (iii) between C - C double bonds and aromatic benzene ring.

Thus the structure of several vitamins and steric hindrance of the molecule can be determined using UV spectroscopy.

## 2. Qualitative analysis

UV absorption spectroscopy is used for characterizing and identification of aromatic compounds and conjugated olefins by comparing the UV absorption spectrum of the sample with the same of known compounds available in reference books.

## 3. Detection of impurities

UV absorption spectroscopy is the best method for detecting impurities in organic compounds, because

- (i) The bands due to impurities are very intense.
- (ii) Saturated compounds have little absorption band and unsaturated compounds have strong absorption band.

## 4. Quantitative analysis

*Determination of substances:* UV absorption spectroscopy is used for the quantitative determination of compounds, which absorbs UV. This determination is based on Beer's law

$$A = -\log T = \log \frac{I_0}{I_t} = \epsilon Cx$$

Where,

$\epsilon$  = molar extinction coefficient (constant)

$C$  = concentration

$x$  = length of the cell.

First, absorbance (optical densities) of the different solutions of known concentrations are measured. Then the graph is plotted between absorbance vs concentration (calibration curve). A straight line is obtained.

Then absorbance of unknown solution is measured. From the graph the concentration of unknown substance is found out.

## 5. Determination of molecular weight

Molecular weight of a compound can be determined if it can be converted into a suitable derivative, which gives an absorption band.

## 6. Dissociation constants of Acids and Bases

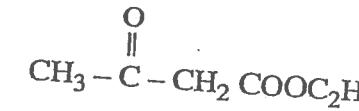
The dissociation constant ( $pK_a$ ) of an acid ( $HA$ ) can be determined by determining the ratio of  $\frac{[HA]}{[A^-]}$  spectrophotometrically from the graph plotted between absorbance vs wavelength at different pH values. These values are substituted in the equation -

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

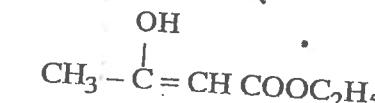
## 7. Study of tautomeric equilibrium

The percentage of various keto and enol forms present in a tautomeric equilibrium can be determined by measuring the strength of the respective absorption bands using UV spectroscopy.

Example: Ethylacetooacetate



Keto form;  $\lambda_{max} = 275\text{nm}$ ;



Enol form;  $\lambda_{max} = 244\text{nm}$

## 8. Studying kinetics of chemical reactions

Kinetics of chemical reactions can be studied using UV spectroscopy by following the change in concentration of a product (or) a reactant with time during the reaction.

## 9. Determination of calcium in blood serum

Calcium in the blood can be determined by converting the 'Ca' present in 1 ml of the serum as its oxalate and

redissolving it in  $H_2SO_4$  and treating it with dilute ceric sulphate solution. The absorption of the solution is measured at 315 nm. Thus, the amount of 'Ca' in the blood serum can be calculated.

## 4.11 INFRARED SPECTROSCOPY

### 4.11.1 Principle

IR spectra is produced by the absorption of energy by a molecule in the infrared region ( $300 - 1 \mu m$ ) and the transitions occur between vibrational levels. So, IR spectroscopy is also known as *Vibrational spectroscopy*.

#### Requirement for a molecule to impart IR spectrum

The essential requirement for a molecule to show vibrational spectrum is that the dipole moment of the molecule must change during vibration. This type of spectra is given by heteronuclear diatomic molecules, and poly atomic molecules with and without dipole moment. In polyatomic molecule, having no dipole moment, the exciting radiation can induce an oscillating dipole moment, hence it becomes IR active. Homonuclear diatomic molecules such as  $O_2$ ,  $N_2$ ,  $H_2$ , etc., are IR inactive because they have no dipole moment. The vibration of a diatomic molecule may be considered as the vibration of a simple harmonic oscillator. The vibrational energy of a diatomic molecule is given as  $E_{vib} = (v + 1/2) h \nu$ , where,  $v$  = the vibrational quantum number 0, 1, 2, 3 etc., and  $\omega$  = fundamental vibrational frequency.  $\nu = 1/2\pi (k/\mu)^{1/2}$ ,  $k$  = force constant and  $\mu$  = reduced mass.

When a molecule is in the ground state ( $V = 0$ ),  $E_{vib} = 1/2 h \nu$ . This is the energy of the lowest vibrational level called the zero point energy. The selection rule is  $\Delta E = \pm 1$ ,  $\Delta E_{vib} = h \nu$ . i.e., For a vibrational transition the energy is absorbed from IR region and also by obeying

the selection rule, the energy difference between two vibrational levels, involved in a transition, will always be equal spacing. Therefore the spectrum is expected to consist of a single line. Most of the molecules are in the  $v = 0$  level at ordinary temperature. Therefore the single vibrational line corresponds to the transition from  $v = 0$  to  $v = 1$  level by absorption of IR radiation called the fundamental line. But in actual practice the molecular vibrations are not harmonic, so it violates the selection rule and the transition from  $v = 0$  to  $v = 2$  and  $v = 0$  to  $v = 3$  may occur called first and second overtone lines. Overtone lines are less intense than the fundamental line.

#### Sources of IR

Electrically heated rod of rare - earth oxides.

### 4.11.2 Range of Infrared Radiation

The range in the electromagnetic spectrum extending from  $12500$  to  $50 \text{ cm}^{-1}$  is commonly referred to as the infrared (IR). This region is further divided into three sub regions.

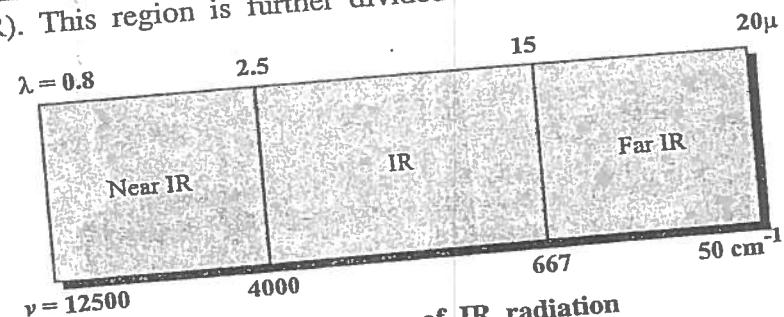


Fig. 4.6. Range of IR radiation

#### 1. Near infrared:

This region is from  $12500$  to  $4000 \text{ cm}^{-1}$

#### 2. Infrared (or) ordinary IR:

This region is from  $4000$  to  $667 \text{ cm}^{-1}$

### 3. Far infrared:

This region is from  $667$  to  $50\text{ cm}^{-1}$

### 4. Finger print region

The vibrational spectral (IR spectra) region at  $1400 - 700\text{ cm}^{-1}$  gives very rich and intense absorption bands. This region is termed as finger print region. The region  $4000 - 1430\text{ cm}^{-1}$  is known as Group frequency region.

### Uses of finger print region

Finger print region can be used to detect the presence of functional group and also to identify and characterise the molecule just as a finger print can be used to identify a person.

### 4.11.3 Origin of IR Spectrum and Molecular Vibrations

Since atoms in a molecule are continuously vibrating, molecules are also vibrating. There are two kinds of fundamental vibrations in the molecule.

#### 1. Stretching vibrations

During stretching the distance between two atoms decreases (or) increases, but bond angle remains unaltered.

#### 2. Bending (or) deformation vibrations

During bending bond angle increases and decreases but bond distance remains unaltered.

Vibrational changes depend on the masses of the atoms and their spatial arrangement in the molecule. When IR light of the same frequency is incident on the molecule, energy is absorbed resulting in increase of amplitude of vibration. When the molecule returns from the excited state to the original ground state, the absorbed energy is released as heat.

Thus, every compound shows characteristic absorption bands in the IR region of the spectrum. Different functional

groups produce easily recognisable band at definite positions in the IR spectral range ( $12500$  to  $50\text{ cm}^{-1}$ ).

### 4.11.4 Types of stretching and bending vibrations

The number of fundamental (or) normal vibrational modes of a molecule can be calculated as follows.

#### 1. For Non-linear molecule

A non-linear molecule containing ' $n$ ' atoms has  $(3n - 6)$  fundamental vibrational modes.

#### Examples

(i)  $\text{CH}_4 \rightarrow (3 \times 5 - 6) = 9$  fundamental vibrational modes.

(ii)  $\text{C}_6\text{H}_6 \rightarrow (3 \times 12 - 6) = 30$  fundamental vibrational modes.

#### 2. For linear molecules

A linear molecule containing ' $n$ ' atoms has  $(3n - 5)$  fundamental vibrational modes.

#### Example

$\text{CO}_2 \rightarrow (3 \times 3 - 5) = 4$  fundamental vibrational modes.

### 4.11.5 Applications of IR spectroscopy

#### 1. Identity of the compound can be established

The IR spectrum of the compound is compared with that of known compounds. From the resemblance of the two spectra, the nature of the compound can be established. This is because a particular group of atoms gives a characteristic absorption band in the IR spectrum.

**Example**

IR spectra of both benzaldehyde ( $C_6H_5 - C = O$ ) and phenylmethylketone ( $C_6H_5 - C - CH_3$ ) show a sharp absorption peak at  $1700\text{ cm}^{-1}$ . This indicates the presence of  $C = O$  group in both the compounds.

**2. Detection of functional groups**

In a given environment, a certain functional group will absorb IR energy of very nearly the same wavelength in all molecules.

**Examples**

(i) Acetone ( $CH_3 - C = O - CH_3$ ) and diethylketone ( $C_2H_5 - C = O - C_2H_5$ ) give absorption peak at the same place.

(ii) But, acetic acid ( $CH_3COOH$ ) and cyclobutanone  

$$\begin{array}{c} CH_2 - CH_2 \\ | \quad | \\ C = O \text{ give absorption peak at different places.} \\ | \quad | \\ CH_2 - CH_2 \end{array}$$

**3. Testing purity of a sample**

Pure sample will give a sharp and well-resolved absorption bands. But impure sample will give a broad and poorly resolved absorption bands. Thus by comparison with

IR spectra of pure compound, presence of impurity can be detected.

**4. Study of progress of a chemical reaction**

The progress of a chemical reaction can be easily followed by examining the IR spectrum of test solution at different time intervals.

**Example**

(i) Progress of oxidation of secondary alcohol to ketone is studied by getting IR spectra of test solution at different time intervals.

The secondary alcohol absorbs at  $2.8\mu$  ( $\sim 3570\text{ cm}^{-1}$ ) due to O-H stretching. As the reaction proceeds this band slowly disappears and a new band near  $5.8\mu$  ( $\sim 1725\text{ cm}^{-1}$ ), due to  $C = O$  stretching appears.

(ii) Similarly, the progress of any chromatographic separations can be readily monitored by examining the IR spectra of the selected fractions.

**5. Determination of shape or symmetry of a molecule**

Whether the molecule is linear (or) non-linear (bend molecule) can be found out by IR spectra.

**Example**

IR spectra of  $NO_2$  gives three peaks at  $750$ ,  $1323$ , and  $1616\text{ cm}^{-1}$ .

