

UNIT - I

STRUCTURE AND BONDING MODELS

Structure and bonding are about explaining the behavior, reactions, properties and uses of macroscopic substances using models of matter at a sub-microscopic level. This topic plays a very large part in understanding the basics of structure and bonding in chemistry. Quantum mechanics play a big role in the understanding of structure and bonding models. Properties of materials are determined by their bonding and structure. This is clearly illustrated by considering different allotropes of carbon, where applications range from diamond in drill tips and graphite in pencil leads to carbon nanotubes for structural reinforcement in construction and for drug delivery to cells in pharmacy.

To understand structure and bonding, the orbital model of the atom as well as covalent, ionic and metallic bonding is important. In an atom the positive nucleus is surrounded by constantly moving electrons which occupy different energy levels containing one or more sub-levels. Electronic structure influences the chemical properties of an element. Molecules are groups of atoms held together by intramolecular forces, such as covalent bonds. Weaker intermolecular forces exist between molecules. Valence Shell Electron Pair Repulsion (VSEPR) can be used to work out the shape of molecules and molecular ions.

Fundamentals of Quantum mechanics

Plank's quantum theory

In 1900, Max plank proposed the theory of radiation. It explains the quantum nature of the energy of electromagnetic waves.

According to the theory,

1. Different matter (atoms or microscopic particles) can emit or absorb energy in discrete quantities only.
2. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum or quanta.
3. The energy of the radiation absorbed or emitted is directly proportional to the frequency of radiation

$$E \propto \nu$$

$$E = h \nu$$

Where, E = Energy of the radiation

h = Planks constant (6.626×10^{-34} J/s)

c = Velocity of light

λ = Wavelength

4. The total energy of radiation is represented as multiple whole numbers of energy of quantum as $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$ and so on.

Dual nature of matter

The matter such as electron, proton, atom etc. can show wave nature and also particle nature which is known as dual nature of matter.

In the case of light, some phenomenon like diffraction and interference can be explained on the basis of wave nature. However, the other phenomenon such as black body radiation and photoelectric effect can be explained by its particle nature. Thus, light is said to have a dual character.

De-Broglie's dual nature hypothesis

According to De-Broglie's hypothesis, all the microscopic particles such as electrons, protons etc. should possess not only the particle nature but also the wave nature.

If a particle of mass ' m ' moving with velocity ' v ', then the wavelength of this moving particle is given by

$$\lambda = \frac{h}{mv}$$

h = Planks constant (6.626×10^{-34} J/s)

m = Mass of particle

v = Velocity of particle

The De-Broglie's equation is derived using the two equations, i.e., Plank's quantum theory and Einstein energy mass relationship.

According to Plank's quantum theory,

$$E = h\nu \text{ ----- (1)}$$

According to Einstein's energy mass relation,

$$E = mc^2 \text{ ----- (2)}$$

Where, m = mass of photon

c = velocity of light

From equation (1) and (2),

$$h\nu = mc^2$$

$$\frac{hc}{\lambda} = mc^2$$

$$\frac{h}{\lambda} = mc$$

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

Since, $p=mc$ is momentum of particle.

The above equation is known as De-Broglie's equation. It is applicable to small particles like electrons only. For, macroscopic particles, it cannot be applicable.

Heisenberg's Uncertainty Principle

The wave nature of particle is further explained by Heisenberg's uncertainty principle. According to this theory, it is impossible to determine accurately and simultaneously both the position and momentum of a particle.

If Δx and Δp are the uncertainties in the position and momentum respectively, then

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Where, Δx = Uncertainty in position

Δp = Uncertainty in momentum

An attempt to reduce Δx will raise Δp and vice-versa. If the position of the particle is known exactly, i.e., $\Delta x=0$, the Δp becomes infinity and vice-versa.

Schrodinger Wave Equation

Schrodinger equation was developed by Erwin Schrodinger in 1925 based on De-Broglie's dual nature, Heisenberg uncertainty principle and classical energy theory.

It describes the energy and position of a particle in space and time. This equation is the keynote of wave mechanics and is based on the idea that electrons are standing waves around the nucleus.

The total energy of any particle or electron is given by

$$E = K.E. + P.E.$$

K. E. = Kinetic Energy

P. E. = Potential Energy

We know that, $K. E. = \frac{1}{2} mv^2$ and let $P.E. = V$

So, $K. E. = \frac{1}{2} mv^2 + V$ -----(1)

$K. E. = \frac{1}{2} mv^2$ can be expressed as $\frac{1}{2} mv^2 = \frac{1}{2} mv^2 * \frac{m}{m} = \frac{1}{2} \frac{(mv)^2}{m}$

From the de-Broglie's hypothesis, we know that

$$\lambda = \frac{h}{mv}$$

Rearranging the above equation, we get, $mv = \frac{h}{\lambda}$

Substituting the mv value in the above equation, $\frac{1}{2} mv^2 = \frac{1}{2} \frac{(\frac{h}{\lambda})^2}{m}$

$$= \frac{1}{2} \frac{h^2}{\lambda^2 m} \text{ ----- 2}$$

Substituting equation no. 2 in no. 1

$$E = \frac{h^2}{2\lambda^2 m} + V$$

or

$$E - V = \frac{h^2}{2\lambda^2 m}$$

Rearranging the above equation,

$$\lambda^2 = \frac{h^2}{2m(E-V)} \text{ ----- 3}$$

Since, electron is exhibits wave like character, the equation describing the wave motion of a particle along the x - axis can write as,

$$\varphi = A \sin 2\pi \frac{x}{\lambda} \text{ ----- 4}$$

φ = Wave function

A = Maximum value of φ

x = Displacement in a given direction

λ = Wave length

Differentiating the above equation twice with respect to 'x'

$$\begin{aligned}\frac{d\varphi}{dx} &= A \frac{2\pi}{\lambda} \cos 2\pi \frac{x}{\lambda} \\ \frac{d^2\varphi}{dx^2} &= -\frac{4\pi^2}{\lambda^2} A \sin 2\pi \frac{x}{\lambda} \\ \frac{d^2\varphi}{dx^2} &= -\frac{4\pi^2}{\lambda^2} \varphi \text{ ----- 5 (From eq. 4, } \varphi = A \sin 2\pi \frac{x}{\lambda})\end{aligned}$$

Rearranging the equation no. 5

$$\frac{d^2\varphi}{dx^2} + \frac{4\pi^2}{\lambda^2} \varphi = 0$$

Substituting the λ^2 value from eq. no. 3 in above equation

$$\frac{d^2\varphi}{dx^2} + \frac{4\pi^2\varphi}{\left[\frac{h^2}{2m(E-V)}\right]} = 0$$

For one dimension,

$$\frac{d^2\varphi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V)\varphi = 0 \text{ ----- 7}$$

For electrons, which can move along any of the three axis, x, y, z, the equation can be written as,

$$\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} + \frac{8\pi^2m}{h^2} (E - V)\varphi = 0$$

The above equation is called as Schrodinger wave equation.

Here, x, y, z = Coordinates in three dimensions

m = Mass of electron

E = Total energy of electron

V = Potential energy

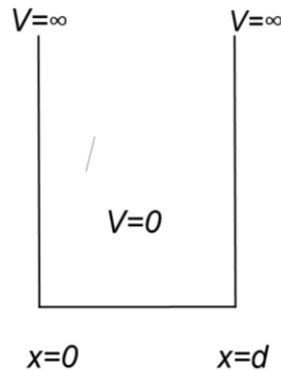
φ = Amplitude of electron wave

Significance of φ and φ^2

1. φ is the wave function. It takes a positive value above the axis and negative value below the axis and it becomes zero while crossing/intercepting the axis. It is a state function but it has no physical significance, it only represents the amplitude of electron wave.

2. ϕ^2 is the probability of finding an electron around the nucleus and the point where the values of ϕ^2 is maximum is called the orbital. The value of ϕ^2 is always positive.

Particle in one dimensional box



Consider a particle of mass ‘m’ confined to one-dimensional region, which is free to move along x-direction between $x=0$ and $x=d$ is inside a box bounded by infinity rigid walls. As per quantum mechanics, the potential energy (V) of the particle infinite on both sides of the box and inside the box ‘V’ is constant ($V=0$). ϕ function has to be zero at $x=0$ and all negative values of x, since the particle is not allowed over the walls of the box.

Similarly, ϕ function must be zero for all values $x>d$. Therefore, it can be stated that the particle is combined with the box and cannot exist outside the box.

The potential energy inside the one-dimensional box can be represented as,

$$V_{(x)} = 0 \quad \text{for } 0 \leq x \leq a$$

$$V_{(x)} = \infty \quad \text{for } 0 > x > a$$

The Schrodinger wave equation for one dimensional given as

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

Inside the box, $V_{(x)} = 0$, then

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

Inside the box, the Schrodinger’s wave equation is

$$\frac{\partial^2\phi}{\partial x^2} + \frac{4\pi^2}{h^2} m (E)\phi = 0 \quad \text{Since } V=0$$

$$\frac{\partial^2 \varphi}{\partial x^2} + K^2 \varphi = 0 \text{ ----- 2 } [\because K^2 = \frac{8\pi^2 m}{h^2}]$$

The solution of the above equation can be written as.

$$\varphi_{(x)} = A \sin Kx + B \cos Kx \text{ ----- 3}$$

The wave function $\varphi_{(x)}$ should be zero everywhere outside the box since the probability of finding the particle outside the box is zero.

Thus, the boundary conditions for this problem are

$$\varphi_{(x)} = 0 \text{ for } x = 0$$

$$\varphi_{(x)} = 0 \text{ for } x = a$$

Applying the boundary condition in equation no. 3, we get

$$0 = A \sin K(0) + B \cos K(0)$$

$$0 = 0 + B(1)$$

$$B = 0 \text{ ----- 6}$$

Substitute the B value in equation no. 3

$$\varphi_{(x)} = A \sin Kx + 0$$

$$\varphi_{(x)} = A \sin Kx \text{ ----- 7}$$

Now applying the boundary condition, equation no. 7 can write as

$$0 = A \sin Ka$$

This equation will satisfy only for certain value of K. Since A cannot be zero. Hence,

$$\sin Ka = 0$$

$$\sin Ka = \sin n\pi$$

$$Ka = n\pi$$

$$K = \frac{n\pi}{a}$$

$$K^2 = \frac{n^2 \pi^2}{a^2} \text{ ----- 8}$$

Comparing K^2 values of equation no. 2 and equation no. 8,

$$\frac{8\pi^2m}{h^2}[E] = \frac{n^2\pi^2}{a^2}$$

$$E = \frac{n^2\pi^2h^2}{8\pi^2ma^2}$$

$$E = \frac{n^2h^2}{8ma^2}$$

Where, n = 1, 2, 3, 4 etc.

Thus, a particle in a box does not possess any arbitrary amount of energy, rather it possesses a discrete set of energy values, i.e., its energy is quantized. Some of the energy levels are

$$E_1 = \frac{h^2}{8ma^2}$$

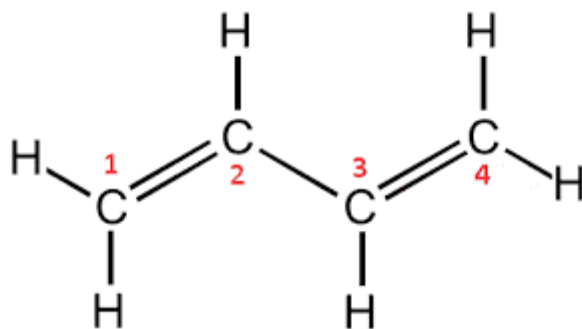
$$E_2 = \frac{4h^2}{8ma^2}$$

$$E_3 = \frac{9h^2}{8ma^2}$$

Therefore, according to the above equation, a particle in a box (bound particle) possesses quantized energy but a free particle does not.

II-Molecular orbitals of Butadiene

Butadiene is composed of four carbons with conjugated π bonds. All the four p-orbitals are aligned with each other and make up into a larger π system. Since, butadiene consists of four individual p-orbitals, the π system of butadiene contains 4 π molecular orbitals. The π electrons in a conjugated molecule are filled according to the Aufbau principle.



1,3-Butadiene

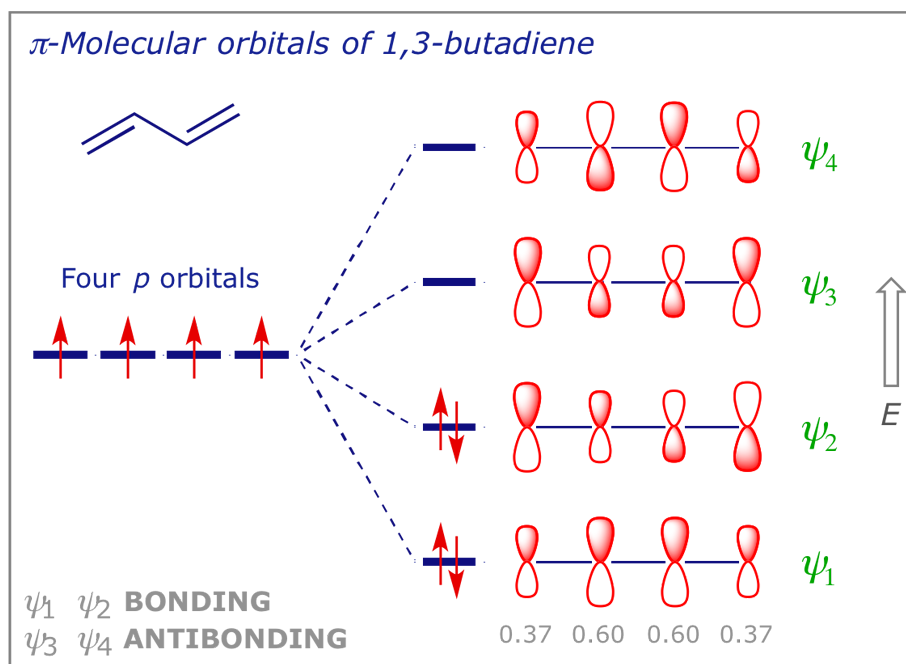
The molecular orbitals of butadiene can divide into two types, bonding molecular orbitals and anti-bonding molecular orbitals. From the all the orbitals, the high energy orbital which having electrons is known as Highest occupied molecular orbital (HOMO) and the low energy orbital which is empty is known as Lowest unoccupied molecular orbital (LUMO).

1. Highest occupied molecular orbital (HOMO)

Π^2 orbital is HOMO in butadiene because of this orbital having the electrons with comparatively higher energy than other electrons. They will be readily lost. When butadiene participates in a reaction as a nucleophile, these electrons are used.

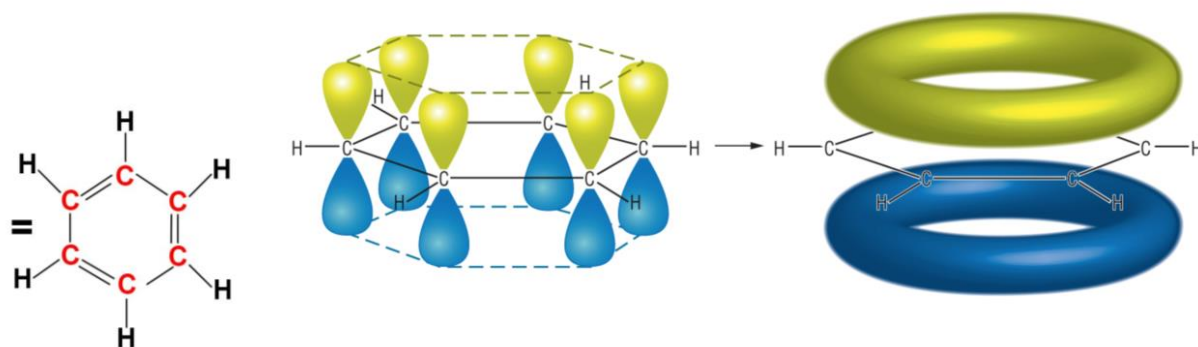
2. Lowest unoccupied molecular orbital (LUMO)

Π^3 orbital is LUMO because of low level energy unoccupied or free orbitals which useful to accept electrons. If it is act as an electrophile, the electrons are accepted into this orbital.

