



**ANNAMACHARYAINSTITUTE OF TECHNOLOGY & SCIENCES::TIRUPATI**  
(AUTONOMOUS)  
Karakambadi Road, Venkatapuram (Vi), Tirupati.



## **Dept. of Humanities and Basic Sciences**

Subject	: <b>Chemistry Digital Notes</b>
Academic Year	: 2023-24
Department	: Humanities and Basic Sciences
Year & Sem	: I B.TECH & I / II SEM



AK23 Regulations

**ANNAMACHARYA INSTITUTE OF TECHNOLOGY & SCIENCES:**  
**TIRUPATI**  
**(Autonomous)**

(Effective for the batches admitted from 2023-24)

**Year: I B.Tech Common to I Sem-CSE,CSD, CIC & EEE, II Sem ECE,AI&DS,AI&ML**

<b>Subject Code:</b> 23ABS9901	<b>Subject Name:</b> Chemistry	L	T/CLC	P	<b>Credits:</b> 3
		4	2	0	

**Course Outcomes (CO):** At the end of the course students will be able to

1. Understand the interaction of energy levels between atoms and molecules
2. Apply the principle of Band diagrams in the conductors and semiconductors
3. Apply the electrochemical principles to the construction of batteries, fuel cells and sensors
4. Analyze the preparation and mechanism of plastics, Elastomers and conducting polymers
5. Analyze the separation of liquid mixtures using instrumental methods.

CO	Action Verb	Knowledge Statement	Condition	Criteria	Blooms level
1	<b>Understand</b>	the interaction of energy levels		between atoms and molecules	L2
2	<b>Apply</b>	principle of Band diagrams	conductors and semiconductors		L3
3	<b>Apply</b>	electrochemical principles to the construction of batteries, fuel cells and sensors			L3
4	<b>Analyze</b>	preparation and mechanism of plastics, Elastomers and conducting polymers			L4
5	<b>Analyze</b>	the separation of liquid mixtures	using instrumental methods		L4

### UNIT I

#### Structure and Bonding Models

Fundamentals of Quantum mechanics, Schrodinger Wave equation, significance of  $\Psi$  and  $\Psi^2$ , particle in one dimensional box, molecular orbital theory– bonding in homo-and hetero nuclear diatomic molecules – energy level diagrams of O<sub>2</sub> and CO, etc.  $\pi$ -molecular orbitals of butadiene and benzene, calculation of bond order.

### UNIT II

#### Modern Engineering materials

**Semiconductors:** Introduction, basic concept, application

**Superconductors:** Introduction basic concept, applications.

**Super capacitors:** Introduction, Basic Concept-Classification–Applications.

**Nano materials:** Introduction, classification, properties and applications of Fullerenes, carbon Nanotubes and Graphines nano particles.

### UNIT III

#### Electrochemistry and Applications

Electrochemical cell, Nernst equation, cell potential calculations and numerical problems, Potentiometry- potentiometric titrations (redox titrations), concept of conductivity, conductivity cell, Conductometric titrations (acid-base titrations).

**Electrochemical sensors** – potentiometric sensors with examples, amperometric sensors with examples.

**Primary cells**–Zinc-air battery, Secondary cells–lithium-ion batteries-working of the batteries including

cell reactions; Fuel cells, hydrogen-oxygen fuel cell– working of the cells. Polymer Electrolyte Membrane Fuel cells (PEMFC).

## UNIT IV Polymer Chemistry

Introduction to polymers, functionality of monomers, chain growth and step growth polymerization, coordination polymerization, with specific examples and mechanisms of polymer formation.

**Plastics** –Thermo and Thermosetting plastics, Preparation, properties and applications of –PVC, Teflon, Bakelite, Nylon-6, 6, Carbonfibres.

**Elastomers**–Buna-S, Buna-N–preparation, properties and applications.

**Conducting polymers**–polyacetylene, polyaniline,–mechanism of conduction and applications. Bio-Degradable polymers-Poly Glycolic Acid (PGA), Poly Lactic Acid (PLA).

## UNIT V Instrumental Methods and Applications

Electromagnetic spectrum. Absorption of radiation: Beer-Lambert’s law. UV-Visible Spectroscopy, electronic transition, Instrumentation, IR spectroscopy, fundamental modes and selection rules, Instrumentation. Chromatography-Basic Principle, Classification-HPLC: Principle, Instrumentation and Applications.

### Text books:

1. Jain and Jain, Engineering Chemistry, 16/e, Dhanpat Rai, 2013.
2. Peter Atkins, Juliode Paula and James Keeler, Atkins’ Physical Chemistry, 10/e, Oxford University Press, 2010.

### Reference Books:

1. Skoog and West, Principles of Instrumental Analysis, 6/e, Thomson, 2007.
2. J.D. Lee, Concise Inorganic Chemistry, 5<sup>th</sup> Edition, Wiley Publications, Feb. 2008
3. Textbook of Polymer Science, Fred W. Billmeyer Jr, 3<sup>rd</sup> Edition

Mapping of COs to POs and PSOs

CO	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PSO1	PSO2
1	2												
2	3												
3	3												
4		3											
5		3											

(Levels of Correlation, viz., 1-Low, 2-Moderate, 3 High)

CO	Percentage of contact hours over the total planned contact hours				CO		Program Outcome (PO)	PO(s): Action verb and BTL (for PO1 to PO5)	Level of Correlation (0-3)
	Register (Hrs)	Lesson Plan (Hrs)	%	corr	Verb	BTL			
1	10	10	15.6	2	Understand	L2	PO1	PO1: Apply (L3)	2
2	10	17	26.5	3	Apply	L3	PO1	PO1: Apply (L3)	3
3	10	12	18.7	3	Apply	L3	PO2	PO1: Apply (L3)	3
4	10	13	20.3	3	Analyze	L4	PO2	PO2: Analyze (L4)	3
5	10	12	18.7	3	Analyze	L4	PO1	PO2: Analyze (L4)	3

**CO1: Understand the fundamentals of Atoms and Molecules**

**Action Verb: Understand (L2)**

PO1 Verbs: Apply (L3)

CO1 Action Verb is less than PO1 verb by one level; Therefore correlation is moderate (2).

**CO2: Apply electrochemical principles to construct batteries**

**Action Verb: Apply (L3)**

PO1 Verbs: Apply (L3)

CO2 Action Verb is equal to PO1 verb; Therefore correlation is high (3).

**CO3: Apply electrochemical principles to the construction of batteries, fuel cells and electrochemical sensors**

**Action Verb: Apply (L3)**

PO2 Verb: Apply (L3)

CO3 Action Verb level is equal to PO1 verb; Therefore correlation is high (3).

**CO4: Analyze the preparation and mechanism of polymers**

**Action Verb: Analyze (L4)**

PO2 Verb: Analyze (L4)

CO3 Action Verb level is equal to PO2 verb; Therefore correlation is high (3).

**CO5: Analyze the identification of individual components**

**Action Verb: Analyze (L4)**

PO1 Verb: Analyze (L4)

CO5 Action Verb level is equal to PO2 verb; Therefore correlation is high (3).

## UNIT—1

### StrUctURe AND BONdIng MOLECuLes

#### Introduction:

All atoms except hydrogen atom are composed of three fundamental particles namely electron, protons and neutrons. A bonding model is a theoretical model used to explain atomic bonding structure, molecular geometry properties and reactivity of physical matter.

#### Plank's quantum theory:

1. Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum or photon.
2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of radiation

$$E = h\nu = \frac{hc}{\lambda}$$

Where E =energy of the radiation

h =planks constant ( $6.626 \times 10^{-34}$  J.S)

c =velocity of light

$\lambda$  =wavelength

$$1/\lambda =\nu \quad E =h\nu$$

$\nu$ =wavenumber

#### Dual nature of matter:

Einstein had suggested that light has dual character, i.e as wave and also as particle. Lewis de-broglie proposed that electrons also a dual character, as a wave and as a particle.

De-broglie equation: If a particle of mass 'm' moving with velocity 'v', then the wave length of this moving particle is given by

$$\lambda = h/mv$$

where h = planks constant

m = mass of particle

v = velocity of particle

According to planks quantum theory

$$E = hv \quad \text{equation(1)}$$

According to einsteins energy mass relation, the energy E of the photon is given by

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

Where m = mass of photon

C = velocity of light

From equation (1) and equation (2)

$$hv = mc^2$$

$$hc/\lambda = mc^2$$

$$h/\lambda = mc$$

$$\lambda = h/mc = h/p \quad \text{equation(3)}$$

where  $p = mc$  is the momentum of photon having mass 'm' and travelling with velocity 'c'. The above equation is known as the de-broglies wave equation.

### Uncertainty principle :

The wave nature of particle is further explained by Heisenbergs uncertainty principle. It is impossible to measure exactly and simultaneously both position and momentum of a particle and momentum respectively when they are simultaneously measured.

$$\Delta x \cdot \Delta p \geq \hbar/2$$

$$\text{where } \hbar = h/2\pi$$

An attempt to reduce  $\Delta x$  will raise  $\Delta p$  and vice-versa.

This is the consequence of diffraction of electron.

### Schrodinger Wave Equation:

Schrodinger derived a mathematical equation to derive the dual nature of matter waves.

Definition: The mathematical equation that describes the wave of a particle is known as schrodinger wave equation

Schrodinger time independent wave equation:

If a particle of mass 'm' moving with a velocity 'v' is associated with a group of waves , let  $\Psi$  be the wave function of the particle. Also let us consider a simple form of progression wave like the one represented by equation

$$y = A \sin(\omega t - kx) \quad (1)$$

$$\Psi = \Psi_0 \sin(\omega t - kx) \quad (2) \quad \text{\_Assumption(solution)}$$

Where  $\Psi = \Psi(x, t)$  and

$\Psi_0$  is amplitude

And  $\omega =$  angular frequency

$K =$  angular wave number,  $k = 2\pi/\lambda$

$Y =$  displacement

$A =$  Amplitude

So,  $\Psi = \Psi_0 \sin(\omega t - kx)$

Differentiating with respect to  $x$

$$\partial\Psi/\partial x = \Psi_0 \cos(\omega t - kx)(-k)$$

Again differentiating with respect to  $x$

$$\partial^2\Psi/\partial x^2 = -\Psi_0 \sin(\omega t - kx)(k^2)$$

$$= -k^2\Psi_0 \sin(\omega t - kx)$$

$$= -k^2\Psi$$

And since  $k = 2\pi/\lambda$

$$\partial^2\Psi/\partial x^2 = -4\pi^2/\lambda^2 \Psi$$

From de-broglie wavelength expression

$$\lambda = h/mv$$

By substituting

$$\partial^2\Psi/\partial x^2 = -4\pi^2 \cdot m^2 v^2 / h^2 \Psi$$

We know total energy of a particle is sum of kinetic energy ( $k$ ) and

Potential energy (v)

i.e.  $E=k+V$

$$E-V=k$$

$$E-V=1/2mv^2$$

$$2(E-V)=mv^2$$

$$2m(E-v)=m^2v^2 \quad (\text{ by multiplying with } m)$$

So by substituting

$$\partial^2\Psi/\partial x^2 = -8\pi^2m(E-V)/h^2.\Psi$$

In quantum mechanics, the value  $h/2\pi$  occurs most frequently. Hence

We denote  $\hbar = h/2\pi$  Where  $\hbar$ =reduced plank constant

Using this notation, we have

$$\partial^2\Psi/\partial x^2 + 2m(E-V)/\hbar^2\Psi=0$$

For simplicity, we considered only one dimensional wave extending equation for three dimensional wave

$$\partial^2\Psi/\partial x^2 + \partial^2\Psi/\partial y^2 + \partial^2\Psi/\partial z^2 + 2m(E-V)/\hbar^2.\Psi=0 \quad \text{Where } \Psi=\Psi(x,y,z)$$

Here, we have considered only stationary states of  $\Psi$ , after separating the time dependence of  $\Psi$

Using laplacian operator

$$\text{i.e. } \nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

Equation can be written as

$$\Delta^2\Psi + 2m(E - V)/\hbar^2 \Psi = 0$$

∇ This is Schrodinger wave equation. Since time factor doesn't appear, it is called time independent wave equation

→ Significance of  $\Psi$  and  $\Psi^2$ :

The wave equation  $\Psi$  associated with a moving particle is not an observable quantity and does not have any direct physical meaning. It is a complex quantity. This can represent the probability density of locating the particle at a place in a given instant of time. In all wave equations the square of the wave function is the property which has physical significance. In case of light wave, square of the amplitude of the wave at a point is proportional to the intensity of the light wave. Similarly in electron wave motion  $\Psi^2$  should represent intensity. According to the uncertainty principle, greater is the probability of locating the electron at the point. Thus  $\Psi^2$  may be interpreted as being proportional to electron density. The wave function  $\Psi$  may be positive, negative or imaginary but the probability density  $\Psi^2$  will always be positive and real. The probability of finding the electron is finite, which means  $\Psi^2 dt$  must give real values.

$$\Psi = a + ib \quad (\text{where } a, b \text{ are real numbers})$$

$$\Psi^* = a - ib$$

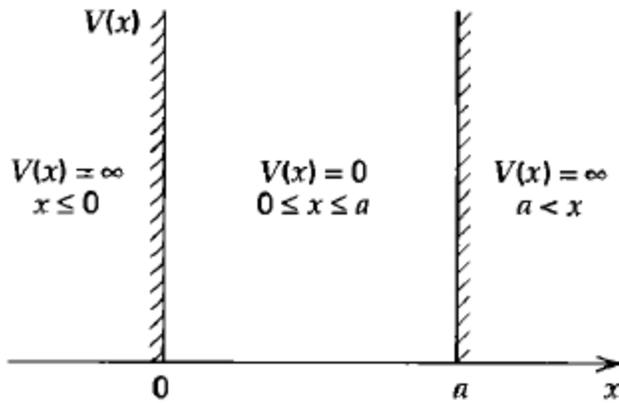
$$\Psi\Psi^* = |\Psi|^2 = a^2 + b^2$$

Applications of Schrodinger's wave equation:

- It helps us to know Bohr quantum number (i.e. principle Quantum number)
- It helps us for finding a particle in one dimensional box .
- It is also used for calculation of energy level.
- It also explains band theory(semiconductors, conductors and insulators)

### **a) Particle in an infinite potential well (or) potential box:**

Consider a particle of mass 'm' moving back and forth between the walls of a one dimensional box separated by a distance 'a' as shown in figure. Let the particle travel along the x-axis and is confined between  $x=0$  and  $x=a$  by two infinitely hard walls so that the particle has no chance of penetrating them. Thus it doesn't lose energy and its total energy remains constant. This box is represented by a potential box of width 'a' with potential walls of infinite height at  $x=0$  and  $x=a$ , so that the potential energy 'v' of the particle is infinitely high on both sides of the box inside it 'v' is uniform.



Let us assume that  $v = 0$  inside the box

$$V(x) = 0 \quad \text{for } 0 < x < a$$

$$V(x) = \infty \quad \text{for } x \leq 0 \text{ and } x \geq a$$

Then the wave function  $\Psi(x)$  of the particle in the region  $0 < x < a$  where  $v=0$  is described by Schrodinger's one dimensional time independent wave equation i.e,

$$\partial^2 \psi / \partial x^2 + [2m(E-v)\psi(x)] / \hbar^2 = 0$$

$$\partial^2 \psi / \partial x^2 + [2m(E-V) / \psi(x)] / \hbar^2 = 0$$

Since  $v=0$  by substituting " $v=0$ " in the above equation

$$\partial^2 \psi / \partial x^2 + 2mE\psi(x) / \hbar^2 = 0$$

$$\text{i.e. } \partial^2 \psi / \partial x^2 + k^2 \psi(x) = 0 \quad \text{-----} \rightarrow \textcircled{1}$$

Where  $k^2 = 2mE / \hbar^2$  or  $K = \sqrt{2mE} / \hbar$

The solution of above equation is given by

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad \text{-----} \rightarrow \textcircled{2}$$

When A and B are arbitrary constants applying the first boundary condition

i.e. at  $x=0$  and  $\psi(x)=0$

$$\psi(x) = A\sin(0) + B\cos(0)$$

$$0 = 0 + B$$

$$B = 0$$

Now when  $x=a$ ,  $\psi(x)=\psi(a)=0$

$$\psi(x) = A\sin(ka) \quad (\text{Since } A \neq 0)$$

$$\sin(ka) = 0$$

We know that  $k = n\pi/a$

$$\sin(n\pi/a)a = 0 \quad \text{Where } n \text{ value is equal to } 1, 2, 3, \dots$$

We cannot take  $n=0$  because for  $n=0$ ,  $k=0$ ,  $E=0$  here  $\psi(x)=0$  everywhere in the box. Thus the particle with zero energy cannot be present in the box i.e. a particle in the box cannot have zero energy. The wave function for the motion of the particle in the region  $0 < x < a$  are given by

$$\Psi_n(x) = A\sin Kx$$

$$\Psi_n(x) = A\sin(n\pi x/a)$$

### Eigen values of energy:

We know that  $K^2 = (2m/\hbar^2)E$

$$E = K^2\hbar^2/2m$$

$$\text{But } K = n^2\pi^2/a^2$$

$$E = (n^2\pi^2/a^2) \quad (\hbar = h/2\pi)$$

$$E = [n^2\pi^2/a^2][h^2/8\pi^2m]$$

$$E_n = n^2h^2/8ma^2$$

From the above equation it is clear that

i. The lowest energy of the particle obtained by putting  $n=1$

i.e.  $E_1 = h^2/8ma^2$  and  $E_n = n^2E_1$

This is known as zero point energy of the system

ii. For  $n=1, 2, 3$  we get discrete energy values of the particle in the

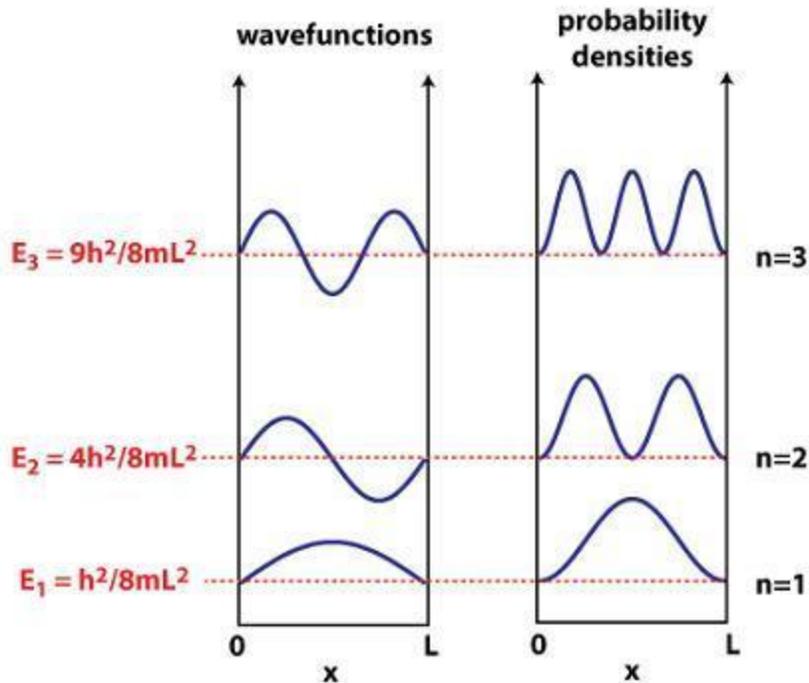
box  $E_1 = h^2/8ma^2$   $E_2 = 2^2h^2/8ma^2 = 4E_1$

$$E_3 = 3^2h^2/8ma^2 = 9E_1$$

The spacing between then the energy level and next higher level increases as  $(n+1)^2E_1 - n^2E_1 = (2n+1) E_1$

iii. These values of  $E_n$  are known as Eigen functions of the particle. The integer 'n' is the quantum number of energy.

iv. In the figure given below shows us the energy level diagram for the particle



### Eigenfunctions:-

The eigen wave function for the motion of the particle in the region  $0 < x < a$  is  $\Psi_n(x) = A \sin(n\pi x/a)$

$$\Psi_n(x) = 0 \quad \text{in region } x \leq 0 \text{ and } x \geq a$$

The total probability that the particle is some in the box must be unity

$$\int P x dx = \int |\psi(x)|^2 dx = 1$$

$$\int A^2 \sin^2(n\pi x/a) dx = 1$$

$$A^2 \int \frac{1}{2} [1 - \cos 2n\pi x/a] dx = 1$$

$$A^2/2 [x - a/2\pi m \sin(2\pi n x/a)] = 1$$

The second term becomes zero at both the limits

Therefore,  $A^2 a/2=1 \rightarrow A=\sqrt{2}/a$

The wave functions are shown in above figure

The wave function  $\psi_1$  has two nodes at  $x=0$  and  $x=a$ . The wave function  $\psi_2$  has three nodes at  $x=0$ ,  $x=a/3$ ,  $x=2a/3$  and  $x=a$

Thus  $\psi_n(x)$  has  $(n+1)$  nodes.

## **Molecular Orbital Theory:**

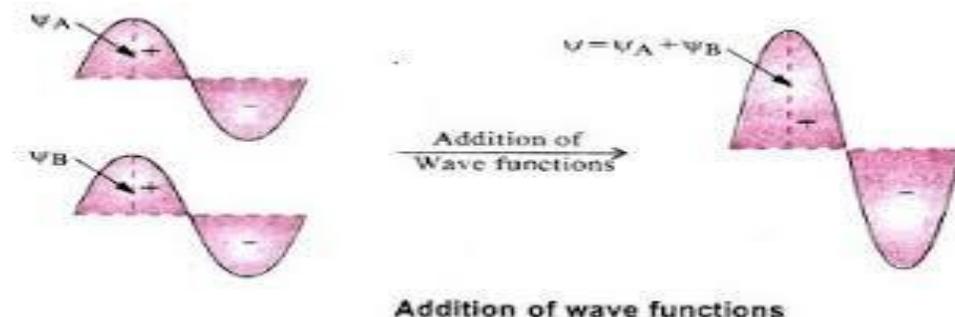
*MOT was given by hund and mulliken in 1932. MOT is a method for describing electronic structure of molecules using quantum mechanics.*

### THE POSTULATES ARE:-

1. When two atomic orbitals overlap they lose their identity and form new orbitals the new orbitals are called molecular orbitals.
2. Molecular orbitals are the energy state orbital of molecule in which the electrons of the molecules are filled.
3. The formation of the orbitals are the energy state of a molecule in which the electrons of the molecule are filled.
4. Only those atomic orbitals can combine to form molecular orbitals which have comparable energies and proper orientation.
5. The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
6. When the two atomic orbitals combine they form two new orbitals called one is Building Molecular Orbital.
7. When the addition of wave function takes place, the type of molecular orbitals formed ; bonding orbitals are formed.

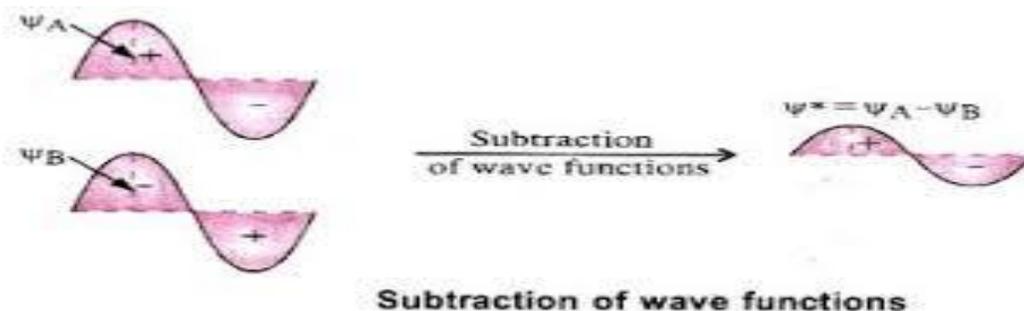
we can represent them by they have lower energy level then atomic orbitals involved.

a.  $\Psi_{MO} = \Psi_A + \Psi_B$



8. When the subtraction of wave function takes place then anti bonding orbitals are formed .this can be represented by

$$\Psi_{AMO} = \Psi_A - \Psi_B$$



they have higher energy then atomic orbitals involved.

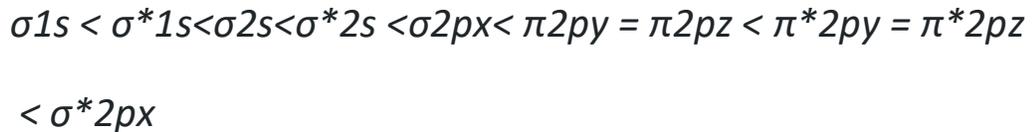
9. The bonding molecular orbitals are represented by sigma ,pie.

10. The filing of molecular orbitals in a molecule takes place in according with auf-bau principle ,pauli-exclusive principle and hund rule.