According to the following calculations,

- (i) For non-linear molecule  $= (3n - 6) = 3$  peaks.
- (ii) For linear molecule  $= (3n - 5) = 4$  peaks.

Since the spectra shows only 3 peaks, it is confirmed that  $\text{NO}_2$  molecule is a non linear (bend) molecule.

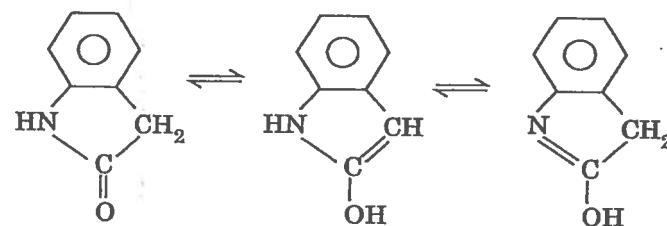
#### 6. To study tautomerism

Tautomeric equilibria can be studied with the help of IR spectroscopy.

##### Example

The common systems such as keto-enol, lacto - lactum, and mercapto - thioamide, contain a group like  $\text{C}=\text{O}$ ,  $-\text{OH}$ ,  $-\text{NH}$  (or)  $\text{C}=\text{S}$ . These groups show a characteristic absorption band in the IR spectrum, which enable us to find at which form predominates in the equilibrium.

##### Example



#### 7. Industrial applications

##### (a) Determination of structure of chemical products

During the polymerisation, the bulk polymer structure, can be determined using IR spectra.

##### (b) Determination of molecular weight

Molecular weight, of a compound can be determined by measuring end group concentrations, using IR spectroscopy.

##### (c) Crystallinity

The physical structure like crystallinity can be studied through changes in IR spectra.

##### Example

The absorption band at  $934 \text{ cm}^{-1}$  is for crystalline nylon 6:6.

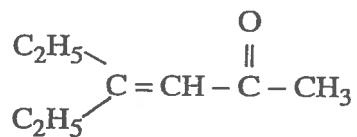
The absorption band at  $1238 \text{ cm}^{-1}$  is for amorphous nylon 6:6.

#### 8. Isomers can be identified in the fingerprint region

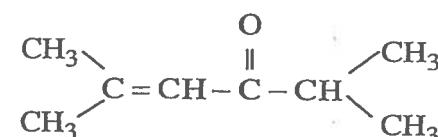
Similar molecules may show very similar spectra in the group frequency region ( $4000 - 1430 \text{ cm}^{-1}$ ). But, they show some differences in the fingerprint region ( $1400 - 700 \text{ cm}^{-1}$ ).

##### Example

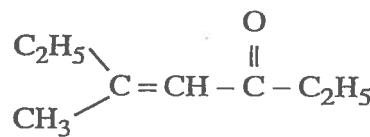
##### Isomers of the compound $\text{C}_8\text{H}_{14}\text{O}$



(a)



(b)



(c)

The IR spectra of the above three isomers in the group frequency region are almost similar. But these are identified from their IR spectra in the fingerprint region, due to three different absorptions.

### 9. Determination of hydrogen bonding in a molecule

To detect the hydrogen bond and also distinguish between inter and intra molecular hydrogen bonding present in a compound, a series of *IR* spectra of the compound at different dilutions are taken.

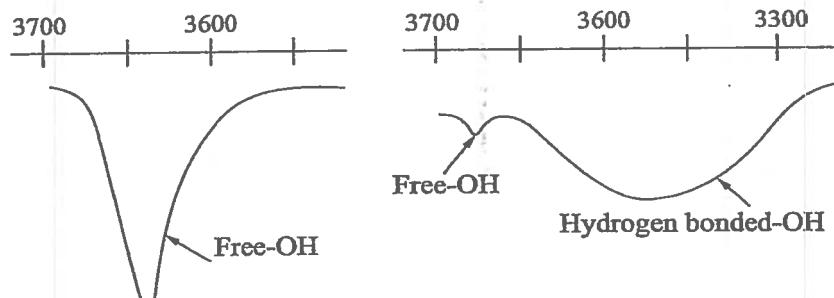
#### Example

The solution of an alcohol at high concentrations gives two peaks i.e.,

(i) one a sharp peak at  $3630\text{ cm}^{-1}$  (due to free  $-\text{OH}$  group)

(ii) another a broad peak at  $3500 - 3200\text{ cm}^{-1}$  (due to  $-\text{H}$  bonded  $-\text{OH}$  group)

On dilution, it is observed that the peak at  $3630\text{ cm}^{-1}$  becomes more intense as the concentration of the free  $-\text{OH}$  group increases. At the same time broader peak at  $3500 - 3200\text{ cm}^{-1}$  becomes less intense and disappears at larger dilutions.



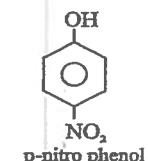
(a) Dilute solution

Fig. 4.7 Effect of hydrogen bonding

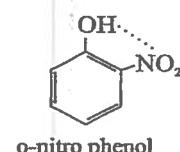
The above explanation is applicable to  $-\text{OH}$  groups involved in intermolecular  $\text{H} - \text{bonding}$ .

If the  $-\text{OH}$  group is involved in intramolecular hydrogen bonding, dilution will not affect the intensity of the peak.

#### Example



Shows intermolecular  $\text{H} - \text{bond}$   
(No effect on intensity on dilution)



Shows intramolecular  $\text{H} - \text{bond}$   
(intensity decreases on dilution)

### 10. Determination of Aromaticity

The difference in the wavelengths of  $\text{C} - \text{H}$  bonds in different environments can be used to determine .

- the relative proportions of saturated and unsaturated rings present in hydrocarbon.
- the % of aromatic compounds or olefines in the mixtures.

### 4.12 $^1\text{H}$ - NMR SPECTROSCOPY

#### 4.12.1 Principle

NMR (Nuclear Magnetic Resonance) is a powerful tool for investigating nuclear structure of atoms and molecules. In NMR, radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

The nucleus of hydrogen (proton) spins about its own axis. Due to its positive charge, the spinning proton generates a magnetic moment and behaves like a tiny bar magnet. If the proton is placed in a strong magnetic field, the two energy levels become separate. But, in the absence of external magnetic field the energy levels are equal.

### 1. Low energy level

It, corresponds to  $m_I = +\frac{1}{2}$ , is due to parallel to the direction of magnetic field.

### 2. High energy level

It, corresponds to  $m_I = -\frac{1}{2}$ , is due to antiparallel to the direction of magnetic field.

The energies of these two states are represented in the following figure.

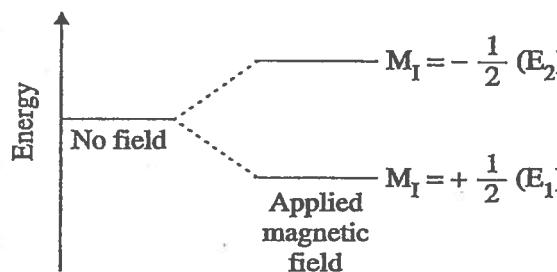


Fig. 4.8. Two energy levels of the nucleus

A transition from the low energy state to the high energy state can be obtained by providing an energy equal to the difference in energy between the two states,  $\Delta E$ .

If the nucleus lies in the upper energy state,  $E_2$ , that will come to lower energy state,  $E_1$ , by emitting energy corresponding to  $\Delta E$ .

The frequency absorbed or emitted by a nucleus in moving from one energy level to another is directly proportional to the applied magnetic field and gives the NMR spectrum. Thus, NMR spectrum is plotted between absorption signal at the detector and the strength of the magnetic field  $H^o$ .

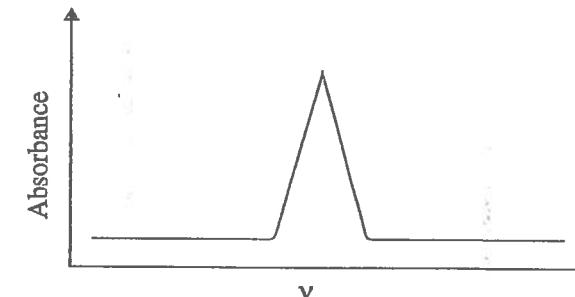


Fig. 4.9. A model NMR spectrum

### Resonance

When a nucleus is placed in a system, it absorbs energy and goes to the excited state. Then it loses energy and returns to unexcited state. Again it absorbs energy and goes to excited state. Thus, the nucleus which alternately becomes excited and unexcited is said to be in a state of resonance.

### 4.12.2 Chemical shift

The position of an NMR signal is determined by the electronic environment of the proton. *The separation in the position of the signal of different types of protons from that of a standard is called chemical shift.*

(or)

Chemical shift is the difference between the resonance frequency of the observed proton and TMS (Tetra methyl silane). TMS is the common reference compound in NMR, its  $\tau = 0$ .

The existence of chemical shift is due to the screening effect of electrons. The position of NMR signal gives an idea

about the kinds of proton (like aliphatic, aromatic, primary, secondary). Different kinds of protons in different electronic environments gives different peaks in NMR. This difference is represented by chemical shift  $\delta$ .

$$\delta = \frac{H_o(\text{reference}) - H_o(\text{sample})}{H_o(\text{reference})} \times 10^6 \text{ ppm}$$

In terms of frequency

$$\delta = \frac{\nu(\text{sample}) - \nu(\text{reference})}{\nu(\text{reference})} \times 10^6$$

The normal reference compound used for H nucleus in organic compounds is tetramethylsilane (TMS).

### Shielding and deshielding (or) causes of chemical shift

#### Shielding

High electron density at around a nucleus shields the nucleus from the external magnetic field. The net magnetic field felt by the nucleus, in a molecule, will be less than the applied (external) magnetic field and the nucleus is said to be shielded. Thus, the NMR signals are upfield (lower  $\delta$  value) in the NMR spectrum.

#### Deshielding

Low electron density at around a nucleus deshields the nucleus from the external magnetic field. The net magnetic field felt by the nucleus in a molecule will be more than the applied magnetic field and the nucleus is said to be deshielded. Thus, the NMR signals are down field (higher  $\delta$  value) in the NMR spectrum.

#### Factors affecting chemical shift

The followings are important factors that influences chemical shift.

#### 1. Electron density

It shields a nucleus from the external field.

#### 2. Electronegativity of neighbouring group

Electronegative groups attached to the  $-\text{CH}_3$  group, decreases the electron density around the protons, and there is deshielding and the chemical shift increases. Thus, the chemical shift increases with increase in electronegativity of the bonded atoms.



#### 3. Magnetic anisotropic effect

Anisotropy means non-uniform, magnetic anisotropy is the non uniform magnetic field. Electrons present in the  $\pi$  systems (alkenes, alkynes, aromatics, etc.,) interact with the applied magnetic field causes anisotropy. It causes both shielding and deshielding effects.

#### 4. Hydrogen bonding

Presence of hydrogen bonding changes the chemical shift values. The more hydrogen bonding, more protons are deshielded and the chemical shift increases.

#### 4.12.3 Spin-Spin splitting (spin-spin coupling)

The NMR spectrum of any compound at low resolution gives broad signal. But the same at high resolution causes further splitting of NMR signal by spin-spin interaction.