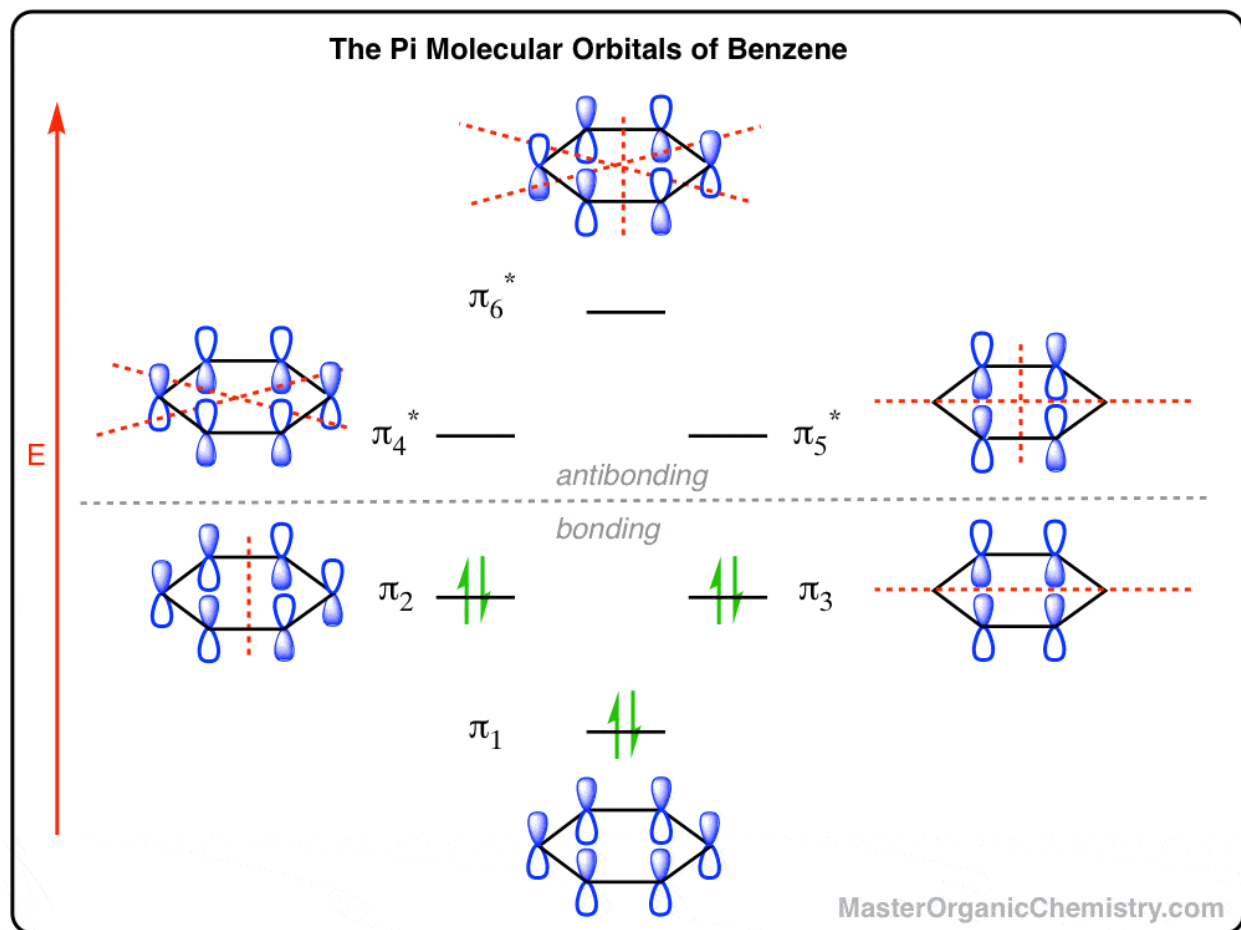


Π -Molecular orbitals of Benzene

Benzene is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached. There are six p -orbitals that form stabilizing electron clouds below and above the ring.



Benzene is sp^2 hybridized and has six molecular orbitals, three are bonding and three are antibonding orbitals (π_1 , π_2 , π_3 , π_4^* , π_5^* , and π_6^*). π_1 orbital has lower energy than other and the two orbitals, i.e., π_2 , π_3 orbitals have same energy and degenerate state as well as the π_4^* , π_5^* orbitals are having the same energy. π_6^* is having higher energy. The six electrons filled in π_1 , π_2 , and π_3 orbitals. π_1 orbital has zero node, π_2 , π_3 orbitals have one node, π_4^* , π_5^* orbitals have two nodes and π_6^* orbital has three nodes.



Molecular orbital theory (MOT)

Molecular orbital theory is proposed by Hund and Mullikan in the year 1932 for describing electronic structure of molecules using quantum mechanics.

Postulates:

1. When the atomic orbitals overlap, they lose their identity and forms a new orbital called molecular orbital.
2. The formation of molecular orbital is because of linear combination of atomic orbitals known as LACO method.
3. Only those orbitals which have similar energies and proper orientation can only combine to form molecular orbitals.
4. The number of molecular orbitals formed is equal to the number atomic orbitals combined.
5. When two atomic orbitals combined to form two molecular orbitals, one is called bonding orbital and another one is called antibonding orbitals.
6. The bonding molecular orbitals are formed by addition of wave functions of atomic orbitals involved whereas the antibonding molecular orbitals are formed by subtraction of wave functions of atomic orbitals involved.
7. The bonding molecular orbitals have lower energy than the atomic orbitals involved whereas anti-bonding orbitals have higher energy than the atomic orbitals involved.
8. The bonding molecular orbitals are represented by σ , π etc. whereas the corresponding anti-bonding molecular orbitals are represented as σ^* , π^* etc.
9. The filling of electrons in molecular orbitals takes place according with three rules, i.e., Aufbau principle, Pauli's exclusion principle and Hund's rule.
10. The number of covalent bonds between two atoms is called bond order and it is called using the given formula.

$$\text{Bond order (B.O.)} = \frac{1}{2} [N_b - N_a]$$

N_b = No. of electrons in bonding molecular orbitals

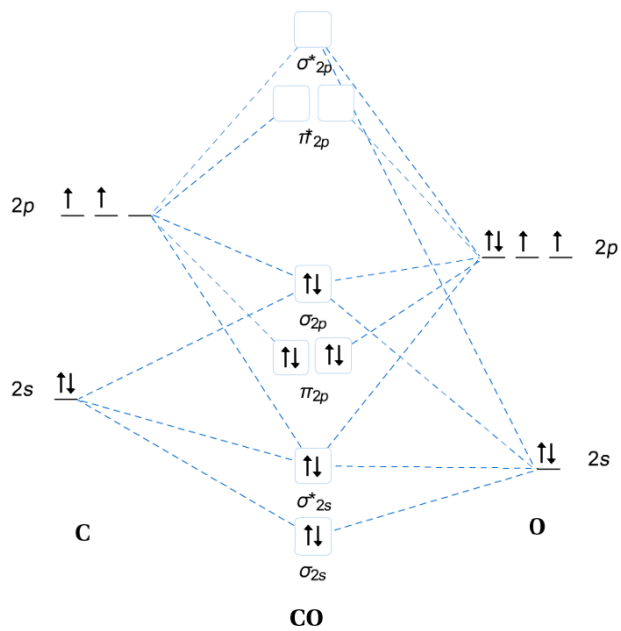
N_a = No. of electrons in anti-bonding molecular orbitals

11. If the molecule contains unpaired electrons, it is paramagnetic, otherwise it is diamagnetic.

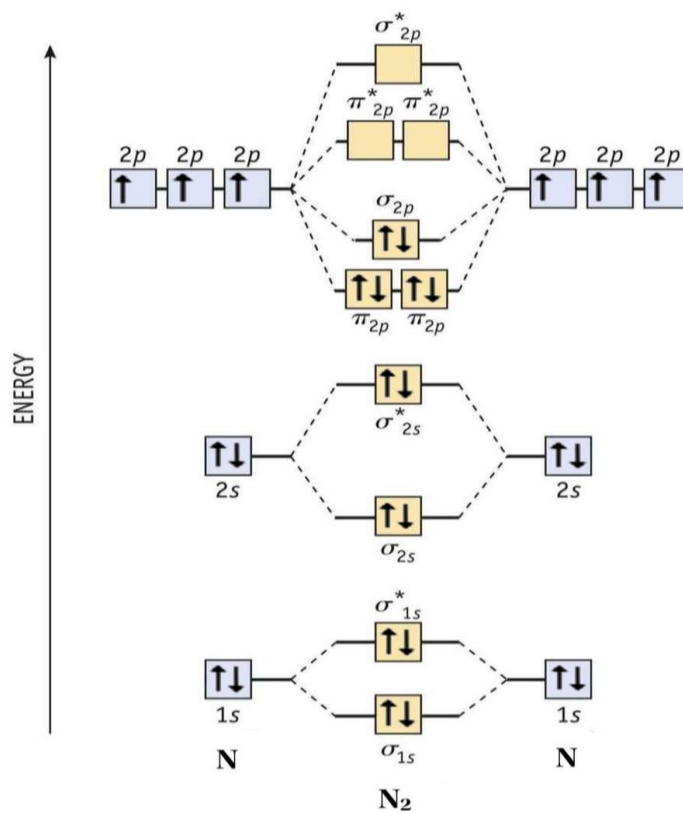
Difference between bonding and antibonding orbitals:

S. No.	Bonding molecular orbitals	Antibonding molecular orbitals
1	The molecular orbital formed by the constructive overlapping of atomic orbitals is called the bonding molecular orbital.	The molecular orbital formed by the destructive overlapping of atomic orbitals is called an antibonding molecular orbital.
2	It has the lower energy and greater stability than the combining atomic orbitals.	It has higher energy and lower stability than the combining atomic orbitals.
3	It has no nodal plane	It has a nodal plane
4	The linear combination of same sign on their lobes takes place	The linear combination of atomic orbitals with opposite signs on their lobes takes place
5	The energy difference between bonding molecular orbitals and the combining atomic orbitals is known as stabilization energy.	The energy difference between the antibonding molecular orbital and the combining atomic orbitals is known as destabilization energy.
6	They are represented as σ , π , δ etc.	They are represented as σ^* , π^* , δ^* etc.

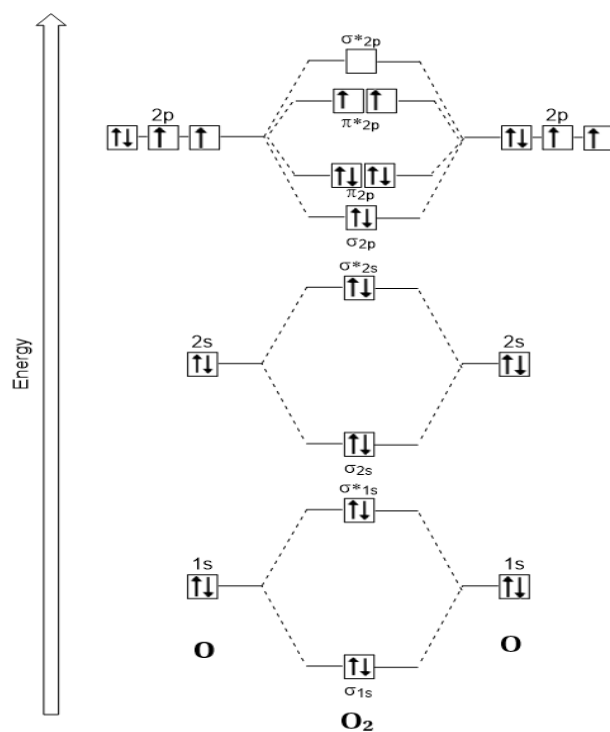
Molecular orbital diagrams of CO



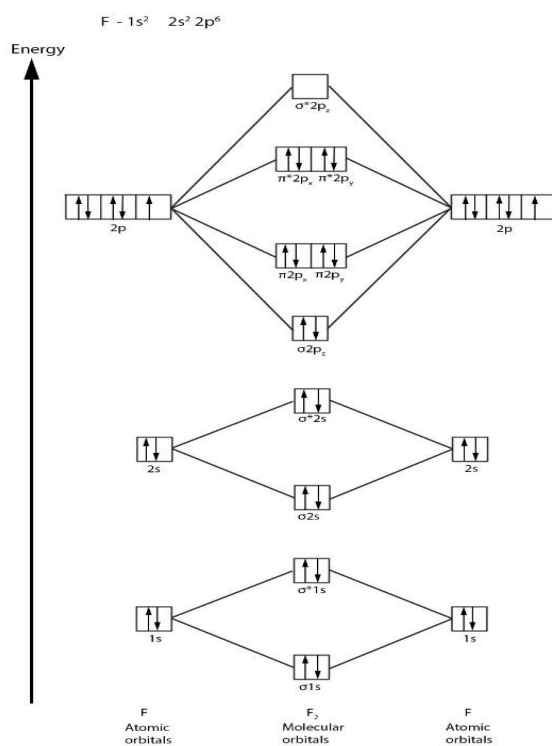
Molecular orbital diagrams of N₂



Molecular orbital diagrams of O₂



Molecular orbital diagrams of F₂



Calculation of Bond Order

The number of covalent bonds between two atoms is called bond order and it is calculated using the given formula.

$$\text{Bond order (B. O.)} = \frac{1}{2} [N_b - N_a]$$

N_b = No. of electrons in bonding molecular orbitals

N_a = No. of electrons in anti-bonding molecular orbitals

If the molecule contains unpaired electrons, it is paramagnetic, otherwise it is diamagnetic.

Ex: 1. Calculate the bond order of O_2 , O_2^- , O_2^{2-} and O_2^+ .

a) The O_2 molecule has the energy order as follows

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1 = \pi^* 2p_z^1 < \sigma^* 2p_x$$

The O_2 molecule has 10 e^- in their bond molecular orbitals and 6 e^- in antibonding molecular orbitals. So, Bond order of the molecule is

$$\text{Bond order (B. O.)} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [10 - 6]$$

$$= \frac{1}{2} [4]$$

$$= 2$$

And, it consists of unpaired electrons in $\pi^* 2p_y^1$ and $\pi^* 2p_z^1$ orbitals. So, it is paramagnetic in nature.

b) The O_2^- molecule has the energy order as follows

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^2 = \pi^* 2p_z^1 < \sigma^* 2p_x$$

The O_2 molecule has 10 e^- in their bond molecular orbitals and 7 e^- in antibonding molecular orbitals. So, Bond order of the molecule is

$$\text{Bond order (B. O.)} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [10 - 7]$$

$$= \frac{1}{2}[3]$$

$$= 1.5$$

And, it consists of unpaired electrons in $\pi^*2p_z^1$ orbitals. So, it is paramagnetic in nature.

c) The O_2^{2-} molecule has the energy order as follows

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^2 = \pi^* 2p_z^2 < \sigma^* 2p_x$$

The O_2 molecule has 10 e^- in their bond molecular orbitals and 8 e^- in antibonding molecular orbitals. So, Bond order of the molecule is

$$\text{Bond order (B.O.)} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[10 - 8]$$

$$= \frac{1}{2}[2]$$

$$= 1$$

And, it does not consist of unpaired electrons in their molecular orbitals. So, it is Diamagnetic in nature.

d) The O_2^+ molecule has the energy order as follows

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1 = \pi^* 2p_z^1 < \sigma^* 2p_x$$

The O_2 molecule has 10 e^- in their bond molecular orbitals and 5 e^- in antibonding molecular orbitals. So, Bond order of the molecule is

$$\text{Bond order (B.O.)} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[10 - 5]$$

$$= \frac{1}{2}[5]$$

$$= 2.5$$

And, it consists of unpaired electrons in $\pi^*2p_y^1$ orbitals. So, it is paramagnetic in nature.

UNIT – II

MODERN ENGINEERING MATERIALS

Based on ability of materials to conduct electricity, the materials are classified into three categories. They are insulators, conductors and semiconductors.