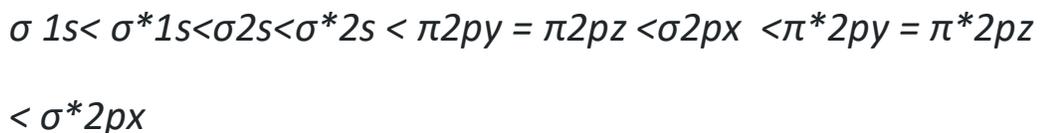
11. Energy level of molecule orbitals when total no of molecules more than 14 , then and when total no of molecules are less

than 14.

*Number of electrons > 14*



*Number of electrons < or = 14, their energy increases in the following order:*



12. Atomic orbitals are mono-centric where as molecular orbitals are poly centric.

13. The no of covalent bond between two atoms is called BOND order .

$$\text{BOND ORDER} = \frac{N_a - N_b}{2}$$

$N_a$  = no of bonding orbitals

$N_b$  = no of anti bonding orbitals

14. If all the electrons in a molecule are paired then the substance is diamagnetic on the other hand. if there are unpaired e<sup>-</sup> in a molecule then the substance is paramagnetic.

15. If the value of bond order is positive then the molecule is

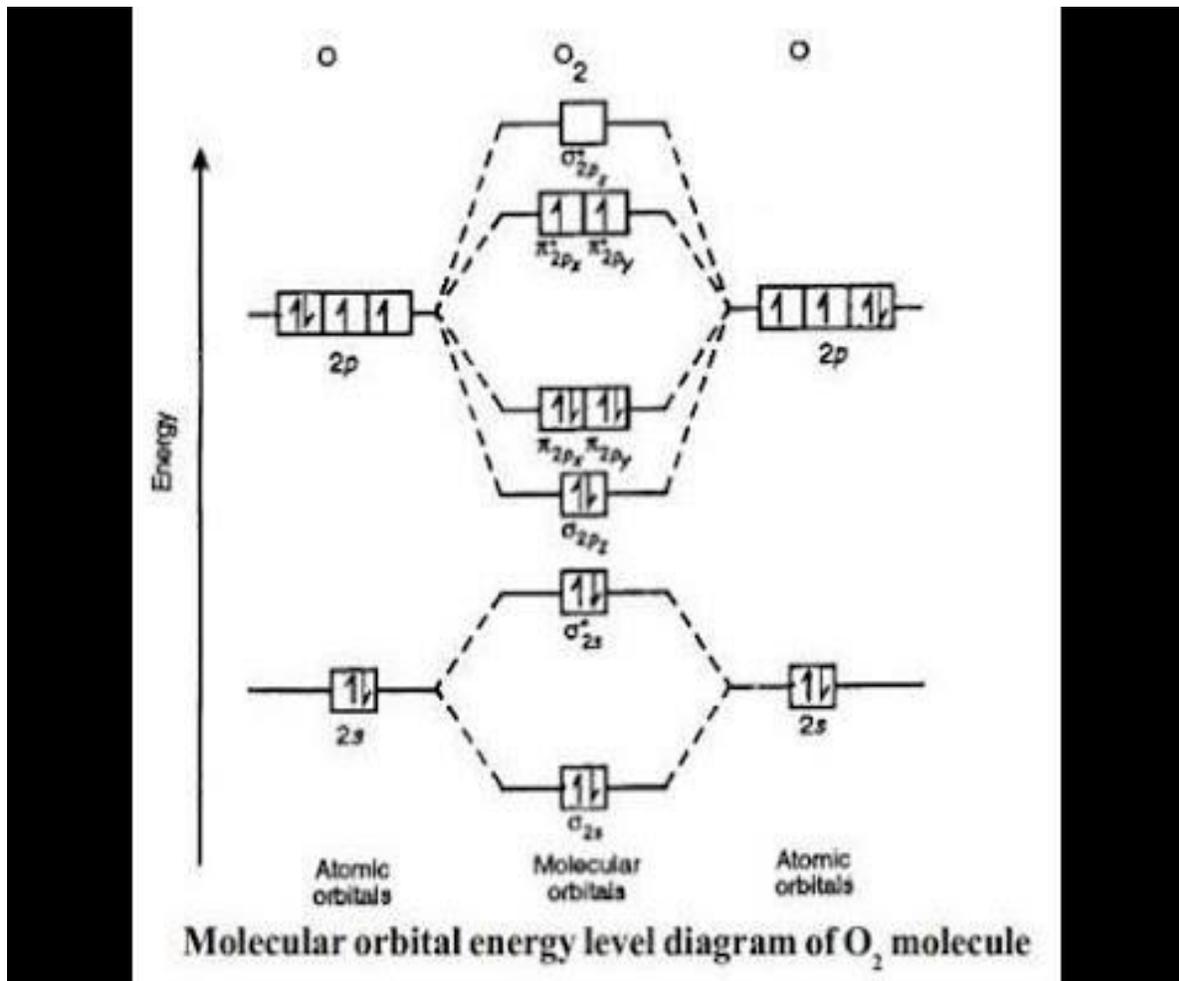
stable and if it is negative or zero then the molecule is unstable.

eg;...H<sub>2</sub>-diamagnetic

H<sub>2</sub><sup>+</sup>-para magnetic

H<sub>2</sub><sup>-</sup>-para magnetic.

## MOLECULAR ORBITALS THEORY FOR NITROGEN AND OXYGEN.

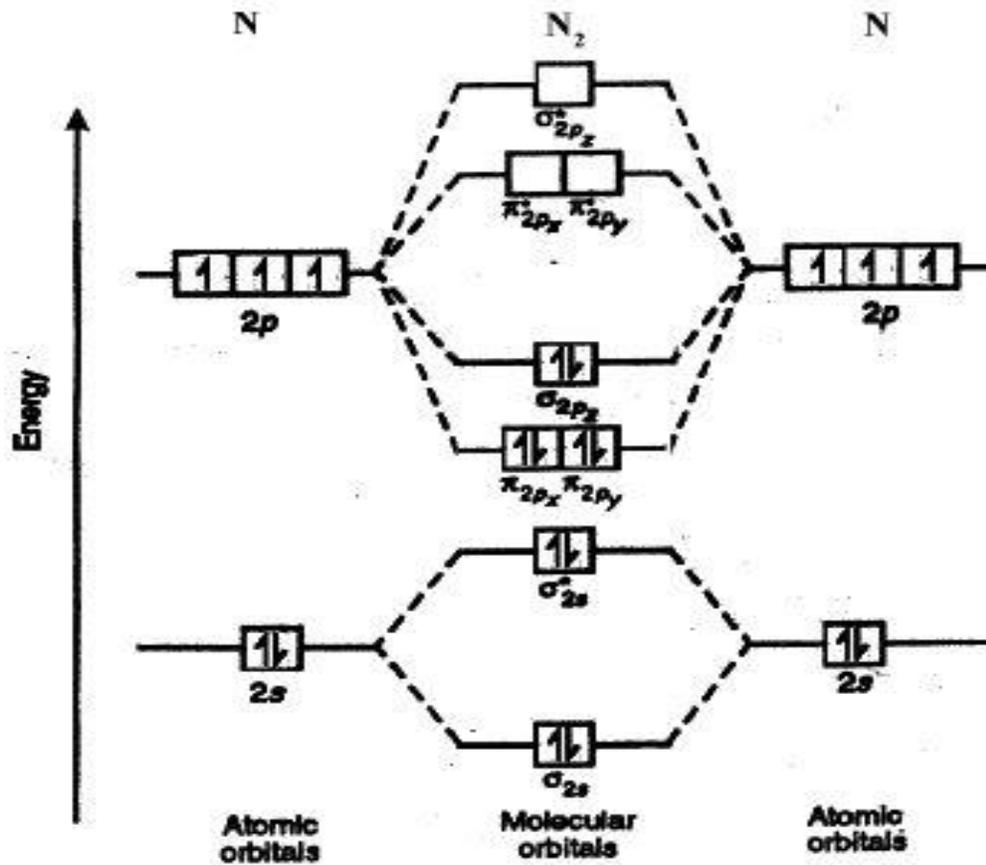


$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{10-6}{2}$$

$$= 2$$

It is a paramagnetic in nature.



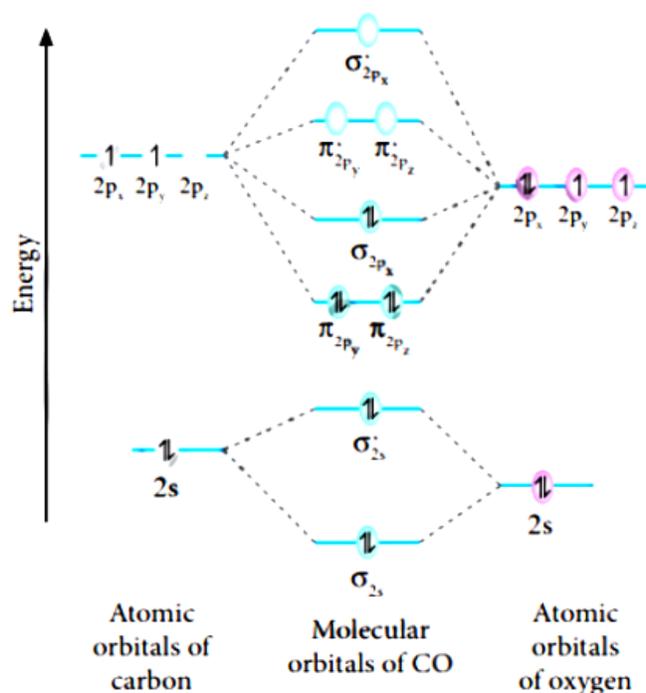
$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{10-4}{2}$$

$$= 3$$

It is a diamagnetic in nature

Molecular orbital diagram for CO molecule



Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom:  $1s^2 2s^2 2p^2$

Electronic configuration of O atom:  $1s^2 2s^2 2p^4$

Electronic configuration of CO molecule :  $\sigma 1s^2, \sigma 1s^{*2}, \sigma 2s^2, \sigma 2s^{*2}, \pi_{2py}2, \pi_{2pz}2, \sigma_{2px}2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

The molecule has no unpaired electrons hence it is diamagnetic.

### $\Pi$ molecular orbital of 1,3 Butadiene:

Butadiene is a **conjugated** diene consisting of two adjacent pi-bonds and comprised of 4 p-orbitals and 4 pi-electrons.

To draw the molecular orbital diagram of butadiene, start by drawing 4 p-orbitals all aligned with the same phase. This has **zero** nodes and is the **lowest energy pi-orbital** ( $\pi_1$ )

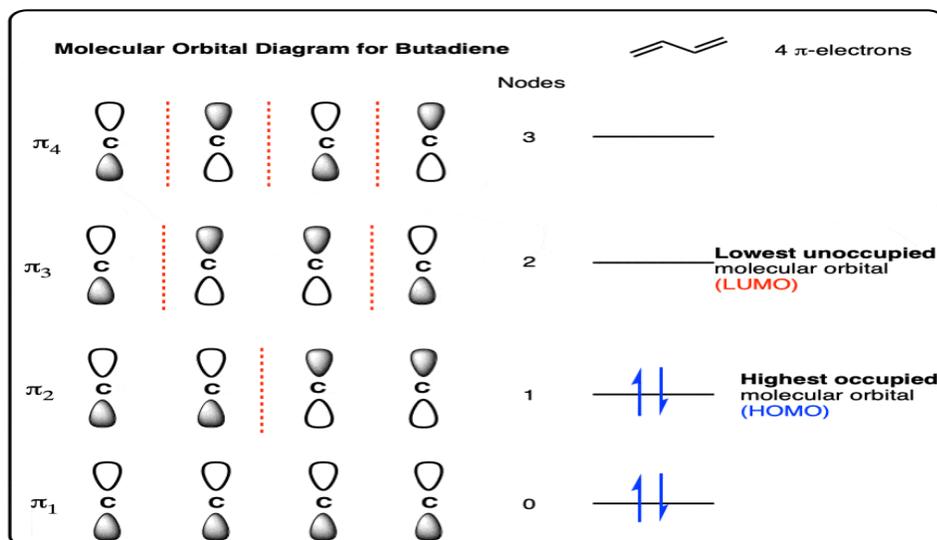
As the number of **nodes** in an orbital increases, so does its energy. The highest-energy molecular orbital has **three** nodes and has all p-orbitals with opposite phases ( $\pi_4$ )

Intermediate orbitals ( $\pi_2$ ) and ( $\pi_3$ ) have one and two nodes, respectively

Once the molecular orbital diagram is built, the next step is to add the 4 **pi-electrons**. This will fill up the lowest-energy orbital ( $\pi_1$ ) and the second-lowest-energy orbital ( $\pi_2$ )

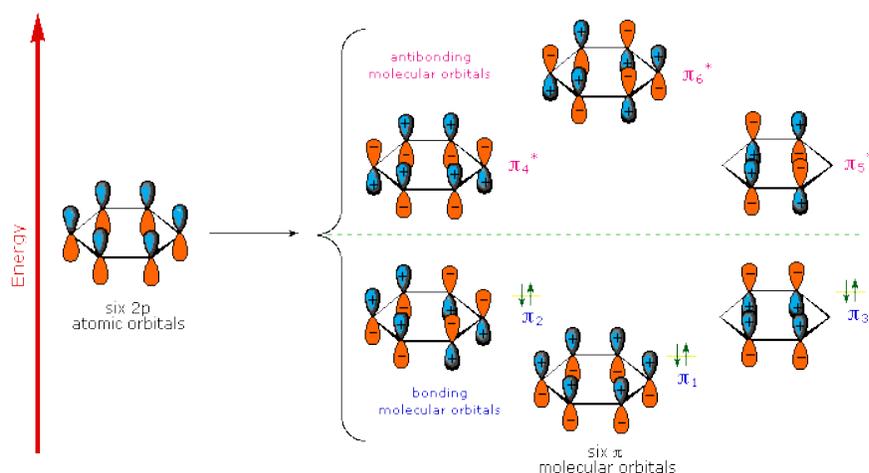
The **highest-occupied** molecular orbital (HOMO) of butadiene is the highest-energy orbital that contains pi-electrons. This is  $\pi_2$

The **lowest-unoccupied** molecular orbital (LUMO) of butadiene is the lowest-energy orbital that has **zero** pi-electrons. This is  $\pi_3$



## $\pi$ molecular orbital of Benzene:

Benzene has a planar hexagonal structure in which all the six carbon atoms are  $sp^2$  hybridized. Four valency electrons of each carbon atom, three forms covalent bonds with two carbon atoms and one hydrogen atoms. The remaining cyclic six p-orbitals(one on each carbon)overlap to generate six molecular orbitals, three bonding and three antibonding. The Molecular Orbitals of Benzene



## UNIT II

### MODERN ENGINEERING MATERIALS

❖ Molecular Orbital Theory was explained properties of liquids and gases the following  
1. Bond order 2. Stability 3. Colour property 4. Magnetic property

❖ But MOT was not explained the properties of solids. So the properties of solids explained by a new theory that is called Band theory.

❖ Band theory is the extension of MOT.

❖ Band theory is used for classification of solids.

❖ Based on the magnetic properties or forbidden gap or energy gap between the energy bands or the distance between the valence band and conduction band in the solid crystals, solid crystals are classified into three types i.e.,

a. Conductors b. Semiconductors c. Insulator

#### **Conductors:**

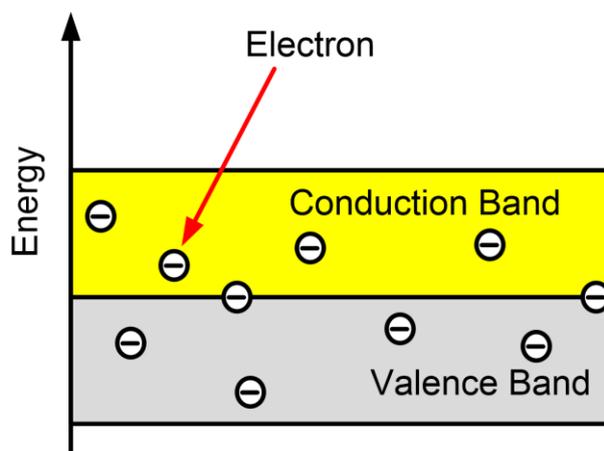
- The electronic conductors which exhibit electrical conductivity in the range of  $10^4 - 10^7 \text{ ohm}^{-1} \text{ cm}^{-1}$  are called as conductors.

- Conductors exhibit conductivity due to motion of electrons.

- Eg: Metals like Cu, Al, Fe, Ag, Mn ---

- The solid crystals in which no energy gap ( $E_g=0$ ) between filled valence band and the empty conduction band are called as conductors.

- Therefore metallic crystals exhibit high conductivity due to electrons can flow easily from valence band to conduction band under an applied electrical field because forbidden gap or energy gap between the valence band and conduction band is zero.

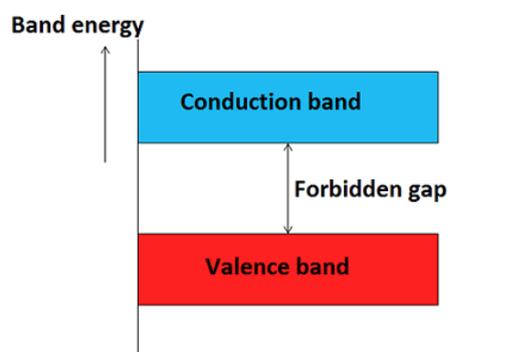


## Insulators:

- The electronic conductors which exhibit electrical conductivity in the range of  $10^{-20}$  –  $10^{-10}$   $\text{ohm}^{-1} \text{cm}^{-1}$  are called as insulators.
- Insulators do not exhibit conductivity due to do not permit electricity to pass.

Eg: Wood, Rubber, Glass and Bakelite ---

- The solid crystals in which large energy gap ( $E_g = \text{max}$ ) between filled valence band and the empty conduction band are called as insulators.
- Therefore insulators does not exhibit conductivity due to electrons does not flow easily from valence band to conduction band under an applied electrical field because forbidden gap or energy gap between the valence band and conduction band is maximum.



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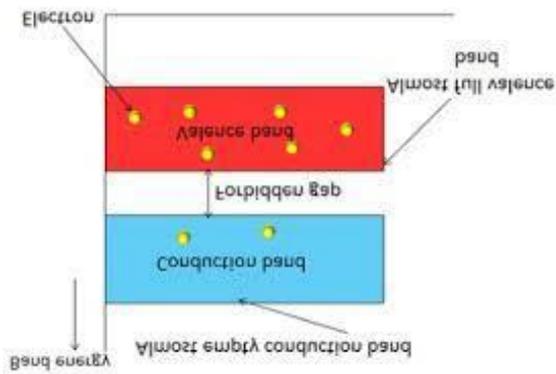
## Semi conductors:

- The electronic conductors which exhibit electrical conductivity in the range of  $10^{-6}$  –  $10^4$   $\text{ohm}^{-1} \text{cm}^{-1}$  are called as semi conductors.
- Semi conductors exhibit conductivity due to motion of interstitial electrons or holes or both.

Eg: Si, Ge, Gallium arsenide ---

- The solid crystals in which very small energy gap ( $E_g = \text{small}$ ) between filled valence band and the empty conduction band are called as semi conductors.
- Therefore semi conductors exhibit low conductivity due to may jump some electrons from valence band to conduction band under an applied electrical field because forbidden gap or energy gap between the valence band and conduction band is very small.
- Electrical conductivity of semi conductors increases due to by the addition of dopants.

- Electrical conductivity of semi conductors increases with rise in temperature.



❖ Based on the energy gap between the valence band and conduction band Semi-conductors are further classified into two types that is

A) Intrinsic semi-conductors.

B) Extrinsic semi-conductors.

A) Intrinsic semi-conductors: The energy gap between valency band and conduction band is a narrow size that type of semiconductors is called as intrinsic semi-conductors.

B) Extrinsic semi-conductors: The energy gap between valency band and conduction band is big size that types of semi-conductors are called as extrinsic semi-conductors. These are further divided into two types based on usage of dopants through doping process that is

1) p-type semi conductors 2) n- type semi conductors

**Doping:** The process in which to enhance the conductivity in semi conductors by adding dopants to the semi conductors is called as doping.

**Dopants:** The chemical substances which are enhance the conductivity in semi conductors by doping process that substances are called as dopants.

Eg: 13th group elements are act as p-dopants (Electron Deficient) and 15th group elements are act as n-dopants(electron rich).

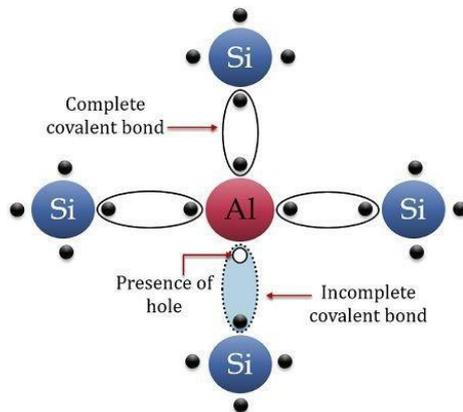
1) P- Type Semi conductors (Electron Deficient):

❖ In these semi-conductors the Si or Ge is doped with B or Al which contains only 3 valence electrons.

❖ Where as in case of Si or Ge, It has 4 valence electrons and formation of 4 bonds with neighboring atoms.

❖ In case of P-Type semi-conductor one electron is deficient to form a bond between Si and B, hence a hole will be generated.

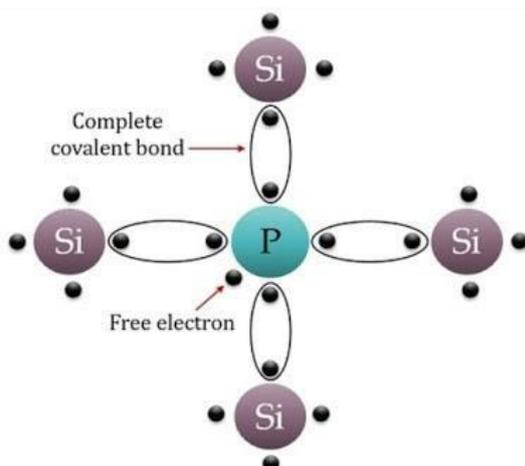
❖ The electron hole is replaced by surrounding Si valence electron, these Si atoms gets hole hence the hole moves through the crystal and this positive charge gives electrical conductivity.



## 2) n-Type semi conductors (electron rich):

- ❖ Silicon or Germanium has 4 valence electrons.
- ❖ In Si and Ge crystal lattice each atom forms four covalent bonds between Si or Ge atoms.
- ❖ If Si or Ge crystal is doped with P or As which contains 5 valence electrons. From these 5 valence electrons occupy some of the lattice sites of Silicon or Ge.
- ❖ Among these 5 valence electrons, 4 valence electrons forms bond between the phosphorus and surrounding Si or Ge atom.
- ❖ The remaining one electron is not used in bonding, hence the non-bonding electron is delocalized in the crystal lattice.
- ❖ The delocalized electron increases the conductivity of doped Si or Ge. Therefore the doped Si or Ge with electron rich impurity is called as electron rich semi-conductors.

Diagrams for Conductors, semiconductors and insulators



## **SUPERCONDUCTORS**

❖ **Conductor:** The materials or substances that allow electricity to flow through them easily that material is called as conductor. Examples of conductor: i. Copper ii. Gold iii. Iron iv. Graphite v. Steel vi. Aluminum Vii. The human body and the earth are good conductors of electricity

❖ **Conductivity:** The ability of a material to allow an electric current through it is called Conductivity.

❖ The history of superconductivity began with Dutch physicist Heike Kamerlingh Onnes's discovery of superconductivity in mercury in 1911.

❖ Superconductivity is a phenomenon displayed by some materials when they are cooled below a certain temperature, known as the superconducting critical temperature,  $T_c$ .

### **Super conductors:**

A superconductor is a material that exhibits zero electrical resistance i.e. there is no opposition for the flow of electrical current.

❖ The main difference between a conductor and superconductor is that a superconductor has zero electrical resistance while conductors have some finite resistance. The superconductor is actually a special type of conductor that achieves superconductivity only when its temperature is brought down below critical temperature.

### **Superconductivity:**

The phenomenon of achieving zero resistivity or infinite conductivity at low temperature is known as superconductivity

➤ When lead, mercury and certain compounds are cooled to extremely cold temperatures, they become superconductors. They stop showing any electrical resistance and they expel their magnetic fields, which makes them ideal for conducting electricity.

➤ The resistance causes loss of energy in the form of heat but since there is no resistance. So there is any loss of energy inside a superconductor.