Further splitting of the NMR signal due to the interaction between protons on adjacent atoms is referred to as spin-spin splitting (or) coupling.

#### Conditions for spin-spin coupling

- Chemically equivalent protons will not cause spin-spin coupling.
- Non-equivalent protons only will couple.

3. Protons present in an adjacent carbon atoms will couple.
4. Protons present in the carbon atom, having multiple bonds, will not couple.

#### *n + 1 rule*

The multiplicity of a signal can be calculated by using  $n + 1$  rule. If  $n$  number of protons are present in a near by nucleus, the peak will split into  $n + 1$  lines.

If no hydrogen is present in neighbour atom, then  $n + 1 = 0 + 1 = 1$  (gives singlet peak)

If one hydrogen is present in neighbour atom, then  $n + 1 = 1 + 1 = 2$  (gives doublet peak)

If two hydrogen is present in neighbour atom, then  $n + 1 = 2 + 1 = 3$  (gives triplet peak)

#### *4.12.4 Applications of NMR spectroscopy*

##### *1. Structural diagnosis by NMR*

The structure of an unknown compound from its NMR spectrum can be confirmed.

##### *Examples*

- (i) The number of main NMR signals should be equal to the number of equivalent protons in the unknown compound.
- (ii) The chemical shift indicates that what type of hydrogen atoms are present.
- (iii) From the area of peaks, the number of hydrogen present in each group can be known.

##### *Quantitative analysis*

NMR spectroscopy is used to determine the molar ratio of the components in a mixture.

#### *3. Hydrogen bonding*

It is used to study the hydrogen bonding in metal chelates and organic compounds.

#### *4. Elemental analysis*

It is used for the determination of total concentration of a given kind of magnetic nucleus in a sample.

#### *5. Study of isotopes other than proton*

Several nuclei, in addition to proton, which have magnetic moments can be studied by the NMR technique.

#### *6. Keto-enol Tautomerism*

It is useful in studying keto-enol tautomerism.

#### *4.13 GAS CHROMATOGRAPHY (GC) (OR) GAS LIQUID CHROMATOGRAPHY (GLC)*

##### *4.13.1 Principle*

Gas chromatography is used to analyse a mixture of volatile organic compounds. The basic principle involved in GC is the differential distribution of various components between a mobile phase and a stationary phase. The mobile phase generally used is nitrogen gas. But the stationary phase may be a solid or liquid.

In GC small amount of sample mixture is vapourised in the carrier gas (mobile phase) and passed at a constant flow rate through a column containing the stationary phase maintained at a particular temperature. The components of the sample mixture get separated due to their differential migration through the column due to differences in their boiling points, solubilities in the stationary phase.

### 4.13.2 Types of gas chromatography

Based on the nature of stationary phase, gas chromatography may be classified into two types

1. Gas-solid chromatography (GSC)
2. Gas-liquid chromatography (GLC)

#### 1. Gas-solid chromatography (GSC)

If the column is packed with a solid stationary phase like silica, alumina, it is known as gas-solid chromatography (GSC). Adsorption occurs between gas and a solid.

#### 2. Gas-liquid chromatography (GLC)

If the column is packed with a non-volatile liquid held as a thin layer over a solid support, it is known as gas-liquid chromatography (GLC). Partition occurs between gas and a solid.

#### Factors affecting separation

The separation efficiency depends on

- (i) Nature of stationary phase
- (ii) Temperature of the column
- (iii) Length of the column
- (iv) Flow rate of the carrier gas

### 4.13.3 Comparison of GSC and GLC

S. No.	Comparison data	GSC	GLC
1.	Stationary phase	solid	liquid
2.	Mobile phase	gas	gas
3.	Packing of the column	fine graded powder absorbent	liquid coated on an inert support

S. No.	Comparison data	GSC	GLC
4.	Length of the column	0.7 to 2 m	3 to 300 m
5.	Thermal stability	thermally stable	less stable above 300°C
6.	Reaction in the column	packing may catalyses some chemical change.	very rarely with stationary liquid, but may occur with solid support.
7.	Application	useful in the separation of permanent gases and low boiling substances.	All volatile material except permanent gases.

### 4.13.4 Applications

1. Separation of components having close boiling points, can be done easily by GC.
2. Ethyl alcohol content in blood can be determined.
3. The multicomponent analysis can be done in a relatively short time.
4. The following analysis may be carried out easily in GC.
  - (i) Refinery gases
  - (ii) Synthetic rubber intermediate
  - (iii) Trace atmospheric constituents

## A.14 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

### 4.14.1 Principle

HPLC is an advanced method of column chromatography. The particle size of the adsorbent, used in the column, is small and it helps to improve the resolution. The solvent is passed through the column under high pressure using pressure pumps. In general, the adsorbent with small particle size ( $3\text{ }\mu\text{m}$ ,  $5\text{ }\mu\text{m}$ ,  $10\text{ }\mu\text{m}$ ) with a very narrow size distribution will greatly improve the resolution. High pressure, in the column, can be created using pump.

#### Instrumentation

The outline of the instrument is shown in fig. 4.10.

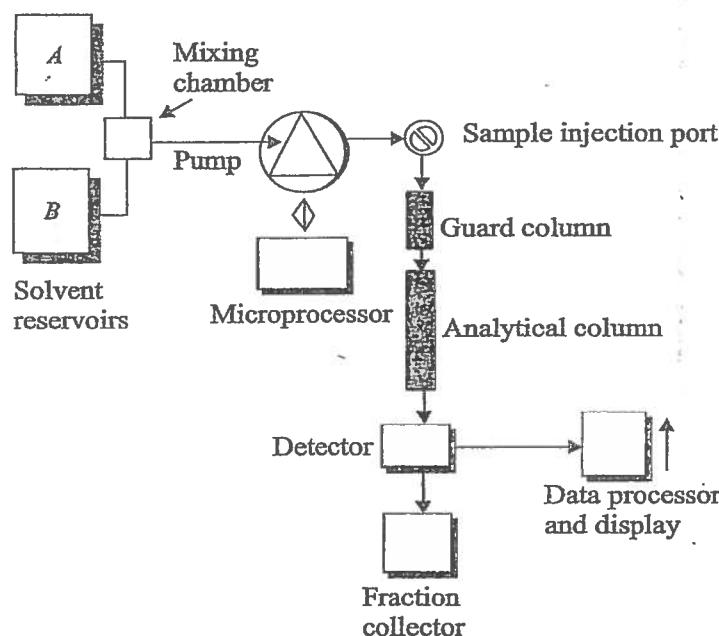


Fig. 4.10 A schematic diagram of a HPLC system

HPLC consists of the following main components

- (i) Solvent reservoir.
- (ii) A microprocessor-controlled high pressure pump to deliver the sample to the column.
- (iii) Sample injection part.
- (iv) Guard column and analytical column containing the adsorbent (stationary phase).
- (v) Detector.
- (vi) Data processor with recorder.
- (vii) Fraction collector.

### 4.14.2 Applications of HPLC

1. Clinical diagnosis of diseases, disorders.
2. In Scientific research for discovery.
3. In food industry for quality control.
4. For separation of similar molecule.
5. In pharmaceutical labs for analysis.

### 4.14.3 Separation of gaseous and liquid compounds by chromatography

Many separation methods are based on chromatography, that is, separation of the components of a mixture by differences in the way they become distributed (or partitioned) between two different phases. This is illustrated with the following example.

#### Illustration 1:

Separation of gaseous methane and ammonia

A mixture of gaseous methane and ammonia is taken and this mixture is contacted with water. Ammonia, being very soluble in water will mostly go into the *water* phase, whereas the methane, being almost insoluble will essentially remain

entirely in the *gas* phase. Such a separation of methane and ammonia would be a one-stage partitioning between gas and liquid phases. It can be made much more efficient by contacting the gas layer repeatedly with fresh water. This partitioning procedure is a tedious process, especially if the compounds to be separated are similar in their distributions between the phases.

However, partitioning can be achieved nearly automatically by using **chromatographic columns**, which permit a **stationary phase** to be contacted by a **moving phase**. This can be illustrated with following example.

#### Illustration 2:

Suppose a sample of a gaseous mixture of ammonia and methane is injected into a long tube (column) filled with glass beads moistened with water (the stationary phase) and a slow stream of an inert **carrier gas**, such as nitrogen (or) helium, is passed in to push the other gases through. A multistage partitioning would occur as the ammonia dissolves in the water and the resulting gas stream encounters fresh water as it moves along the column. Carrier gas enriched with methane would emerge first and effluent gas containing ammonia would come out later.

This technique has become so efficient as to revolutionize the analysis and separation of almost any organic substance that has even a slight degree of volatility at some reasonably attainable temperature. The most modern GLC equipment runs wholly under computer control, with preprogrammed temperatures and digital integration of the detector output. A wide variety of schemes is available for measuring the concentration of materials in the effluent carrier gas and some of these are of such extraordinary sensitivity that only very small samples are necessary.

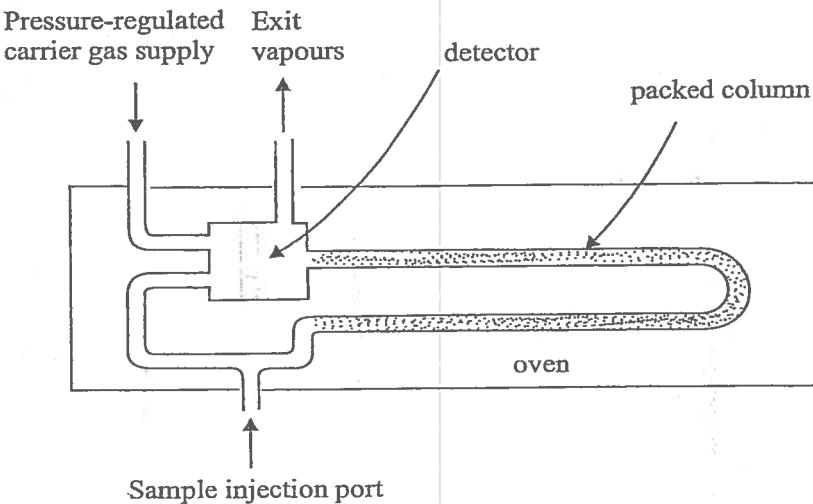


Fig. 4.17 Schematic diagram of a gas-liquid chromatography apparatus.

The detector is arranged to measured the difference in some property of the carrier gas alone versus the carrier gas plus effluent sample at the exit. Differences in thermal conductivity are particularly easy to measure and give reasonably high detection sensitivities.

In the usual GLC procedure, a few microliters of an organic liquid to be analyzed are injected into a vaporizer and carried with a stream of gas (usually helium) into a long heated column that is packed with a porous solid (such as crushed firebrick) saturated with a nonvolatile liquid. Gas-liquid partitioning occurs and small differences between partitioning of the components can be magnified by the large number of repetitive partitions possible in a long column. Detection often is achieved simply by measuring changes in thermal conductivity of the effluent gases. A schematic diagram of the apparatus and a typical separation pattern are shown in Figure. 4.17. The method is extraordinarily useful for detection of minute amounts of impurities provided these are separated from the main peak. GLC can also be used effectively to purify

materials as well as to detect impurities. To do this, the sample size and the size of the apparatus may be increased (or) an automatic system may be used wherein the products from many small scale runs are combined.