Insulators:

The materials which do not allow to pass the electric current through them easily is known as insulators. In this materials, electric current does not flow easily. These materials are independent of temperature. Ex: Glass, plastic, wood etc.,

Conductors:

The materials which allow to pass the electric current through them easily is known as conductors. In these materials, the conductivity decreases as temperature increases.

Ex: Copper, Aluminium etc.

Semiconductors:

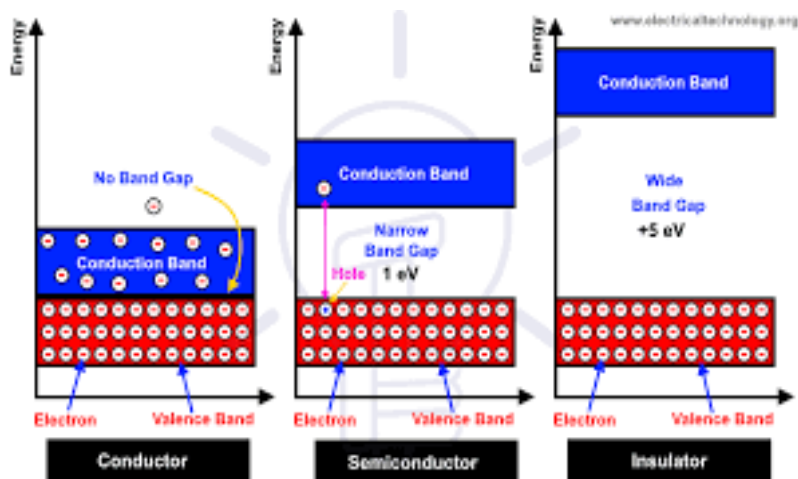
The materials which have electric conductivity more than the insulator but less than the conductor is known as semiconductors. The conductivity increases with the increase in temperature.

Ex: Si, Ge etc.,

Band theory of conduction:

When the atoms brought nearer to each other in their solid state, the energy levels split into two bands, valence band and conduction band. The energy band containing valence electrons is known as valence band. The energy band of unoccupied orbitals is known as the conduction band. The energy gap between the valence band and conduction band is known as the band gap energy. It can be denoted by (E_g). The material can conduct electricity when electrons are promoted from the valence band to the conduction band.

Band diagrams for conductors, semiconductors, insulators:



In conductors, the band gap energy is essentially zero and there is overlapping of conduction band and valence band, so electrons are promoted to conduction band quite easily. Hence, conductors can conduct electricity easily.

In semiconductors, there is narrow band gap between the valence band and conduction band. So, they can conduct electricity less than the conductors and the conductivity increases with increase in temperature because of more no of electrons can promote to conduction band.

In insulator, these is wide band gap energy is present. So, because of lack of electrons in conduction band, the insulators cannot conduct electricity.

Semiconductors:

The materials which conduct electricity more than the insulator such as glass, ceramics but less than the conductor such as copper is known as semiconducting materials. The conductivity of semiconducting materials is in between the insulators and conductors. The conductivity of semiconductors increases with the increase in temperature.

Ex: Si, Ge etc.

Principle of semiconductors:

The chemical bond in semiconductors is primarily covalent, which is quite different from metallic bond.

When the atoms are brought near to each in the solid, the splitting of the energy levels produces two bands and they do not overlap.

The conduction band lies higher in energy and is not occupied with electrons at 0 K and the valence band lies lower in energy and is filled electrons at 0 K

The energy splitting between the top of the valence band and the bottom of the conduction band is called the energy gap (E_g). The energy separating the valence and conduction bands is the intrinsic energy gap.

$$E_g = (E_c - E_v)$$

At room temperature, some of the electrons are promoted to conduction band, so semiconductors can conduct little electricity.

Classification of Semiconductors:

Semiconductors are divided into two types, intrinsic semiconductors and extrinsic semiconductors. The extrinsic semiconductors are divided into two groups, P-Type semiconductors and N-Type semiconductors.

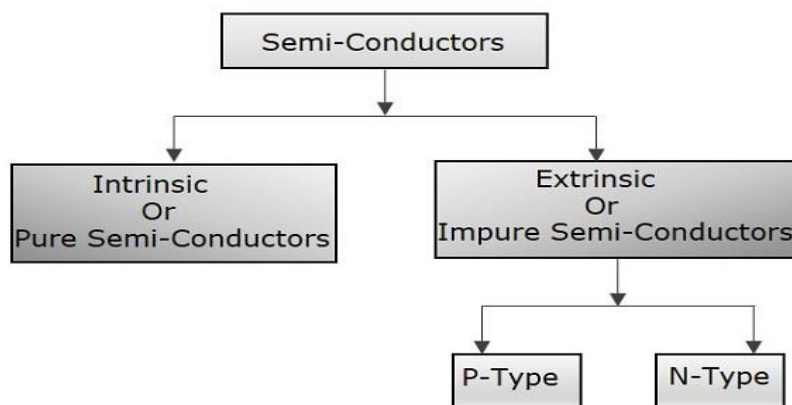
Intrinsic semiconductors:

The pure form of semiconductor is known as intrinsic semiconductor. Only one type element present and these are substances without the presence of any impurity or doping.

They have low conductivity when compared to extrinsic semiconductors. Si, Ge are the examples.

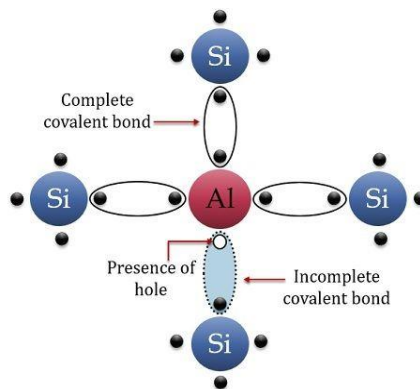
Extrinsic semiconductors:

Impure form of semiconductor is known as extrinsic semiconductor. This semiconductor consists of more than one element. The conductivity is high when compare to intrinsic semiconductors. The impurity that is added is known as dopant. Based on the impurity added, extrinsic semiconductors are divided into two types, P-type semiconductor and N-type semiconductor.



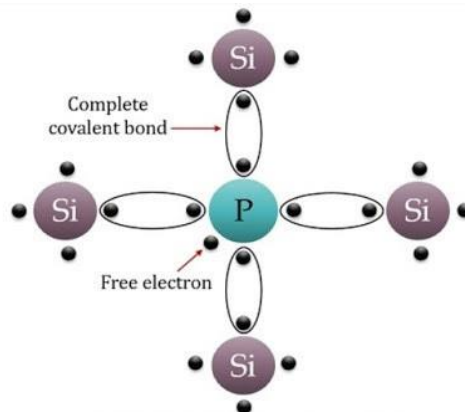
P-type semiconductor:

These are obtained by adding extremely small amount of trivalent impurity like boron, aluminium, etc. (IIIA group elements) to the pure semiconductor (Si, Ge) crystal lattice. The trivalent impurity has three outer electrons which are insufficient to make four bonds with silicon. One electron on silicon is left over and found nonbonding electron. This extra electron can move freely through the crystal lattice to increase the conductivity of Silicon. The lack of an electron between the boron and silicon atoms creates a small positive charge in that area and is often called as positive hole, hence the name of P-type semiconductor. The diagrammatic representation is shown in figure.



N-type semiconductor:

These are obtained by adding small amount of pentavalent impurity like phosphorus, arsenic etc. (VA group elements), to the pure semiconductor (Si, Ge) crystal lattice. The pentavalent impurity has five outer electrons so there is one left over electron after the formation of four bonds with silicon. This extra electron can move freely through the crystal lattice to increase the conductivity of Silicon. The extra electron between the P and Si creates a small negative charge in that area hence the name N-type semiconductor. The diagrammatic representation is shown in figure.



Applications of semiconductors:

1. Semiconductors are the foundation for modern electronics which includes radio, computers and telephones.
2. Semiconductor-based electronic components employed in various applications including transistors, solar cells, LEDs, and digital and analog integrated circuits.
3. The resistivity of semiconductors changes with temperature. On the basis of this, semiconductors enable to be used as thermometers.
4. Semiconductors are used in making of Hall Probes. These are measure magnetic field strengths with a small piece of semiconductors with known properties.

5. IR Sensors / Optoelectronic devices are made using semiconductors.
6. Semiconductors are useful to prepare rectifiers which having p-n junction diode.

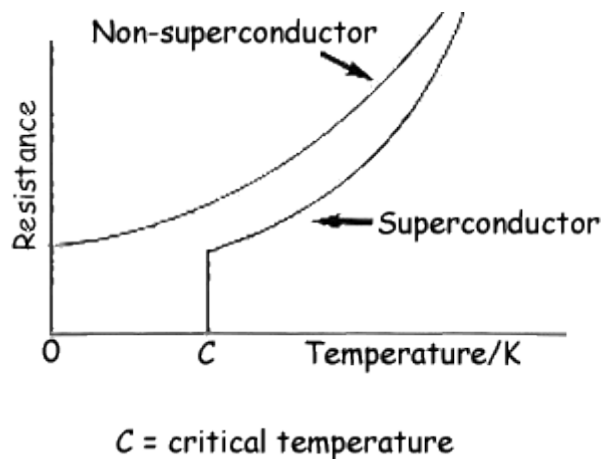
Superconductors:

The material which can conducts electricity or transport electrons from one atom to another atom with zero (or) no resistance is called the superconducting materials.

(OR)

The materials which can conducts electricity with zero resistivity or infinite conductivity is called the superconducting materials.

The temperature at which a material electrical resistivity drops to absolute zero is called the critical temperature. It is denoted by T_c . At the crucial temperature, the materials behave as superconductors. superconductor can conduct electricity with no resistance, which means no heat, sound, or other forms of energy would be discharged from the material when it reaches the “critical temperature” (T_c). Superconductivity is not exhibited by any of the magnetic material such as Chromium, Manganese, Iron, Cobalt and Nickel.



Principle:

Superconductivity can be explained by examining various formulas.

First law of resistance in current carrying superconductors can be illustrated by Ohm's law.

$$R = \frac{V}{I}$$

Here, R = Resistance

V = Voltage

I = Current

$$I = \frac{V}{R}$$

If resistance is zero,

$$I = \frac{V}{0}$$

$$I = \infty$$

Since, superconducting material, carrying current with no applied voltage $R = 0$, Superconductivity also does not involve power loss. Since power is defined as

$$P = I^2 R$$

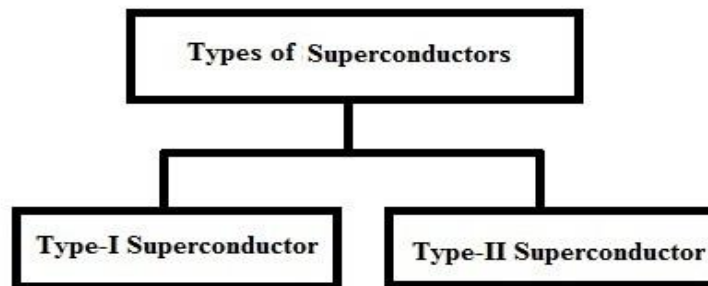
$R = 0$ in a superconducting material power loss is zero.

$$P = 0$$

Classification of Superconductors:

Superconductors are classified into two types. They are

- (i) Type – I Superconductors
- (ii) Type – II Superconductors



Type – I Superconductors:

Type – I Superconductors also called as soft superconductors. They are low temperature superconductors. A type I superconductor consists of fundamental conductive elements that are used in everything from electrical wiring to computer microchips. Presently, type I superconductors have critical temperatures between 0.000325 °K and 7.8 °K. Type I superconductors cannot be penetrated by a magnetic field known as it exhibits Meissner effect.

Some of the metals and its critical temperature value for type – I superconductors can be given below:

Material	Critical temperature (K)
Aluminium	1.2 K
Cadmium	0.52 K
Lead	7.2 K
Mercury	4.15 K
Tin	3.72 K

Type – II Superconductors:

Type – II Superconductors also called as hard superconductors. They are high temperature superconductors. Type II superconductors comprise metallic compounds and alloys. Type II superconductors can be penetrated by a magnetic field, that means they do not exhibit Meissner effect. They reach the superconductive state much higher temperature than type – I superconductors.

Some of the metals and its critical temperature value for type – II superconductors can be given below:

Material	Critical temperature (K)
NbTi	10 K
Nb ₃ Al	18 K
Nb ₃ Sn	18.1 K
Nb ₃ Ge	23.2 K
MgB ₂	39 K

Applications:

1. Superconductors widely used in construction of electromagnetic materials which have variety of applications ranging from electric power transmission to high-speed computing.
2. High temperature superconductors have applications in metrology, electromagnetic sensing, analog and digital circuits.
3. Superconducting materials are useful in Magnetic Resonance image (MRI) machines.
4. They are useful in particle accelerators.
5. Superconductors are used in Generators.
6. Superconductors are used for achieving magnetic levitation.
7. They have wide applications in Power transmission, Electric motors, Military, etc.

Supercapacitors:

Supercapacitors are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolytes.

The supercapacitor is also known as an ultracapacitor. This capacitor is called an ultracapacitor since it has a higher capacitance value than other regular capacitors. These components consume less power and are absolutely safe and easy to operate.

Principle:

The basic principle of supercapacitor energy storage is to store electrical energy through the electric double-layer capacitance formed by the charge separation on the interface between the electrolyte and the bath solution as well as electron charge transfer between electrode and electrolyte that can be done by a reduction-oxidation reaction commonly known as a redox reaction.

Classification:

Supercapacitors are classified into three types:

1. Electrostatic double-layer capacitors
2. Pseudo-capacitors
3. Hybrid capacitors

1. Electrostatic Double Layer Capacitors

These types of capacitors include two electrodes, a separator, and an electrolyte. The electrolyte is the mixture that constitutes positive and negative ions. The two electrodes are separated by a separator. The electrodes are generally made with carbon or carbon derivatives. The separation of charge in electrostatic double-layer capacitors is less than in a conventional capacitors that ranges from 0.3–0.8 nm.

2. Pseudo Capacitors

Pseudo capacitors are also known as electrochemical supercapacitors. These capacitors make use of metal oxide or conducting polymer electrodes. These types of components store electrical energy by electron charge transfer between electrode and electrolyte. This can be done by a reduction-oxidation reaction commonly known as a redox reaction.

3. Hybrid capacitors

The hybrid capacitors are mixed capacitors of double-layer capacitors and pseudo-capacitors. In these components, electrodes with different characteristics are used. One electrode with the capacity to display electrostatic capacitance, and the other electrode with electrochemical capacitance. The lithium-ion capacitor is example for hybrid capacitors.

Applications:

Supercapacitors are used in the following:

1. Supercapacitors are used in electric cars.
2. Supercapacitors are used in Wind turbines.
3. Supercapacitors are used in Photographic flash.
4. Supercapacitors are used in Flywheel in machines.
5. Supercapacitors are useful in MP3 players.
6. Supercapacitors are used in Regenerative braking in the automotive industry.
7. Supercapacitors are useful to prepare Static memories (SRAM).
8. Supercapacitors have applications in Industrial electrical motors.

Nanomaterials:

The particles whose external dimensions or internal structure dimension or surface structure dimension lies in the range of 1nm to 10 nm are considered as Nanomaterials.

The term nano stands for 1 billionth of a meter in a physical scale length. Nano chemistry is defined as the study of synthesis and properties of materials in nanoscale range 1-10 nm including large organic molecules, inorganic cluster compounds and metallic or semiconducting materials.

The nanomaterials have the distinct properties when compared to their bulky counterparts. The distinct properties of nanomaterials are due to increase in relative surface area and quantum effect.

Classification:

Nanomaterials are classified into 3 types based on atoms/molecules array:

One dimensional nanomaterials

Materials with one dimension in the nano scale. For example, thin films, surface coatings, etc.

Two dimensional nanomaterials

Materials that have two dimensions in nano scale. For example, nanowires, nano-tubes, biopolymers, inorganic nano tubes, etc.

Three dimensional nanomaterials

Materials in three dimensions in nano scale. For example, tiny particles of semiconductors materials such as nanometre sized grains, fullerenes, nano particles, dendrimers.