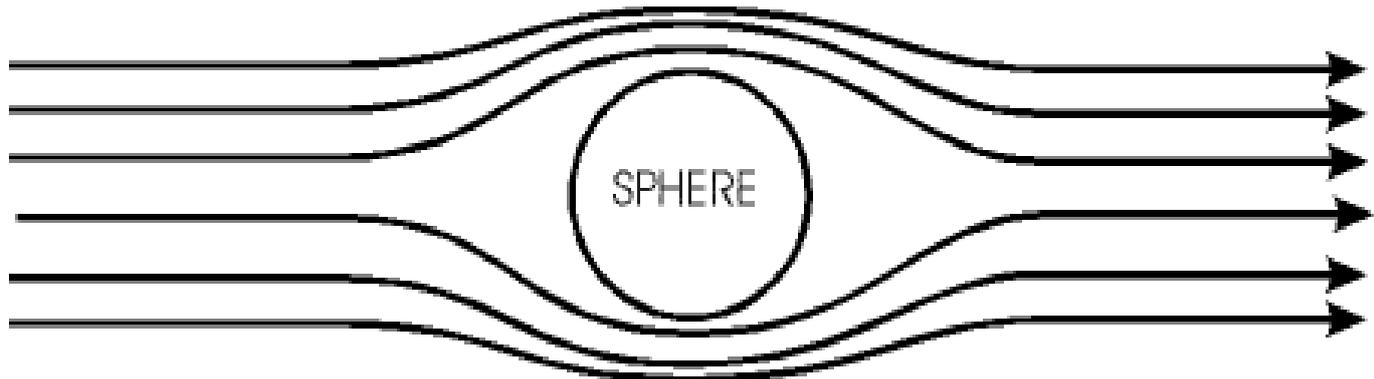
➤ The resistance is directly proportional to the temperature. But unlike normal conductors whose resistance decreases slowly, the resistance of superconductors falls to zero below a fixed temperature known as critical temperature.

❖ Below  $T_c$ , superconducting materials exhibit two characteristic properties i.e, A. Zero electrical resistance B. Perfect diamagnetism (the Meissner effect) A. Zero electrical resistance: No energy is lost as heat as the material conducts electricity is called zero

electrical resistance. B. Perfect diamagnetism (the Meissner effect): Material exhibit perfect diamagnetism means that the superconducting material will exclude a magnetic field - this is known as the Meissner effect and can be used to display extraordinary physical effects.

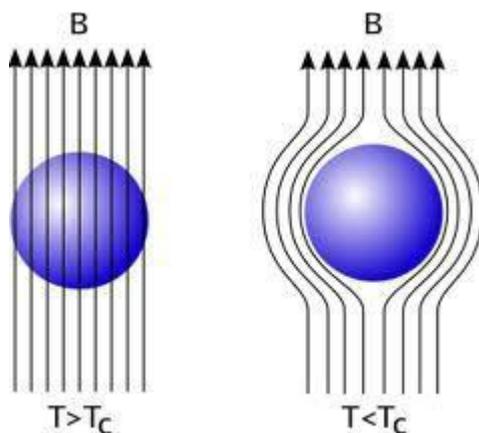
### The meissner Effect:

When a superconductor is cooled under the critical temperature, then it doesn't permit the magnetic field to go through in it. This occurrence in superconductors is known as the Meissner effect.



$$B = \mu_0(H + M)$$

❖ Where B is the magnetic flux density,  $\mu_0$  is the magnetic permeability, H is the external applied magnetic field and M is the magnetization produced inside the specimen.



### Properties:

❖ **Critical temperature/Transition temperature:** The temperature below which the material changes from conductors to superconductors is called critical temperature or transition temperature. The transition from conductors to superconductors is sudden and complete.

❖ **Zero Electric Resistance/Infinite Conductivity:** In the superconducting state, the material has zero resistance. When the temperature of the material is reduced below the critical temperature, its resistance suddenly reduces to zero. Mercury is an example of a superconductor that shows zero resistance below 4 kelvin.

❖ **Expulsion of Magnetic Field:** Below the critical temperature, superconductors do not allow the magnetic field to penetrate inside it. This phenomenon is called Meissner Effect.

❖ **Critical Magnetic Field:** The certain value of the magnetic field beyond which the superconductors return to conducting state is called the critical magnetic field. The value of the critical magnetic field is inversely proportional to the temperature. As the temperature increases, the value of the critical magnetic field decreases

### ❖ **Applications:**

- Superconductors mainly used for creating powerful electromagnets in MRI scanners.
- Superconductor is used to transmit power for long distances.
- Superconductor is used in memory or storage elements.
- Superconductors are used in electric motors and generators.
- These are used in, transportation, computing, medical, power transmission, etc.
- Ore separation can be done efficiently by using superconducting magnets.
- Superconductors used in rail gun (Type of weapon that uses powerful electromagnets to accelerate projectiles to very high speeds) and coil gun magnets (accelerate projectiles to very high speeds).
- Superconductors used in RF and microwave filters (Eg: For mobile phone base stations, as well as military ultrasensitive/selective receivers).
- Superconductors can be used to transmit electrical power over very long distances without any power loss or any voltage gap.
- Superconductor generator has the benefits small size and low energy consumption than the conventional generators.
- Superconducting coils are used in NMR (Nuclear Magnetic Resonance) imaging equipments which are used in hospitals for scanning the whole body diagnoses medical problems.

# **SUPER CAPACITORS**

**Capacitor:** The capacitor is a two terminal electrical device that can store energy in **the** form of an electric charge.

It consists of two electric conductors that are separated by a distance. The space between the conductors may be filled by vacuum (or) with an insulating material known as a dielectric.

## **SUPER CAPACITORS**

Super capacitor is an electrochemical capacitor that has high energy density and better performance efficiency as compared to the common capacitor

It stores and releases energy by reversible desorption/absorption of ions at the electrode – electrolyte interface.

Super capacitors have high capacitance over a lower limit of cell voltage.

## **TYPES OF SUPERCAPACITORS**

On the basis of their charge storage mechanism these are classified into three types

1. Electrostatic double layer capacitor
2. Pseudo capacitor
3. Hybrid capacitor

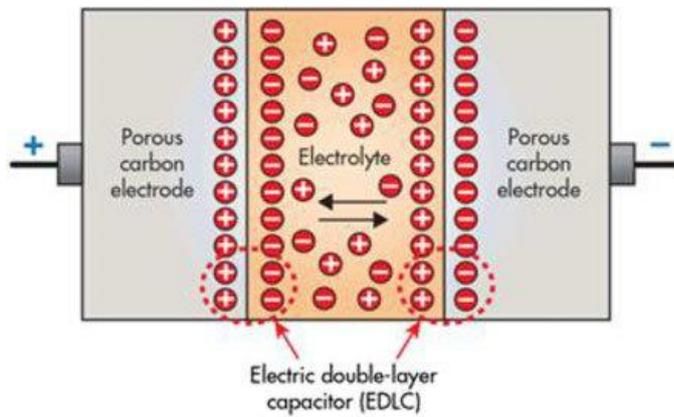
### **1. Electrostatic double layer capacitor**

This type of capacitor works on the charge storage mechanism where charge is physically stored on the surface of the electrodes without causing any irreversible chemical reactions via the formation of an electrical double layer.

Carbon based electrodes are used in this super capacitors which are separated by dielectric substance that act as an insulator and possesses electrical properties that affect the performance of the super capacitor.

Charges are electrostatically stored in super capacitors. An electric field is generated at each electrolyte at each electrode as soon as the voltage is applied across the terminals which leads to the polarization of the electrolyte

As a result of which ions diffuse through the dielectric to the porous electrodes of opposite charges. In such a way the formation of an electric double layer takes place at each electrode. This results in the increased surface area of each electrode and decreased distance between the electrodes.

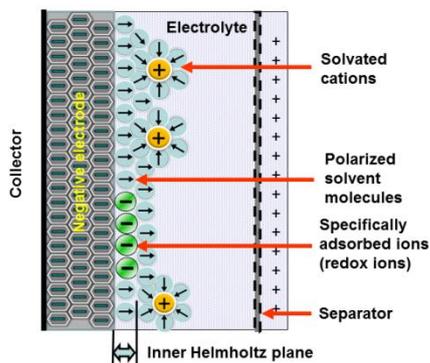


## PSUEDO CAPACITOR:-

Pseudo capacitor are also called faradaic super capacitors. These devices are electrodes made up of redox active materials such as metal oxides( $MnO_2, RuO_2$ ) and conducting polymers (poly anilines, poly pyrroles, polythiophenes) .

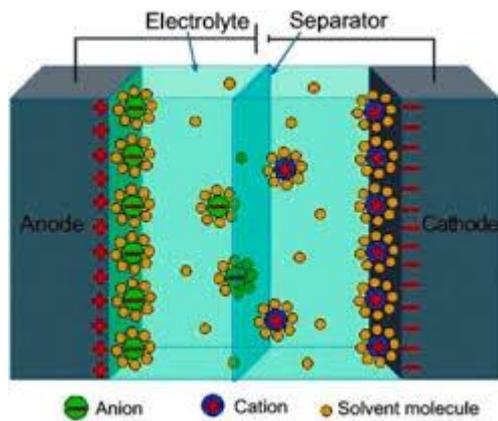
These electrodes store charge through reversible faradic reaction mechanisms near the electrode .(or) at the electrode surface ehere charges are transferred across the metal-electrolyte interface.

Pseudocapacitance with specifically adsorbed ions



## HYBRID CAPACITORS :

These capacitors have adopted both the mechanisms of EDLC and Pseudo capacitors. Hybrid capacitors are composed of electrodes with different characteristics based in chemical as well as electrical mechanisms. As a result at one electrode exhibits electrochemical capacitance. The advantage include higher operating voltage increased capacitance and energy density



## Applications:

- ☐ The super capacitor mainly used in where very fast charging and discharging needed.
- ☐ The super capacitor is used in digital cameras for flashing of light.
- ☐ Waterproof/weatherproof energy storage (e.g. remote wind farms)
- ☐ Military vehicles (starter engines for tanks, submarines, compact power for missiles)
- ☐ Power source for Laptops and flash in cameras.
- ☐ Backup power systems in missiles.
- ☐ Super capacitors are used to power emergency systems in aircrafts.
- ☐ Super capacitors provide burst power in stop and go vehicles( In buses, trains)
- ☐ Super capacitors are used in startup mechanism for automobiles.
- ☐ Super capacitors make a great tool for regenerative breaking in vehicles due to very charging and discharging.
- ☐ Super capacitors are used in industrials lasers and medical equipment.
- ☐ Super capacitors provide backup or emergency shutdown power to low-power equipments. Eg: ups
- ☐ They are also used in many portable gadgets and devices.

## 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 nanotubes 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  $\mu\text{m}$ . 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.

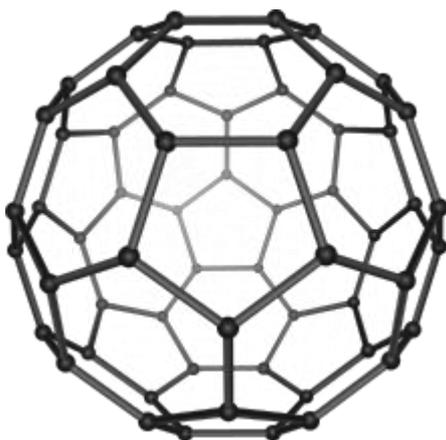
**Zig – zag structures:** The lines of carbon bonds are down the centre.

### 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.

## Fullerenes

Fullerenes are carbon molecules with unique, cage-like structures, including spherical, cylindrical, and ellipsoidal forms. Discovered in 1985, the most well-known fullerene is  $\text{C}_{60}$ , or buckyball, which resembles a soccer ball made of 60 carbon atoms. Other forms include carbon nanotubes and graphene. Fullerenes are notable for their strength, electrical conductivity, and stability, making them valuable in materials science, nanotechnology, and medicine.



## preparation of fullerenes

**Arc Discharge Method:** It involves creating an electric arc between two carbon electrodes in a vacuum. The high temperature of the arc vaporizes the carbon, and as the vapor cools, fullerenes such as  $\text{C}_{60}$  and  $\text{C}_{70}$  condense and form.

## properties of fullerenes

1. Like graphite and diamond, Fullerenes are closed cage like structure or looks like soccer ball.
2. It consists of number of five membered rings and six membered rings.
3. It consists of 12 pentagons and 20 hexagons
4. The bonds in  $C_{60}$  are two kinds. The bond length in a pentagon is  $1.45\text{\AA}$  units and the bond length between the pentagon is  $1.40\text{\AA}$  units.
5. At room temperature the solubility of  $C_{60}$  is  $2.8\text{Mg/lit}$  in Toulene.
6. As the size of  $C_{60}$  increases the heat of sublimation also increases.
7. Fullerenes are ready to reduce and it acts as good oxidizing agent.
8. It is unstable at high temperature.
9. It is poor conductor of electricity, but when it reduces it conducts electricity.

## Applications of fullerenes:

**Drug Delivery:** Fullerenes can be used to deliver drugs to specific cells or tissues due to their ability to encapsulate other molecules. Their size allows them to penetrate biological membranes easily.

☒ **Cancer Therapy:** Modified fullerenes can be used in photodynamic therapy to target and destroy cancer cells.

☒ **Solar Cells:** Fullerenes are used in organic photovoltaic cells (solar cells) due to their ability to accept electrons, which improves the efficiency of these devices.

☒ **Transistors:** Fullerenes can be used to create organic field-effect transistors (OFETs), which are components of flexible electronics.

☒ **Superconductors:** Certain fullerene-based materials exhibit superconductivity at relatively high temperatures, making them useful in various electronic applications.

☒ **Pollution Control:** Fullerenes can be used to remove pollutants from the environment due to their ability to interact with various contaminants.

**Water Purification:** They can be used in water purification systems to remove toxins and pathogens.

☒ **Chemical Sensors:** Fullerenes can be used to develop sensitive chemical sensors due to their ability to interact with a wide range of substances.

☒ **Biosensors:** They can be used in biosensors for detecting biological molecules, providing high sensitivity and specificity.

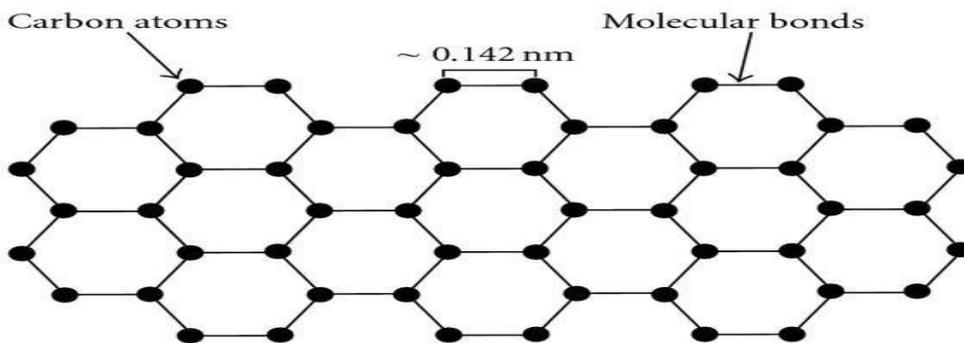
## Graphenes:

Graphene is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice.

Each carbon atom is bonded to three other carbon atoms through  $sp^2$  hybridization, forming strong covalent sigma bonds.

The remaining p orbital forms pi bonds with adjacent carbon atoms, creating a delocalized electron cloud above and below the plane.

The distance between carbon atoms is about  $1.42 \text{ \AA}$ , and the material is only one atom thick, approximately 0.34 nanometers.



## PREPARATION OF GRAPHENE

1. **Mechanical Exfoliation** : This involves peeling off layers from graphite using adhesive tape.
2. **Chemical Vapor Deposition (CVD)** : Hydrocarbon gases (like methane) are decomposed at high temperatures on a metal substrate (such as copper), forming a graphene layer.
3. **Liquid-Phase Exfoliation**: Graphite is dispersed in a solvent and exfoliated into graphene sheets using ultrasonication or shear mixing.

## PROPERTIES OF GRAPHENE

1. **Strength**: Graphene is one of the strongest known materials, with a tensile strength of about 130 GPa, approximately 200 times stronger than steel.
2. **Elasticity**: It can be stretched by up to 20% of its initial length without breaking.
3. **Flexibility**: Graphene is highly flexible and can be bent without damage.
4. **Conductivity**: Graphene exhibits exceptional electrical conductivity, with electron mobility at room temperature reaching up to  $200,000 \text{ cm}^2/\text{Vs}$ .

- 5. Thermal Conductivity:** Graphene has a thermal conductivity of about 5,000 W/mK, making it an excellent heat conductor.
- 6. Stability:** It remains thermally stable up to temperatures of around 2600°C in a vacuum.
- 7. Transparency:** Graphene is nearly transparent, absorbing only about 2.3% of visible light. This makes it suitable for use in transparent conductive films and optoelectronic devices.

## **APPLICATIONS OF GRAPHENE:**

- 1. Batteries:** Graphene can enhance the performance of lithium-ion batteries, providing faster charging times, higher capacity, and longer lifespan.
- 2. Solar Cells:** Graphene's transparency and conductivity improve the efficiency and flexibility of solar cells, potentially leading to more efficient and cheaper photovoltaic devices.
- 3. Drug Delivery:** Graphene can be used to deliver drugs directly to targeted cells or tissues, improving the efficacy and reducing side effects.
- 4. Medical Imaging:** Graphene-based contrast agents enhance the quality of MRI and other imaging techniques.
- 5. Biosensors:** Graphene's high sensitivity allows for the detection of biomolecules at very low concentrations, aiding in early diagnosis of diseases.
- 6. Desalination:** Graphene oxide membranes can filter out salts and other impurities from water, providing an efficient method for desalination.
- 7. Water Filtration:** Graphene-based filters can remove contaminants, bacteria, and viruses from water, improving water purification processes.
- 8. Lightweight Materials:** Graphene-reinforced composites are lightweight yet strong, making them ideal for aerospace and automotive applications where reducing weight is crucial.

## UNIT-III

### Electrochemistry and Applications

#### Electro chemistry: -

Electrochemistry is a branch of science that deals with conversion of chemical energy into electrical energy and vice versa.

#### Electrolyte: -

A substance, which decomposes as a result of passing of electric current is called 'Electrolyte' and the phenomena of decomposition of electrolyte through passage of electricity is called 'electrolysis'.

#### Concepts of electrolysis: -

- (1). A conductor used to electrical contact as a non-metallic part of a circuit.
- (2). An element in a semi conductor device (such as a transistor) That emits or collects electrons or holes containing their movement.

Electrode are:-(1) Cathode (+)

(2) Anode (-)

#### Reference electrodes: -

The electrodes of standard potential with which one can compare the potentials of another electrodes of interest is called reference electrode. The standard hydrogen electrode is used as reference electrode for determined single electrode potential whose potential arbitrarily taken as zero.

#### **ELECTROCHEMICAL CELL:**

An electrochemical cell is a device in which redox reaction is utilised to get electrochemical energy. This type of cell is commonly known as voltaic or galvanic cell. The electrode where oxidation occurs is called anode, while the electrode where reduction occurs is called cathode. In redox chemical reaction, oxidation can take place only if reduction can also take place at the sometime.

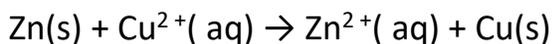
EXAMPLE: -

Zn-  $\text{CuSO}_4$  solution in a beaker. Oxidation of zinc metal by  $\text{Cu}^{2+}$  ions. If a zinc rod is placed in a solution of  $\text{CuSO}_4$  .The following observation will be made.

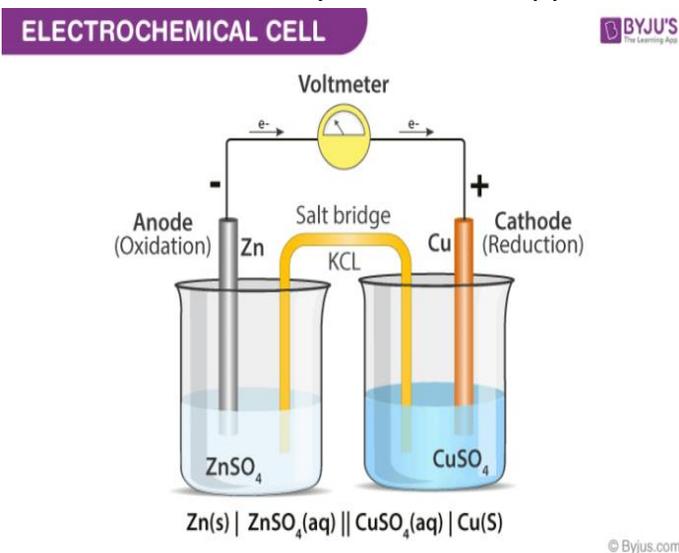
$\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  ( oxidation half reaction) -----(1) At the same time starts to precipitate out from the solution.



The reaction 1 and 2 are called half reactions. The overall reaction is a redox reaction and obtained by adding two half reactions.



Zn metal can be oxidised by  $\text{Cu}^{2+}$  ions. Copper metal cannot be oxidised by  $\text{Zn}^{2+}$  ions.



**NERNST EQUATION:** The Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient. Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.

The Nernst **equation is often used to calculate the cell potential** of an electrochemical cell at any given temperature, pressure, and reactant concentration. The equation was introduced by a German chemist Walther Hermann Nernst.

### Expression of Nernst Equation

Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (**standard reduction potentials**) of 298K and one molar or one atmospheric pressure.

### Nernst Equation for Single Electrode Potential

$\Delta G = \Delta G^\circ + RT \ln Q$

where:

- $\Delta G$  is the Gibbs free energy change.
- $\Delta G^\circ$  standard Gibbs free energy change.

$R$  is the gas constant (8.314 J/mol·K).

- $T$  is the temperature in Kelvin.
- $Q$  is the reaction quotient.

$$\Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

$n$  is the number of moles of electrons transferred.

- $F$  is the Faraday constant (approximately 96485 C/mol).
- $E$  is the cell potential.
- $E^\circ$  is the standard cell potential.

Substitute the expressions for  $\Delta G$  and  $\Delta G^\circ$  into the Gibbs free energy equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$-nFE + nFE^\circ = RT \ln Q$$

$$nF(E^\circ - E) = RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

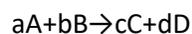
$Q = \frac{[\text{reactants}]}{[\text{products}]}$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{0.0592}{n} \log Q$$



Ans.



we start by considering the relationship between the Gibbs free energy change ( $\Delta G$ ) and the cell potential ( $E$ ).

$$\Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

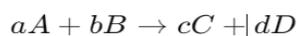
- where:
  - $R$  is the universal gas constant (8.314 J/mol).
  - $T$  is the temperature in Kelvin.
  - $Q$  is the reaction quotient.

Substituting  $\Delta G = -nFE$  and  $\Delta G^\circ = -nFE^\circ$  into the equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$



The reaction quotient  $Q$  is:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where  $[C]$ ,  $[D]$ ,  $[A]$ , and  $[B]$  are the concentrations (or activities) of the reactants and products.

$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

### Applications of Nernst equations

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

### Electrochemistry problems

1. Calculate the standard emf of the cell;  $\text{cd(s)}/\text{cd}^{+2}(\text{aq})//\text{cu}^{+2}(\text{aq})/\text{cu}$  and determine the cell reaction ( $E^\circ_{\text{cu}^{+2}/\text{cu}} = 0.34$ ;  $E^\circ_{\text{cd}^{+2}/\text{cd}} = -0.40$ )

**Sol.**

$$E^\circ_{\text{cell}} = E^\circ_{\text{cell}}(\text{Right}) - E^\circ_{\text{cell}}(\text{Left})$$

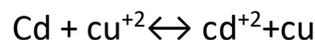
$$= E^\circ_{\text{cu}^{+2}/\text{cu}} - E^\circ_{\text{cd}^{+2}/\text{cd}}$$

$$= 0.34 - (-0.40)$$

$$= 0.74 \text{ volts}$$

**Cell reaction:**  $\text{cd} \leftrightarrow \text{cd}^{+2} + 2\text{e}^-$  (oxidation)

$\text{cu}^{+2} + 2\text{e}^- \rightarrow \text{cu}$  (Reduction)



2. Calculate the emf of the cell represented the cell as as  $\text{Zn}/\text{Zn}^{+2}//\text{H}^+/\text{H}_2$  at  $[E_{\text{zn}^{+2}}(\text{Zn} = -0.7618\text{v})$

**Sol:**

$$E^\circ_{\text{cell}} = E^\circ_{\text{Right}} - E^\circ_{\text{Left}}$$

$$= 0 - (-0.7618\text{V})$$

$$=+0.7618V$$

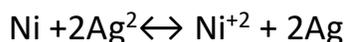
3. Calculate the emf of the cell Cd/Cd<sup>2+</sup>//Cu<sup>2+</sup>/Cu at 25<sup>o</sup>c. The standard reduction potential of cadmium and copper electrodes are -0.40 and 0.34volts respectively

**Sol:**

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{Right}} - E^0_{\text{Left}} \\ &= 0.34 - (-0.40) \\ &= 0.34 + 0.40 \\ &= 0.74\text{volt} \end{aligned}$$

4. Calculate the standard emf of Ni-Ag cell whose E<sup>o</sup><sub>Ni</sub> and E<sup>o</sup><sub>Ag</sub> are -0.25 and 0.83 v Also write cell representation.