#### 4.15. DESCRIPTIVE TYPE QUESTIONS

1. What are the changes observed during the absorption of radiation. Explain the factors affecting it.
2. Explain the characteristics of electromagnetic spectrum.
3. Write notes on
  - (i) pH - metry
  - (ii) Conductrometry.
4. Write notes on principle and applications of UV-visible spectroscopy.
5. Explain the applications of IR spectroscopy.
6. Write notes on NMR spectroscopy.
7. Explain the principle and applications of HPLC.

## Molecular Machines and Molecular Switches

### 5.1 SUPRAMOLECULAR CHEMISTRY

Supramolecular chemistry refers to the study of supramolecular assemblies. Traditional chemistry generally focuses on the covalent bonding, but supramolecular chemistry is monitored by weak interactions of non-covalent bonds like hydrogen bonds, hydrophobic forces, VanderWaals forces,  $\pi - \pi$  interactions.

**Supramolecular structures:** Supramolecular structures are large molecules formed by grouping (or) bonding smaller molecules together.

#### 1. Molecular self-assembly

Molecular self-assembly is the construction of systems without guidance (or) management from an outside source. The molecules get assembled through non-covalent interactions. Molecular self-assembly also allows the construction of larger structures like micelles, membranes and liquid crystals. Molecular self-assembly may be sub-divided into two types.

- (i) Intermolecular self-assembly
- (ii) Intramolecular self-assembly

#### 2. Molecular recognition and complexation

Molecular recognition is the specific binding of a guest molecule to a complementary host molecule to form a host-guest complex. Which species is the "host" and which is the "guest" is arbitrary. These are identified using non-covalent interactions.

### 3. Template-directed synthesis

Non-covalent bonds between the reactants and a "template" hold the reactive sites of the reactants close together. This technique is useful for situations where the desired reaction conformation is thermodynamically (or) kinetically unlikely like preparation of larger macrocycles

### 4. Mechanically interlocked molecular architectures

Mechanically interlocked molecular architectures consists of molecules that are linked only as a consequence of topology. Some non-covalent interactions may exist between the different components.

**Examples:** Catenanes, rotaxanes, molecular knots are some examples for the mechanically interlocked molecular architectures.

### 5. Dynamic covalent chemistry

In dynamic covalent chemistry, covalent bonds are broken and formed in a reversible reaction under thermodynamic control.

### 6. Imprinting

Molecular imprinting describes a process by which a host is constructed from small molecules using a suitable molecular species as a template. After construction the template is removed leaving only the host.

### 7. Molecular machinery

Molecular machines are molecules (or) molecular assemblies that can perform functions such as linear (or) rotational movement, switching and entrapment.

### 8. Molecular switch

It is a molecule that can be reversibly shifted between two (or) more stable states. It may happen in response to environmental stimuli such as changes in pH, light, temperature (or) in the presence of ions and other ligands.

### 5.1.2 Important terms of supramolecular chemistry

#### 1. Host

It is the organic molecule containing convergent binding sites. Synthetic counter parts to receptor sites in enzymes, genes, antibodies and ionophores.

#### 2. Guest

Molecules or ions containing divergent to binding sites counter parts to substrates, inhibitors, cofactors, antigens.

#### 3. Complexes

Hosts and guests held together in solution in definable structural relationship by electrostatic forces such as hydrogen bond, metal ion-to-ligand attraction, dipole-dipole interactions and Vander Waals attraction.

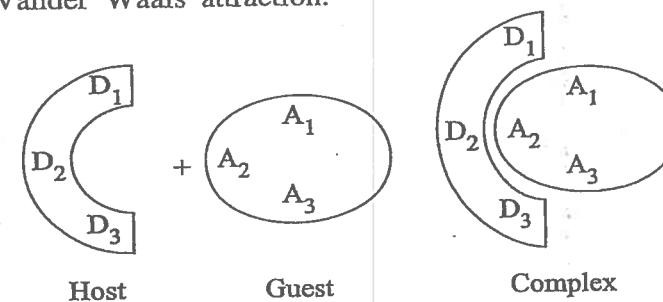


Fig. 5.1 Structural relationship between host and guest

### 5.2 COMPLEMENTARITY

The principle of complementarity states that, "to complex, host must have binding sites which can simultaneously contact and attract the binding sites of the guests without generating internal strains (or) strong non-bonded repulsions."

### 5.2.1 Types of complementarity

Complementarity are of two types

1. Size complementarity
2. Electronic complementarity

#### 1. Size complementarity

A host must have binding sites that of the correct size and electronic character (polarity, hydrogen bond, donor/acceptor ability, hardness (or) softness etc., to complement those of the guest.

Examples

- (i) Hydrogen bond donors must match acceptors
- (ii) Lewis acids must match Lewis bases and so on,

Furthermore, those binding sites must be spaced out on the host in such a way as to make it possible for them to interact with the guest in the binding conformation of the host molecule. If a host fulfills these criteria, it is said to be complementarity.

Factor affecting size complementarity

#### 1. Size-match selectivity

This factor is significant when the metal radius matches the ligand cavity radius. It mainly comes into account if the ionophore has cyclic and fixed cavity.

*Example*

18-crown-6, whose cavity (2.60-3.20 Å) can accommodate a guest potassium ion (2.66 Å).

#### 2. Electronic complementarity

The principle of hard and soft acids and bases states that hard acids form more stable complexes with hard bases and soft bases form more stable complexes with soft acids.

HSAB theory deals predominantly with electronic (ionic and covalent) effects. It has been suggested that there is also a significant steric component based on size of donor atoms.

### 5.3 LOCK AND KEY MODEL

Enzymes make reactions go faster. Enzymes are specific to the specific substrate. Enzymes react with the substrate and enhance the reaction process. The enzyme-substrate reaction was well explained by Lock and Key model.

The lock represents an enzyme and the key represents a substrate. It is assumed that both the enzyme and substrate have fixed confirmation that lead to an easy fit. Because the enzyme and the substrate are at a close distance with weak attraction, the substrate must need a matching shape and fit to join together. At the active sites, the enzyme has a specific geometric shape and orientation that a complementary substrate fits into perfectly. The theory behind the Lock and Key model involves the complementarity between the shapes of the enzyme and the substrate. Their complementary shapes make them fit perfectly into each other like a lock and a key. According to this theory, the enzyme and substrate shape do not influence each other because they are already in a predetermined perfectly complementary shape. As a result, the substrate will be stabilized. This theory was replaced by the induced fit model which takes into account the flexibility of enzymes and the influence the substrate has on the shape of the enzyme in order to form a good fit.

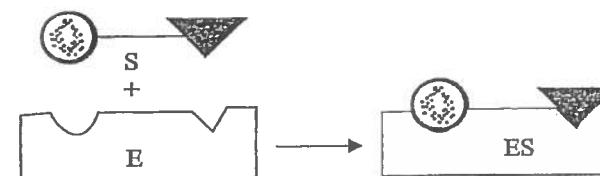


Fig. 5.2 Lock and Key model

### 5.3.1 Induced Fit Theory

This is modified from lock and key hypothesis and was suggested by Koshland in 1959. In the presence of substrate the active site of the enzyme may change shape to fit the substrate i.e., the enzyme is flexible and moulds to fit the substrate molecule. This theory is stated based on the nature of enzyme. Protein molecule is flexible enough to allow conformational changes.

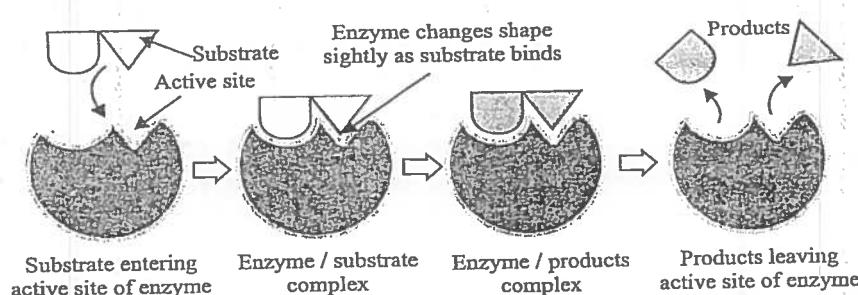


Fig. 5.3 Modified lock and key model

## 5.4 EXAMPLES OF SUPRAMOLECULES

### 1. Fullerenes

These are closed carbon structures constructed from pentagonal and hexagonal carbon units. The fullerene(C<sub>60</sub>) consisting of sixty carbon atoms has a structure similar to a soccer ball. Fullerenes possess very different properties; some of their electronic properties are similar to those of a semi-conductor.

### 2. Carbon Nanotubes

A carbon nanotube is carbon-based tube with a diameter ranges in nanometers. These are single walled and double walled structures. Nanotubes have interesting electronic characteristics that are expected to lead to their widespread use in molecular electronics.

### 3. Dendrimers (Molecular Trees)

Dendrimers have systematic branching structures and they are built in a stepwise manner. Supra molecules from this family can be used to shield functional groups and to collect energy.

### 4. Rotaxane

Rotaxanes are obtained by threading linear polymers through molecular rings such as cyclodextrins,crown ethers and cyclophanes.

### 5. Catenane

A catenane is a mechanically-interlocked molecular architecture consisting of two (or) more interlocked macrocycles, i.e. a molecule containing two (or) more intertwined rings. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles.

### 6. Micelle

It is an aggregate of surfactant molecules dispersed in a liquid colloid. The formation of a micelle is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic regions as well as hydrophobic regions. The polar head groups of micelles form the outside surface of the molecule, facing the aqueous environment and their hydrophobic chains are clustered in the interior, where water is excluded since they are nonpolar.

### 7. Vesicle

Vesicles are self-assembled nanoscale capsules consisting of a molecular layer enclosing an inner solvent compartment. In particular, the range of building blocks for vesicles has expanded from "conventional" (i.e., phospholipid-like) amphiphiles to block copolymers, giant amphiphiles and supramolecular amphiphiles. Increasingly, vesicles are also assembled from nonconventional (i.e., non-amphiphilic) components in aqueous as well as organic solvents. Vesicles

can be tailor-made to respond to external stimuli. Vesicles are also highly interesting biomimetic structures. Molecular recognition of vesicles is a powerful model system in biological membranes.

### 8. Cyclodextrins

These are a family of cyclic oligosaccharides composed of a (1,4) linked glucopyranose subunits. Cyclodextrins are useful molecular chelating agents. They possess a cage-like supramolecular structure, which is the same as the structure's formed from cryptands, calixarenes, cyclophanes, spherands and crown ethers. These compounds, having supramolecular structures, carry out chemical reactions that involve intramolecular interactions where covalent bonds are not formed between interacting molecules, ions (or) radicals. The majority of all these reactions are of 'host-guest' type. Compared to all the supramolecular hosts mentioned above, cyclodextrins are most important.