Properties:

The properties of nanomaterials depend on size, crystal structure and surface characteristics.

1. Size:

Nano materials have a large surface area. For example, nano crystals of 10 nm size have approximately 15% of its atoms on the surface and smaller nano crystal of 1nm size will be about 30% of its atoms on the surface. Hence, size of crystal is important for available active surface area.

2. Electrical properties:

Nanomaterials shows electrical properties vary between semiconducting to metallic depending upon the diameter and chirality of the molecules. For example, carbon nano tubes reveal electrical properties and act as semiconducting and metallic nature on the basis of chirality and diameter of a tube.

3. Mechanical properties:

Nanomaterial exhibits unusual mechanical properties. For example, the tensile strength of carbon nano tube is about 604 Pa. They are among the strongest and stiffest.

4. Optical properties:

Nanomaterials that are provided large surface area exhibit better optical properties. For example, silicon nanowires show photoluminescence characteristics. Indium phosphide nanowire shows photoluminescence used in the construction of photodetectors.

5. Semiconductors:

Most of the nanomaterials exhibit semiconductivity properties. For example, carbon nanotubes, nanowires, some metal oxides (MoS_2 and WS_2) Shows semiconductor properties.

6. Superconductors:

Some nanomaterials which show superconductivity properties. For example, nanotubes of NbS_2 and NbSe_2 are metallic in nature with NbSe_2 becomes a superconductor at low temperature.

7. Catalytic activity

Nanomaterials are very good catalyst for variety of transformations. They are useful in heterogenous catalyst. For example, Rhodium nanomaterials have been shown to be effective catalyst in hydrogenation of oils. Palladium nanomaterials useful in organic transformations.

Applications:

Nanomaterials show potential applications because of their unusual and unique properties. Some of the other applications of nanomaterials and their uses

1. The nanomaterials are used in Sunscreens, Cosmetics.
2. They are useful for Coating on surfaces, Hard cutting tools.
3. They are useful for preparation of Fuel cells, Batteries.
4. They are important catalysts in hydrogenation and catalysis.
5. They have potential applications in magneto optical storage and drug transport.
6. They are used in fluorescent displays.
7. They are useful to prepare field effect transmitter.
8. They have wide applications in Displays, Lubricants, Machinable ceramics, Military bottle suits etc.

Fullerenes:

A Fullerene is an allotrope of carbon whose molecules consists of carbon atoms connected by single and double bonds so as to form closed or partially closed mesh, with fused rings at five to seven atoms. The molecules may be a hollow sphere, ellipsoid, tube or many other shapes and sizes.

Classification:

The fullerenes can be classified into the following types.

i) Buckminster fullerene: First fullerene with 60 carbon atoms arranged as 12 pentagons and 20 hexagons in the form of a sphere is called Buckminster fullerene C_{60} . It is a smallest fullerene molecular containing pentagonal and hexagonal rings in which no two pentagons share an edge. The Vander wall diameter is about 1.1 nanometres.

ii) Nanotubes: These are the hollow tubes of very small dimensions having single or multiple walls. It is used mainly electronic industries.

iii) Mega tubes: These are larger in diameter than nanotubes. These are prepared with walls at different thickness. It is used for the transport of a variety of molecules

iv) Nano anions: These are spherical particles based on multiple carbon layers surrounding a bucky ball core. It is proposed to use in lubricants.

Properties:

1. Solubility:

Fullerenes are sparingly soluble in many solvents, but soluble in toluene.

2. Colour:

Fullerene is fine black powder. Solutions of pure Buckminster fullerene have deep purple colour, solutions of C_{70} have a reddish-brown colour.

3. Conductivity:

Fullerene are electrical insulators as there is no movement of electrons available from one molecule to another.

4. Hydrogenation:

C_{60} exhibits a small degree of aromatic character, it undergoes addition reaction with hydrogen.

5. Halogenation:

C_{60} undergoes halogenation with F, Cl and Br under variety of conditions.

Applications:

1. Fullerenes are used as a powerful antioxidant, so it used in health and personal care areas.
2. Used as a tip in scanning probe microscopy.
3. Very good medium to make hydrogen fuel.
4. Used in organic photovoltaics.
5. Act as a catalyst in some organic reaction, water purification and fuel cell membrane materials.

Carbon Nanotubes:

Carbon nanotubes also called Bucky tube which is allotrope of carbon with a cylindrical nano structure. It was discovered by S. Limija in 1991. When graphite sheets are rolled into a cylinder, their edges join to each other to form carbon nanotubes. Each carbon atom in the carbon nanotubes is linked by covalent bonds. But the number of nanotubes align into ropes and are held together by weak Vander wall forces.

Types of Carbon nanotubes:

Depending upon the way in which graphite sheets are rolled, two types of carbon nano tubes are formed.

1. Single walled nanotubes
2. Multi walled nanotubes

1. Single walled nanotubes: Single walled nanotubes consist of one tube of graphite. It is one atom thick having a diameter of 2 nm and a length of 100 μm . It is an excellent conductor. Three kinds of nanotube are resulted based on the orientation of the hexagon lattice.

Arm – chair structures: The lines of hexagons are parallel to the axis of the nanotube.

Zig – zag structures: The lines of carbon bonds are down the centre.

Chiral nanotubes: It exhibit twist or spiral around the nanotube.

2. Multi walled nanotubes:

Multi walled nanotubes consist of multiple layers of graphite rolled in on themselves to form a tube shape. It exhibits both metallic and semiconducting properties.

Properties:

1. Strength

Carbon nanotubes are the strongest and stiffest materials in terms of tensile strength and elastic module. A multi walled carbon nanotubes was tested and found tensile strength 63 GPa.

2. Hardness

The diamond is considered as hardest material. The compressed SWNT has 462-546 GPa surpassing the value of 420 GPa for diamond.

3. Thermal conductivity

Carbon nanotubes exhibit good thermal conductivity exhibiting a property known as ballistic conduction. The SWNT has a room-temperature thermal conductivity along its axis of about $3500 \text{ Wm}^{-1}\text{K}^{-1}$ compare this to copper, a metal well known for its good thermal conductivity, which transmits $385 \text{ Wm}^{-1}\text{K}^{-1}$.

4. Temperature stability

Carbon nanotubes are estimated to be up to 2800°C in vacuum and about 750°C in air of temperature stability.

5. Optical properties

Carbon nanotubes have useful absorption, photoluminescence (fluorescence) properties. Carbon nanotube optical properties have been explored for use in applications such as for light-emitting diodes and photo-detectors.

Applications:

1. It is used in battery technology and in industries as catalyst.
2. CNTs is used effectively for drug delivery.
3. Used for water softening process.
4. Act as efficient catalyst for some chemical reactions.
5. Used as light weigh shielding materials.

Graphene materials:

Graphene is a single layer of carbon atoms arranged in a hexagonal lattice structure, forming a two-dimensional (2D) material with exceptional mechanical, electrical, and thermal properties. It is widely studied for its potential use in various fields such as electronics, energy storage, and biomedicine.

Classification:

1. Graphene Oxide

Graphene oxide (GO) is a single atom carbon layer where both surfaces of the layer are modified by oxygen containing functional groups. In multi-layer graphene oxide, the carbon layers are separated by functional groups bonded to each layer of carbon atoms. Although graphene oxide is a 2D material, its properties are very different from that of graphene. It does not absorb visible light, has very low electric conductance compared to that of graphene, and demonstrates significantly higher chemical activity.

2. Graphene quantum dots

A graphene quantum dot is a graphene fragment with size less than 100 nm. The properties of GQDs are different from 'bulk' graphene due to the quantum confinement effects which only becomes apparent when size is smaller than 100 nm.

3. Reduced graphene oxide

Reduced graphene oxide is obtained from chemically or thermally treated graphene oxide to eliminate most of the oxygen groups and sp^3 carbon to generate a more graphene like material. They are 2D material with a large specific surface area, high chemical stability, and carrier mobility. Reduced graphene oxide has commonly been used to prepare composites with various materials, such as metal and metal oxides.

Properties:

1. Electronic properties

Graphene is one of the best electrical conductors. The unique atomic arrangement of the carbon atoms in graphene allows its electrons to easily travel at extremely high velocity without the significant chance of scattering due to overlapped pi-electrons, allowing for an easy movement of electrons. A single layer of graphene shows 10,000 times higher electrical conductivity than few layers graphene.

2. Mechanical properties

Graphene is one of the strongest materials ever discovered with a tensile strength of 130 GPa. In addition to having strength, it is also very lightweight (0.77 mg/m^2). The mechanical properties of graphene, its stiffness, strength and toughness, are one of the reasons that make graphene stand out both as an individual material and as a reinforcing agent in graphene composites.

3. Thermal Properties

Graphene has extremely high intrinsic thermal conductivity. The repeating structure of graphene makes it an ideal material to conduct heat in plane. Graphene has a thermal conductivity of 5300 W/mK , which is ten times the thermal conductivity of copper.

4. Flexibility/Elasticity

The repeating sp^2 hybridized backbone of graphene molecules allow for flexibility, as there is rotation around some of the bonds, whilst still providing enough rigidity and stability that the molecule can withstand changes in conformation and support other ions. In terms of its elasticity, graphene has found to have a spring constant between $1\text{-}5 \text{ Nm}^{-1}$, with a Young's modulus of 0.5 TPa .

5. Optical properties

Graphene is highly transparent to visible light, with a transparency of 97.7 %. This is taken advantage of when determining the number of graphene layers. The optical properties of graphene do vary by the layer number. For example, a single layer of graphene only absorbs 2.3% of light, so 97.7% of light passes through a single layer, with around 0.1% reflected from its initial trajectory.

Applications:

1. Energy storage and solar cells

Graphene-based nanomaterials have many promising applications in energy-related areas such as rechargeable batteries, superior supercapacitors for energy storage, solar cell.

2. Graphene sensor applications

Functionalized graphene holds exceptional promise for biological and chemical sensors.

3. Graphene membranes

The use of graphene membranes is ranging from water filtration, industrial gas separation such as CO_2 capture, separator membranes for redox flow batteries, or as filtration membrane in the food industry such as for filtering lactose from milk.

4. Biomedical uses

Graphene is used as a biosensor. Emerging uses are in stem cell therapies where graphene is used as biocompatible structures.

5. Electronics

Graphene has a unique combination of properties that is ideal for next-generation electronics, including mechanical flexibility, high electrical conductivity, and chemical stability.

6. Photodetectors

Graphene can be used for telecommunications applications for ultrafast photonics applications, optoelectronics.

7. Coatings

Graphene sheets to create a superhydrophobic coating material that shows stable super hydrophobicity under both static as well as dynamic (droplet impact) conditions, thereby forming extremely water repelling structures.

UNIT – III

ELECTROCHEMISTRY AND APPLICATIONS

Electrochemistry is a branch of chemistry which deals with the conversion of electrical energy into chemical energy as well as chemical energy into electrical energy. The setup that is used to achieve the transformations is known as electrochemical cell.

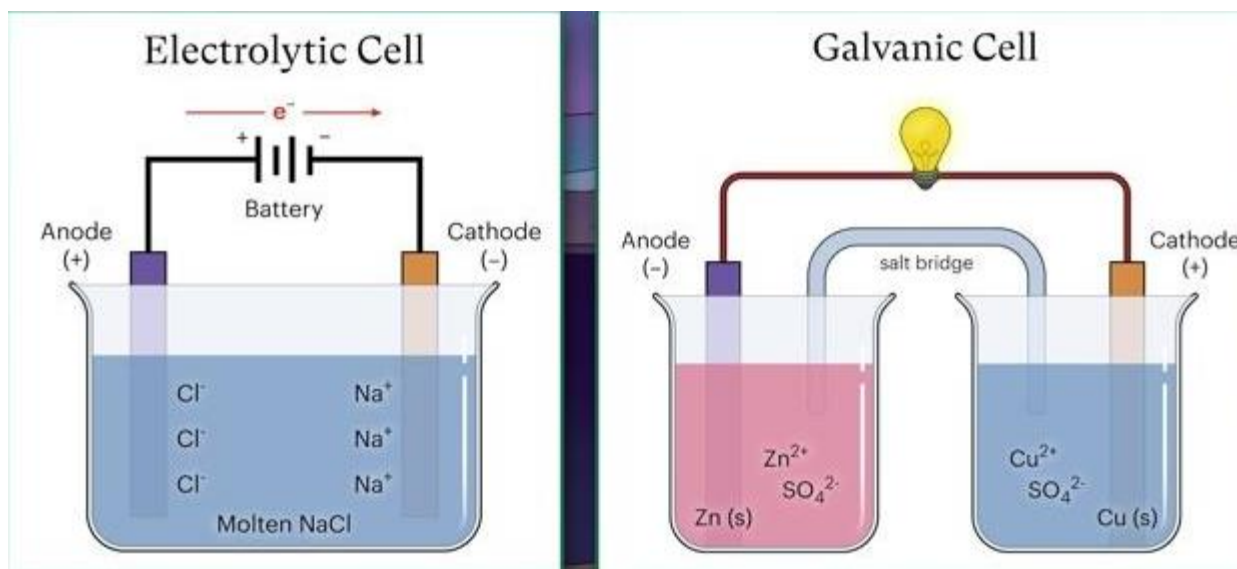
An electrochemical cell is an apparatus or device that convert chemical energy of spontaneous redox reactions into electrical energy or uses electrical energy supplied to it to facilitate chemical reactions within it.

Electrochemical cells broadly classified into two categories.

1. **Galvanic Cell or Voltaic Cell**
2. **Electrolytic Cell**

A Galvanic Cell or Voltaic Cell produces electric current from chemical change and energy released by spontaneous redox reaction. Electrons are transferred from one chemical species to another, so an electric current is produced.

An Electrolytic cell uses the electrical energy to facilitates the chemical reactions to occur, so it converts electrical energy into chemical energy.



Basics of Electrochemistry:

Electrochemical cell:

An electrochemical cell is an apparatus or device that convert chemical energy of spontaneous redox reactions into electrical energy or uses electrical energy supplied to it to facilitate chemical reactions within it.

Galvanic or Voltaic cell:

A Galvanic Cell or Voltaic Cell produces electric current from chemical change and energy released by spontaneous redox reaction. Electrons are transferred from one chemical species to another, so an electric current is produced.

Electrolytic cell:

An Electrolytic cell uses the electrical energy to facilitates the chemical reactions to occur, so it converts electrical energy into chemical energy.

Anode:

The electrode where oxidation takes place is known as anode. It is a negative electrode. The oxidation reaction occurs here and produces the electrons.

Cathode:

The electrode where reduction takes place is known as cathode. It is a positive electrode. The reduction reaction occurs here and consumes the electrons.

Oxidation:

The loss of electrons or increase in oxidation number or addition of oxygen or removal of hydrogen is known as Oxidation.

Reduction:

The gain of electrons or decrease in oxidation number or addition of hydrogen or removal of oxygen is known as Reduction.

Electrolyte or Electrolytic solution:

A substance that dissociates into ions in *solution* and conducts electrical current is known as electrolytic solution.

Electrode:

Electrode is a material or a metallic rod/bar/strip which conducts electrons.

Half Cell:

Half cell is a part of cell, containing electrode dipped into an electrolytic solution. The cell consists of two half cells, i.e., Anode half-cell where the oxidation occurs and Cathode half-cell where the reduction occurs.

Single electrode potential or electrode potential:

The potential generated due to an electrode lose or gain electrons when the electrode is in contact with the solution of its own metal ions is known as single electrode potential.

Standard electrode potential:

The electrode potential of electrode when it contacts with a solution of its own metal ions at standard conditions such as 1 M concentration and at 25 °C.

Cell potential:

The *cell potential*, E_{cell} , is the measure of the potential difference between two half cells in an electrochemical cell.

According to latest conventions, the electrode potential must be in their reduction potentials.

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}} \quad (\text{or})$$

$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

Introduction to Electrochemical Cell:

The devices in which electrical energy is produced from chemical reactions are called electrochemical cells or galvanic cells. In these cells, oxidation and reduction reactions occur in separate containers are called half cells and the redox reaction is spontaneous electrical energy is produced during such reactions.