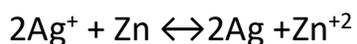
**Sol:**



$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{Ag}} - E^0_{\text{Ni}} \\ &= 0.83 - (-0.25) \\ &= 1.08\text{v} \end{aligned}$$

5. Calculate the emf of the Zinc=silver all at 25<sup>o</sup>c when [Zn<sup>2+</sup>]=0.10 M & [Ag<sup>+</sup>]=10.0M [E<sup>o</sup><sub>cell</sub> at 25<sup>o</sup>c =1.56v]

**Sol.**



$$E^0_{\text{cell}} = E^0_{\text{cell}} + \frac{RT}{nf} \ln \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$$

$$1.56 + \frac{0.0592}{2} \log \frac{[10]^2}{[0.1]}$$

$$= 1.56 + \frac{0.0592}{2} \log 100 \cdot 10$$

$$= 1.56 + 0.0888$$

$$= 1.6488 \text{ volts}$$

6. The emf of a cell, mg/mg<sup>2+</sup>(0.01//cu<sup>2+</sup>/cu is found to 2.78 volts at 300K. The standard electrode potential of mg electrode is -2.371v. what is electrode potential of copper electrode

$$\begin{aligned} E_{\text{mg}} &= E^0_{\text{mg}^{2+}/\text{mg}} + \frac{0.0591}{n} \log [\text{mg}^{2+}] \\ &= -2.37 + \frac{0.0591}{2} \log (0.01) \\ &= -2.37 - 0.0591 \\ &= -2.4290\text{v} \end{aligned}$$

$$E_{\text{cell}} = E_{\text{cu}} - E_{\text{mg}}$$

$$2.78 = E_{\text{cu}} - (-2.4290)$$

$$E_{\text{cu}} = 2.78 + 2.4290$$

$$E_{\text{cu}} = +0.3509\text{V}$$

7. Calculate the electrode potential of Zinc electrode dipped in 0.1M ZnSo<sub>4</sub> solution at 25<sup>0</sup>c [ E<sup>0</sup> Zn<sup>+2</sup>/Zn = -0.763v]

**sol:**

$$\begin{aligned} E &= E^0 + \frac{0.0591}{n} \log(0.1) \\ &= -0.763 + \frac{0.0591}{2} \log(0.1) \\ &= -0.763 - 0.02955 \\ &= -0.79255\text{v} \end{aligned}$$

8. Find the oxidation potential of Zn/Zn<sup>+2</sup> = 0.2M electrode at 25<sup>0</sup>c standard reduction potential of Zn/Zn<sup>+2</sup> is 0.763v

**Sol:**

$$\begin{aligned} [\text{Zn}^{+2}] &= 0.2\text{M} \\ E^0_{\text{Zn}/\text{Zn}^{+2}} &= 0.763 \\ E &= E^0 - \frac{0.0591}{n} \log [\text{Zn}^{+2}] \\ &= 0.763 - \frac{0.0591}{2} \log [0.2] \\ &= 0.763 - (0.02955 - 0.69897) \\ &= 0.763 + 0.02065 \\ &= 0.78365\text{v} \end{aligned}$$

### **Potentiometric Titrations:**

A titration in which the end for equivalence point is estimated with the help of measurement of the potentials of the reaction mixture is called a potentiometric titration.

Without using indicator, we can determine the end point.

### **Potentiometry Principle:**

When the pair of electrodes are placed in the sample solution or analyte it shows the potential difference between two electrodes by addition of the titrant or by the change in the concentration of ions.

Potentiometric titration is of three types.

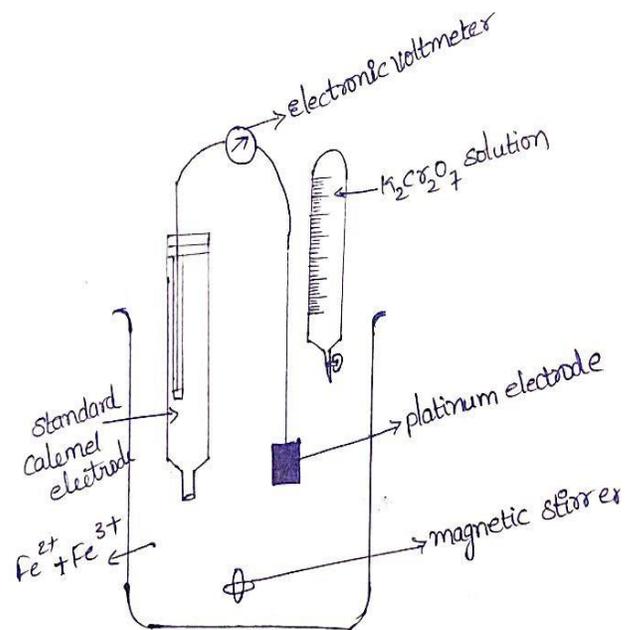
ii) Redox titrations

3) Precipitation titration

### Redox titrations:

Potentiometric titration was first used for redox titration by Crotono. He titrated alkali ions with  $KMnO_4$  using a platinum electrode and calomel electrode.

In this titration, it will be observed that at the end point, there is a sharp increase in PH for the addition for a very small quantity  $K_2Cr_2O_7$ . The variation of  $P^H$  value can be measured potentiometrically by immersing a bright platinum working electrodes. The emf of the electrode is measured by activity ration of the substance being oxidized or reduced.



### Calibration:

Let us consider the titration of ferrous ammonium sulphate against potassium dichromate.

A known volume of ferrous salt solution is placed in the beaker and transferred to 100 ml of distilled water and 10 ml of dilute  $H_2SO_4$ . Then a bright platinum electrode is dipped in the solution and connected with a saturated Calomel reference electrode with the help of a salt bridge.

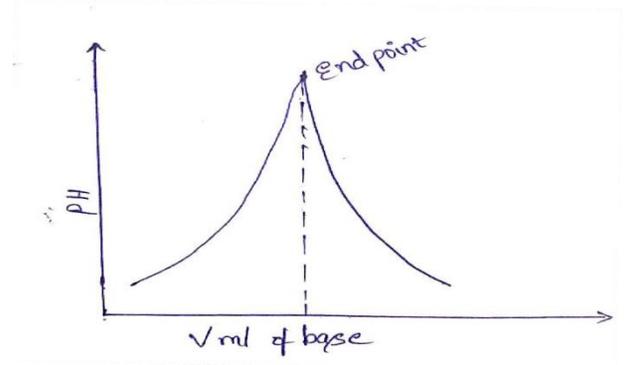
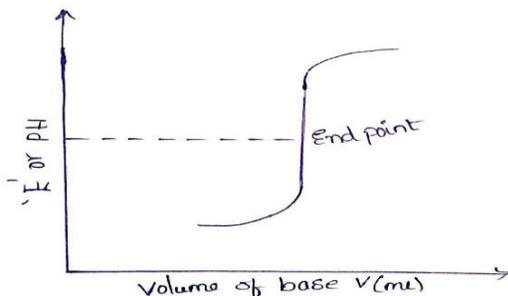
The emf of the cell is observed for each addition of  $K_2Cr_2O_7$  solution from the burette is noted. The observed value of  $E(\text{emf})$  is then plotted against 'V' and the steepest portion of the curve indicates its equivalence point. If there is difficulty in finding the end point, in such cases, for obtaining a sharp end point, plot  $\delta E/\delta v$  instead of 'E' against the volume of base. At the volume corresponding to the equivalence point of the titration, the differential curve shows a maximum

### Applications:

It is used in clinical chemistry for analysis of metals.

It is used for analysis of cyanide, ammonia etc. in water or wastewater.

It is used in agriculture for detection of different elements in soils, fertilizers etc.



It is used in detergent manufacturing, food processing etc.

Conductivity of electrolytes: -

(1) Specific conductance: -

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

$R \propto l/A$   $R$ =resistance in ohms.

$R = \frac{\rho l}{A}$   $\rho$ = specific resistance.

$l$ =length in cm.

$A$ =Area of cross section.

If  $l=1$  and  $A=1 \text{ cm}^2$ .

Then  $R=\rho$

Resistivity of specific resistance of a conductor the resistance between two opposite faces of a centimeter cube.

Units --ohm-cm.

(2) Specific conductivity:-

It is reciprocal of specific resistance an electrolytic solution.

$$k = 1/\rho = l/AR$$

$$\text{Units} = \text{ohm}^{-1} \text{ cm}^{-1}$$

(3) Equivalent conductivity:-

The conductivity of all the ions present in equivalent of the electrolyte in solution. 1 equivalent of electrolyte is contained in then

$$\begin{aligned}\lambda_{\text{eq}} &= v \times \text{specific conductance} \\ &= v \times k\end{aligned}$$

If the normality of electrolytic solution is

$$V = (1/N)L = 1000/N \text{ ml}$$

$$\lambda_{\text{eq}} = \frac{1000K}{N}$$

$$\text{Units} = \text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

(4). Molar conductivity: -

The conductance of all ions presents in one mole of electrolyte in the solution.

$$\lambda_M = \frac{1000K}{M}$$

$$\text{Units} = \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Classification of electrolytes: -

Electrodes like NaOH, NaCl, HCl, KCl have value of conductance even at low dilution and there is no rapid change or increasing in their equivalent conductance on dilution. Such electrolytes are called as strong electrolytes.

Electrolytes like acetic acid have a low value of equivalent conductance even at higher concentrations and there is rapid increase in the conductance of dilution. Such as weak electrolytes

### Conductometric Titrations:

It is a method of volumetric analysis based on the change in conductance of the solution, at equivalence point during titration. The conductance of an electrolyte mainly depends on

- ▮ No. of free ions in the solution
- ▮ Charge on the free ions
- ▮ Mobility of the ions

During the course of titration, the number of free ions in the solution changes and also the identity of the ions also changes. As a result, conductance of the solution also changes.

Conductometric titrations are four types.

- i) Acid-base titrations
- ii) Redox titrations
- iii) Precipitation titrations
- iv) Complex titrations

### **i) Acid –Base titration:**

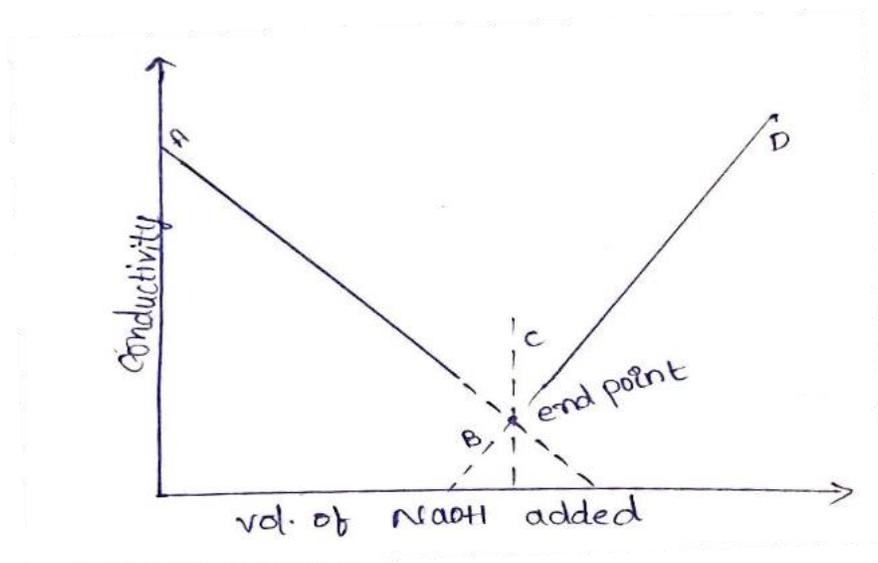
#### **a) Strong acid with strong base:**



The acid is taken into the conductivity vessel and the alkali in the burette. Before base is added, the conductivity of acid solution is high due to high mobile hydrogen ions. As alkali is added, the hydrogen ions are replaced by slowly moving sodium ions. This will result in the decrease conductivity rapidly. The solution at neutralization point containing only sodium and chloride ions will have minimum conductivity.

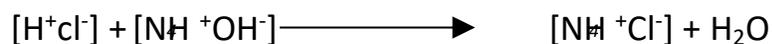
Any subsequent addition of NaOH will cause introduction of fast moving hydroxide ions will result in increase of conductivity on plotting the conductance against the volume of NaOH added, the points will lie on two straight lines AB & CD. The point of intersection

of two lines 'X' gives the end point and will give volume of alkali required for the neutralization.

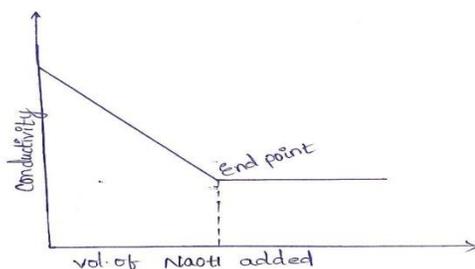


### **b) Strong acid with a weak base:**

Let us consider titration of HCl with  $\text{NH}_4\text{OH}$ . When  $\text{NH}_4\text{OH}$  is added to HCl, the conductivity decreases because of the replacement of the fast-moving  $\text{H}^+$  ions by slow moving  $\text{NH}_4^+$  ions.



The addition of  $\text{NH}_4\text{OH}$  after the end point does not change the conductance because  $\text{NH}_4\text{OH}$ , a weakly ionized electrolyte has a very small conductivity with acid or its salt.

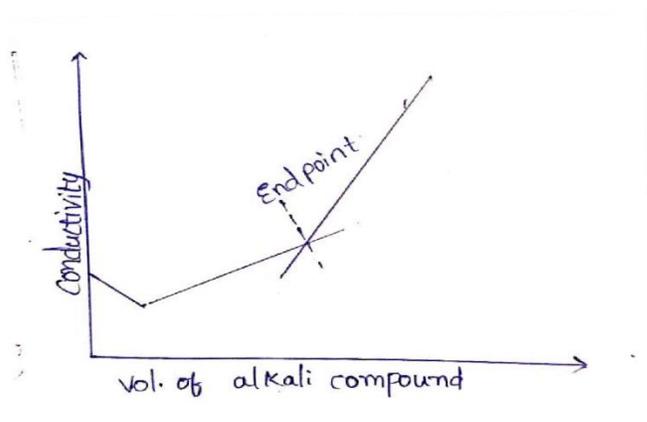


### c) Weak acid with a strong base:

Let us consider the titration of  $\text{CH}_3\text{COOH}$  with a  $\text{NaOH}$ . The conductance of acid will be low on account of its poor dissociation. When a small amount of  $\text{NaOH}$  is added to  $\text{CH}_3\text{COOH}$ , the conductivity decreases initially then increases with the further addition of  $\text{NaOH}$ .

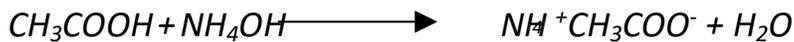


When the neutralization of acid is completed, further addition of alkali produces excess of  $\text{OH}^-$  ions. The conductance of solution therefore begins increasing rapidly.

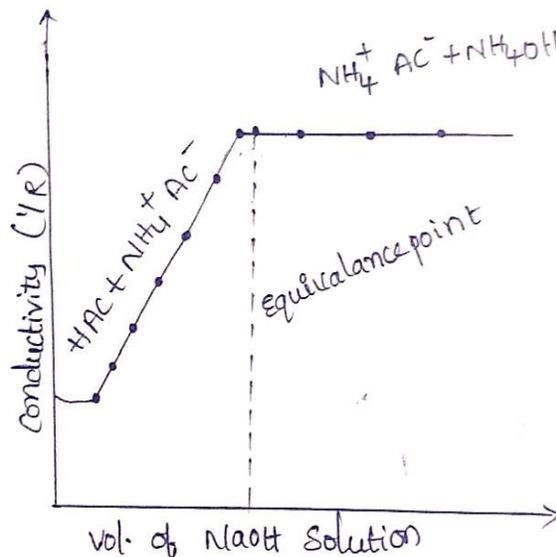


#### d) Weak acid with weak base:

Let us consider the titration of  $\text{CH}_3\text{COOH}$  with  $\text{NH}_4\text{OH}$ , the addition of  $\text{NH}_4\text{OH}$  may cause decrease in conductance in the beginning, because the common ions formed depresses the dissociation of their respective electrolyte.



On further addition of  $\text{NH}_4\text{OH}$ , an increase in the conductivity of the solution results, because the conductance of highly ionized salt exceeds the conductance of the weak acid it replaces. After the neutralization of the acid, further addition of  $\text{NH}_4\text{OH}$  does not cause any change in the conductance.



## Applications:

Check water pollution in rivers and lakes

Alkalinity of fresh water

Salinity of sea water (oceanography)

Deuterium ion concentration in water – deuterium mixture.

Food microbiology – for tracing micro organisms

Tracing antibiotics.

Estimate ash content in sugar juices

Purity of distilled and de – ionized water can determine

Solubility of sparingly soluble salts like AgCl, BaSO<sub>4</sub> can be detected

Determination of atmospheric SO<sub>2</sub>, estimation of vanillin in vanilla flavor.

## **Electro chemical sensors:**

### History: -

The history of electro chemical sensors starts basically with the development of glass electrode by Cremer in 1906.

### Definition: -

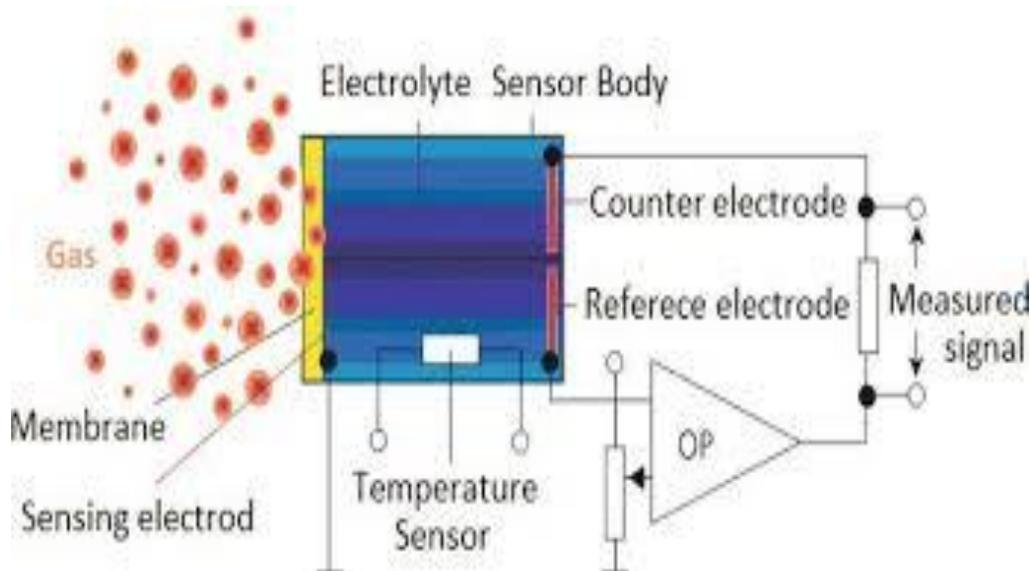
Electro chemical sensors are devices that extract information about sample from measurement of some electrical parameters.

### **SCHEMATIC REPRESENTATION OF ELECTROCHEMICAL SENSORS:**

The electrochemical sensors mainly consist of outer frame containing an electrolyte gel and three electrodes. At the top of the frame it should have gas

permeable membrane. The electrodes are carefully constructed with high sensitivity, long life and allow large surface area. Each cell shall construct with special filter electrodes and electrolytes for high specificity as possible. This will helpful for allowing of larger signal immediate response and even a smaller volume of electrolyte sensor.

### **Block diagram of electro chemical sensors**



### **Classification of electro chemical sensors:**

Electro chemical sensors are devices that extract information about sample from measurement of some electrical parameters.

Sensors are divided into three kinds.they are:

1. Potentiometric sensors(if we measure difference of two potentials)
2. Amperometric sensors(if the parameters of intrest is current)
- 3.Chemiresistors [or]conductometric sensors(if we measure resistance or conductance)

These three kinds of sensors are working based on the basic principle of ohms law stating that the potential difference in a circuit is equal to the product of the current and the resistance i.e  $\text{volt} = \text{ampere} \times \text{ohm}$ . They all have two things in common. First, the measurement must be done with closed electrical circuit, meaning that a hypothetical (test) charge can be passed through the electrical circuit and return to its origin. Second electrical neutrality must be preserved. Example a positive charge (+ve) is added at one place of the closed circuit another positive charge must be taken out (or negative charge added) somewhere else.

### Potentiometric sensors:

Ion-selective electrode is electrode with a potential that is dependent on the concentration of an ionic species in the last solution and is used for electro analysis. Most common ion-selective electrode are often membrane type electrode. Ion-selective electrode the reorganization of hydrogen ion is done by the glass electrode sensing element. Here develops a potential between ISE and reference electrode and the sensor measures the potential differences between these two electrodes. Since the electrode is selective for one ion. The mother of all ions selective electrode is the glass electrode which is selectively sensitive to hydrogen ions.

### Working principle of potentiometric sensors:

The working principle of glass electrode is similar and common to all ISE's.

The glass electrode may be represented as



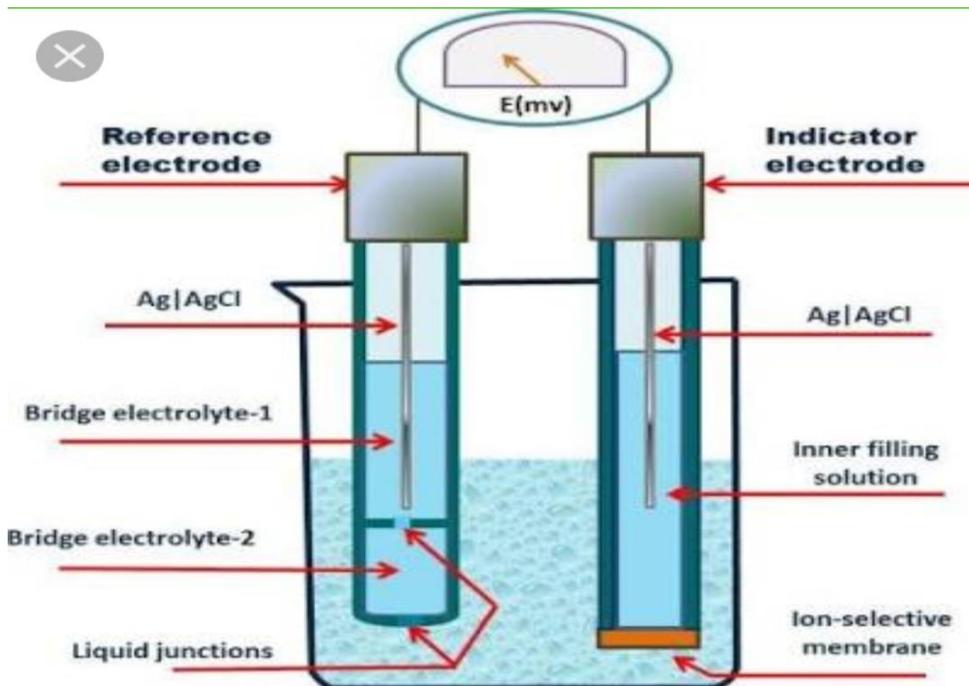
When placed in a solution, the potential of glass electrode depends on like concentration of  $\text{H}^+$  ions in the solution. The potential develop across glass membrane as the result of a concentration differences of  $\text{H}^+$  ions on its two sides of membrane.

Glass, it has been exposed to water adsorbs and develops a very thin film gel like layers at its surface. Hydrogen ion available in the solution likes to be in this gel layers, more so than in its solutions. The charges have been separated

and when that happens an equilibrium potential is formed. This potential is detected by the  $p^H$  sensors.

Eg: For reference electrode are AgCl, calomel and electrodes.

These sensors are used to measure the acidity/ alkalinity of solutions, a parameter protection, agriculture, biology, medicine and many chemical processes.



### Working of potentiometric sensors

#### Glucose – potentiometric sensors:

Glucose is an electrically neutral molecule. Hence, it does not produce signal. The neutral glucose molecule has to be converted into ions, which are then selectively detected. Enzymatic oxidation of glucose to gluconic acid and the subsequent measurement of this liberated hydrogen ions.