### 9. Host-guest complex

The simplest example of supramolecular structure is a host-guest complex.

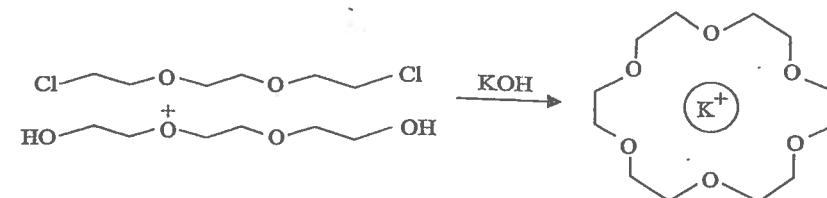
The host (receptor) is a large organic molecule with a cavity in the centre and a guest is a simple molecule or ion.

**Example:** Different size cyclic polyesters (crown esters) are strongly bound by alkali metal ions.

### 10. Metal-ion-templating

**Example:** 18-crown-6

18-crown-6 strongly coordinates potassium ion thus can be prepared through the williamson ether synthesis using potassium ion as the template metal.



### 5.5 MOLECULAR RECOGNITION

The molecular recognition is the most fundamental kind of supramolecular chemistry, because all supramolecular chemistry is based on how to recognize molecules, how to influence molecules and how to express specific functions due to molecular interactions. The origin of "molecular recognition" is "lock and key" principle. This concept proposed that the mechanism by which an enzyme recognizes and interacts with a substrate.

The term **molecular recognition** refers to the specific interaction between two (or) more molecules through noncovalent bonding such as hydrogen bonding, metal coordination, hydrophobic forces, Vander Waals forces,  $\pi - \pi$  interactions, halogen bonding, electrostatic (or) electromagnetic effects. The host and guest involved in molecular recognition exhibit molecular complementarities. "Molecular recognition", which may be both inter and intramolecular phenomena is also encompasses the "host-guest chemistry", "supramolecular chemistry" and "self-assembly", though these are limited to intermolecular processes. Protein folding is a classic example of intramolecular recognition. It is seen in the Host-Guest interactions and in enzymology lock and key interaction.

#### 5.5.1 Types of Molecular Recognition

Molecular recognitions are of two types

1. Static molecular Recognition
2. Dynamic molecular Recognition

### 1. Static molecular Recognition

Static molecular recognition involves interaction between a key and a keyhole; it is a 1:1 type complexation reaction between a host molecule and a guest molecule to form a host-guest complex. To achieve advanced static molecular recognition, it is necessary to make recognition sites that are specific for guest molecules.

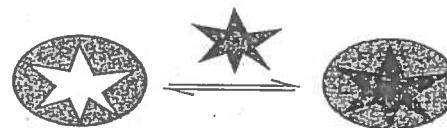


Fig: 5.4 Static recognition between a single guest and a single host binding site.

In dynamic recognition binding the first guest at the first binding site induces a conformation change that affects the association constant of the second guest at the second binding site, a positive allosteric site.

### 2. Dynamic molecular Recognition

In the case of dynamic molecular recognition the binding of the first guest to the first binding site of a host affects the association constant of a second guest with a second binding site. In the case of positive allosteric systems the binding of the first guest increases the association constant of the second guest. While for negative allosteric systems the binding of the first guest decreases the association constant with the second. The dynamic nature of this type of molecular recognition is particularly important since it provides a mechanism to regulate

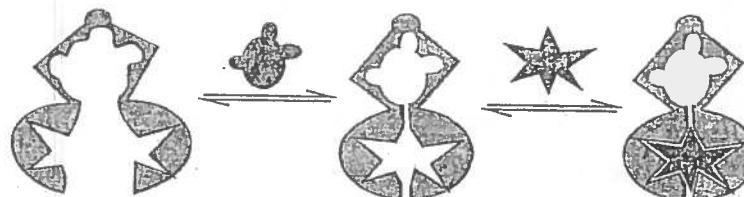
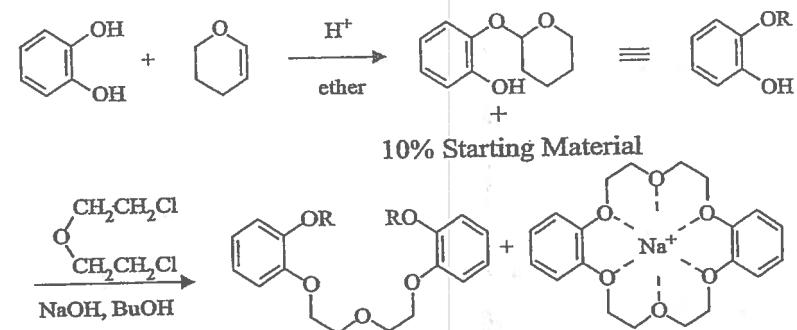


Fig. 5.5 Dynamic molecular recognition

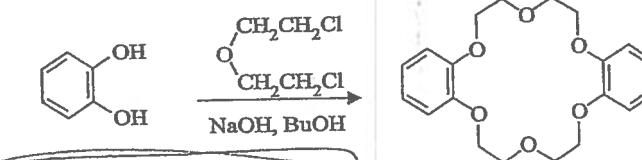
binding in biological systems. Dynamic molecular recognition is also being studied for application in highly functional chemical sensors and molecular devices.

### 5.5.2 Molecular Recognition in Supramolecular Systems with example

The artificial supramolecular systems designed, exhibit molecular recognition. One of the earliest examples of such a system is crown ethers which are capable of selectively binding specific cations. However, a number of artificial systems have been established. "For their development and use of molecules with structure-specific interactions of high selectivity,"



#### Facile Synthesis of Crown Ethers



### 5.5.3 Cation binding

#### Definition

Interacting selectively and non-covalently with cations, charged atoms (or) groups of atoms with a net positive charge.

### Factors affecting selectivity of cation complexation

- Size match between cation and host cavity;
- electrostatic charge;
- solvent (polarity, hydrogen bonding and coordinating ability);
- degree of host preorganisation;
- enthalpic and entropic contributions to the cation-host interaction;
- cation and host free energies of solvation;
- nature of the counter-anion and its interactions with solvent and the cation;
- cation binding kinetics; and
- chelate ring size

### Complexation of Organic Cations(example for cation binding)

Cryptate is a million times less likely to deprotonate than its uncomplexed analogue.

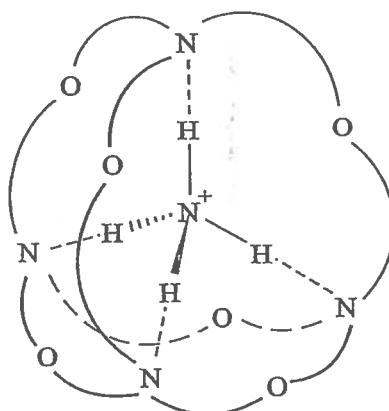


Fig. 5.6 Tetrahedral recognition of  $\text{NH}_4^+$  by a "soccer ball" cryptand

### 5.5.4 Anion binding

#### Definition

Interacting selectively and non-covalently with anions, charged atoms (or) groups of atoms with a net negative charge.

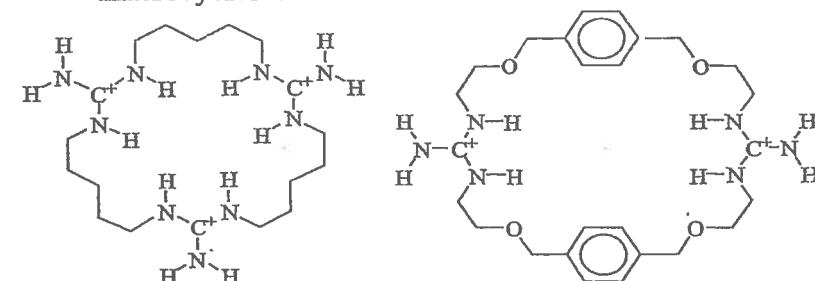
Hexacyclen cavity is partially filled with NH protons, it is too small to include anions. Its  $4\text{H}^+$  form binds halide and nitrate anions via hydrogen bonds with perching geometry

#### Factors affecting anion complexation

1. Size match between anion and host cavity
2. Complementarity (topological and shape selectivity)
3. Anion and host charge and anion polarisability
4. Solvent (polarity, hydrogen bonding and coordination ability), anion and host free energies of solvation
5. Anion basicity and host acidity
6. Other kinetic, enthalpic and entropic contributions to the anion-host interactions, prevailing interactions which take place in anion binding:
7. Hydrogen bonding
8. ion-dipole and ion-ion interactions
9. Vander Waals interactions.

#### Example: Guanidium Based Hosts(Anion binding)

- low charge density at the guanidinium moiety
- macrocycles are too small

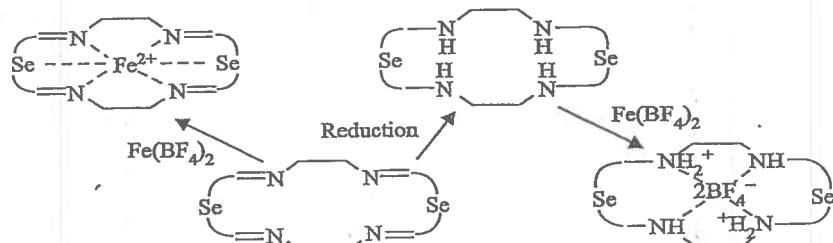


- high degree for solvation of the guanidinium ion

### 5.5.5 Simultaneous binding of anion-cation in supramolecules

Selenazamacrocycles hosts that are the first system to change guest binding affinity from cation to anion depending upon macrocycle oxidation/reduction. Selective cation ( $\text{Fe}^{2+}$ ) (or) anion ( $\text{BF}_4^-$ ) binding occurs with both ions present and under identical reaction conditions. The first macrocyclic complex with a  $\text{Fe}-\text{Se}$  bond.

Example: Selenazamacrocycle host



## 5.6 SUPRAMOLECULAR REACTIVITY AND CATALYSIS

Supramolecular reactivity and catalysis involve two main steps.

### (i) Binding

Binding selects the substrate.

### (ii) Transformation

Transformation of the bound species into products within the supramolecule formed.

Both the steps take part in the molecular recognition of the productive substrate and require the correct molecular information in the reactive receptor.

### 5.6.1 Mechanism of reactivity and catalysis

There are three modes of catalysis

#### 1. Orienting reactive and labile groups

A supramolecular host could bind to a guest molecule in such a way that the guest's labile group is positioned close to the reactive group of the host. The proximity of the two groups enhances the probability that the reaction could occur and thus the reaction rate is increased. This concept is similar to the principle of preorganisation, which states that complexation could be improved if the binding motifs are preorganized in a well-defined position so that the host does not require any major conformational change for complexation. In this case, the catalyst is preorganized such that no major conformational changes are required for the reaction to occur.

#### 2. Raising the effective substrate concentration

Biomolecular reactions are highly dependent on the concentration of substrates. Therefore, when a supramolecular container encapsulates both reactants within its small cavity, the effective local concentration of the reactants is increased and, as a result of an entropic effect, the rate of the reaction is accelerated. So that an intramolecular reaction is more accelerated than its corresponding intermolecular reaction.