1. The arrangement consists of two beakers, one of which contains 1.0M solution of zinc sulphate and the other 1.0M solution of copper sulphate.
2. A zinc rod is dipped into zinc sulphate sulphate while a copper rod is dipped into copper sulphate solution. These metallic rods are known as electrodes.
3. The metallic rods in the beaker are connected to the voltmeter. The solutions in the two beakers are connected by an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO₃, or NH₄NO₃ which does not undergo a chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatine.
4. The two openings of the U-tube are plugged, with some porous material such as glass wool or cotton. The U-tube which connects the two glass beakers is called a salt-bridge.

Functions of salt bridge: - Salt bridge is used to prevent or avoid the mixing of electrolytic solutions. Salt bridge allows only ions. Salt bridge is used to maintain electrical neutrality between the two electrolytic solutions.

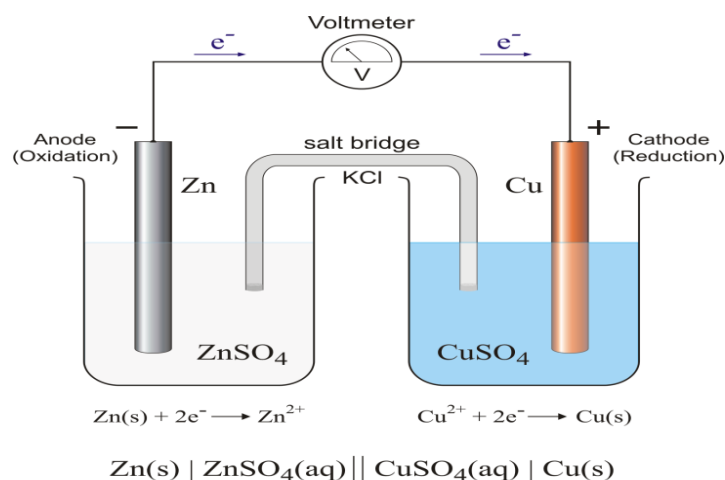


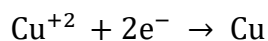
Fig. 3.1: Galvanic Cell or Voltaic Cell

Working:

1. At anodic half-cell, Zn gets oxidized and converts into Zn^{+2} ions. Zn rod gradually loses its weight. The concentration of Zn^{+2} in the ZnSO_4 solution increases.



2. At cathode, copper ions get reduced to copper. Copper gets deposited on the electrode. The concentration of Cu^{+2} in the CuSO_4 solution decreases.



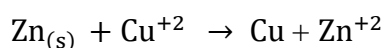
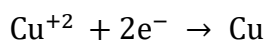
3. There is a flow of electrons in the external circuit from zinc rod to copper rod. Therefore, the current flows from copper to zinc. The flow of electric current is taken opposite to the flow of electrons. During the reaction, zinc is oxidized to Zn^{+2} ions which go into the solution.

Overall cell reaction:

At anode: Oxidation



At cathode: Reduction



Representation of Electrochemical cell:

An electrochemical cell or galvanic cell consists of two electrodes: anode and cathode. The electrolytic solution containing these electrodes is called half cells. When these two half cells are combined, a cell is formed.

- A galvanic cell is represented by writing the anode on the left-hand side and cathode on the right-hand side.
- The anode of the cell is represented by writing metal or solid phase first and then the electrolyte while the cathode is represented by writing the electrolyte first and then metal and solid phase.
- The metal and the electrolyte are separated either by a semicolon (;) or by a vertical line.

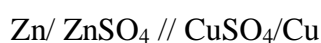


(Anode)

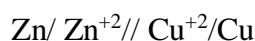


(Cathode)

- The salt bridge which separates the two-half cells is indicated by two vertical lines.



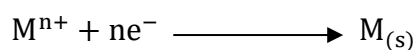
(or)



Nernst equation for Single Electrode Potential:

Nernst equation gives the relationship between the electrode potential and the concentration of the electrolyte solution.

Consider a general electrode reaction,



For a reversible reaction, the free energy change and its equilibrium constant are related by the Van't Hoff's reaction isotherm as

$$\Delta G = -RT\ln K + RT\ln Q$$

$$\Delta G = -RT\ln K + RT\ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= G^{\circ} + RT\ln \frac{[\text{Product}]}{[\text{Reactant}]} \text{ -----(1) [Since, } G^{\circ} = -RT\ln K \text{]}$$

$$\Delta G^{\circ} = \text{Standard free energy}$$

The electrical energy is produced at the expense of decrease in free energy, that is

$$\Delta G = -nFE \text{ and } \Delta G^{\circ} = -nFE^{\circ} \text{ -----(2)}$$

n = No. of e^{-} liberated at one electrode

F = Faraday's constant ($1F=96500$ Coulomb)

E = Electrode Potential

E° = Standard electrode potential

Substituting these values in equation (1), we get

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

By simplifying the equation, dividing the equation with nF , we get

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

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]} \text{ -----(3)}$$

At $T=298\text{ K}$, $F=96500$, $R=8.314\text{ JK}^{-1}$, the equation reduces to

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]} \text{ -----(4)}$$

Applications:

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metal can be predicted.
3. Useful in the calculation of standard EMF of the cell.

Numerical problems:

Conductivity:

Conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to conduct electricity. The SI unit of conductivity is siemens per meter (S/m).

The conductivity of a liquid solution depends on the three factors

1. No. of ions or concentration of ions
2. Charge on the ions
3. Mobility of ions

1. No. of ions or concentration of ions:

The reason for the conductivity of electrolytes is the ions present in them. The conductivity of electrolytes increases with an increase in the concentration or number of ions as there will be more charge carriers if the concentration of ions is more and hence the conductivity of electrolytes will be high.

2. Charge on the ions:

The charge on the ions also influences the conductance of the liquid solution.

3. Mobility ions

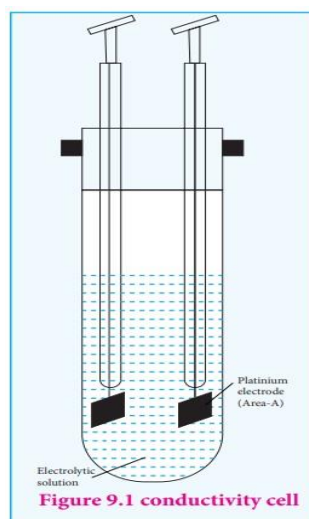
The mobility of ions is one of the important parameters to consider for conductance. The low mobility ions can contribute lower value to the conductance whereas high mobile ions can contribute the higher value to the conductance.

Conductivity cell:

It is an instrument to measure the ionic conductivity/resistivity of electrolytic solution. Conductivity cells, also called conductivity electrodes or probes, are constructed with metal electrodes placed at a fixed distance in either glass or plastic body and surrounded by an outer tube.

The conductivity cell is made of Pyrex or quartz and are fitted with two platinum electrodes that are coated with platinum black. These electrodes are welded to platinum wires fused into the bottom of two thin glass tubes containing some mercury for making contact with the circuit by means of copper wires. These glass tubes are usually fixed rigidly into an ebonite cover so that the distance between electrodes remain constant.

For any given conductivity cell, the distance between the two electrodes and the area of cross section are constant. The distance between the electrodes divided by their surface area is known as cell constant. Hence, the quantity (l/a) is constant which is called cell constant.



Conductometric titrations (Acid-base titrations):

The measurement of conductivity of the solution during the course of titration to find out the end point is known as conductometric titrations. The principle involved is that electrical conductance of a solution depends upon the number of ions and mobility of ions.

During a titration process, one ion is replaced with another and the difference in the ionic conductivities of these ions directly impacts the overall electrolytic conductivity of the

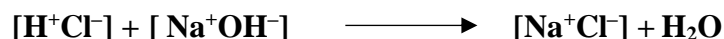
solution. In conductometric titrations, the titrant is added from the burette and conductivities are measured during the course of titration. The values of conductivities are then plotted against the volume of the titrant with the measured conductance. The graph two lines will be obtained which will intersect each other at a point known as end point or equivalence point.

Acid – Base conductometric titrations:

There are four types of acid base conductometric titrations can be carried out

1. Strong acid vs strong base

Consider the titrations of a strong acid with strong base by taking HCl as a strong acid and NaOH as a strong base. The acid is taken into the conductivity vessel and the alkali in the burette. The reaction is as follows.



At the beginning of the experiment before base is added, the conductivity of acid solution is high due to a greater number of high mobile hydrogen ions.

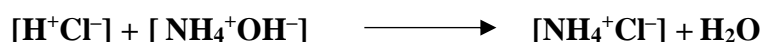
During the course of titration, as base is added, the fast-moving hydrogen ions are replaced with the slow-moving sodium ions, so the conductivity decreases gradually up to endpoint. At end point, all the high mobile H^+ ions are replaced with low mobile Na^+ ions, so, the conductivity reaches the minimum.

After the endpoint, any subsequent addition of NaOH will cause introduction of fast-moving hydroxide ions will result in increase of conductivity abruptly.

By plotting the conductance against the volume of NaOH added, the point where two straight lines intersect gives the end point and will give volume of alkali required for the neutralization.

2. Strong acid vs weak base

Consider the titrations of a strong acid with weak base by taking HCl as a strong acid and NH_4OH as a weak base. The reaction is as follows.



At the beginning, the conductivity is high due to the greater number of high mobile H^+ ions in solution.

During the course of titration, the conductivity decreases because of fast moving H^+ ions are replaced with slow moving NH_4^+ ions.

At the end point, the conductivity reaches the minimum because of all the fast-moving H^+ ions are replaced with slow moving NH_4^+ ions.

After the end point, addition of NH_4OH does not change the conductance because of it is a weak base which have low ionization.

3. Weak acid vs strong base

Consider the titrations of a weak acid with strong base by taking CH_3COOH as a weak acid and NaOH as a strong base. The reaction is as follows.



At the beginning, the conductivity is low due to less number of ions present in the solution because of it is a weak acid so it cannot completely dissociates.

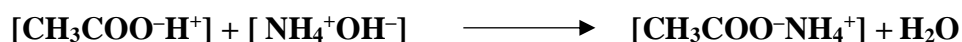
During the course of titration, the conductance decreases initially and increase with further addition of NaOH due to the formation of strong conjugate base.

Upto end point, the conductivity gradually increases.

After the end point, the conductivity increases abruptly or sharply because of the solution gets the fast moving OH^- ions.

4. Weak acid vs weak base

Consider the titrations of a weak acid with weak base by taking CH_3COOH as a weak acid and NH_4OH as a weak base. The reaction is as follows.



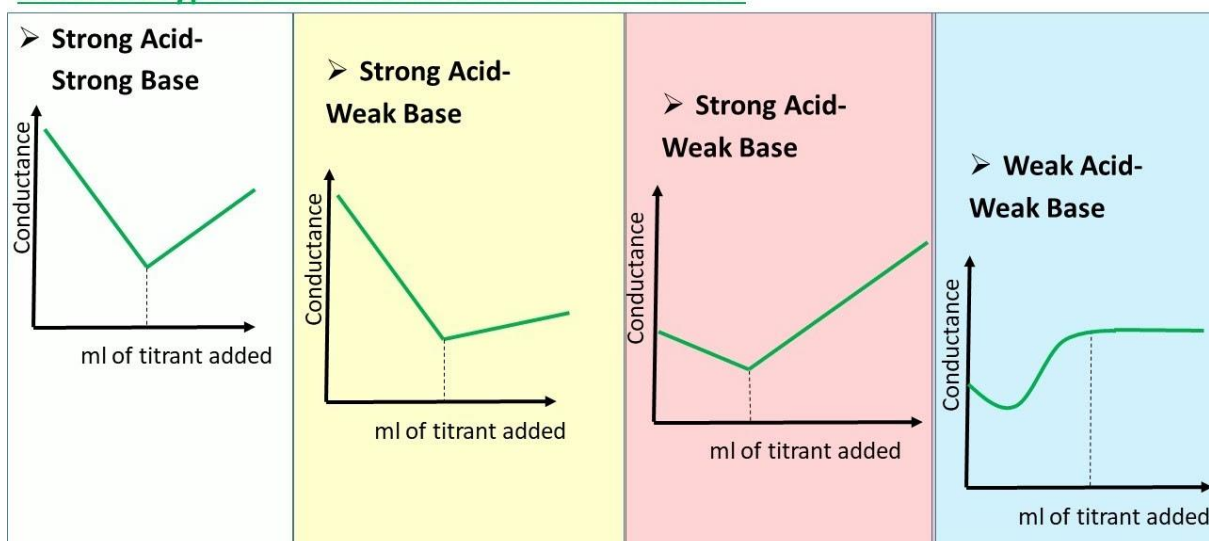
At the beginning, the conductivity is low due to a smaller number of ions present in the solution because of it is a weak acid so it cannot completely dissociate.

During the course of titration, the conductance decreases initially and increase with further addition of NH_4OH due to the formation of strong conjugate base.

Upto end point, the conductivity gradually increases.

After the end point, the conductivity does not change much because of the NH_4OH which is a weak base, so it cannot ionizes completely.

Different Types of Conductometric Titration Curve



Potentiometric titrations

The measurement of potential difference between two electrodes during the course of titration to determine end point is known as potentiometric titration.

Potentiometric titrations have certain advantages over conventional methods such as no indicator required and analysis of colour solutions etc.

The potentiometric titrations are three types like acid-base titrations, redox titrations and precipitation titrations.

Redox titrations

The experimental produce adopted in redox titrations is similar as acid base titrations with the only difference that a bright platinum working electrode is used instead of hydrogen working electrode. The emf of this electrode is measured by activity ratio of the substance being oxidized or reduced.

Consider the titration of ferrous ammonium sulphate against potassium dichromate. A known volume of ferrous salt solution is taken in a beaker and 10 ml of H_2SO_4 is added. Then, the bright platinum electrode and saturated calomel electrode are dipped into solution and connected with potentiometer.

The cell emf observed for each addition of $\text{K}_2\text{Cr}_2\text{O}_7$ solution from the burette is noted. The observed value of emf is then plotted against Volume of dichromate. The 'S' type will be obtained. The steepest portion of the curve indicates the endpoint.

Electrochemical Sensors

The electrochemical sensors are the devices that evaluate information about sample from measurement of some electrical parameters continuously.

Generally, a chemical sensor follows the changes of concentration of some chemical in a predictable and continues fashion. The electrochemical sensor can direct conversion of chemical information into an electrical signal. One of the important applications of electrochemical sensor is a well-known blood glucose test employed for diabetic patient.

Principle

The electrochemical sensors are working based on the basic principle of ohm's law i.e., the potential difference in a circuit is equal to the product of the current and the resistance.

$$V = I \cdot R$$

V= Voltage Difference

I= Current

R= Resistance

Classification of electrochemical sensor

The electrochemical sensors are divided into three types

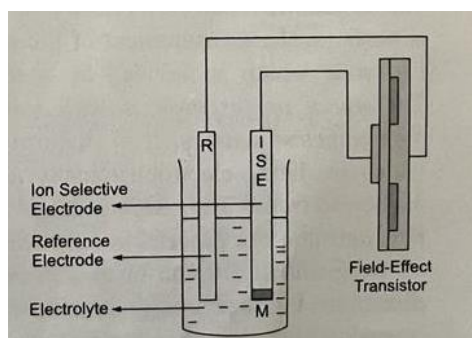
1. Potentiometric Sensors
2. Amperometric Sensors
3. Chemiresistor or Conductometric Sensors

1. Potentiometric Sensors:

If electrochemical sensor measures the potential difference, it is known as potentiometric sensor. The potential difference of two electrodes depends on the concentration of analyte solution. So, the potentiometric sensors give information of the electrical parameters continuously.

Construction and working principle:

The potentiometric sensor consists of two electrodes, reference and indicator electrode. Generally, ion selective electrode is taken as indicator electrode. When electrodes are placed in an analyte solution, the potential of ion selective electrode depends on the concentration of test species in analyte. So, the electrode can measure the concentration of the analyte and gives an electrical signal. Glucose meter is one of the best examples for potentiometric sensors.