When glucose de-hydrogenase (GDH) was applied, the electro chemical reactions using electron transfer mediator in the glucose sensors.



- In presence of glucose and oxidase



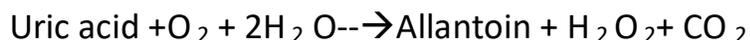
### Amperometric sensors {or} Voltametric sensors

The principle of Amperometric is based on the measurement of the current between the working and counter electrode which is induced by a redox reaction at the working electrode. The signal or response is with respect to the diffusion current, i.e. in Amperometric sensors

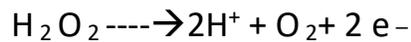
#### Estimation of uric acid:

Uric acid is a major nitrogenous compound in urine, is the product of urine metabolism in the human body and is related to many clinical disorders. One of the major problems in biological determinations of UA comes from electro chemical interferences such as ascorbic acid which has similar oxide potential. There are two methods for the measurement of UA i.e. enzymatic and non-enzymatic.

The enzymatic procedures using uricase



- In presence of uricase



Other enzymatic procedures are based on electron transfer mediators



#### Advantages:

- These can be used for non optically active compounds.
- Many inorganic ions .
- Electro chemically not active anions.

#### Some more applications:

- Detection of  $\text{O}_2$  and toxic gases like  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .
- For checking the race level construction of fertilizers, pesticides, drugs etc.

#### **BATTERY:**

It is a device consisting of 100 galvanic cells connected in series of parallel or both.

#### **PRINCIPLE COMPONENT:**

- A anode oxidation occurs
- A cathode reduction occurs
- An electrolyte, which is ionically conducting
- A separator to separate anode and cathode compartment.

#### **CLASSIFICATION OF BATTERIES:**

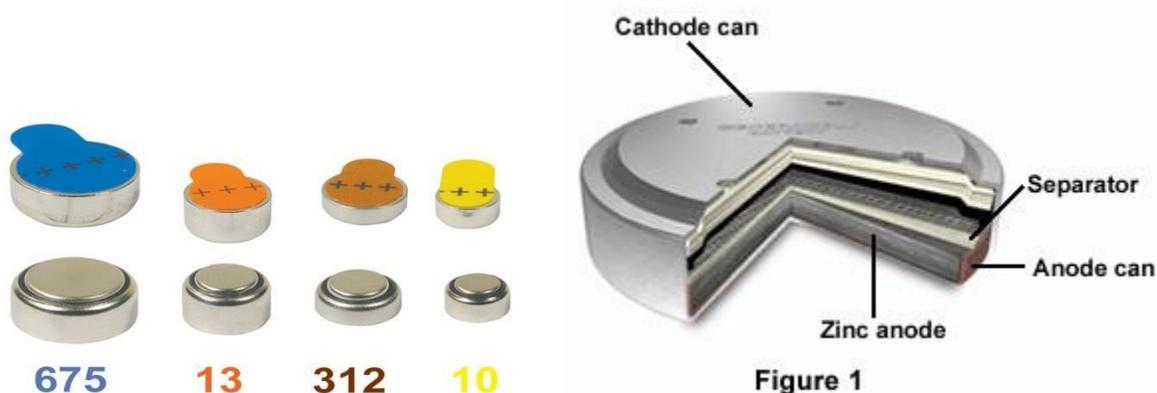
Batteries are of two types:

- Primary Batteries
- Secondary Batteries

## Primary batteries

These are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted. An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. In such cells, a zinc container acts as the anode and a carbon rod acts as the cathode. A powdered mixture of manganese dioxide and carbon is placed around the cathode. The space left in between the container and the rod is filled with a moist paste of ammonium chloride and zinc chloride. The redox reaction that takes place in these cells is:

### 1. ZINC AIR BATTERIS



These are non-rechargeable batteries and zinc-air fuel cells (mechanically rechargeable) are metal-air batteries powered by oxidizing zinc with oxygen from the air. These batteries have high energy densities and are relatively inexpensive to produce. Sizes range from very small button cells for hearing aids.

During discharge, a mass of zinc particles from a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate ( $\text{Zn}(\text{OH})_4^{2-}$ ) releasing electrons to travel to the cathode. The zincate oxidized to zinc oxide and water returns to the electrolyte. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed. The reactions produce a theoretical 1.65v.

Location	HALF CELL REACTION	VOLTAGE
ANODE	$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$	1.25
CATHODE	$1/2 O_2 + H_2O + 2e^- \rightarrow 2 OH^-$	0.4
OVERALL	$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$	1.65

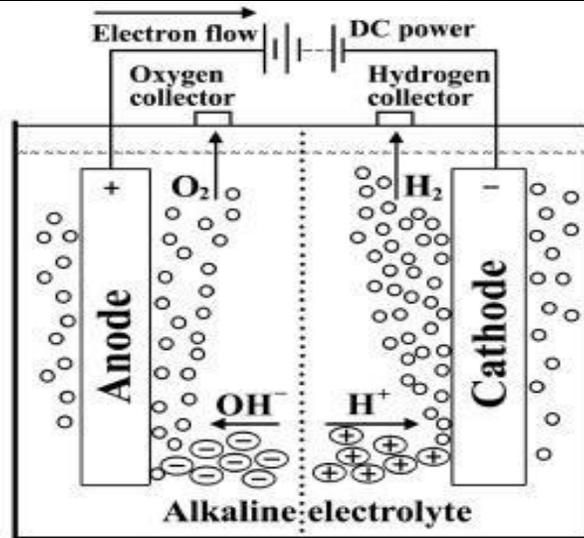


Figure 3. Basic scheme of a water electrolysis system

## Applications

1. Used as power source in hearing aids
2. Used in electronic pagers
3. Used in military radio receivers
4. Used in voice transmitters

## SECONDARY CELL:

These chemical reactions are reversed by passing direct electric current in opposite directions. The cell is designed for repeated use and they are able to be rechargeable.

e.g.: ni-cd storage cell, lithium batteries.

## LITHIUM IONS CELLS: (RECHARGEABLE)

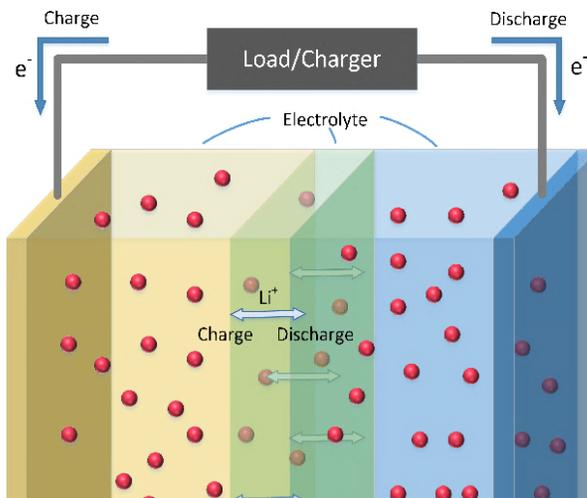
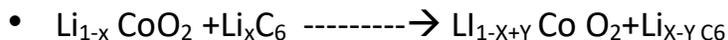
These cells do not contain metallic lithium hence they are called as lithium ion cells.

The cell operation does not actually involve oxidation and reduction. But it was the transport of  $\text{Li}^+$  ions through the electrolyte from one electrode to the other by the transport of electrons through the external circuit to maintain charge balance.

When the cell of  $\text{Li CoO}_2$  and graphite is constructed it is in uncharged state with no  $\text{Li}^+$  ions between the layers of carbon atoms in the graphite when the cell is discharging, lithium ions leave  $\text{Li CoO}_2$  and travel through the electrolyte to the graphite.



When the cell is spontaneous discharging to provide electrical power,  $\text{Li}^+$  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  $\text{Li}^+$  transferring by 'y'. The charge reaction is



## APPLICATIONS:

- Power backups/ ups, Mobile, Laptops, and other commonly used consumer electronic, electric mobility, Energy storage system.

## Fuel cells:

The galvanic cell can only produce. Electrical energy for a limited time because the electrode reactant is eventually depleted.

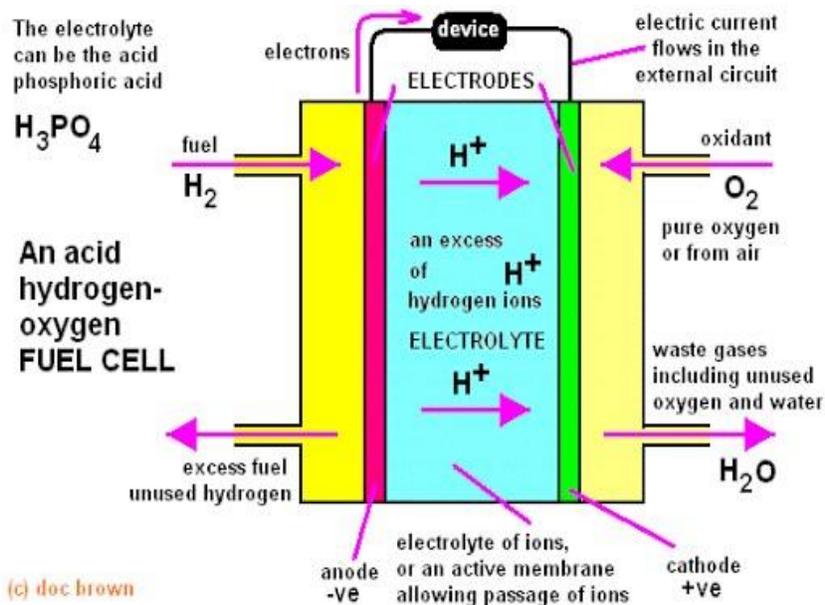
Fuel cells are the electro chemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limits as long as the apply of reactant is maintained. In fuels cells electrical energy is obtained without combination from oxygen and a gas that can be divided.

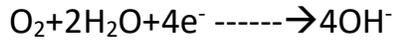
A Fuel cells convert the chemical energy of the fuel directly to electricity.



## Hydrogen-oxygen fuel cell:

It consists of a hot concentrated solution. Of KOH as an electrolyte in the entire compartment which is in contact with two process electrode that contain catalyst to the electrode reactions. Gaseous hydrogen and oxygen under pressure as circuited as to come in contact with the electrode.





The standard EMF of the cell is

$$\begin{aligned} E^0 &= E^0_{\text{RED}} - E^0_{\text{OX}} \\ &= 0.83 + 0.4 \\ &= 1.23\text{V} \end{aligned}$$

Large number of these cells are connected in series to make a battery called fuel cell battery or fuel battery.  $\text{H}_2$ - $\text{O}_2$  fuel cells are an attractive alternative to gasoline because the only product of the reaction is harmless water. These are thermodynamically efficient converting as much as 75% of available energy to useful work.

### Disadvantages:

- Energy cost of generating  $\text{H}_2$  fuel.
- Problem in storing.
- Availability of alternative fuels.

### Application:

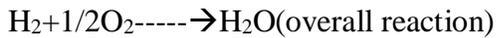
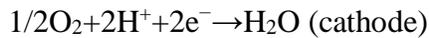
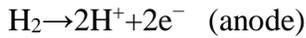
- Used as an energy resource in space vehicles, submarines, military vehicles.
- The weight of fuel battery for 15 days is about 25kg.
- The product of water pores to be a valuable source of fresh water to the astronauts.

Polymer electrolyte membrane fuel cell

A Polymer Electrolyte Membrane (PEM) Fuel Cell, also known as a Proton Exchange Membrane Fuel Cell, is a type of fuel cell that uses a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst.

It consists of anodic and cathodic compartments, which is connected with platinum catalyst which facilitates electrode reactions. These two compartments connected by external circuit and this compartments are separated by polymer electrolyte membrane (nafion).

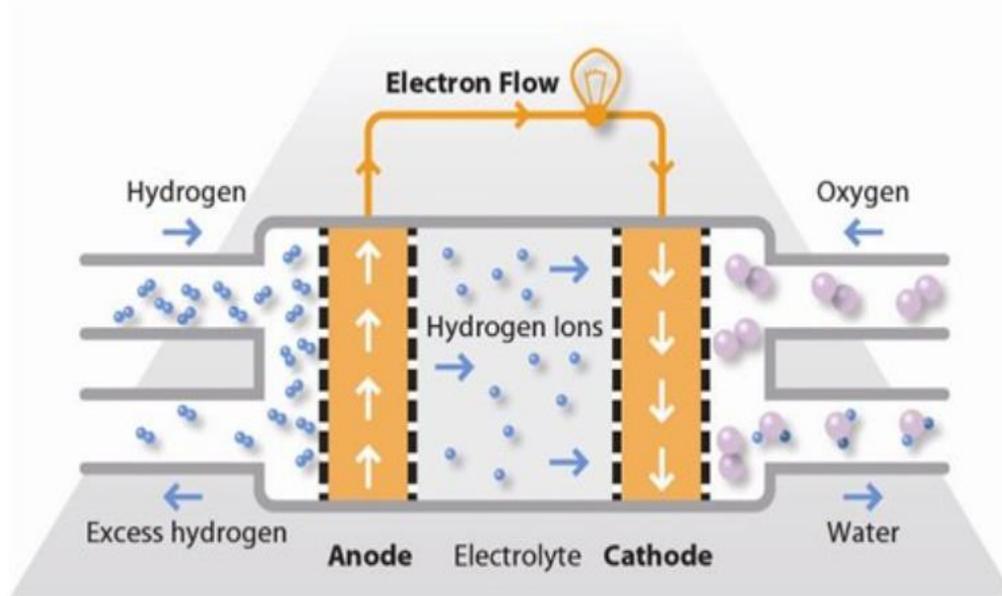
Now, hydrogen gases caused through anodic compartment where as oxygen from air is caused through cathodic compartment.



In anodic compartment hydrogen undergoes oxidation and loses electrons and protons. These electrons travel through external circuit to the cathodic compartment and protons pass through polymer electrolyte membrane to the cathodic compartment, where protons and electrons are gained by oxygen molecule and convert into water.

### Applications:

- Transportation:** Used in fuel cell vehicles (FCVs) like cars, buses, and trains.
- Stationary Power Generation:** Used for backup power and distributed generation systems.
- Portable Power:** Used in portable electronic devices and small-scale applications..



## INTRODUCTION

Matter is composed of many small units called molecules, which are in different sizes and shapes and associated with atoms. Polymers are giants or macro molecules which play a vital role in our daily life and provide the basic needs of our life (food, clothing and shelter).

The word polymer was derived from Greek word 'poly' = 'many' and 'mers' = 'parts /units'.

### Polymer:

- The large number of small molecules are combine together to form a big molecule or high molecular weight compound is called as Polymer.

### Monomer:

The basic repeating units present in a polymer are called monomer.

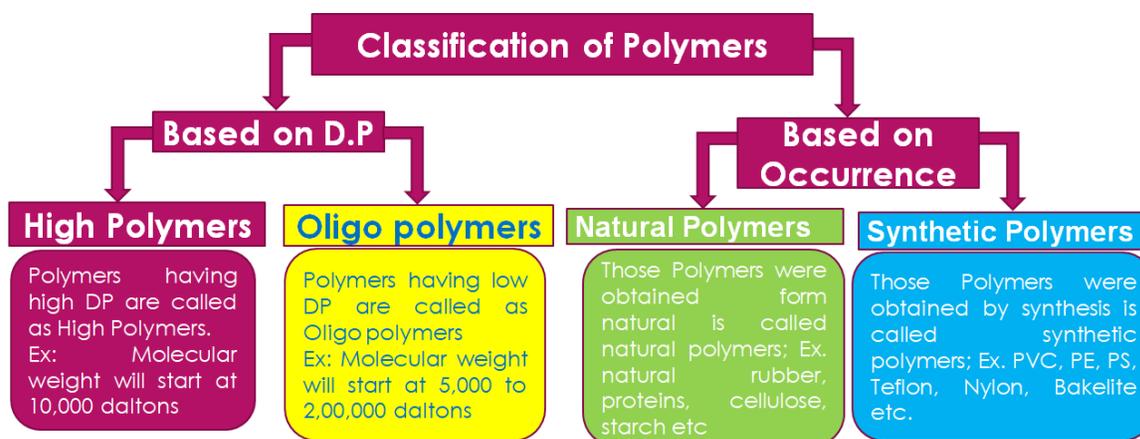
Ex: Vinyl chloride is a monomer of PVC; Ethylene is a monomer of poly ethylene; Glucose is a monomer of starch; Styrene is a monomer of polystyrene; Amino acids are the monomers of proteins; Nucleotides are the monomers of Nucleic acids.

### Degree of polymerization:

The number of repeating units (or) monomers present in the polymer is called as degree of polymerization. They may be hundreds (or) thousands (or) ten thousands and it's denoted as D.P.

$$\text{Degree of polymerization (D.P)} = \frac{\text{Mol. Wt of Polymer}}{\text{Mol. wt of Monomer}}$$

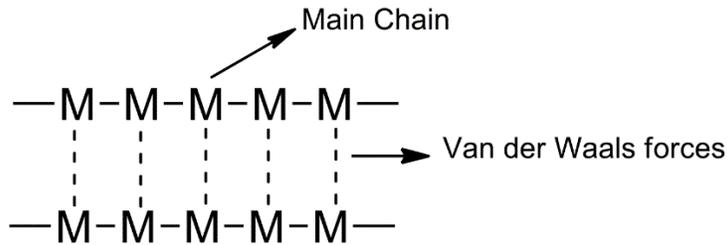
Molecular wt of polymer = D.P X Mol.wt of monomer.



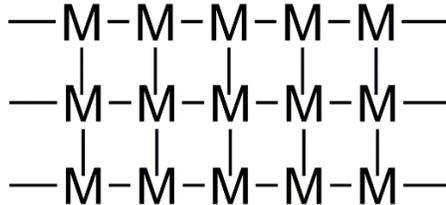
### Functionality of Monomers

The number of bonding sites (or) reactive sites present in a monomer is called as functionality. Each monomer should have minimum two bonding sites for polymerization.

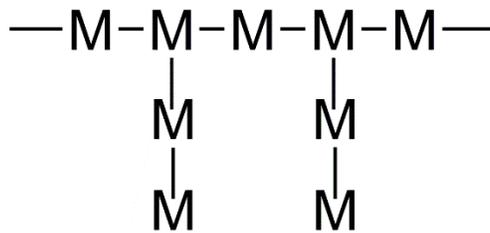
- If the functionality of monomer is 2, the resulting polymer is linear(or) straight chain. Ex: Ethylene, styrene, vinyl chloride.



- If the functionality of monomer is three (trifunctional), Cross linked three dimensional polymers are obtained; Ex: Bakelite



- If a mixture of bi functional and tri functional monomers is present, branched chain polymers are formed; Ex: Buna – S – Rubber



**Polymerization:**

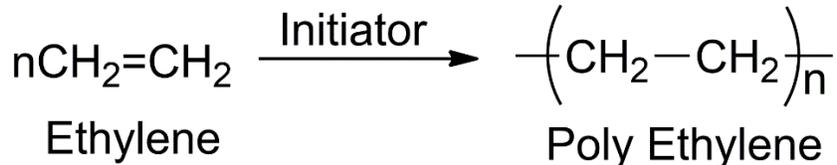
- The process of large number of monomers are combined together to form a polymer is called polymerization.

These are classified in to 4 types.

- Addition Polymerization (or) Chain growth Polymerization.
- Condensation Polymerization (or) Step growth Polymerization.
- Co-Polymerization.
- Coordination Polymerization (or) Zeigler-Natta Polymerization (or) Stereo specific Polymerization.

**Addition Polymerization:**

- A Polymerization reaction in which monomers containing one or more double bonds are linked to each other without any elimination of by product is called as Addition Polymerization. Generally the addition polymerization is initiated by free radicals and formation of Chain reaction hence it's called as Chain Polymerization.



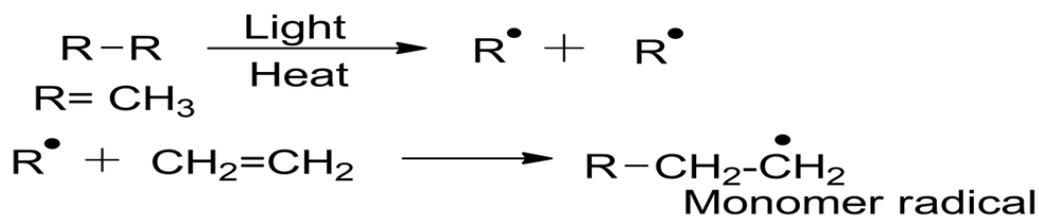
The main Feature of Addition Polymerization are as follows.

- Only Olefin or Vinyl compounds can undergo addition polymerization.
- No elimination of by product.
- The double bond provides required bonding sites.
- The addition of monomers takes rapidly.
- Polymerization is carried out by initiators like free radicals.
- The elemental composition of the polymer is the same as the monomer.

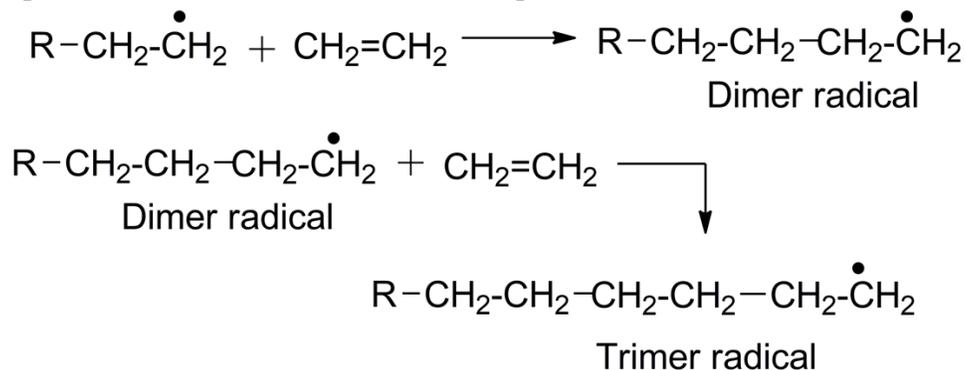
### Mechanism of Addition Polymerization:

The addition polymerization which takes place via free radical mechanism involves 3 significant steps which are; (i) Initiation; (ii) Propagation; (iii) Termination.

Initiation: This step involves the generation of free radicals by the hemolytic cleavage of an initiator, such as ethane, peroxides, per acids, per esters----etc.

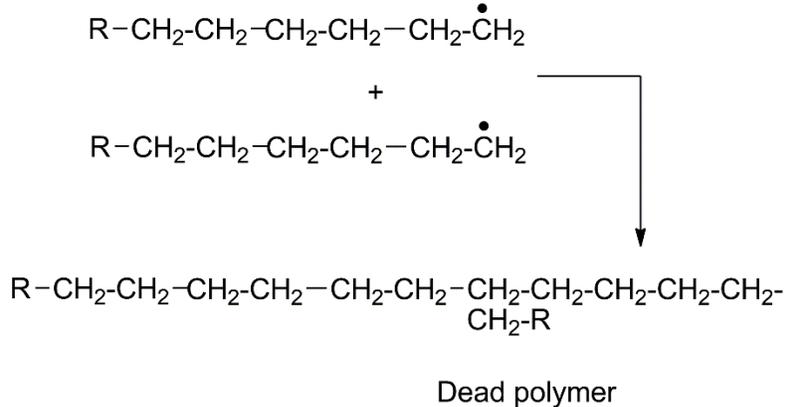


Propagation: In propagation, the radical attacks monomer to produce monomer free radical, this again react with another monomer to produce dimer free radical, this again react with another monomer to produce trimer free radical----etc. The process continues until termination occurs.



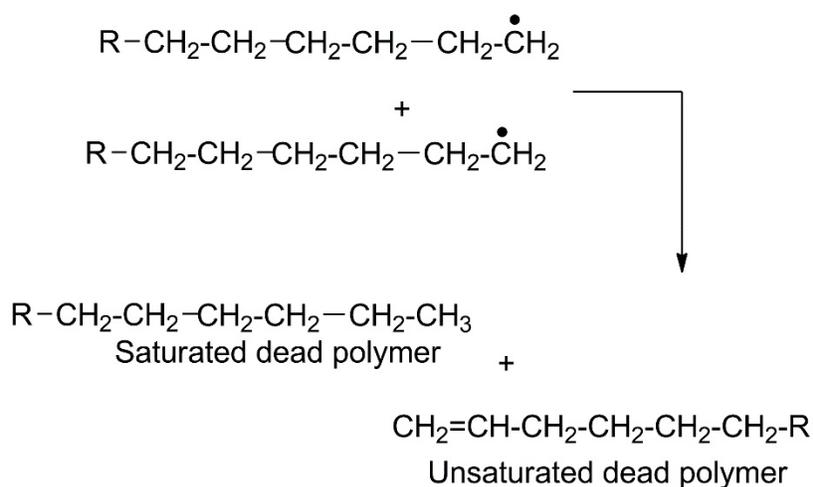
Termination: Chain termination occurs in two ways.