Although a large raise in effective concentration is observed, molecules that employ this mode of catalysis have tiny rate acceleration compared to that of enzymes. A proposed explanation is that in a container the substrates are not as tightly bound as in enzyme.

#### 3. Stabilizing transition state

Supramolecular catalysts can accelerate reactions not only by placing the two reactants in close proximity but also by stabilizing the transition state of the reaction and reducing activation energy. While this fundamental principle of

catalysis is common in small molecule (or) heterogeneous catalysts, supramolecular catalysts however has a difficult time utilizing the concept due to their often rigid structures. Unlike enzymes that can change shape to accommodate the substrates, supramolecules do not have that kind of flexibility and so rarely achieve sub-angstrom adjustment required for perfect transition state stabilization.

A Diels Alder reaction between two pyridine functionalized substrates normally yield a mixture of endo and exo products. In the presence of the two catalysts, however, complete endo selectivity or exo selectivity could be obtained. The underlying cause of the selectivity is the coordination interaction between pyridine and the zinc ion on porphyrin. Depending on the shape of the catalysts, one product is preferred over the other.

## 5.7 SELF ASSEMBLY IN BIOLOGICAL SYSTEMS

Controlled molecular association results in the spontaneous formation of supermolecules with specific shapes and characteristics. This process is called self-assembly (or) self-organization.

### 5.7.1 Types of self assembly in biological systems

Self-assembling processes are classified into two types.

#### 1. Strict associations

The first type involves "strict" associations formed through hydrogen bonding.

#### *Example*

Assemblies are constructed from blocks of a defined shape, and these blocks are used to build the final supramolecule shape according to a specific construction program.

#### 2. Looser molecular interactions

Another type of self-assembly mode is based on "looser" molecular interactions, where one of the main binding forces comes from hydrophobic interactions in aqueous media. Amphiphilic molecules (amphiphiles) that have a hydrophilic part and a hydrophobic part form various assemblies in water and on water.

#### *Example*

The simplest example of this kind of assembly is a micelle, where amphiphiles self-assemble in order to expose their hydrophilic part to water and shield the other part from water due to hydrophobic interactions. A similar mechanism also leads to the formation of other assemblies, such as lipid bilayers. These molecules form spherical assemblies and/or two-dimensional membranes that are composed of countless numbers of molecules. These assemblies are usually very flexible. When external signals are applied to them, they respond flexibly while maintaining their fundamental organization and shape.

A variety of naturally occurring biological materials exhibits supramolecular self-assembly properties. By incorporation of signaling motifs, biological information and functional units, these biological materials can find extensive applications in developing nanotechnology, material science, tissue engineering and nanomedicine.

## 5.8 SELF ASSEMBLY IN SYNTHETIC SYSTEMS

The idea of synthesizing, efficiently and precisely, large and complex artificial molecular assemblies and supramolecular arrays from simple modular components has resulted in some chemical processes by using self-assembly in chemical synthesis, thus mimicking the many examples of this paradigm in nature. Coordination of organic ligands around metal centres, hydrogen bonding interactions and donor/acceptor  $\pi-\pi$  interactions.

stacking interactions have been employed to self-assemble numerous structures and superstructures, such as double and triple helices, grids, cages, and square-like networks, two and three-dimensional aggregates, tubular ensembles, as well as a large number of mechanically interlocked molecular compounds, such as catenanes, rotaxanes, and knots.

### 5.8.1 Catenane

Catenane is derived from the Latin word *catena* meaning "chain". A catenane is a mechanically-interlocked molecules consisting of two (or) more interlocked macrocycles, i.e., a molecule containing two (or) more intertwined rings. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles.

#### Synthesis: Clipping method

In catenane synthesis, clipping reactions are also prevalent synthesis methods in the formation of catenanes. In a clipping method, there can be one (or) two cyclisation reactions involved. In double-clipping, two macrocycles which are not fully closed are interlocked and two subsequent ring-closing reactions are performed in order to form the catenane. Catenanes can be prepared in this way by using template directed clipping reaction by making use of a dialkylammonium recognition site.

Threading followed by clipping

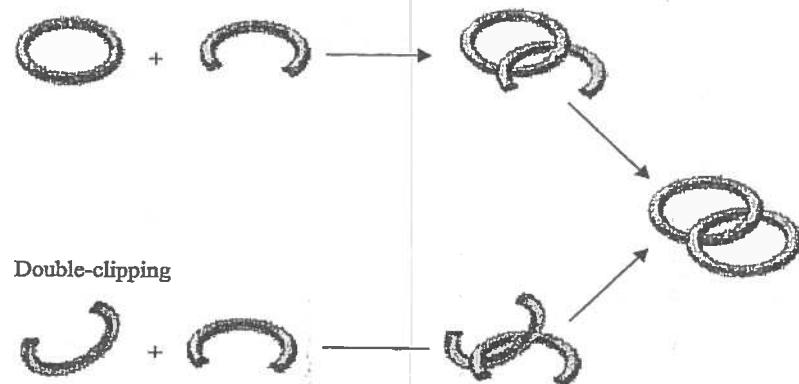
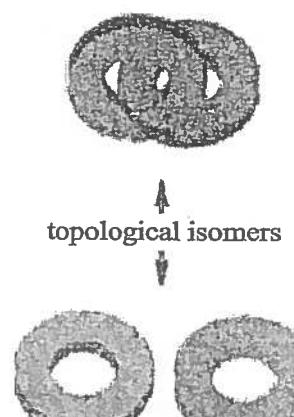


Fig. 5.7 Synthesis by clipping method

One can also have one full macrocycle and one macrocycle which is not fully closed yet, which threads through the full macrocycle. Ring-closing reaction is then used to lock the two macrocycles together and to create the catenane.

#### (a) Catenane



#### (b) Rotaxane

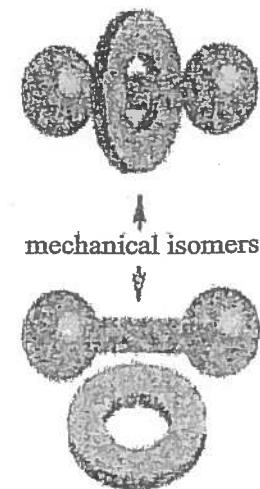


Fig. 5.8 Catenane and rotaxane

### 5.8.2 Rotaxanes

Rotaxanes are interlocked molecules composed of a macrocycle with an axle molecule threaded through it, kept in place by bulky end groups. Structurally, they consist of molecular rings threaded by molecular wires that have stoppers at both the ends to keep the rings in place. When more than one ring is threaded by a single wire, the structure is called a polyrotaxane. Sometimes a rotaxane with no stoppers are found and called as pseudorotaxane.

#### Synthesis

Two more recent approaches in the synthesis of rotaxanes are threading followed by shrinking (or) swelling respectively.

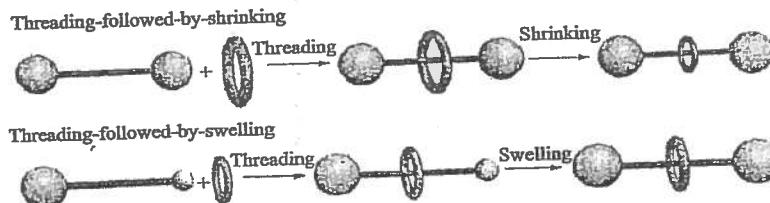


Fig. 5.9 Synthesis of rotaxane by shrinking (or) swelling

#### 1. Threading followed by shrinking

In threading followed by shrinking, a big macrocycle is used to thread the thread through the macrocycle. Then, the coordination between the macrocycle and the thread causes the macrocycle to shrink, effectively locking the thread into place. With this principle by making use of a macrocycle in which the arylmethyl sulfone group extrudes  $\text{SO}_2$  under photochemical conditions. This effectively makes the ring structure smaller by lowering the amount of atoms in the ring.

#### 2. Threading followed by swelling

In threading followed by swelling, a thread is used in which one of the bulky groups is smaller than the other one,

enabling it to thread easily through the macrocycle. Then the small group swells and locks the macrocycle into place. This approach is used in synthesising molecular rotaxanes by conversion of a *cis*-1-[*(Z*)-alk-1'-enyl]-2-vinylcyclopropane terminal group to a bigger cycloheptadiene moiety by a Cope rearrangement under ambient conditions.



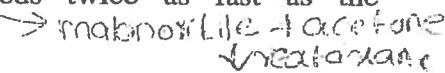
### 5.8.3 Applications of rotaxanes and catenanes

#### 1. Chemical Applications



##### (a) Catalyst

The Knoevenagel reaction between malononitrile and acetone was carried away by the presence of a rotaxane catalyst. The proposed malononitrile reacted with the rotaxane via its active hydrogens, creating a zwitter ion which initiates the reaction. The reaction proceeds twice as fast as the rotaxane-catalysed reaction.



##### (b) Chemical Sensors

Recently, Beer.P.D designed a rotaxane which incorporates a tris(bipyridine)ruthenium(II)-based macrocycle unit for the luminescent detection of halide ions in water. The selectivity for specifically the iodide ion, makes this rotaxane useful in detecting iodide ions in water.

##### (c) Polymers

Crystallisation of the polyethylene oxide catenane polymer slowed down with respect to common polyethylene oxide polymers, due to the catenane acting as a defect in the polymer chain which slows down crystallisation. By the addition of even a single catenane moiety to a polymer chain influenced the properties of the polymer. Future design of mechanically interlocked polymers could therefore rely on less catenane moieties for getting the desired physical properties.

## 2. Biological Applications

### (a) Drug Delivery Agents

$\alpha$ -chymotrypsin is used to hydrolyse the amide bond to release the macrocycle into the cell. If the macrocycles are biologically active molecules, this pathway opens up the possibility of using this system as a vehicle to transport drugs into the cell through the cell membrane and to release the active macrocycle inside the cell by hydrolysing the amide bond holding the macrocycle onto the thread.

### (b) Optical Bio-Imaging Agents

Enhancement of MRI measurements can be measured by the presence of rotaxane. Catenane composed of two macrocycles, one containing a endoperoxide which is the source of chemiluminescence and another macrocycle containing a squaraine moiety that is responsible for fluorescence. These catenanes undergo thermally- activated cycloreversion reaction which emits light and an excited singlet oxygen. Nanoparticles stained with this catenane dye were injected into mice and chemiluminescence and fluorescence was detected.

## 3. Applications in Materials Research.

### (a) Molecular Switches

TEFM (Mitochondrial transcription and elongation factor) switches on (or) off the replication (or) transcription of DNA.

### (b) Molecular Motors

Molecular motors are employed in biology for a wide variety of functions that often have macroscopic equivalents in engineering. The applications of motors in intracellular transport, in cellular motility and as key elements of muscle tissue are important.

## 5.9 METAL ION ASSISTED ASSEMBLIES

Metal ions are frequently used for assembly of large supramolecular structures. Metal organic frame works (MOFs)

are one example. MOFs are infinite structures where metal serve as nodes to connect organic ligands together.