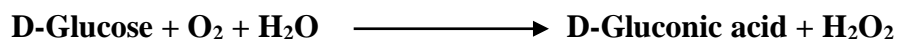


Glucose potentiometric sensor

Glucose is an electrically neutral molecule. Hence, the potentiometric sensor cannot measure the concentration and does not yield a signal. For the determination of glucose, one more step has to be made. That is, initially the neutral glucose molecule has to be converted into ions, which are then selectively detected.

At first, glucose is oxidized by enzymatic oxidation to gluconic acid and subsequent measurement of the liberated hydrogen ions to be done.

The electrochemical reactions proceed as follows

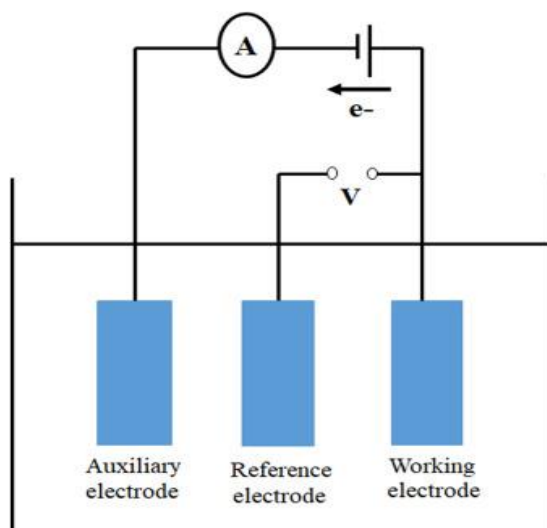


Amperometric sensors:

If an electrochemical sensor measures the current between working and counter electrode which is induced by a redox reaction at the working electrode, it is known as an amperometric sensor.

The signal in this sensor is due to the diffusion current and it is proportional to the concentration of the analyte species.

Construction:

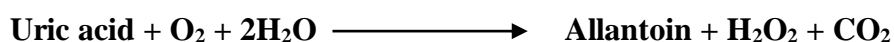


The amperometric sensor usually consists of three electrodes, reference and indicator electrode and counter electrode (auxiliary electrode). When electrodes placed in an analyte solution, the current produced at electrode depends on the concentration of test species in analyte. So, the electrode can measure the concentration of the analyte and gives as electrical signal. Estimation of Uric acid is the one of the best examples for amperometric sensors.

Estimation of uric acid

Uric acid is a major nitrogenous compound in urine, is the product of purine metabolism in the human body. It is related to many clinical disorders. There are two methods are there for measurement of uric acid, enzymatic and non-enzymatic.

The enzymatic procedures using uricase enzyme involves the conversion of uric acid into allantoin along with H_2O_2 and CO_2 . Then, the released H_2O_2 is ameprometrically determined.



Battery:

A battery is a power source device in which one or several galvanic cells or electrochemical cells are connected in a series.

Like galvanic cell, a battery also consists of electrodes, i.e., anode and cathode and an electrolyte. The electricity energy is produced by spontaneous redox reactions occur inside the battery.

Batteries can be classified as follows

1. Primary Battery
2. Secondary Battery

1. Primary Battery:

In those batteries, electrode chemical reactions are irreversible is known as primary batteries.

Once the product is formed, it won't be converted into reactant again by application of external current. The reactions occur only once and after use they become dead. They are not rechargeable. They are also called as non-rechargeable batteries.

Ex: Zinc-air battery, Mercury battery etc.

2. Secondary Battery:

In those batteries, electrode chemical reactions are reversible is known as secondary batteries. The reactions can be reversed by passing an external electrical energy, so they can be rechargeable for number of cycles and used again and again.

They are also called rechargeable batteries.

Zinc-air battery:

It is a primary battery, which means it is non-rechargeable.

They are relatively inexpensive to produce and have high energy densities. They are available in many sizes from small button cells to large batteries. They are able to produce around 1.35 V – 1.4 V of electrical energy.

Construction

The battery consists of two electrodes, anode and cathode.

The anode is made up of Zinc. The cathode is made up of porous carbon paste which is capable of allowing into electrode.

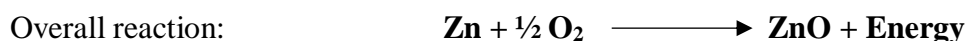
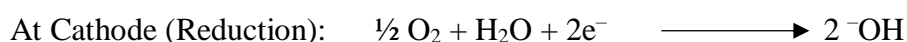
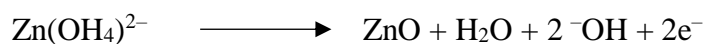
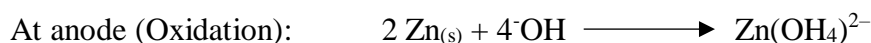
The alkaline solution such as NaOH or KOH act as an electrolyte.

Working and cell reactions

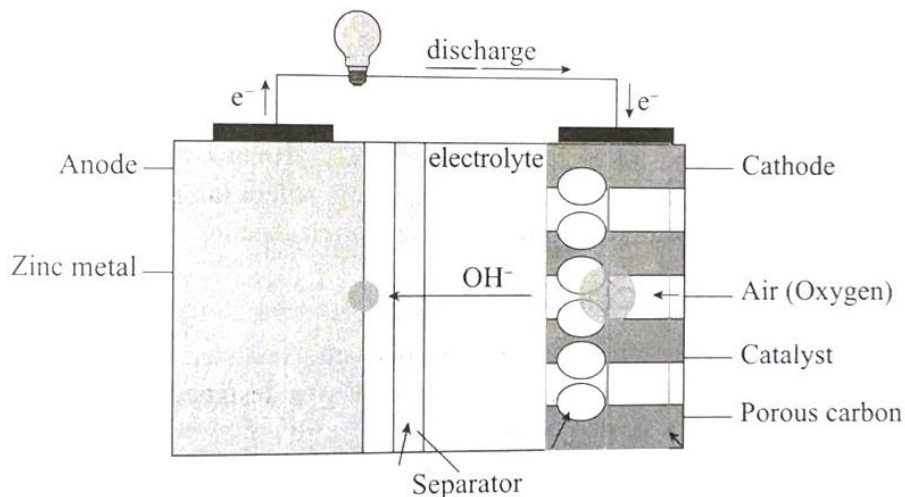
At anode, Zinc oxidizes into Zn^{+2} , further reacts with electrolyte to form zincate ions which in turn decay into zinc oxide and water.

At cathode, the electrons released of the anode, travel to the cathode where O_2 of the air accepts the electrons to form hydroxide ions.

The cell reactions are



Diagram



Advantages:

1. These batteries are inexpensive to fabricate
2. They have high energy density
3. They are available in many sizes.
4. They have excellent shelf life

Disadvantages:

1. These batteries are sensitive to extreme temperature and humid conditions.
2. These batteries have high self-discharge.
3. Carbon dioxide from the air forms carbonate which reduces the efficiency of electrode.

Applications

1. They are commonly used in watches and hearing aids.
2. They are used in telecoms and railway remote signaling,
3. Safety lamps.
4. Flim cameras.
5. Power sources for electric fences.

Lithium-ion battery:

It is a secondary battery, which means rechargeable.

These cells uses lithium ions instead of lithium metal, hence they are called as lithium-ion cells.

In fact, the cell operation does not actually involve oxidation and reduction like other batteries. But it uses the transport of Li^+ ions through the electrolyte from one electrode to another electrode, so that to maintain charge balance, the transport of electrons through the external circuit occurs. It was found that, the Li^+ ions are able to slip between two layers of atoms in certain crystal such as graphite and $LiCoO_2$.

Construction:

The battery consists of two electrodes, anode and cathode,

The anode is made up of Graphite and the cathode is made up of $LiCoO_2$.

Generally, solid electrolytes such as Lithium hexafluorophosphate ($LiPF_6$) is used.

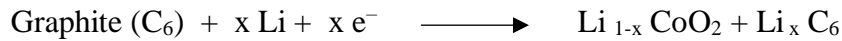
Working and cell reactions:

When the cell of LiCoO_2 and graphite is constructed, Lithium ions leave LiCoO_2 and travel through the electrolyte to the graphite.

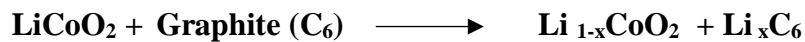
At cathode:



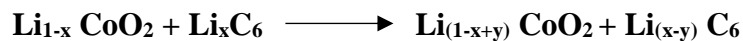
At anode:



Overall reaction:



When the cell is spontaneous discharging to provide electrical power, Li^+ ions move track through the electrolyte to the cobalt oxide while the electrons move through external circuit from graphite electrode to the cobalt oxide electrode if we represent amount of Li^+ transferring by 'y'. The charge reaction is



Advantages:

1. It has high energy density which is two times compare to Ni-Cd.
2. Low self-discharge rate.
3. Light weight and compact.
4. They can produce high voltage

Disadvantages:

1. Expensive to manufacture.
2. Extreme sensitive to high temperatures.
3. Short life span.

Applications

1. Power backups/UPS.
2. Electronic gadgets such as laptops, computers, mobile phones etc.
3. Tele-communication.
4. Aerospace.
5. Industrial applications.
6. Power source for electric and hybrid electric vehicles.

UNIT – II

POLYMER CHEMISTRY

Polymers are the high molecular weight macromolecules that are obtained by combination of number of small molecules (Monomers). Polymer is a Greek word which means ‘many parts’. Polymers can be found all around us. From the strand of our DNA, which is a naturally occurring biopolymer, to polypropylene which is used throughout the world as plastic. Polymers may be naturally found in plants and animals (natural polymers) or may be man-made (synthetic polymers). Different polymers have a number of unique physical and chemical properties, due to which they find usage in everyday life.

The polymers are a very large molecules having high molecular mass which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerization.

Basic concepts

Polymers

High molecular weight macromolecules that are obtained by combination of number of small molecules is known as polymer.

Ex: Polyethylene, Poly vinyl chloride (PVC), Bakelite, Nylon- 6,6 etc.

Monomers

The repeating unit that presents in polymer is known as Monomer. Monomers when joined together in large numbers give rise to a polymer. These are the building blocks of Polymers.

Ex: Ethene, Vinyl chloride, propylene etc.

Polymerization

The chemical reaction in which the monomers are combine to form polymer is known as polymerization reaction.

Degree of polymerization

The number of repeating units present in a polymer chain is known as degree of polymerization. It is calculated using below formula.

$$\text{Degree of Polymerisation (D. P.)} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of monomer}}$$

Nomenclature of Polymers

The polymers can classify based on the monomer or repeating unit present in it.

1. Homopolymer
2. Heteropolymer

1. Homopolymer: A polymer containing same type of monomer is known as Homopolymer.

Ex: Polyethylene, Polyvinyl chloride etc.

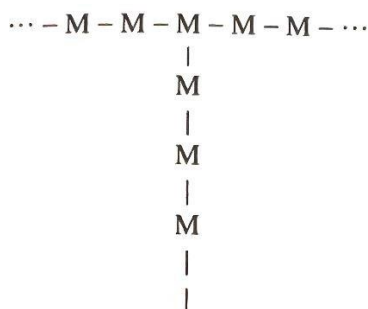
The homopolymers are subdivided into three types depending upon the monomer's arrangement in the polymer chain.

- i) Linear homopolymer
- ii) Branched homopolymer
- iii) Cross linked homopolymer

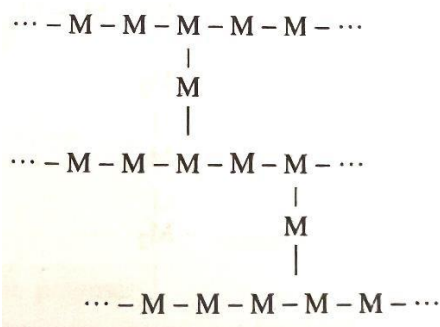
i) Linear homopolymer: A linear polymer is a macromolecule made out of many monomer units arranged in a long straight chains.



ii) Branched homopolymer: In this polymer, branching is the regular or irregular attachment of side chains to a polymer's backbone chain.

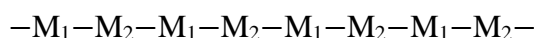


iii) Cross linked homopolymer: Cross linked polymers are polymers in which monomer units are cross linked together with covalent bonds to form a three dimensional network polymers.



2. Heteropolymer or Copolymer: A polymer containing more than one type of monomer is known as Heteropolymer or Copolymer.

Ex: Nylon, Terylene.



Heteropolymer are also subdivide into three types.

- i) Random copolymer: Two monomer units like M_1 and M_2 are randomly arranged in this polymer.
- ii) Block copolymer: The monomer units appear as a blocks in this polymer
- iii) Graft copolymer: In this polymer, one kind of monomer constitutes the main chain and another kind of monomer in the side chain.

The polymers can classify based on same or different atoms in the polymer backbone chain.

- i) Homochain polymers
- ii) Heterochain polymers

Functionality of monomer

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

If the monomer is bifunctional, i.e., functionality is 2, it mainly forms linear or straight chain polymer.

If the monomer is mixed functional, i.e., functionality of 2 and 3, it mainly forms branched chain polymer.

If the monomer is polyfunctional, i.e., functionality is 3, it mainly forms cross-linked polymers of three-dimensional network.

Polymerization reactions

The polymerization reactions may be carried out by the following pathways.

1. Addition or chain growth polymerization
2. Condensation or step-wise polymerization
3. Co-polymerization
4. Co-ordination (or) Ziegler-Natta Polymerization

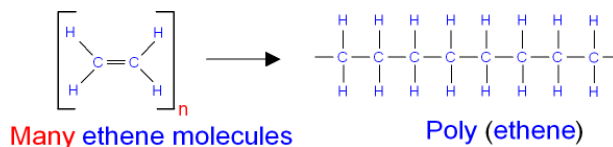
1. Addition or chain growth polymerization

In this polymerization reaction, several bifunctional monomers combine to form polymer by addition reaction without elimination of any by products.

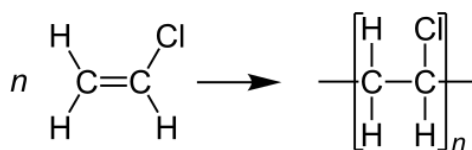
Generally, the monomer with double or triple bonds undergoes addition polymerization

and produce linear polymers. The polymer contains the same elemental composition as that of monomer and molecular weight is integral multiple of the original monomer.

Ex: 1. Polymerization of Ethylene



2. Polymerization of Vinyl chloride



Mechanism of addition polymerisation

In addition polymerisation, three different kinds of active initiating species such as free radicals, carbonium ions, carbanions are found to be formed. Based on initiating species, the mechanism divided into following types.

1. Free radical polymerisation
2. Ionic polymerisation
 - i) Cationic polymerisation
 - ii) Anionic polymerisation

1. Free radical polymerisation

If the addition polymerisation reaction was initiated by an active intermediate free radical, it is known as free radical polymerisation. The free radical polymerisation has three steps

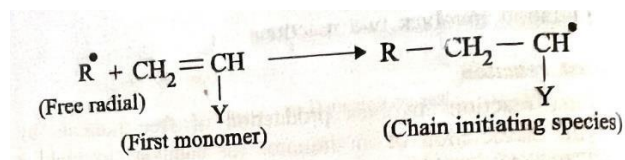
1. Initiation
2. Propagation
3. Termination

1. Initiation:

The initiation step involves two reactions. The first reaction involves the production of free radicals by homolytic dissociation of an initiator (or catalyst).

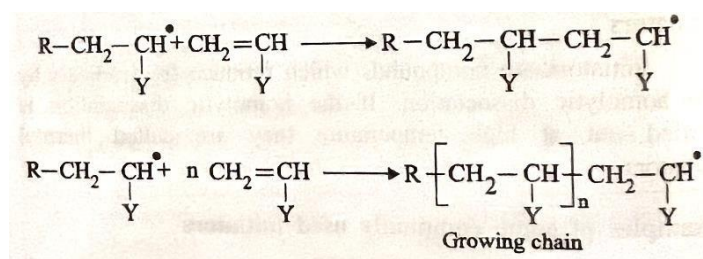


The second reaction involves the addition of monomer to the free radical to form chain initiating species.