1. Coupling or combination of two growing chains.



Disproportionation.

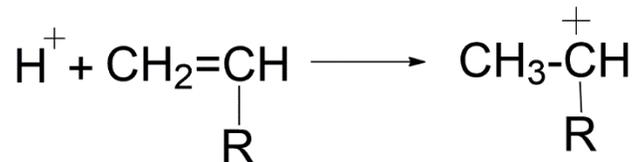
In which a hydrogen atom of one growing chain is transferred to another growing chain. This result in formation of two dead polymer chains; one is having saturated and the other having unsaturated end



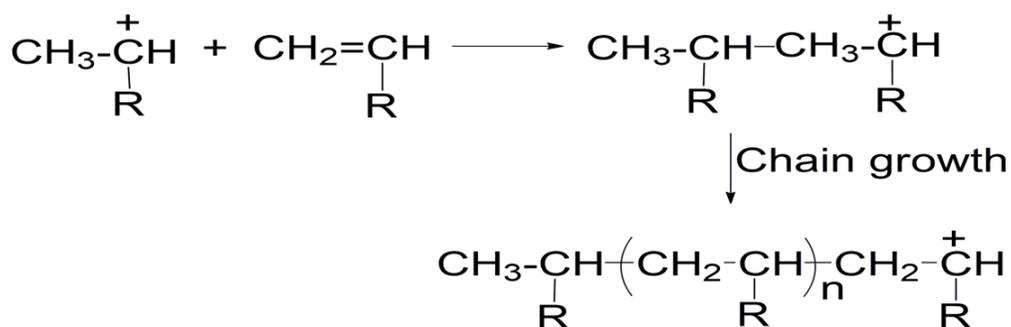
Ionic Polymerization: Addition polymerization can also be initiated by ionic species instead of free radicals and this is known as ionic addition polymerization. It can be classified in to two types-cationic and anionic, based on the nature of ionic initiator involved.

Cationic Polymerization: In cationic addition polymerization, the initiator is a cation obtained either from protic acids (HCl, H<sub>2</sub>SO<sub>4</sub>) OR Lewis acids (FeCl<sub>3</sub>, ZnCl<sub>2</sub>---etc). In case of Lewis acid, presence of water is essential as a co-catalyst. Ex. Homopolymerization Isobutylene and Co-polymerization of isobutylene with 2-methyl Propene.

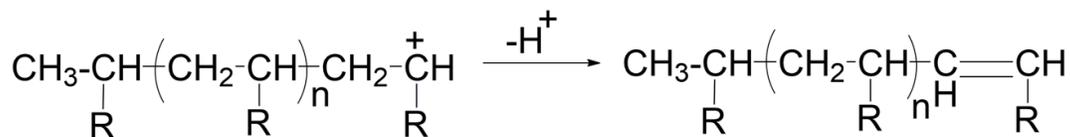
Initiation: The addition of cation to the double bond of the monomer leads to the formation of a carbonium ion and this initiates the polymerization.



Propagation: In the next step, the carbonium ion formed adds to the double bond of another monomer, generating a bigger carbonium ion and the chain propagates in a similar manner.



Termination: The chain is terminated by the removal of  $\text{H}^+$

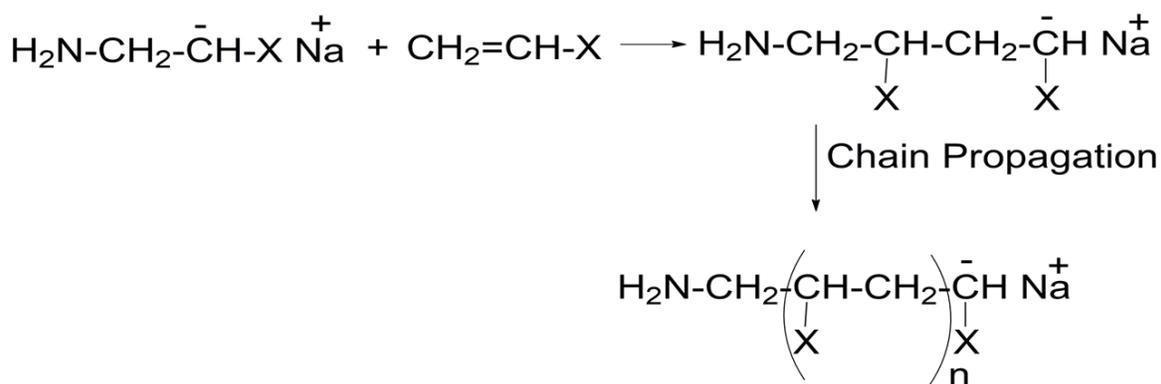


Anionic Polymerization: Addition polymerization the initiator is a anion obtained from Lewis bases ( $\text{NH}_3$ ,  $\text{PH}_3$ ) or alkali metal amides ( $\text{NaNH}_2$ ). Ex. Polymerization styrene, acrylonitrile, methyl methacrylate.

Initiation: The anionic initiator adds to the double bond of the monomer leads to the formation of a carbanion and this intitates the polymerization.



Propagation: In the next step, the carbanion formed adds to the double bond of another monomer, generating a bigger carbanion and the chain propagates in a similar manner.



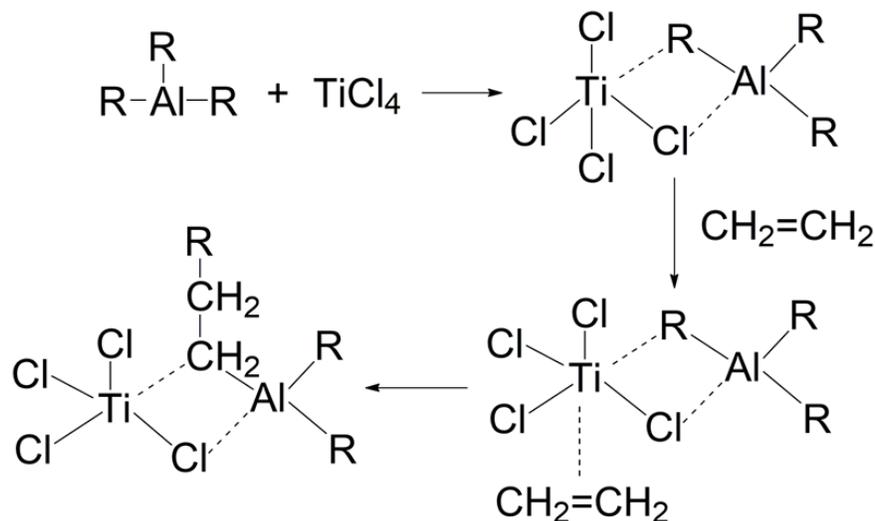
Termination: In this step termination is not spontaneous process. If any impurities are added then only termination occurs otherwise chain growth can live in the system for long time. If monomer is added, again polymerization starts growing. Hence this type of polymerization is called living polymerization and the polymer are known as living polymers.

Co-ordination addition polymerization: The polymerization in which coordination bond is involved b/w a carbon atom of a monomer and metal of the catalyst is called coordination addition polymerization.

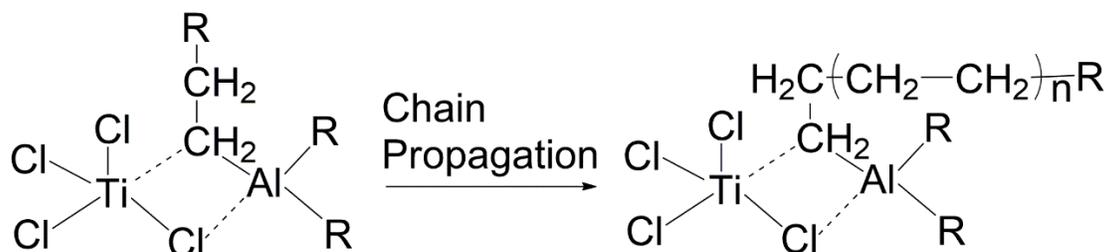
This polymerization is catalyzed by Zeigler-Natta catalyst complex formed b/w trialkyl aluminum and transition metal halides.



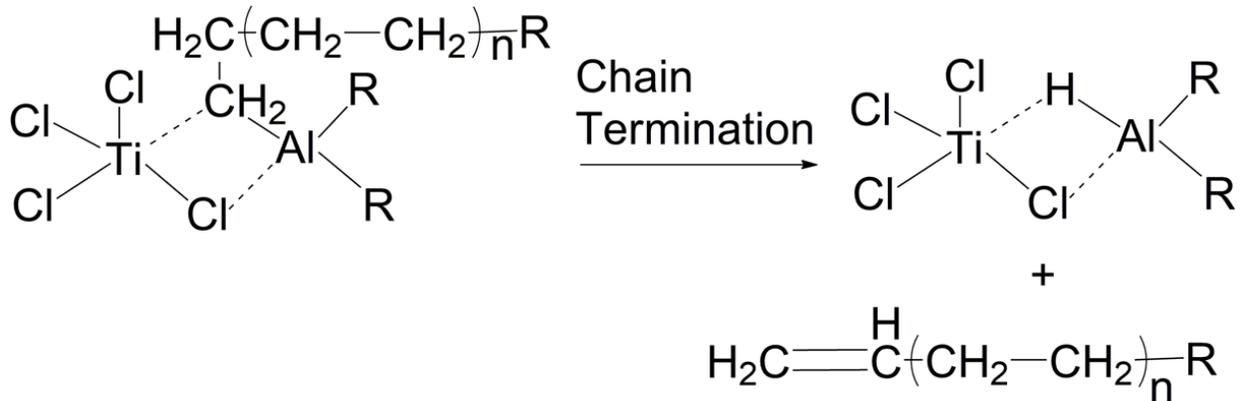
Initiation: The transition metal serves as the active site. The alkene monomer is held at the active site by formation of  $\Pi$ -complex with the transition metal (Titanium). It gets inserted b/w the metal and the alkyl group R. This coordination process results in the stereo specificity of the polymerization.



Propagation: The migration of alkene monomer b/w metal and alkyl group initiates the polymerization by facilitating the formation of  $\Pi$ - complex with new monomer and the process continues in a similar manner.

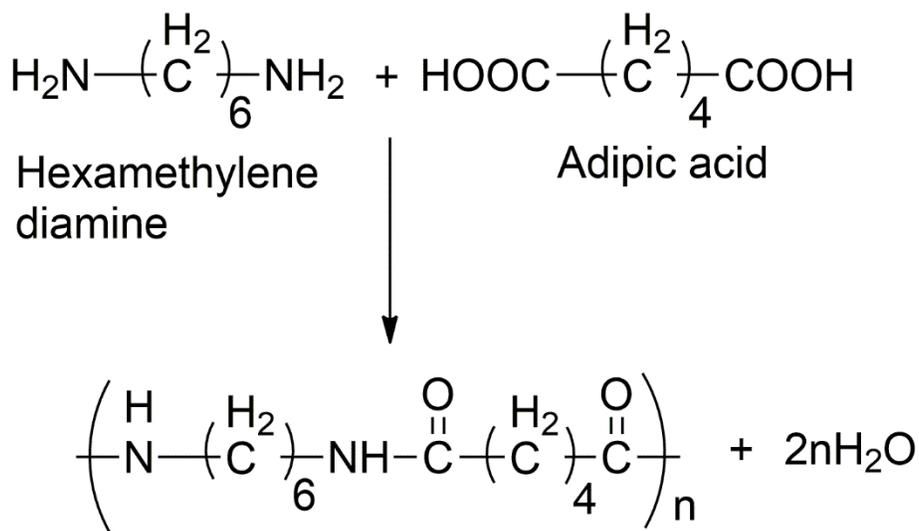


Termination: The termination of the chain occurs when the monomer migrates and forms an inactive site, so that polymerization does not proceed further.



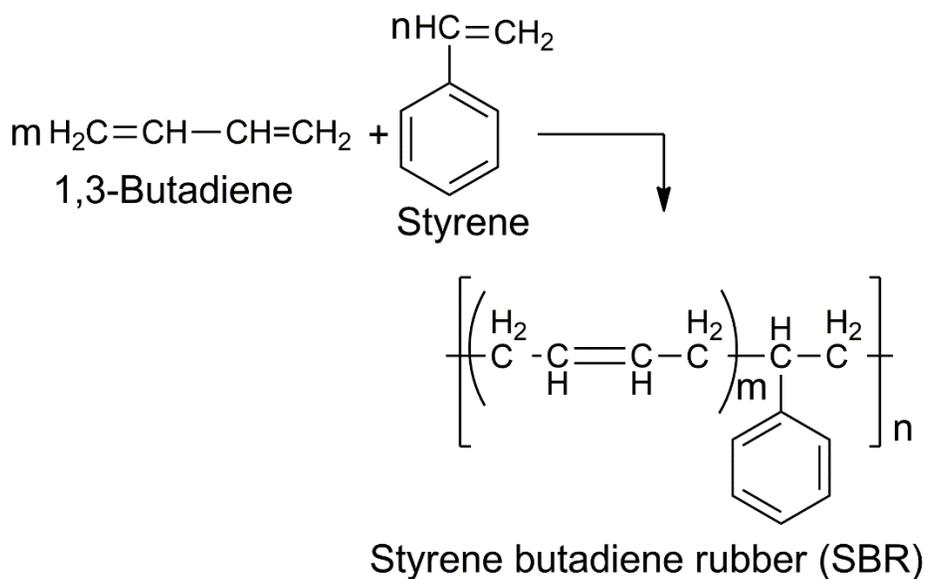
Condensation Polymerization: Large number of monomeric units of same or various Monomers undergoes a chemical process by liberation of small molecules like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ --etc to give a polymer is called as condensation polymerization.

Ex. Nylon 6:6



Co-Polymerization: The polymer obtained or synthesized from two or more type of monomers are called as co-polymers. Thus copolymers contain more than one type of repeating units in the chain and this type of polymerization is called copolymerization.

Ex. Styrene butadiene rubber (SBR)



### Plastics

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

#### Advantages:

- They are light in weight.
- They possess low melting point.
- They can be easily moulded and have excellent finishing.
- They possess very good strength and toughness.
- They possess good shock absorption capacity.
- They are corrosion resistant and chemically inert.
- They possess good thermal and electrical insulating property.
- They are very good water-resistant and possess good adhesiveness.

#### Disadvantages:

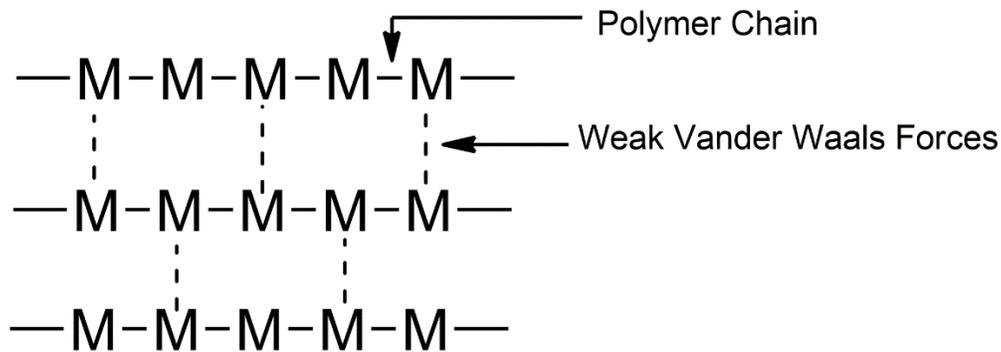
- They have high softness.
- They undergo embrittlement at low temperature.
- They undergo deformation under load.
- They possess low heat-resistant and poor ductility.
- They undergo degradation upon exposure to heat and UV- radiation.
- They are Non bio-degradable.

### Classification of Plastics

#### Thermoplastics

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

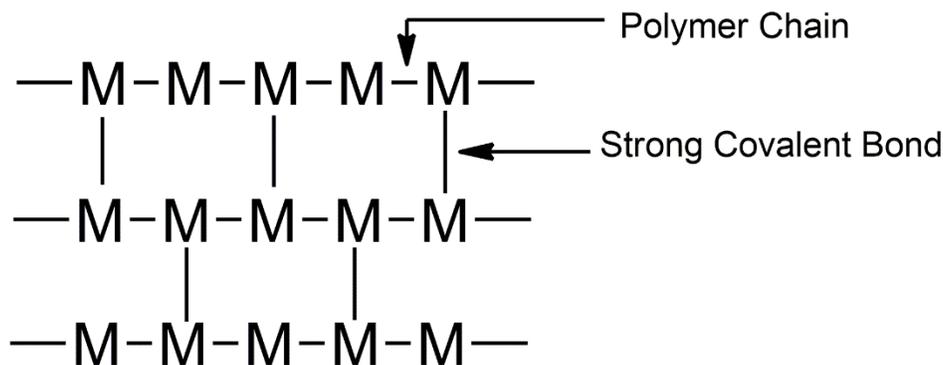
Ex. Poly Ethylene; Polyvinyl chloride; Polystyrene; Polyaniline (PAN)



### Thermosetting plastics

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

Ex. Bakelite; Polyester; Urea-formaldehyde; Epoxy-resin



### Comparison b/w thermoplastic and thermosetting resins

#### Thermoplastics

- They are formed by addition polymerisation.
- They consist of linear long chain polymers.
- All the polymer chains are held together by weak Vander Waals forces.
- They are weak, soft and less brittle.
- They soften on heating and harden on cooling.
- They can be remoulded.
- They have low molecular weights.
- They are soluble in organic solvents.
- The resin is synanomus with plastics.

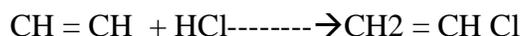
Example: Polyethelene, PVC, Teflon etc.

#### Polyvinyl chloride

#### Preparation:

Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared

by reacting acetylene with hydrogen chloride at 100-150<sup>0</sup>C in the presence of metal salt catalyst



PVC is prepared by heating a water- emulsion of vinyl chloride in presence of Benzoyl Peroxide in a autoclave under pressure.

**Properties:**

- PVC is colorless and odorless Powder.
- It is non-inflammable and chemically inert.
- It is soluble in chlorinated hydrocarbons like ethyl chloride, etc. and ketones.
- It has high resistance to light, inorganic acids, alkalis, and atmospheric oxygen.

**Uses:**

- Plasticized PVC is used for making table cloths, rain coats, coatings for electric wire and cables, toilet articles, radio, T.V components, pipes, coupling valves, etc.
- Un-plasticized PVC or rigid PVC is used for making refrigerator components, cycle and motor cycle mudguards, tubes, pipes, etc.

Thermosetting Plastics

- They are formed by condensation polymerisation.
- They consist of three dimensional network structure.
- All the polymer chains are linked by strong covalent bonds.
- They are strong, hard and more brittle.
- They do not soften on heating.
- They cannot be remoulded.
- They have high molecular weights.
- They are insoluble in organic solvents.
- Resin is not synanomous with plastics.

Example: Bakelite, Ureaformaldehyde resin, etc.,

**Bakelite (or) Phenolic resin**

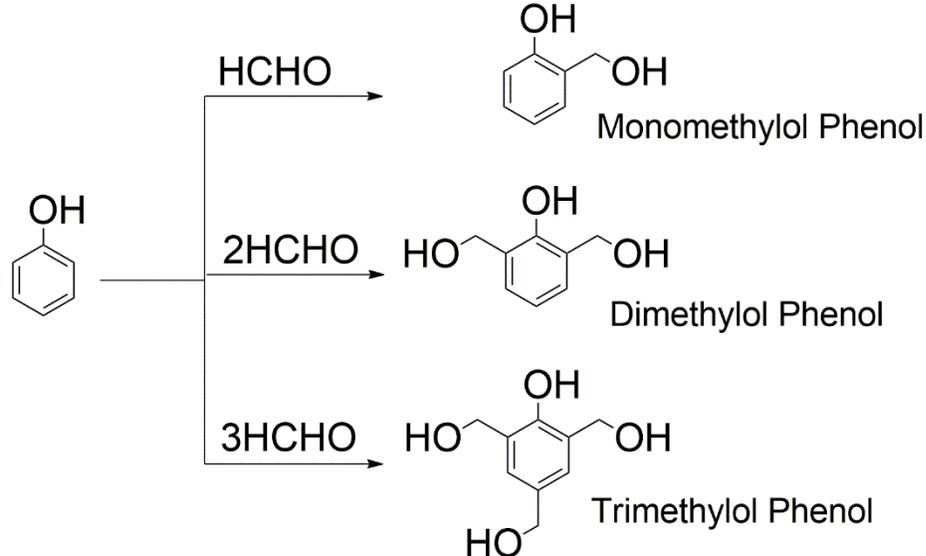
- It is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of acid catalyst.

**Synthesis:**

- The reaction involves the following 3 steps.

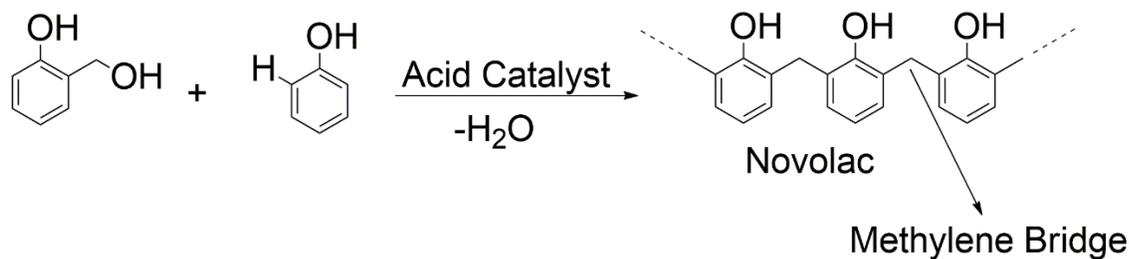
**Step-I****Methylation**

The first step is the reaction between phenol and formaldehyde in presence of acid catalyst, forms mono, di and tri-methylol phenols.



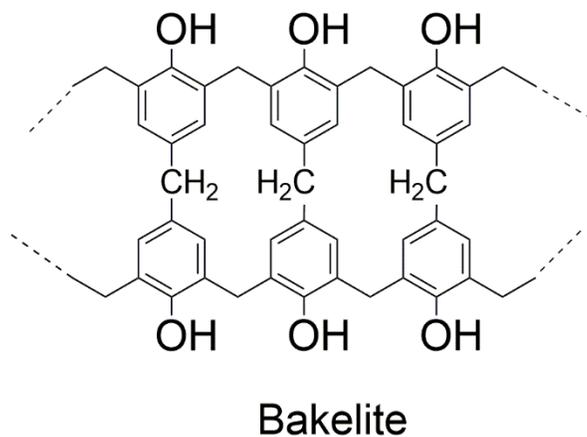
### Step-II

When methylol phenols are heated with excess of phenol in presence of acid catalyst, the methylol phenols condense with phenol through methylene linkages to form novolacs. Novolac is a high molecular weight linear polymer. It is insoluble in alkaline solutions.



### Step-III

Further heating of novolac resin in the presence of a curing agent (Hexamethylenetriene) produces hard, rigid, infusible, cross-linked polymer called bakelite.



### Properties and Uses

#### Properties

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

## Uses

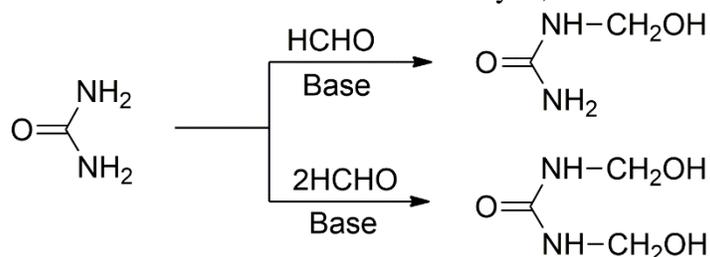
- Bakelite is used as an adhesive in plywood laminations & in grinding wheels, etc.
- It is also widely used in paints, varnishes.
- It is used for making electrical insulator parts like plugs, switches, heater handles, etc.,

## Amino Resins or Urea-formaldehyde

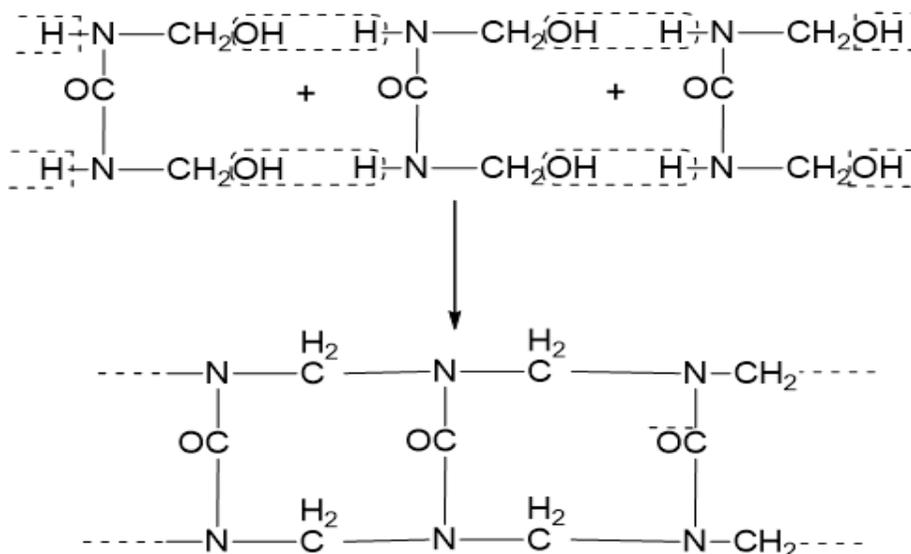
- Urea formaldehyde is obtained by the condensation polymerisation of urea and formaldehyde in the presence of base catalyst.