SSCs are discrete systems where selected metals and ligands undergo self-assembly to form finite supramolecular complexes. Usually the size and formed can be determined by the angularity of chosen metal-ligand bonds.

### Example

Self assembly of peptide-decorated AuNPs into three dimensional NP networks using divalent metal ions. Disassemblies can be induced using a strong chelator for metal ions such as EDTA.

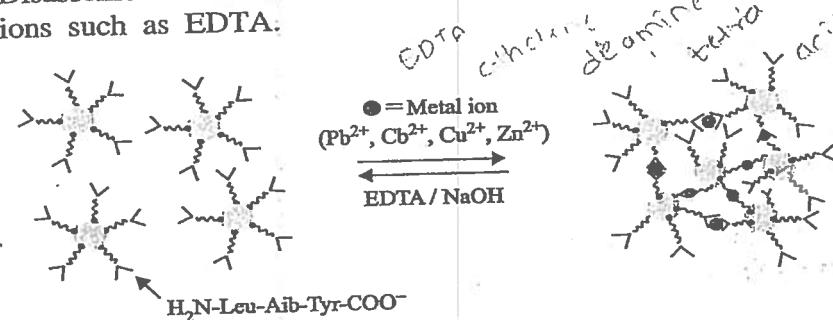


Fig. 5.10 Assembly and Disassembly of peptide-decorated AuNPs

## 5.10 TERMS IN TEMPLATE SYNTHESIS

### 1. Template centre

The metal ion (or) another particle (molecule, anion) which can orientate and activate the ligands for their subsequent interaction.

### 2. Positive template

A template which brings together the reactive end groups of a molecule (molecules) facilitating intramolecular coupling.

### 3. Negative template

The template which prevents the reactive end groups of a molecule (molecules) coming together suppressing intramolecular coupling and favouring intermolecular reactions.

### 4. Template bonds

Forces by means of which the corresponding template orients (and/or activates) the reacting ligands, organising their preparation for the reaction. Metal-ligand binding, hydrogen bonding can be successfully exploited with a high degree of control in synthesis of macrocycles.

### 5. Ligand synthon (or) ligson

A polyfunctional, usually chelating ligand that takes part in the assemblage reactions at the template centre (a building block for the template synthesis).

### 6. Chelant (chelator)

The open-chain ligand which occupies several coordination places in the inner sphere (coordination shell) of the template centre.

### 7. Assemblage reaction

The organic reaction at the template centre, by means of which coupling of ligands occurs.

### 8. Construction (Chelatogene) bonds

Covalent bonds formed as a result of assemblage reactions and providing the skeleton of the appearing chelatocycles.

### 9. Ligand product

The final organic product (ligand) which is formed as a result of ligsons interaction.

### 10. Template information

The totality of coordinative-stereochemical characteristics of the template centre which stipulates a definite spatial arrangement of ligsons.

### 11. Template complementarity

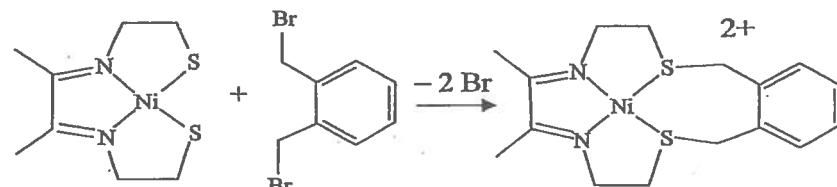
A matching between the template information of the matrix and the geometrical (conformational) and electron donor-acceptor parameters of the ligsons and of the ligand product.

#### 5.10.1 Template synthesis of Macrocyclic Ligands

A metal ion template reaction is one in which coordination of at least one reactant molecule to a metal ion is necessary either for the reaction to proceed (or) to change the product distribution in favour of a specific macrocyclic compound. This means that the presence of metal is controlling the synthesis. This is known as the template effect. An example of its use is the production of the phthalocyanines, which are used as dye pigments and semiconductors and also as the model ligand for biological macrocycles such as porphyrins.

#### Examples

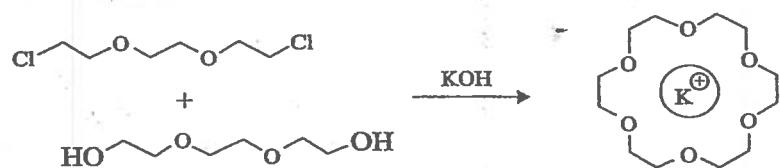
In chemistry, a **template reaction** is any of a class of ligand-based reactions that occur between two (or) more adjacent coordination sites on a metal center. In the absence of the metal ion, the same organic reactants produce different products. The term is mainly used in coordination chemistry. The **template effects** emphasizes the pre-organization provided by the coordination sphere, although the coordination modifies



the electronic properties (acidity, electrophilicity, etc.) of ligands.

An early example is the dialkylation of a nickel dithiolate:

The corresponding alkylation in the absence of a metal ion would yield polymers. Crown ethers arise from dialkylations that are templated by alkali metals. Other template reactions include the Mannich and Schiff base condensations. The condensation of formaldehyde, ammonia, and tris(ethylenediamine)cobalt(III) to give a clathrochelate complex is one example.



18-Crown-6 can be synthesized by the Williamson ether synthesis using potassium ion as the template cation.

## 5.11 APPLICATIONS OF SUPRAMOLECULAR DEVICES

These are molecules (or) assemblies that can perform functions such as linear (or) rotational movement, switching and entrapment. These devices exist at the boundary between supramolecular chemistry and nanotechnology. The applications of supramolecular devices are explained under the following headings.

1. Switching Devices
2. Ionic devices
3. Electronic Devices

g

### 5.11.1 Switching Devices

Electrical switch is used for regulating electron flow. Certain supramolecules mimics this electric switch are called as molecular switches.

There are two kinds of molecular switches

1. Photoregulated molecular switch
2. Chemically controlled molecular switch.

An electrical switch is another important element for regulating electron flow. Direct connection and disconnection between lead wires is usually used to regulate electricity flow. The molecule shown in the fig.5.10 mimics this kind of switch. When the center of the molecule is uncyclized, a fully conjugated path (a path of conduction) through the molecule is not available and so the molecular switch is in the OFF state. Irradiating the molecule with light at 365 nm induces cyclization of the molecule. When it is cyclized, a fully conjugated path through the molecule becomes available and so the molecular switch is turned ON. The molecule can revert its OFF state by irradiating it with light of > 600 nm. If this kind of molecular switch was introduced into a supramolecular system, molecular electric circuits switched by photoirradiation could be constructed.

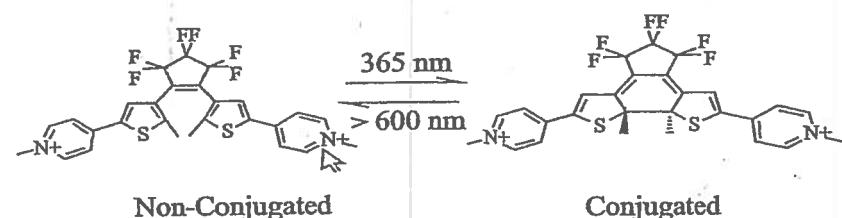


Fig. 5.10 Molecular switch

### 5.11.2 Ionic devices

The response to external physical (or) chemical stimuli (light, electrons, ions, molecules) that may regulate the operation of the device and switch it on (or) off. The nature of the signals generated and of the signal conversion effected (photon-photon, photon-electron, electron-electron, electron-ion, ion-ion). Selective ion carriers corresponds to ion transducers.

- (i) Carboxylic acid functional group represents a proton switch and leads to proton greater receptors and carriers responding to pH changes.
- (ii) In the cell membrane there are ion selective pumps, composed of proteins, which pump  $K^+$  into the cell and  $Na^+$  out of the cell. This creates an electrochemical gradient across the membrane known as the resting potential. The neuron receives signals from other neurons at its dendrites through structures called synapses.
- (iii) The  $Ca^{2+}$  ion plays an important role in a wide range of cellular processes, from neurotransmitter exocytosis to cell proliferation (hours). The versatility of the  $Ca^{2+}$  ion is a result of the highly spatiotemporal nature of  $Ca^{2+}$  signaling

### 5.11.3 Electronic Devices

Supramolecular electronics is the experimental field of supramolecular chemistry that bridges the gap between molecular electronics and bulk plastics in the construction of electronic circuitry at the nanoscale. In supramolecular electronics, assemblies of  $\pi$ -conjugated systems on the 5-100 nanometer length scale are prepared by molecular self-assembly with the aim to fit these structures between electrodes.

#### 1. Molecular wires

Electron-conducting wire is the first requirement for molecular electronics. Molecules with conjugated linkages, such as conductive polymers, are strong candidates for this "molecular wire". Their typical diameters are less than three nanometers, while their lengths may be macroscopic, extending to centimeters. Organic molecular wires include carbon nanotubes and DNA. Electrons are transmitted through this molecular wire. This system can therefore be regarded as a form of molecular wiring. Electron transfer via a noncovalent junction was achieved artificially. In this system, the electron donor zinc porphyrin was covalently connected to guanosine and an electron-accepting quinone was linked to the cytosine. These two parts associate through complementary hydrogen bonding between the guanosine and cytosine. When this pair were irradiated with light of an appropriate wavelength, electron transfer occurred from the zinc porphyrin to the quinone. This example demonstrates that electrical connections can be achieved between molecular parts via noncovalent supramolecular interactions.

#### 2. Molecular machines (or) Molecular motors

Molecular motors, also called molecular machines, are either natural (or) synthetic molecules that convert chemical energy into mechanical forces and motion. An example of a biological motor is the protein kinesin, which uses the hydrolysis of adenosine triphosphate to move along microtubule filaments.

- (a) Biomolecular motors achieve the cold conversion of chemical energy into mechanical work, in contrast to heat engines such as the internal combustion engine. The transition from heat engines to cold engines seems just as desirable as the transition from hot incandescent lamps to cold lightemitting diode (LED) lamps.
- (b) Intracellular transport comprises a range of motor-driven mechanisms, including, for example, anterograde and

- retrograde transport in neurons and cytoplasmic streaming in algae
- (c) The transport of molecules, supramolecular complexes, and nano- (or) microparticles is a prime application for molecular motors
- (d) The detection of chemical and biological entities is a complex process that often requires the capture, aggregation and identification of the target molecules. Active transport of captured analyte molecules and particles can be exploited to enhance the mass transport to a sensor under specific conditions

### 5.12 DESCRIPTIVE TYPE QUESTIONS

1. Explain principles of complementarity and its types.
2. Explain lock and key model for enzyme substrate reaction.
3. Write notes on molecular recognition and their types.
4. Write notes on (i) cation binding (ii) anion binding.
5. Explain the various modes of supramolecular reactivity and catalysis.
6. Write notes on self assembly in biological systems.
7. Explain the applications of supramolecular devices.

### 1. Structure and Bonding Models

#### 1. Define black body and black body radiation.

An ideal body which can emit and absorb radiation of all frequencies is called a **black body**.

The radiation emitted by such bodies is called black body radiation.