2. Propagation:

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

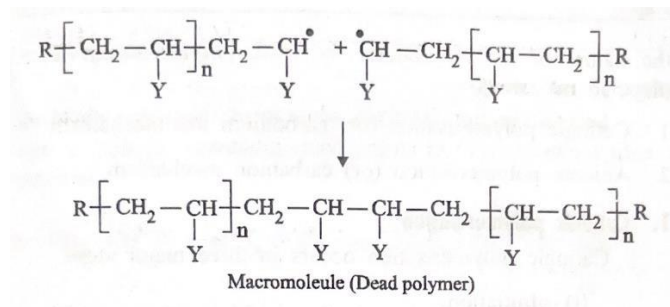


3. Termination:

The termination of polymer chain can be done either by coupling reaction or disproportionation reaction.

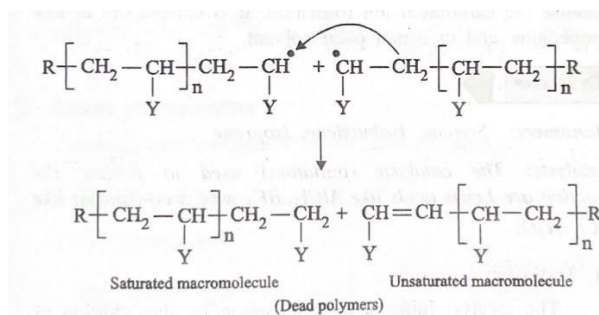
i) Coupling reaction:

It involves coupling of free radical of one chain end with free radical of another chain to form dead polymer.



ii) Disproportionation:

It involves transfer of a hydrogen atom of one radical centre to another to form two dead polymers.



2. Ionic polymerisation

The ionic polymerisation reaction is faster than the free radical mechanism. This

polymerisation is initiated by either a cation or anion. Depending on the type of initiator, this polymerisation can be divided into two types.

- i) Cationic Polymerisation
- ii) Anionic Polymerisation

i. Cationic polymerisation

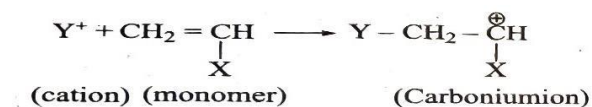
This polymerization is initiated and propagated by carbocation (a cation) intermediate, so it is called cationic polymerization.

The cationic polymerization occurs in three steps.

- a) Initiation
- b) Propagation
- c) Termination

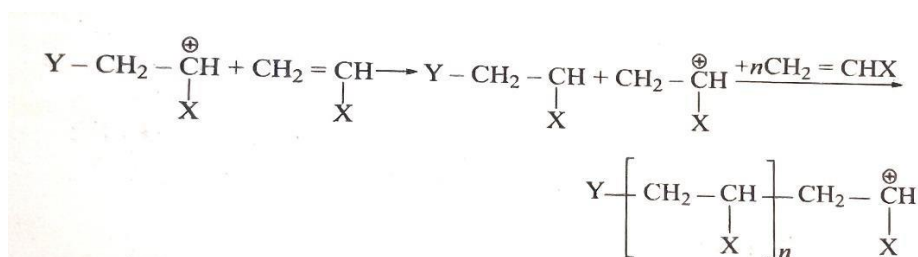
a) Initiation:

The catalyst (usually H^+) initiates the polymerisation by the addition of cation to the one of the monomer to form chain initiating species.



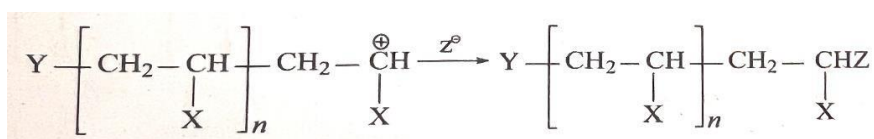
b) Propagation:

This step involves the successive addition of number of monomers to the chain initiating species for the growth of chain initiating species.



c) Termination:

Termination of polymer chain involves the removal of proton from the polymer chain to form dead polymer.



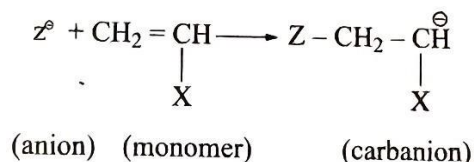
ii) Anionic polymerisation

The anionic polymerization is initiated and propagated by carbanion (a anion) intermediate, so it is called anionic polymerization.

This polymeisation involves three steps

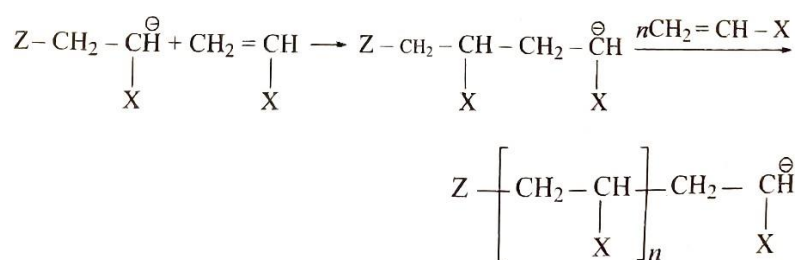
a) Initiation:

Usually the catalyst initiates the polymerisation by the addition of anion to the monomer to form chain initiating species.



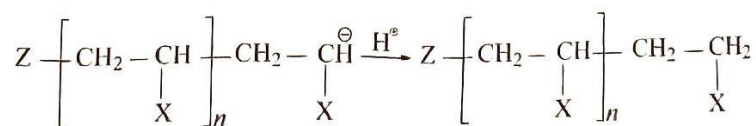
b) Propagation:

This step involves the successive addition of number of monomers to the chain initiating species for the growth of chain initiating species.



c) Termination:

Termination of growing polymer chain occurs by the addition of suitable terminating agents such as active hydrogen compounds (HX).



2. Condensation or step-wise polymerization

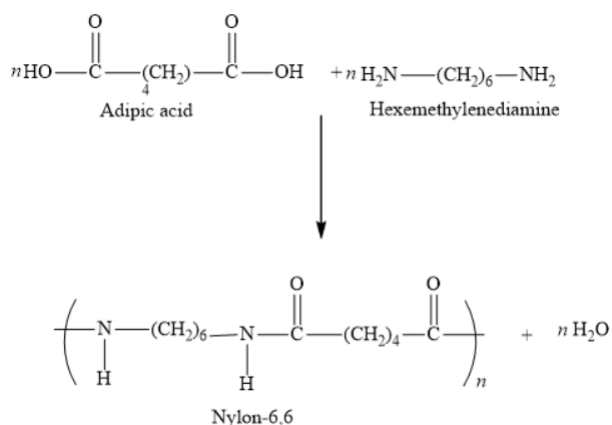
The stepwise reaction between the same or different polar groups containing monomers with the elimination of small molecules like H₂O, HCl and NH₃ etc. to form polymer is known as condensation or step-wise polymerization.

Polymerization proceeds through inter molecular condensation and forms linear or cross-linked polymers. The polymers may not contain same elemental composition as monomer and the molecular weight of the polymer is not an integral multiple of monomer's molecular

weight.

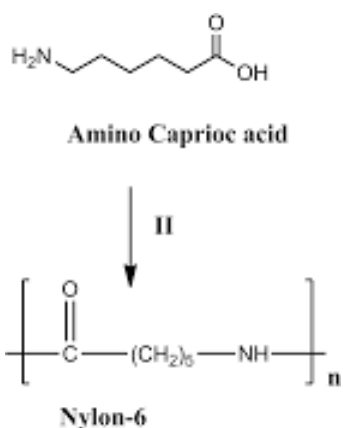
Ex: 1. Preparation of Nylon – 6,6

Nylon -6,6 obtain by condensation polymerization between two monomers, Hexamethylenediamine and Adipic acid.



2. Synthesis of Nylon -6

Polymerization of ω -amino caproic acid to form Nylon – 6.



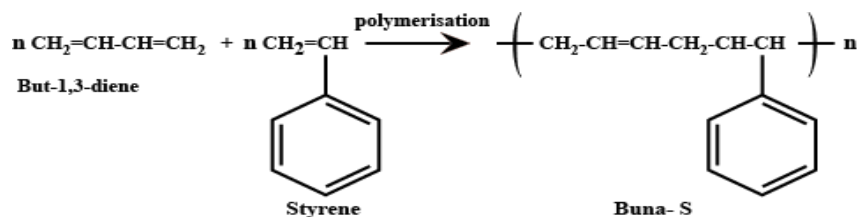
3. Co-polymerization

When two or more different types of monomers undergoes polymerization to form a polymer is called copolymerization.

It is a joint polymerization. The polymers obtained by copolymerization is called copolymers. This polymerization mainly carried out to vary the properties of polymers such as hardness, strength, rigidity, heat resistance etc.

Ex: 1. Synthesis of BUNA-S or SBR or GR-S rubber

Butadiene and styrene copolymerize to form GR-S or SBR rubber.



4. Co-ordination (or) Ziegler-Natta Polymerization

Zeigler – Natta catalyst is used to achieve stereo specific polymerization. The mechanism. The catalyst is prepared by reacting transition metal halide like TiCl_4 with trialkyl aluminum. The structure of typical Zeigler – Natta catalyst is given below.

The coordination polymerization involves three steps. In order to explain the mechanism, the catalyst is represented as Cat-R.

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

Biodegradable polymers

Those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes.

Poly Glycolic Acid (PGA)

Polyglycolide or polyglycolic acid (PGA) is a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester. PGA has been known since 1954 as a tough fiber-forming polymer. The

solubility of this polyester is somewhat unique, in that its high molecular weight form is insoluble in almost all common organic solvents (acetone, dichloromethane, chloroform, ethyl acetate, tetrahydrofuran), while low molecular weight oligomers sufficiently differ in their physical properties to be more soluble. However, polyglycolide is soluble in highly fluorinated solvents like hexafluoroisopropanol (HFIP) and hexafluoroacetone sesquihydrate that can be used to prepare solutions of the high molecular weight polymer for melt spinning and film preparation. Fibers of PGA exhibit high strength and modulus (7 GPa) and are particularly stiff [9].

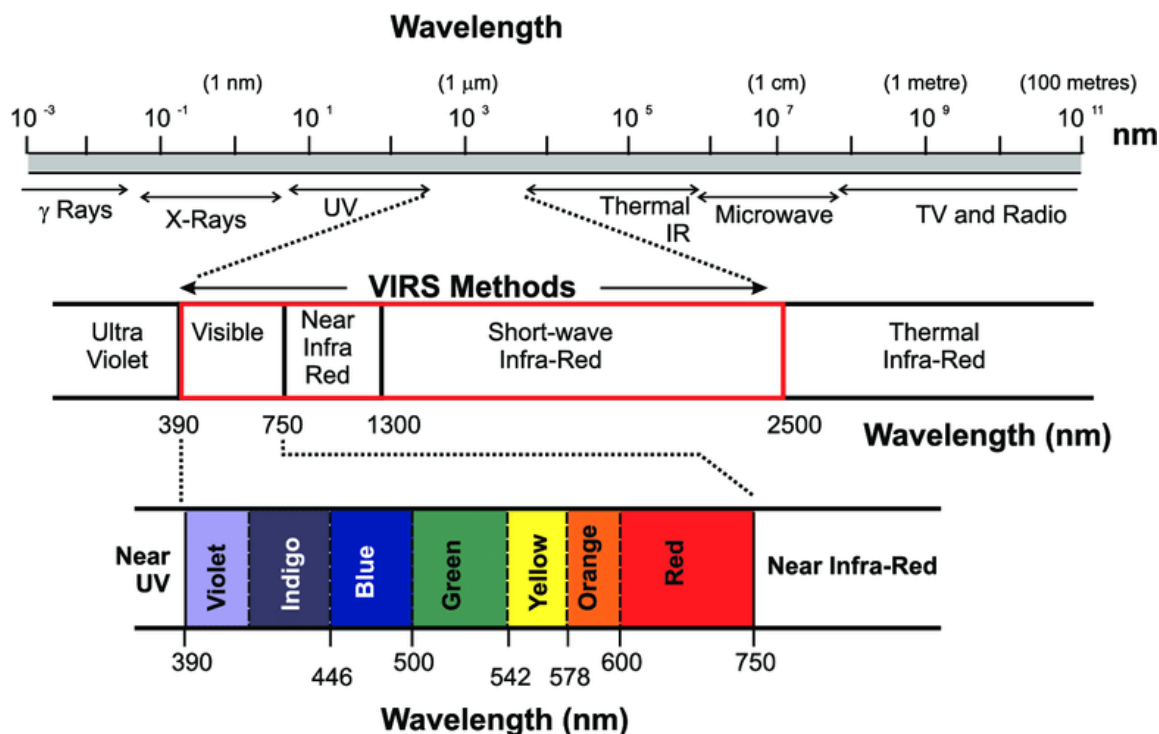
UNIT - V

INSTRUMENTAL METHODS AND APPLICATIONS

Instrumental methods analysis is a field of analytical chemistry that investigates analytes using scientific instruments. Instrumental methods have become the principal means of obtaining information in diverse areas of science and technology. The speed, high sensitivity, low limits of detection, simultaneous detection capabilities, and automated operation of modern instruments, when compared to classical methods of analysis, have created this predominance. Spectroscopy and chromatography are the two major instrumental methods. Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Chromatography useful to separate the individual components from the mixture of compounds.

Regions of Electromagnetic Spectrum

The electromagnetic spectrum is a range of frequencies, wavelengths and photon energies covering frequencies from below 1 Hz to above 10^{25} Hz corresponding to wavelengths which are a few kilometres to a fraction of the size of an atomic nucleus in the spectrum of electromagnetic waves. The electromagnetic spectrum consists of a span of all electromagnetic radiation which further contains many subranges which are commonly referred to as portions. The entire range (electromagnetic spectrum) is given by radio waves, microwaves, infrared radiation, visible light, ultra-violet radiation, X-rays, gamma rays and cosmic rays in the increasing order of frequency and decreasing order of wavelength. The type of radiation and their frequency and wavelength ranges are as follows:



Absorption of radiation

Absorption of electromagnetic radiation is how matter takes up a photon's energy and so transforms electromagnetic energy into internal energy of the absorbed matter. When a beam of radiation passes through a homogeneous medium the radiant energy may be partially or entirely absorbed, transmitted, reflected and scattered.

Beer-Lambert's law

The absorption of light in the visible and near UV region is governed by photo physical law known as Beers- Lambert's law.

Beer's law

This law states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

Lamberts law

The lamberts law states that where a monochromatic light passes through a transport medium the rate of decrease in the intensity with the thickness of medium is proportional to the intensity of light, mathematically.

Beer- Lambert's law:

$$dI / dx \propto I \text{ — — — — — (1)}$$

Where dI is a small decrease in intensity of light upon passing through a small distance dx and I is the intensity of the monochromatic light just before entering the medium.

Equation (1) may be written as

$$- dI / dx = aI \text{ — — — — — (2)}$$

Where $- dI / dx$ is the rate of decrease of intensity with thickness dx , a is called the absorption co-efficient.

Integration of equation (2) after rearrangement gives,

$$- \ln I = ax + C \text{ — — — — — (3)}$$

At $x=0$, $I=I_0$.

$$\ln I / I_0 = - ax \text{ — — — — — (4)}$$

Equation (4) can also be written as,

$$I = I_0 e^{-ax} \text{ ————— (5)}$$

Equation (5) can also be written as,

$$\log I / I_0 = -a / 2.303 \times \text{ ————— (6)}$$

$$\text{or, } \log I / I_0 = -a \times \text{ ————— (7)}$$

Lambert's law was extended.....

$$-dI / dx \propto c \text{ ————— (8)}$$

The two laws may be combined to write

$$-dI / dx \propto I \times c$$

$$\text{Or, } -dI / dx = b \times I \times c \text{ ————— (9)}$$

When the concentration, c, is expressed in mol /L, b is called the molar absorption co-efficient.

As in the case of Lambert's law equation (9) may be transformed into,

$$\log I / I_0 = -b / 2.303 \times c \times x \text{ ————— (10)}$$

$$\log I / I_0 = -\epsilon \times c \times x \text{ ————— (11)}$$

The expression (equation 11) is commonly known as Beer-Lambert's law.