### Synthesis:

- The reaction involves the following 2 steps
- The first step is the reaction between urea and formaldehyde, forms mono or dimethylol urea.



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



## Properties and Uses

### Properties

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

### Uses

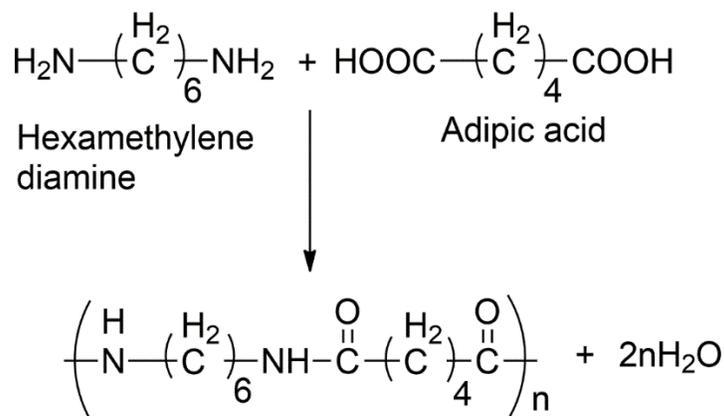
- It is used in bonding of grinding wheels, plywood.
- It is used as a binder of glass fibres, rock wool and foundry cores.
- It is used as decorative articles like plates, drinking glasses, dishes, electrical insulators.

- It is used as lacquers and surface adhesives.

## Nylon-6:6

### Synthesis:

- Nylon-6,6 is obtained by the polymerization of adipic acid with hexamethylene diamine.



### Properties and Uses

#### Properties

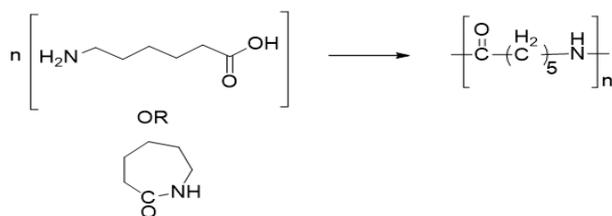
- Nylon 6:6 is a less soft and stiff material when compared to nylon 6.
- Its melting point is 264°C.

#### Uses:

- Nylon 6:6 is used for fibers, which are used in making socks, ladies shoes, dresses, carpets, etc.,.
- Nylons are used for making filaments for ropes, bristles for tooth-brushes, films and tyre-cords.

## Nylon-6

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



### Properties and Uses

#### Properties:

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

#### Uses:

- Nylon 6 is mainly used for moulding purposes for gears, bearings, electrical mountings, etc.,. Nylon bearings work without any lubrication.

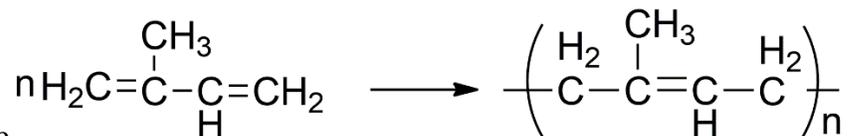
#### General Properties:

- They behave as plastic as well as fiber.
- They are translucent, white, horny and high melting polymers.

- They are insoluble in common organic solvents but soluble in phenol and formic acid.
- They possess good mechanical properties and fairly resistant to moisture.

### **Rubbers (or) Elastomers**

- Rubbers (or) elastomers are non-crystalline high polymers (linear polymers), having elastic and other rubber-like properties.
- These are two types.
- **Natural Rubber**
- Natural rubber is obtained from the tree as a latex, which is a dispersion of isoprene. During the treatment of latex, these isoprene molecules undergo polymerisation to form long coiled chain of polyisoprene.



- Ex: Polyisoprene

### **Synthetic Rubber (Elastomers)**

- An elastomer (synthetic rubber) is any vulcanisable man made rubber like polymer, which is superior to natural rubber in certain properties.
- Ex: Buna-S-Rubber; Buna-N-Rubber; Polyurethane Rubber; Silicone Rubber.

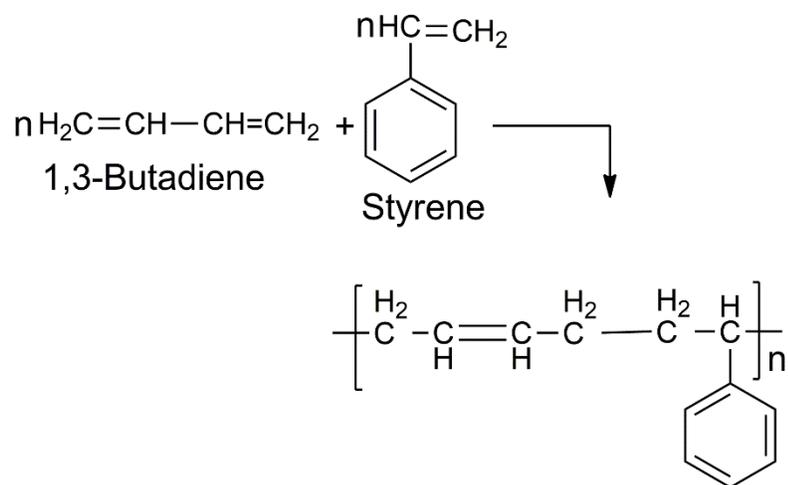
### **Synthetic rubber**

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

### **SBR (Styrene-butadiene rubber) (GR-S (or) Buna-S:**

#### **Synthesis:**

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



Styrene butadiene rubber (SBR)

### **Properties and Uses**

Properties:

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

It undergoes oxidation readily, when traces of ozone is present in the atmosphere.

It requires less sulfur for vulcanization when compared to natural rubber.

Tensile strength and flexibility of SRB are inferior to those of natural rubber.

Uses:

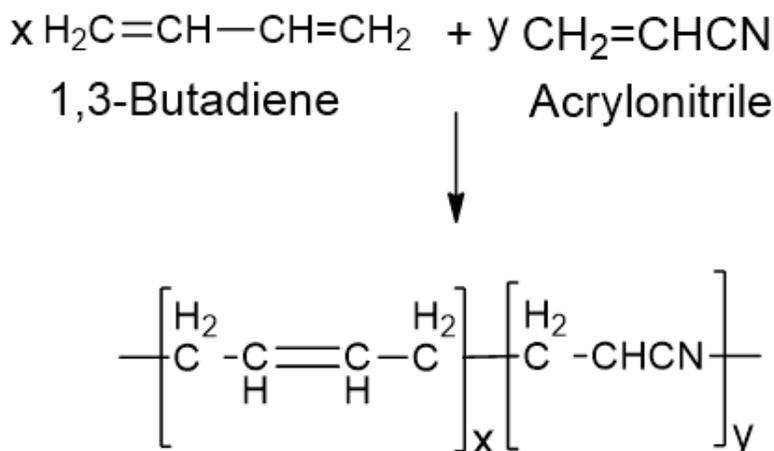
SRB is used for making light duty tyres, belts hoses and gaskets.

It is also used in footwear industry.

It is used as an adhesives and in electrical insulation.

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

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



#### ● **Properties:**

- It has excellent resistance to heat and sunlight.
- It is easily affected by alkali.
- It can be vulcanized in the same way as natural rubber.
- It is resistant to oils, acids and salt.
- Uses:
- It is used in making conveyor belts and tank linings.
- It is used in the production of hoses and gaskets.
- It is also used in the production of resistant foams and automobile parts.

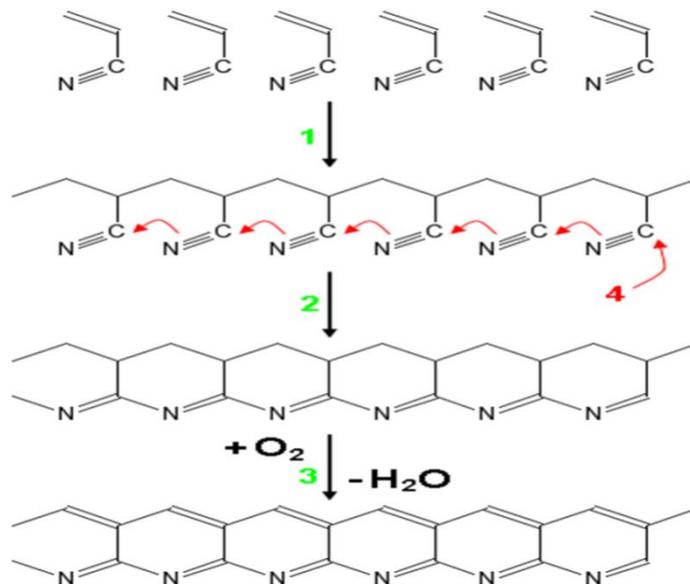
#### **Carbon fibres**

- Carbon fibers are fibers about 5–10 micrometres in diameter and composed mostly of carbon atoms.
- Carbon fibers are obtained as a continuous filament, by the pyrolysis of organic fibers such as cellulose, polyacrylonitrile (PAN) in an inert atmosphere.

#### **Synthesis:**

- A common method of manufacture involves heating the PAN filaments to approximately 300 °C in air, which breaks many of the hydrogen bonds and oxidizes the material. The oxidized PAN is then placed into a furnace having an inert atmosphere of a gas such as argon, and heated to approximately 2000 °C, which induces graphitization of the material, changing the molecular bond structure. When heated in the correct conditions, these chains bond side-to-side (ladder

polymers), forming narrow graphene sheets which eventually merge to form a single, columnar filament. The result is usually 93–95% carbon.



### Properties:

- High stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion. These properties have made carbon fiber very popular in aerospace, civil engineering, military, and motorsports.

### Uses:

They are used as reinforcing material with polyester resins (or) epoxy resins to form composites, which have higher specific strength than metals.

### CONDUCTING POLYMERS

- In General polymers such as plastics, elastomers are regarded as insulators due to the presence of strong C - C covalent bond. But, under certain circumstance, these can be made to behave like a metal (conductor).
- Thus, those polymers, which conduct electricity are called conducting polymers. The conduction in the polymers is mainly due to the following reasons.
- Presence of unsaturated conjugated double bonds in the polymer.
- Addition or removal of electrons (doping) in to the polymer.
- Examples: Two important examples for conducting polymers are Polyacetylene, Polyaniline, Polypyrrole, etc.,

### Preparation of conducting polymers

- Conducting polymers are mainly prepared by the doping method.
- Doping
- To becoming electrically conductive, the electrons of the polymer need to be free to move. The polymers having conjugated double bond has to be disturbed either by removing electron from or inserting the electron into the polymer by oxidation or reduction. This process is known as doping.
- Types of doping
- p - doping: Oxidation with Lewis acids (or) halogens.

- n - doping: Reduction with Lewis bases (or) alkali metals.

p - doping

- In p - doping an intrinsically conducting polymer or the polymer having conjugated C = C bonds are treated with Lewis acids or halogens, which oxidises the polymers and creates positively charged sites on polymer back bone.
- Due to the positive charge on the polymer backbone, they are acting as good conductors of electricity like metal.
- Examples: Examples for p-dopant: I<sub>2</sub>, Br<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub>

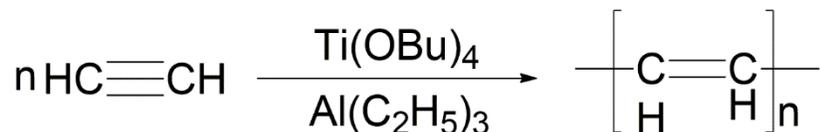
### n - doping

- In n - doping an intrinsically conducting polymers or the polymers having conjugated C = C bonds are treated with Lewis bases or alkali metals, which reduces the polymers are creates negatively charged sites on polymer back bone.
- Due to the negative charge on the polymer back bone, they are acting as good conductor of electricity like metal.
- Examples: Examples for n-dopant: Na, K, Lithiumnaphthalides, etc.,

### Polyacetylene

- Polyacetylene is prepared by the addition polymerisation of acetylene. Acetylene gas is passed over the Ziegler - Natta catalyst to get polyacetylene.

Polyacetylene is a infusible, insoluble and becomes brittle on exposure to air.



The conductivity of cis - polyacetylene is less when compare to trans polyacetylene.

The conductivity of polyacetylene can be improved by either p - doping (or) n - doping.

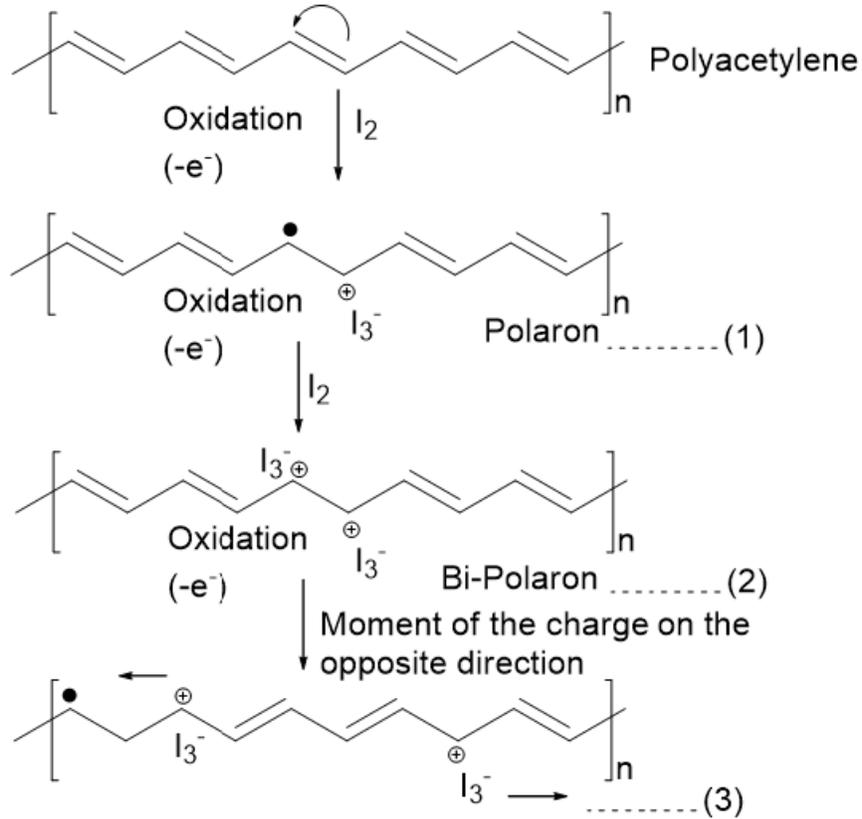
p - doping

It involves, the following two steps.

I step involves the oxidation of a polyacetylene with iodine vapour (Lewis acid).

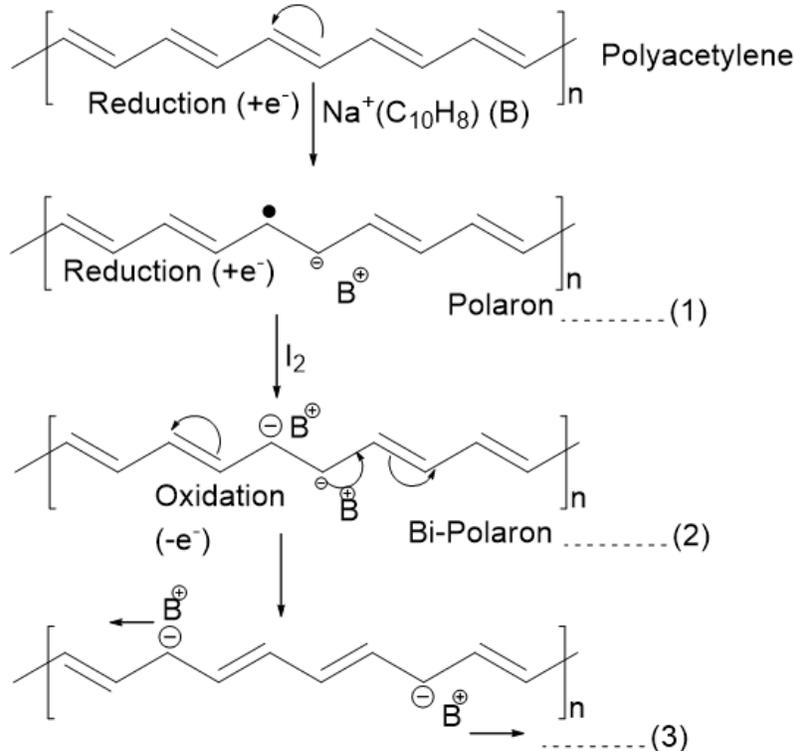
During oxidation, (as shown in reaction 1) the iodine molecules remove an electron from polyacetylene chain and becomes I<sub>3</sub><sup>-</sup>. Now the polyacetylene chain carrying the +ve charges is called polaron.

The second oxidation of polaron (as shown in reaction2) produces two +ve charges on the chain called bipolaron. This +ve charges are mobile because of delocalization and responsible for electrical conductance (as shown in reaction 3).



### n - doping

- n - doping also involves two steps
- Step 1 involves reduction of polyacetylene with sodium naphthalide Na<sup>+</sup> (C<sub>10</sub>H<sub>8</sub>)<sup>-</sup>. During the reduction (as shown in reaction 1) sodium naphthalide donates an electron to polyacetylene chain. Now the polyacetylene carrying the (-)ve charge is called polaron.
- Step 2 involves second reduction of polaron (as shown in reaction 2) to produce two (-ve) charges on the chain called bipolaron. This (-ve) charges are mobile because of delocalization and responsible for electrical conductance (as shown in reaction 3).



### Applications of Polyacetylene

- It is used in various electronic devices as active and passive electrodes.
- The main area of its application are batteries, nonlinear optics and microelectronics.
- PA with various conductivities are used for the formation of schottky barriers, p-n transitions, and heterojunctions.
- It is also used in the development of photovoltaic devices.
- It is used as an electrode material in solid-state batteries operating at room temperature.

### • *Polyaniline*

Synthesis:

- Polyaniline is prepared by the slow addition of aqueous solution of ammonium per sulphate to a solution of aniline in aqueous HCl at lower temperature (0 - 5°C). The precipitate formed is separated by filtration, which is emeraldine hydrochloride.

•



- Polyaniline is a transparent and stable material. It shows green colour in conducting state. It turns to red under reducing condition and blue under oxidizing condition.

### • Mechanism of conduction in polyaniline

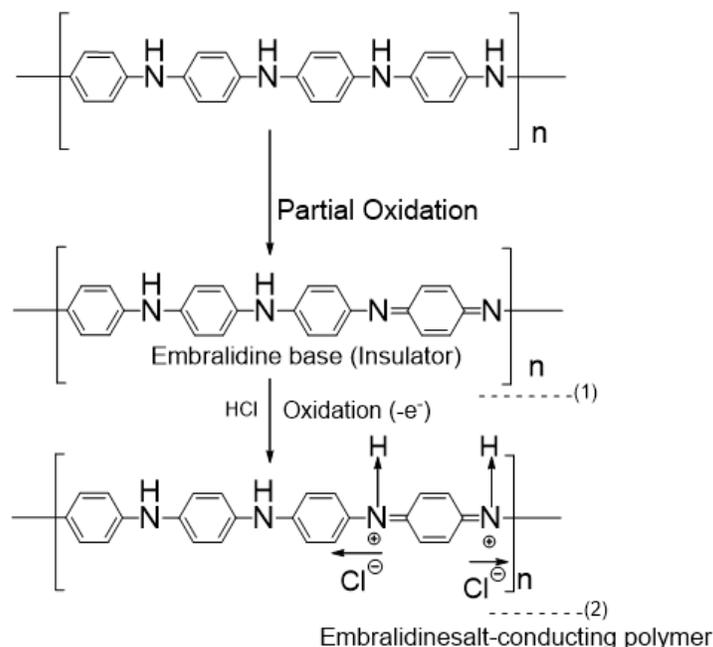
- The conductivity of polyaniline can be improved by either p-doping or n-doping.

#### • p-doping

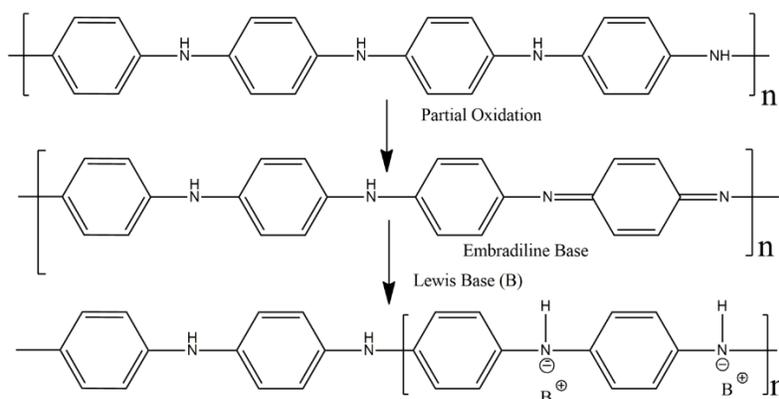
- It involves the following two steps.

- Step 1 involves partial oxidation of polyaniline to emeraldine base, which is non conductive (as shown in reaction 1).

- Step 2 involves oxidation of emeraldine base (as shown in reaction 2) using Lewis acid like HCl to emeraldine salt, which is a conducting polymer. During oxidation HCl removes electron from polyaniline chain and creates (+) ve hole in the polymer back bone, which is responsible for conduction.



- n-doping
- It involves the following two steps.
- Step 1 involves partial oxidation of polyaniline to form emeraldine base, which is nonconductive (as shown in 2 line ).
- Step 2 involves reduction of emeraldine base (as shown in 3 line) using Lewis base to emeraldine salt, which is a conducting polymer. During reduction lewis base donates electron to polyaniline chain and creates (-) ve charge in the polymer back bone, which is responsible for conduction.



### Applications of polyaniline

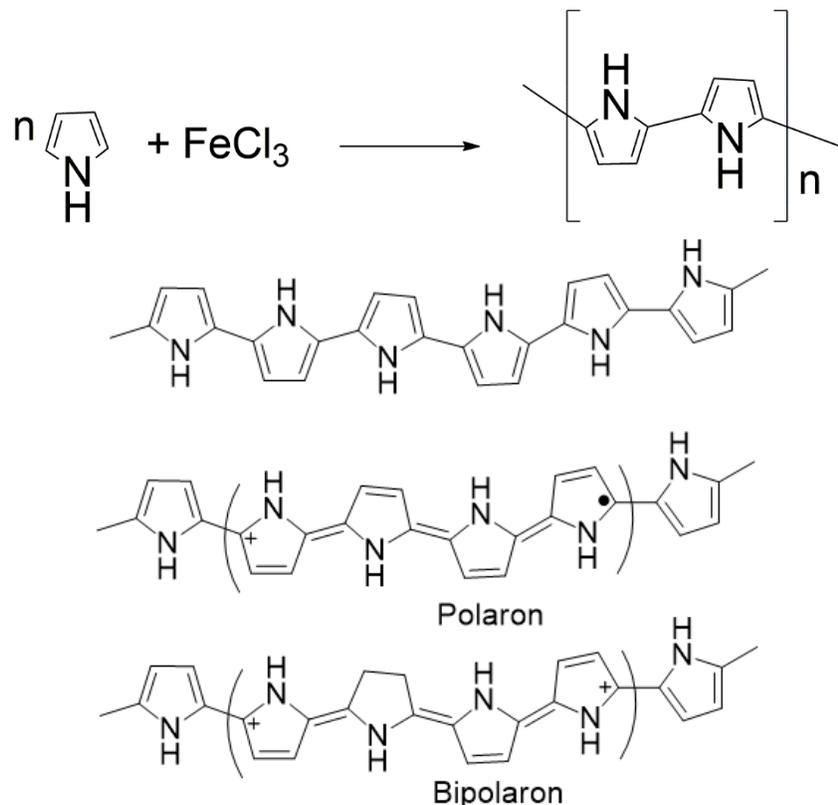
- Polyaniline is used in sensors, PCB (Printed Circuit Boards), conductive fabrics, smart windows.
- It is used as a corrosion resistant.
- It is used as a coating for films and semi-finished articles.
- In rechargeable batteries, polyaniline is used as a secondary electrode.