#### 2. What are the significance of bonding and antibonding orbitals?

To understand the significance of bonding and antibonding molecular orbitals in terms of wave functions, it is necessary to know the electronic charge distribution of these orbitals.

The electronic charge distribution can be understood from the derivation of molecular orbitals by the Linear Combination of Atomic Orbitals (LCAO method).

#### 3. What is the order of energy levels in homonuclear MOs?

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z)$$

$$< \left\{ \begin{array}{l} \pi(2p_y) \\ \pi(2p_x) \end{array} \right\} < \left\{ \begin{array}{l} \pi^*(2p_y) \\ \pi^*(2p_x) \end{array} \right\} < \sigma^* 2p_z$$

#### 4. Write the order of energy levels in heteronuclear MOs

$$\begin{aligned} \sigma(1s) &< \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \left\{ \begin{array}{l} \pi(2p_x) \\ \pi(2p_y) \end{array} \right\} \\ &< \sigma(2p_z) < \left\{ \begin{array}{l} \pi^*(2p_x) \\ \pi^*(2p_y) \end{array} \right\} < \sigma^*(2p_z) \end{aligned}$$

5. Calculate the bond order of CO.

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8 - 2}{2} = 3$$

Thus, the C-atom and O-atom are bonded through three bonds (one  $\sigma$  and two  $\pi$ ).

6. Write the spectrochemical series?

When different ligands are arranged in increasing order of  $\Delta_0$ , we get the spectrochemical series.

(Weak ligand field)  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{EtOH} < (\text{COO}^-)_2 < \text{H}_2 < \text{EDTA} < \text{NH}_3 < \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2 < \text{NO}_2^- < \text{CN}^- < \text{CO}$  (Strong ligand field).

7. Crystal field splitting of tetrahedral complex is lesser than that in octahedral complex. Why?

This is due to the following reason

- (i) There are only 4 ligands, so the ligand field is small.
- (ii) The direction of the orbitals does not coincide with that of ligands.

Thus, the tetrahedral splitting ( $\Delta_t$ ) is always much smaller than the octahedral splitting ( $\Delta_o$ ).

8. What are diamagnetic and paramagnetic properties?

#### (a) Diamagnetic

The complexes having paired electrons (ie., having no unpaired electrons) are said to be diamagnetic.

#### (b) Paramagnetic

The complexes having one (or) more unpaired electrons are said to be paramagnetic.

9. What is meant by doping. How is it done?

The process by which impurity is introduced in semiconductors to enhance their conductivity is called doping. It can be done with an impurity which is electron rich (or) electron deficient. Such impurities introduce electronic defects in them.

## 2. Electrochemistry and Applications

### 1. What are electrodes? How are they classified?

An electrode is a solid electric conductor that carries electric current into non-metallic solids (or) liquids (or) gases. They are typically good electric conductors.

#### Types of electrodes

**1. Anode:** Anode is an electrode at which oxidation occurs

**2. Cathode:** Cathode is an electrode at which reduction occurs.

### 2. What are the factors affecting electrode potential?

- (i) The nature of the metal.
- (ii) The temperature.
- (iii) The concentration of metal ions in solution.

### 3. Define single electrode potential.

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

### 4. What is standard electrode potential?

It is the measure of tendency of a metallic electrode to lose (or) gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

### 5. How is calomel electrode represented?

It is represented as,

**Hg, Hg<sub>2</sub>Cl<sub>2</sub>(s), KCl (sat.solution); E° = 0.2422 V**

### 6. What are the advantages of glass electrode.

- (i) It can be easily constructed and readily used.
- (ii) The results are accurate.
- (iii) It is not easily poisoned.
- (iv) Equilibrium is rapidly achieved.

### 7. What are electrochemical cells?

Electrochemical cells are Galvanic cells in which the electrons, transferred due to redox reaction, are converted to electrical energy.

### 8. What is the function of salt bridge?

- (i) It eliminates liquid junction potential.
- (ii) It provides the electrical continuity between the two half cells.

### 9. Define emf.

Electromotive force is defined as, "the difference of potential which causes flow of electrons from one electrode of higher potential to the other electrode of lower potential."

### 10. Mention some applications of Nernst equation.

- 1. Nernst equation is used to calculate electrode potential of unknown metal.
- 2. Corrosion tendency of metals can be predicted.

### 11. What is photovoltaic cell?

Photovoltaic cell is the one, which converts the solar energy (energy obtained from the sun) directly into electrical energy.

### 12. What are sensors mention their types?

Sensors are devices which convert one form of energy into another.

There are so many sensors of which the followings are some important sensors.

- 1. Potentiometric sensors
- 2. Amperometric sensors
- 3. Electrochemical sensors

## 13. What are batteries?

A battery is an arrangement of several electrochemical cells connected in series, that can be used as a source of direct electric current.

## 14. Define conductivity

Conductivity (or) conductance of an electrolyte solution is a measure of its ability to conduct electricity.

## 15. What is equivalent conductance?

It is defined as the conducting power of all the ions produced by dissolving 1 gram equivalent of an electrolyte in the solution.

$$\Lambda_{eq} = \frac{1000 \kappa}{C}$$

## 16. What is molar conductance?

It is defined as "the conducting power of all the ions produced by dissolving 1 mole of an electrolyte in a given solution."

$$\Lambda_m = \frac{1000 \kappa}{C}$$

3. Polymer Chemistry

## 1. What are polymers?

Polymers are macro molecules (giant molecules of higher molecular weight) formed by the repeated linking of large number of small molecules called monomers.

## 2. Define functionality of monomers.

The number of bonding sites (or) reactive sites (or) functional groups, present in a monomer, is known as its **functionality**.

## 3. Define polymerisation?

Polymerisation is a process in which large number of small molecules (called monomers) combine to give a big molecule (called a polymer) with or without elimination of small molecules like water.

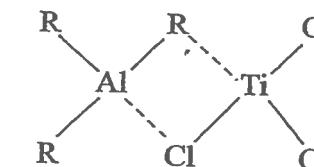
## 4. Define DP.

The number of repeating units (n) in a polymer chain is known as degree of polymerisation. It is represented by the following relationship.

Degree of polymerisation (DP)

$$= \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$

## 5. Draw the structure of Zeigler-Natta catalyst.



6. Write the uses of bakelite?

- (i) Bakelite is used as an adhesive in plywood laminations & in grinding wheels, etc.
- (ii) It is also widely used in paints, varnishes.
- (iii) It is used for making electrical insulator parts like plugs, switches, heater handles, etc.,

7. What are the properties of urea-formaldehyde resin?

1. Urea-formaldehyde resins give white-water soluble products.
2. It has good tensile strength, good electrical insulation, good chemical-resistance, and great hardness.

8. Explain the uses of nylons.

- (i) Nylon 6:6 is used for fibers, which are used in making socks, ladies shoes, dresses, carpets, etc.,
- (ii) Nylon 6 is mainly used for moulding purposes for gears, bearings, electrical mountings, etc., Nylon bearings work without any lubrication.
- (iii) Nylons are used for making filaments for ropes, bristles for tooth-brushes, films and tyre-cords.

9. What are elastomers?

Rubbers (or) elastomers are non-crystalline high polymers (linear polymers), having elastic and other rubber-like properties.

10. What are conducting polymers?

Those polymers, which conduct electricity are called conducting polymers.

11. What are the reasons for conduction in polymer?

- (a) Presence of unsaturated conjugated double bonds in the polymer.
- (b) Addition or removal of electrons (doping) in to the polymer.

12. What are the applications of conducting polymers?

1. Conducting polymers are used in solar cells.
2. It is used in telecommunication systems.
3. It is also used as a very good electrode material for rechargeable batteries.
4. Conducting polymers are used in antistatic coatings for clothing.
5. It is used as a membrane film for gas separations.
6. Conducting polymers are used as electrocatalytic materials in fuel cells.
7. It is used for making analytical sensors.
8. It is used for making ion exchangers.

## Instrumental Methods and Applications

1. Define Beer-Lambert's law.

$$A = \epsilon Cx$$

The absorbance ( $A$ ) is directly proportional to molar concentration ( $C$ ) and thickness (or) path length ( $x$ ).

2. Define pH - metry. How is it carried out.

pH - metry is a scientific method used to measure the hydrogen ion concentration in water based solutions, indicating its acidity (or) alkalinity expressed as pH. The pH metry is usually carried out by pH meter.

3. What is conductometry?

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction.

4. What is meant by chromophores?

The presence of one (or) more unsaturated linkages ( $\pi$ -electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores.

**Examples**



Chromophores undergo  $\pi \rightarrow \pi^*$  transitions in the short wavelength regions of UV-radiations.

5. Define chemical shift.

The separation in the position of the signal of different types of protons from that of a standard is called chemical shift.

6. Define spin-spin splitting.

Further splitting of the NMR signal due to the interaction between protons on adjacent atoms is referred to as spin-spin splitting (or) coupling.

7. What are the conditions required for spin-spin coupling to occur?

1. Chemically equivalent protons will not cause spin-spin coupling.
2. Non-equivalent protons only will couple.
3. Protons present in an adjacent carbon atoms will couple.
4. Protons present in the carbon atom, having multiple bonds, will not couple.
5. Write the important applications of GC
1. Separation of components having close boiling points, can be done easily by GC.
2. Ethyl alcohol content in blood can be determined.
3. The multicomponent analysis can be done in a relatively short time.
4. The following analysis may be carried out easily in GC.
  - (i) Refinery gases
  - (ii) Synthetic rubber intermediate
  - (iii) Trace atmospheric constituents

## 5. Molecular Machines and Molecular Switches

**1. What is supramolecular chemistry?**

Supramolecular chemistry refers to the study of supramolecular assemblies.

**2. What is supramolecular structure?**

Supramolecular structures are large molecules formed by grouping (or) bonding smaller molecules together.

**3. Define host and Guest.**

**1. Host**

It is the organic molecule containing convergent binding sites. Synthetic counter parts to receptor sites in enzymes, genes, antibodies and ionophores.

**2. Guest**

Molecules or ions containing divergent to binding sites counter parts to substrates, inhibitors, cofactors, antigens.

**4. What is the basic principle of complementarity?**

The principle of complementarity states that, "to complex, host must have binding sites which can simultaneously contact and attract the binding sites of the guests without generating internal strains (or) strong non-bonded repulsions."

**5. Define molecular recognition.**

The term molecular recognition refers to the specific interaction between two (or) more molecules through noncovalent bonding such as hydrogen bonding, metal coordination, hydrophobic forces, Vander Waals forces,  $\pi - \pi$  interactions, halogen bonding, electrostatic (or) electromagnetic effects.

**6. What is cation binding?**

Interacting selectively and non-covalently with cations, charged atoms (or) groups of atoms with a net positive charge.

**7. What is catenane?**

A catenane is a mechanically-interlocked molecules consisting of two (or) more interlocked macrocycles.

**8. What is Rotaxanes?**

Rotaxanes are interlocked molecules composed of a macrocycle with an axle molecule threaded through it, kept in place by bulky end groups. Structurally, they consist of molecular rings threaded by molecular wires that have stoppers at both the ends to keep the rings in place.