Spectroscopy:

Spectroscopy is study of the interaction of electromagnetic radiation with matter. Spectroscopy is mainly used to identify and elucidate the elements and compounds of atoms and molecules. They are measured by examining the absorbed or emitted radiant energy by the sample or object. Here, the beam of electromagnetic radiation like infrared rays, UV rays. etc are passed on the sample and the response of the sample is measured through the wavelength of the electromagnetic spectrum.

UV-Visible spectroscopy:

It is also known as electronic spectroscopy. The Principle of UV-Visible Spectroscopy is based on the absorption of ultraviolet light (100 – 400 nm) or visible light (400 – 800 nm) by chemical compounds, which results in the production of distinct spectra. The absorption by a molecule of ultraviolet or visible radiation results in transitions between the molecule's electrical energy. UV-vis spectroscopy is a cost-effective, simple, versatile, non-destructive, analytical technique suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV-vis spectrophotometers measure the absorption or transmission of light that passes through a medium.

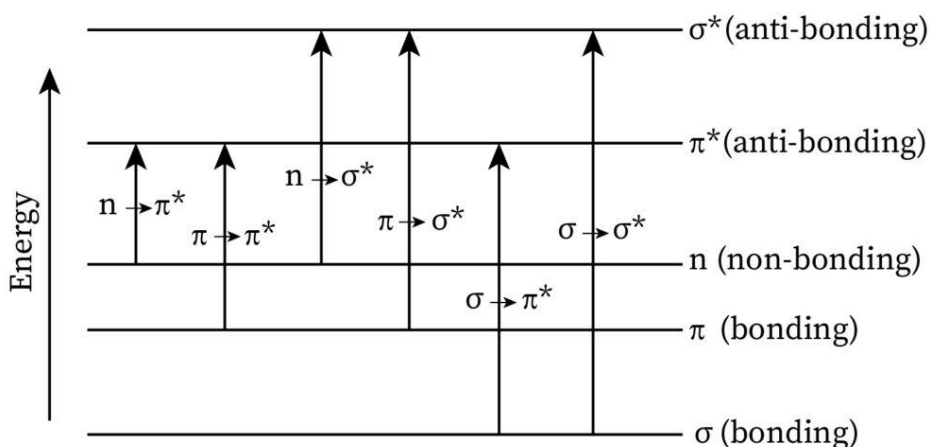
Principle:

When ultraviolet and visible light radiations are absorbed, this results in the excitation of the electrons from the lower energy ground state to higher energy excited state. The amount of the energy required for the transition is equal to energy difference between two energy levels.

$$E = E_1 - E_0$$

There are four possible types of transitions ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, and $n \rightarrow \sigma^*$) in molecules when the UV-Visible radiation absorbs, and they can be ordered as follows: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$. The amount of light absorbed or in form of transmitted is calculated using Beer-Lambert's law.

Electronic transitions:



When

$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

$n \rightarrow \sigma^*$ Transitions

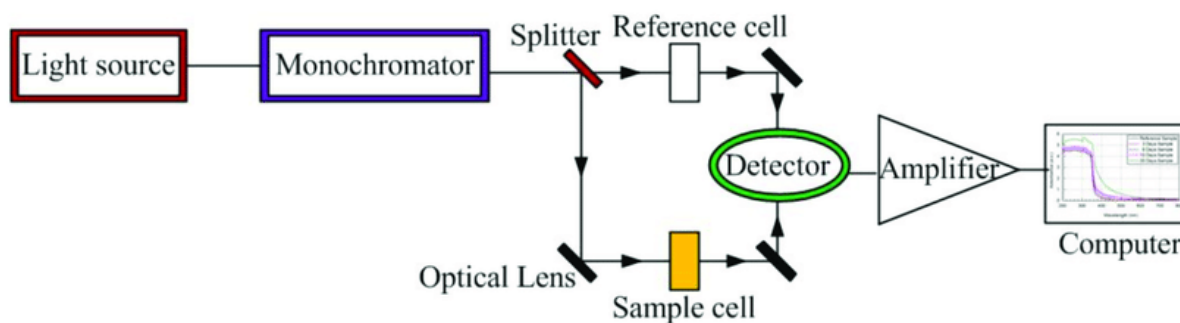
Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

Molar absorptivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to 100 $\text{L mol}^{-1} \text{cm}^{-1}$. $\pi \rightarrow \pi^*$ transitions normally give molar absorptivities between 1000 and 10,000 $\text{L mol}^{-1} \text{cm}^{-1}$.

Instrumentation:



The UV-Visible spectrometer consists of the following components.

1. Light source

Chromatography

The term “*chromatography*” is derived from Greek, *chroma* meaning, “*colour*,” and *graphein* meaning “*to write*”. The Russian botanist Mikhail Tswett coined the term chromatography in 1906.

Chromatography is an analytical separation technique used to separation of individual components from the mixture of components as well as their qualitative and quantitative determination. In chemical laboratories, it is the most used separation technique where it is used for analysis, isolation, and purification.

In this method of separating a mixture of components into individual component through equilibrium distribution between two phases, stationary phase and mobile phase. Chromatography involves a sample (or sample extract) being dissolved in a mobile phase (which may be a gas, a liquid or a supercritical fluid). The substance that has to be separated during the process of chromatography is known as an analyte.

The stationary phase is a phase that is fixed in a place in a column or on a solid surface. The mobile phase is passing through the stationary phase carrying with it the sample solution

Principle:

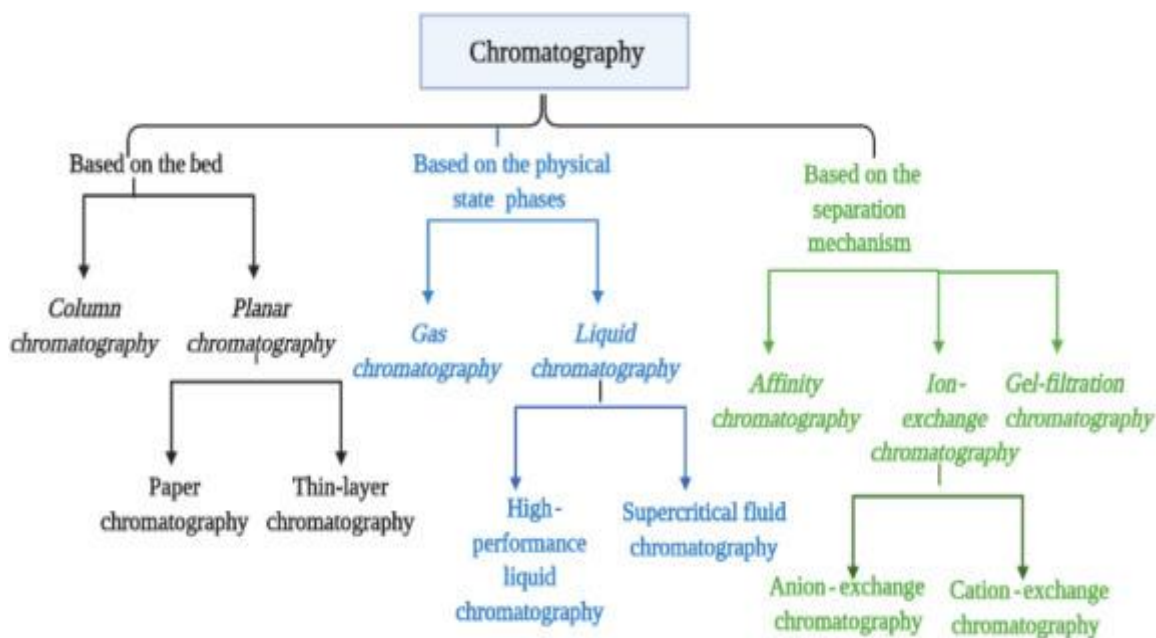
The chromatography is dependent on the principle of partitioning the constituent components (analyte) between two phases, i.e., a Mobile Phase and a Stationary Phase.

The stationary phase in chromatography is composed of either a solid or liquid substance attached to a glass or a metal surface on which the components of the mixture to be separated.

The mobile phase in chromatography is either a liquid or gas, which is passed through a chromatographic column where the components of the mixture are separated at different rates by adsorbing to the stationary phase.

The method of chromatography is based on the fact that the dissolved substances in the same solvent may have differing solubility. The different solubility of the analyte is due to the differential affinity or the different strength of adhesion towards the mobile and stationary phases. The affinity of an analyte can be explained by two terms, the first is adsorption and the second is solubility. Adsorption is the ability to get attached to the surface of the stationary phase while solubility is the ability to dissolve in the mobile phase. Analyte having higher adsorption will slowly pass through the column while analyte having high solubility will move faster through the column. The difference in the solubility and adsorption is due to the difference in polarity towards different phases which determines the extent of adsorption and solubility. For Example, a polar analyte will adsorb better to a polar stationary phase thus moving slowly through the column, and a non-polar analyte will better dissolve in a non-polar mobile phase thus moving faster through the column.

Classification:



Chromatography can be classified into two basic types based on the stationary phase bed.

1. Column chromatography
2. Planar chromatography

In column chromatography, the stationary phase is held in a narrow tube through which the mobile is forced through by pressure. In planar chromatography, the stationary phase is supported on a flat surface or in the pores of a paper, and the mobile passes through the stationary phase by capillary action or under the influence of gravity.

The stationary phase is supported on a flat surface or in the pores of a paper and the mobile phase passes through the stationary phase by capillary action or under the influence of gravity.

A more fundamental classification of chromatographic separations is based on the types of mobile and stationary phases and the kinds of equilibria involved in the transfer of solutes between the phases. Based on the type of mobile phase used, chromatography is divided into three types, Gas chromatography, Liquid chromatography and supercritical fluid chromatography. The mobile phases are gas, liquid and supercritical fluids respectively.

Based on separation mechanism, Chromatography is divided into affinity chromatography, Adsorption chromatography, Partition chromatography and Ion-exchange chromatography.

In adsorption chromatography, a solid stationary phase and liquid or gaseous mobile phase are used. The solute is adsorbed on the surface of the solid particles. The more strongly a solute is adsorbed, the slower it travels through the column.

In partition chromatography, A liquid stationary phase is bonded to a solid surface, which is typically inside the pores of the silica (SiO_2) column. The different components in a mixture equilibrate between the stationary phase and liquid phase.

In ion-exchange chromatography, anions such as $-\text{SO}_3^-$ or cations such as $-\text{N}(\text{CH}_3)_3^+$ are covalently attached to the stationary solid phase, usually a resin. Solute ions of the opposite charge are attracted to the stationary phase. the mobile phase is a liquid.

In gel filtration or size exclusion or gel permeation chromatography, this technique separates the molecules by size, with no attractive interaction between the stationary phase and solute.

The affinity chromatography is most selective kind of chromatography employs specific interaction between one kind of solute molecule and a second molecule that is covalently attached to the stationary phase.

Applications:

1. To identify and analyse samples for the presence of trace elements or chemicals.
2. Separation of compounds based on their molecular weight and element composition.
3. Detects the unknown compounds and purity of mixture.
4. In drug development.

HPLC-High Performance Liquid Chromatography:

High-performance liquid chromatography (HPLC), formerly referred to as high-pressure liquid chromatography, is a separation technique in analytical chemistry used to identify, quantify and separate molecular compounds in a liquid mixture.

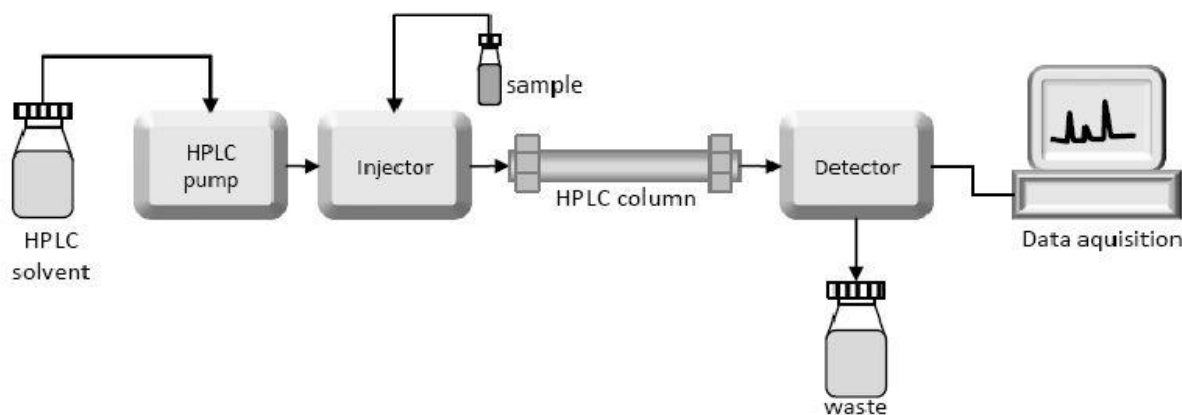
Principle:

The principle of separation on HPLC is based on the distribution of analyte (sample with a different unknown amount of compounds) between the mobile phase and stationary phase (column).

Depending on the chemical structure of the analyte, the molecules are retarded in the column stationary phase due to specific intermolecular interactions between the analyte and the packing material on the column. This defines the analyte's retention time on the column, and therefore different substances elute at different time intervals, thereby achieving the separation of different compounds in an analyte.

The mobile phase is pressurized into the column using solvent delivery pumps with the stationary phase. An analyte sample with unknown compounds is injected into the mobile phase before entering the column. Subsequently, individual compounds in the analyte migrate through the column at different rates achieving separation. Once the analytes exit the column, the detector unit recognizes the compounds in the analyte and exhibits them in electrical signals to generate the chromatogram. Chromatograms are used to identify and quantitate the concentration of analyte constituents.

Instrumentation:



Instrumentation:

Main components in an HPLC system include the solvent reservoir, or multiple reservoirs, a high-pressure pump, sample injector, a column, detector, and the recorder.

1. Solvent Reservoir

A solvent reservoir is used to store the mobile phase. Generally, it is made with steel or glass having capacity of 0.5 L – 2.0 L. It must contain volume enough for repetitive analysis.

2. Pump:

Pump is used to inject the mobile phase in column from the solvent reservoir. It regulates the flow of mobile phase through the column at certain pressure.

If the flow of mobile phase is uniform or constant throughout the experiment, it is known as isocratic elution.

If the flow of mobile phase is variable throughout the experiment, it is known as gradient elution. Generally, this type of elution achieved using two or more pumps.

3. Injectors

It is the device that injects the sample into the stream of mobile phase. Injectors for HPLC should provide the possibility of injecting large liquid sample volume under high pressure. Generally, six-port Rheodyne valve is used as a sample injector for modern HPLC instruments.

4. Column:

The column is an important part of the HPLC instrument where the separation takes place. The stationary phase is immobilized in the column. Nowadays stainless steel is used as a material for the column.

Depending on the chromatographic procedure, the column length and diameter can change. The column is placed in a thermostat to ensure the constant temperature.

5. Detector

A detector is a device that detects and quantifies separated compounds as they elute from the chromatographic column. The main function of a chromatography detector is to translate the physical or chemical properties of the analyte molecules into a measurable signal, typically an electrical signal.

The most commonly used detectors in HPLC are

- Refractive index detector
- UV/Visible detector
- Fluorescence detector
- Conductivity detector
- Mass-spectrometric detector

6. Recorder

The recorder converts the electrical signals into visible chromatograms. Laptops and computers are usually used as a recorder.

Applications:

The HPLC technique has a wide range of applications in

1. Both in laboratory and clinical science
2. Analysis of drugs
3. Analysis of synthetic polymers
4. Analysis of pollutants in environmental analytics
5. Determination of drugs in biological matrices
6. Isolation of valuable products such as proteins, nucleic acids, plant pigments, amino acids, pesticides, hormones etc.
7. Product purity and quality control of industrial products and fine chemicals

8. Separation and purification of biopolymers such as enzymes or nucleic acids
9. Water purification
10. Pre-concentration of trace components
11. Ligand-exchange chromatography
12. Ion-exchange chromatography of proteins