## Polypyrrole

● Polypyrrole is a type of organic polymer formed by the polymerisation of pyrrole. Polymerisation of pyrrole may be carried out chemically (or) electrochemically. It is a very good conducting polymers with conjugated double bonds. Conducting polypyrrole consists of number of connected pyrrole ring structure.

### ● Synthesis:

Polypyrrole is prepared by oxidation (p-doping) of pyrrole using ferric chloride in methanol.



## Applications

- Polypyrrole is used as biosensors, gas sensors, antielectrostatic coatings, light weight rechargeable batteries, etc.
- It is used in carbon composites due to its excellent thermal stability.
- It is used for manufacturing containers for protein, so it can be used for drug delivery.
- The blend of polypyrrole based polymer, protects corrosion of metals.
- It acts as a support for the catalyst used in fuel cells.
- It is used as a counter electrode in dye-sensitized solar cells.

<i>Addition polymerization</i>	<i>Condensation polymerization</i>
1. No by-product is formed.	1. Generally a by-product is obtained.
2. Homo-chain polymer is obtained.	2. Hetero-chain polymer is obtained.
3. Bifunctionality is provided due to the presence of double bond in the monomer.	3. Bifunctionality is provided due to the presence of reactive functional groups present at both ends of the monomer.
4. The chain growth is at one active centre.	4. The chain growth takes place at atleast two active centres.
5. Mostly thermoplastics are formed by this	5. Mostly thermosetting plastics are formed.

### Differences Between Thermoplastics and Thermosetting plastics

S.No	Thermoplastics	Thermosetting plastics
1	Formed either by addition or by Condensation polymerization reactions	Formed by Condensation polymerization reactions
2	They have either linear or branched structures.	They have three dimensional cross linked network structures
3	Adjacent polymer chains are held together by either vanderwaals forces, or by dipole-dipole forces or by hydrogen bonds	Adjacent polymer chains are held together by strong covalent bonds called crossed-links
4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerisation and cross-linking during moulding process.
8	They are soft and flexible	They are hard, rigid and infusible.

9	They can be reclaimed from waste i.e., they can be recycled.	They cannot be reclaimed from waste. They cannot be recycled.
10	They undergo reversible changes, on the application of heat.	They undergo irreversible changes on the application of heat.
11	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
12	They are tough materials	They are brittle materials
13	The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	The moulded articles can be taken out of the moulds even when they are still hot without any deformations
14	Curing can be done by cooling.	Curing can be done by applying heat and pressure.
15	Examples: Polyethylene(PE), bakelite.	Examples: Phenol-formaldehyde resin (PF), urea- formaldehyde resin

### Bio-Degradable polymers-Poly Glycolic Acid (PGA), Poly Lactic Acid (PLA).

#### Bio-Degradable polymers

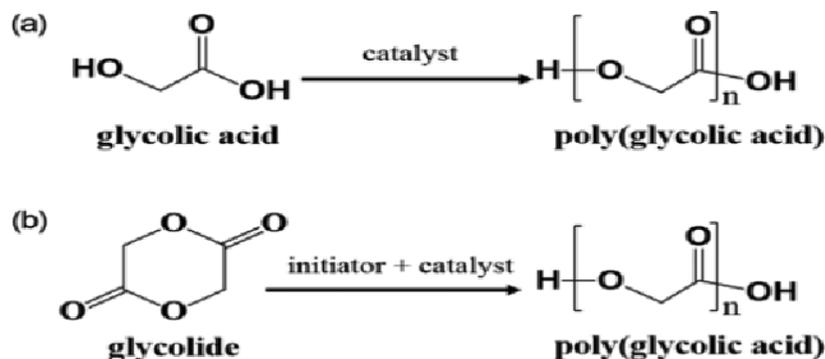
Natural biodegradable polymers are called biopolymers. Polysaccharides, as starch and cellulose, represent the most characteristic family of these natural polymers. Other natural polymers as proteins can be used to produce biodegradable materials. These are the two main renewable sources of biopolymers

#### Poly Glycolic Acid (PGA)

Poly glycolide or poly(glycolic acid) (PGA), also spelled as poly glycolic acid, is a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester. It can be prepared starting from glycolic acid by means of polycondensation or ring-opening polymerization.

#### Preparation

A synthesis method of polyglycolic acid, characterized in that it comprises the steps of: placing the glycolic acid in reaction medium with a catalyst, - using hydrophilic organic solvents for removing the excessive water and monomer formed during condensation, mixing and boiling the mixture, stabilizing the amount of polyglycolic acid



#### Properties

Polyglycolic Acid. PGA is a strong and crystal-like polymer having a melting point of 225°C along with 36°C glass transition temperature. PGA is not soluble in common polymer solvents. Also, it

possesses excellent  
Fiber-forming properties.

### Applications

Poly(lactic acid) (PLA) is an easy-to-process, biocompatible, biodegradable plastic. As such, it is used for medical implants like stents and implantable drug dispensers that are designed to biodegrade over time. PLA is also used in food packaging and disposable cutlery and can be formed into fibers for clothing.

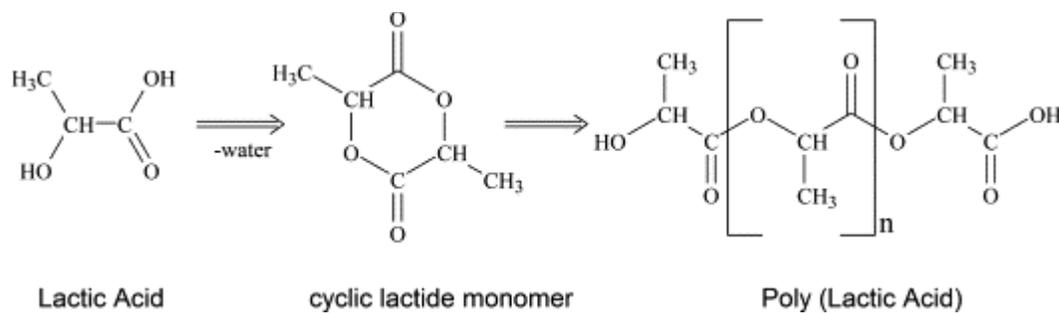
### Poly Lactic Acid

Poly(lactic acid) (PLA) is a bioplastic made from repeating monomers having the chemical formula  $C_3H_4O_2$ . Chemically, PLA is made from lactic acid molecules. The lactic acid is fermented from plant matter under precisely controlled conditions.

### Preparation

The preparation of PLA by direct polycondensation can be divided into three main stages

1. Reducing free water content;
2. Oligomer polycondensation;
- and 3. Melt polycondensation to obtain higher molecular weight PLA.



### Properties

PLA is the most widely used plastic filament material in FDM 3D printing, due to its low melting point, high strength, low thermal expansion, and good layer adhesion, although it possesses poor heat resistance unless annealed.

### Applications

PLA is used in a large variety of consumer products such as disposable tableware, cutlery, housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays. (However, PLA is not suitable for microwavable containers because of its low glass transition temperature.)

# Unit-V

## Instrumental Methods and its Applications

### Introduction:-

Instrumental methods may be used to separate samples using chromatography, electrophoresis or field flow fractionation. Then qualitative and quantitative analysis can be performed, often with the same instrument and may use light interaction, heat interaction, electric fields or magnetic fields.

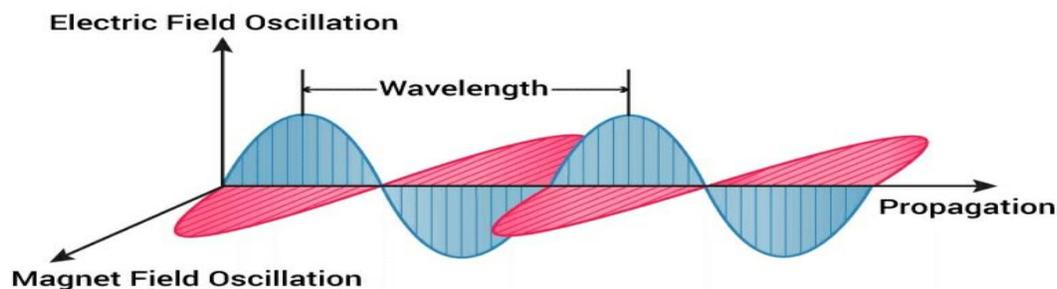
### Spectroscopy:-

- \* Spectroscopy is the study of the interaction between matter and electromagnetic radiation
- \* Spectroscopy and spectrograph are terms used to refer to the measurement of radiation, intensity as a function of wavelength and are often used to describe experimental spectroscopic methods

### Electromagnetic Radiations

The radiation which are having both electric field and magnetic field which are perpendicular to each other and are coplanar are called as “electromagnetic radiations “.

These are produced by the Oscillation of electric field and magnetic field residing on the atom



### Characteristics of Electromagnetic Radiations

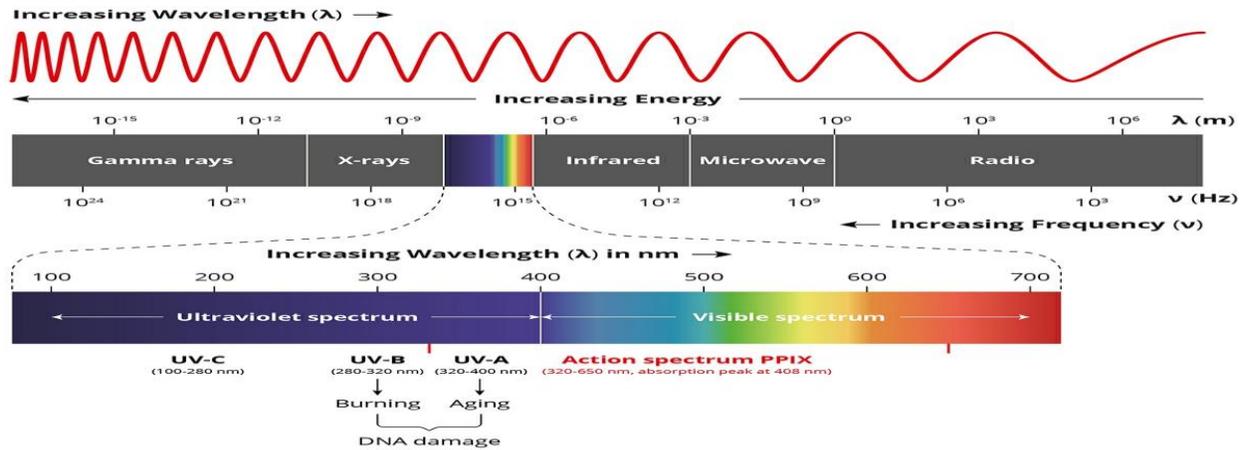
1. These are characterized by their wave lengths or frequencies or wave numbers.
2. The energy carried by an electromagnetic radiation is directly proportional to its frequency.
3. The emission and absorption of radiation is quantized and each quantum of Radiation is called a photon.
4. All types of Electromagnetic radiation travel with the Same velocity and no medium is required for their propagation.
5. When visible light is passed through a prism, it is split up into seven colours. This phenomenon is called dispersion

## Electromagnetic spectrum

The arrangement all types of electromagnetic radiation in order of their increasing wavelengths Or decreasing frequencies is known as electromagnetic spectrum.

Electromagnetic radiation are absorbed, emitted or propagated in the form of Energy packets called quanta or photons.

$$E=h\nu$$



## Observations of Electromagnetic Spectrum

1. Radio waves are longer wave length and less energetic
2. Cosmic waves are shorter wave length and high energetic
3. Ultra violet radiations cover the wave length range from 190-400 nm
4. Visible radiations cover the wave length range from 400-800 nm
5. IR radiations cover the wave length range from 667-4000  $\text{Cm}^{-1}$
6. Radio waves cover the wave length range from 60-300 MHz

## Laws of light absorption

When a beam of radiation passes through a homogeneous medium the radiant energy may be partially or entirely absorbed,transmitted,reflected and scattered

$$I_0=I_a+I_t+I_r$$

Where  $I_0,I_a,I_t,I_r$  are intensity of incident light, absorbed, transmitted, reflected respectively

The process of absorption depends upon the

- a) Molecular structure of the absorbing species

b) Concentration of the solution

c) Length of path of the radiation passing through the absorbing medium

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

### Beer's law, 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.

## Beer-Lambert Law

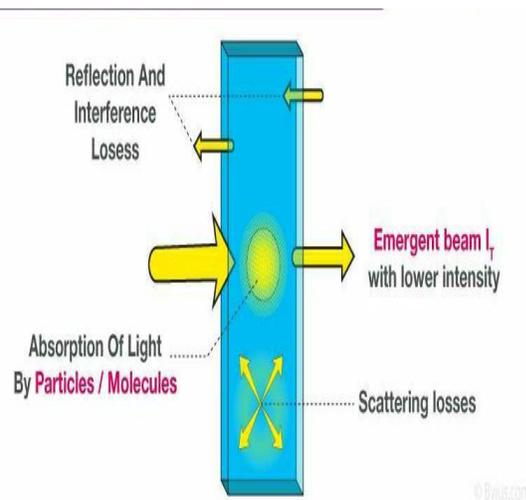
$$A = \epsilon c l$$

$A$  = absorbance (no units).

$\epsilon$  = Molar extinction coefficient ( $M^{-1} \text{ cm}^{-1}$ ).

$c$  = Concentration ( $M$ ).

$l$  = pathlength (cm).



#### 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.

Mathematically it can be expressed as

$$-\frac{dI}{dx} \propto I \text{ ----- (1)}$$

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

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

Where  $-\frac{dI}{dx}$  is the rate of decrease of intensity with thickness  $dx$ ,  $a$  is called the *absorption co-efficient*. Integration of equation (2) after rearrangement gives,

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

Where  $C$  is a constant of integration. At  $x=0, I=I_0$ . So,  $C = -\ln I_0$ . Introducing this in equation (3) we get,

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

Equation (4) can also be written as,

$$I = I_0 e^{-ax} \text{ ----- (5)}$$

### Beer- Lambert's law....

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

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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,

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

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

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.

### Uv- spectroscopy

Ultraviolet –visible spectroscopy or ultraviolet–visible spectrophotometry (UV–Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full adjacent visible spectral regions. This means it uses light in the visible and adjacent ranges.

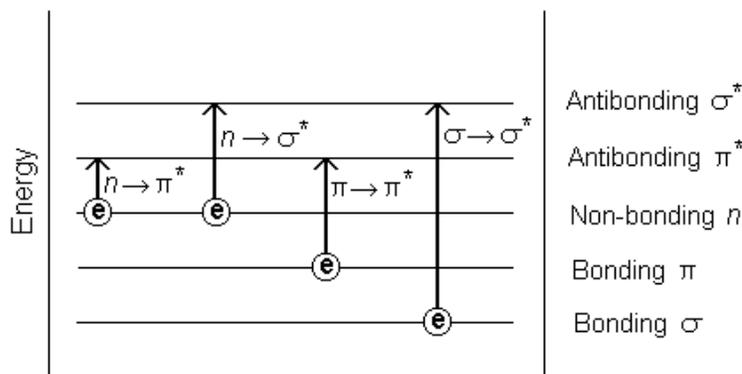
Ultraviolet-visible (UV-Vis) spectrophotometry is a technique used to measure light absorbance across the ultraviolet and visible ranges of the electromagnetic spectrum. A UV-Vis spectrophotometer can use this principle to quantify the analytes in a sample based on their absorption characteristics.

### Principle of ultraviolet–visible absorption:-

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the **HOMO** and the **LUMO**), the longer the wavelength of light it can absorb. There are four possible types of transitions ( $\pi-\pi^*$ ,  $n-\pi^*$ ,  $\sigma-\sigma^*$ , and  $n-\sigma^*$ ), and they can be ordered as follows :  $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$ .

Electronic transitions:

There are four possible types of transitions ( $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ , and  $n \rightarrow \sigma^*$ ), and they can be ordered as follows:  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$ .



### $\sigma \rightarrow \sigma^*$ Transitions:

An electron in a bonding  $\sigma$  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)

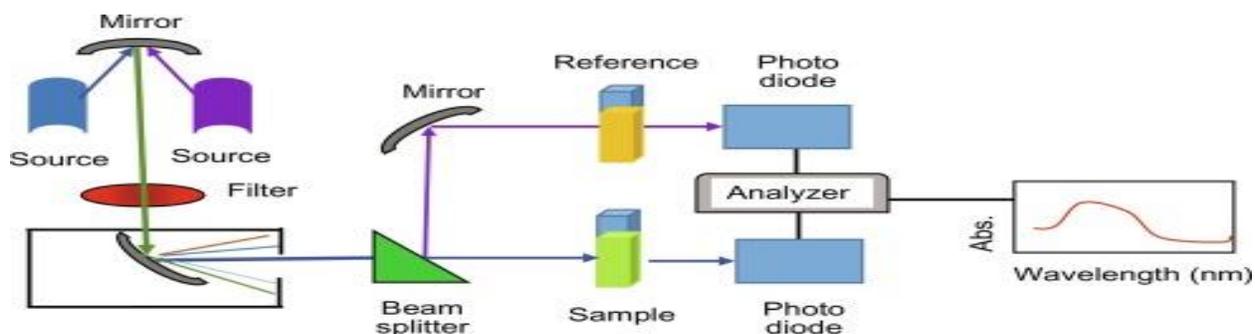
### $n \rightarrow \sigma^*$ Transitions:

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  $\pi$  electrons to the  $\pi^*$  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  $\pi$  electrons.

Instrumentation:



### Basic Components of a UV-Vis Spectrometer:

#### 1. Light Source:

- **Deuterium Lamp:** Provides UV light (usually 190-400 nm).
- **Tungsten-Halogen Lamp:** Provides visible light (usually 400-700 nm).
- Some instruments use a combination of both lamps to cover the full UV-Visible range.

#### 2. Monochromator:

- Used to isolate specific wavelengths of light.
- Consists of a diffraction grating or a prism to disperse light into its component wavelengths.
- A slit selects the desired wavelength from the dispersed light.

#### 3. Sample Holder:

- Typically a cuvette, which is a small, transparent container that holds the sample.
- Cuvettes are made of materials like quartz, glass, or plastic, depending on the wavelength range being studied.

#### 4. Detector:

- Measures the intensity of light passing through the sample.
- Common types of detectors include photomultiplier tubes (PMTs), photodiodes, and charge-coupled devices (CCDs).
- The detector converts the light signal into an electrical signal.

#### 5. Data Processing System:

- Analyzes the electrical signal from the detector.
- Usually involves a computer with software to display and analyze the absorbance or transmittance spectra.

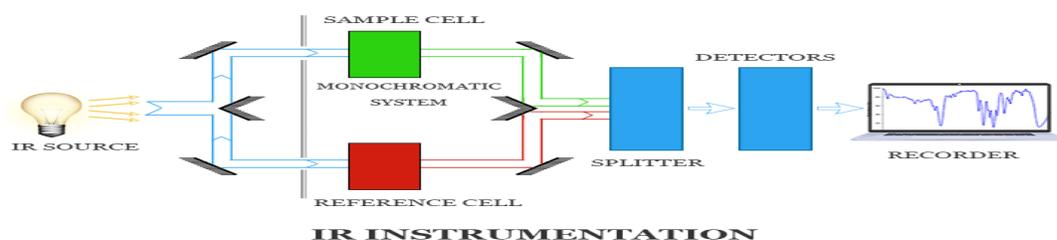
### Applications of UV-Vis Spectroscopy:

- **Quantitative Analysis:** Determining the concentration of a substance in a solution by using Beer-Lambert's law.
- **Qualitative Analysis:** Identifying compounds based on their absorption spectra.
- **Kinetics Studies:** Monitoring the rate of chemical reactions.
- **Protein and Nucleic Acid Analysis:** Measuring concentrations and purity of biological samples.
- **Environmental Analysis:** Detecting pollutants in water and air.

## IR-Spectroscopy:

Infrared (IR) spectroscopy is an analytical technique used to identify and study chemicals through their interaction with infrared light. It measures the absorption of IR radiation by molecules, which causes changes in their vibrational and rotational states.

Instrumentation:



## Basic Components of an IR Spectrometer:

### 1. IR Light Source:

- Common sources include Nernst glowers, Globar sources (silicon carbide), and tungsten filament lamps.
- These sources emit a broad spectrum of infrared radiation.

### 2. Sample Holder:

- Samples can be solids, liquids, or gases.
- Solid samples can be prepared as KBr pellets, Nujol mulls, or thin films on IR-transparent windows.
- Liquid samples are usually placed in cells with IR-transparent windows (e.g., made of NaCl or KBr).
- Gas samples are contained in gas cells with long path lengths.

### 3. Monochromator:

- Disperses the IR light into its component wavelengths.
- Uses gratings or prisms to achieve dispersion.
- Some modern instruments use Fourier Transform (FT) methods, which do not require a monochromator.

### 4. Detector:

- Measures the intensity of IR light.
- Common detectors include thermocouples, thermistors, and pyroelectric detectors (e.g., deuterated triglycine sulfate, DTGS).
- Mercury cadmium telluride (MCT) detectors are used in FT-IR spectrometers for higher sensitivity.

### 5. Interferometer (in FT-IR):

- In FT-IR spectrometers, the Michelson interferometer is used.
- It splits the IR beam into two paths, recombines them, and creates an interference pattern that is transformed into a spectrum using a Fourier transform algorithm.

### 6. Data Processing System:

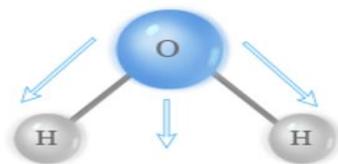
- Converts the detector signal into an absorbance or transmittance spectrum.
- Analyzes and displays the spectral data, often with software for peak identification and quantification.

## Fundamental Modes of Vibration:

### 1. Types of Vibrational Modes:

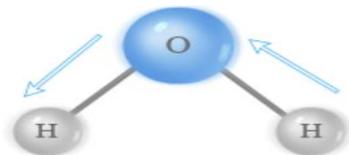
#### ○ Stretching:

- **Symmetric Stretching:** Two bonds increase and decrease in length simultaneously.



*Symmetric stretching*

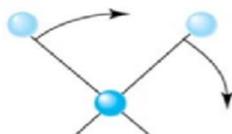
- **Asymmetric Stretching:** One bond lengthens while the other shortens.



*Asymmetric stretching*

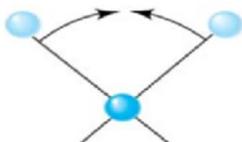
#### ○ Bending:

- **Scissoring:** Two atoms move towards and away from each other, like scissors.



**In-plane rocking**

- **Rocking:** Two atoms move in the same direction, maintaining the angle between bonds.



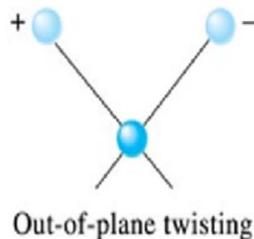
**In-plane scissoring**

#### Torsional :

- **Wagging:** Two atoms move up and down out of the plane.



- **Twisting:** Two atoms move in opposite directions, out of the plane.



### Selection Rules:

Selection rules determine which vibrational transitions are allowed and will appear in the IR spectrum. These rules are based on changes in the dipole moment of the molecule.

#### 1. IR Selection Rule:

- A vibrational mode is IR-active if it involves a change in the dipole moment of the molecule. This means that during the vibration, the distribution of electrical charges in the molecule must change.

#### 2. Dipole Moment:

- The dipole moment is a measure of the separation of positive and negative charges in a molecule.
- For a vibration to be IR-active, the dipole moment must change in magnitude or direction as the molecule vibrates.

### Applications of IR Spectroscopy:

- **Identification of Functional Groups:** Determining the presence of specific functional groups (e.g., OH, NH, CO, etc.) in molecules.
- **Structural Analysis:** Provides information about the molecular structure and bonding.
- **Quantitative Analysis:** Measures the concentration of components in a mixture.
- **Quality Control:** Ensures the quality and purity of products in pharmaceuticals, food, and chemical industries.
- **Environmental Monitoring:** Detects pollutants and contaminants in air, water, and soil.
- **Forensic Science:** Analyzes substances found at crime scenes.
- **Polymer and Material Science:** Studies the composition and properties of polymers and other materials.

## **Chromatography:-**

Chromatography may be defined as method of separating a mixture of components into individual component through equilibrium distribution between two phases.

... Chromatography involves a sample (or sample extract) being dissolved in a mobile phase (which may be a gas, a liquid or a supercritical fluid).

A technique Exploiting the interaction of the components of a mixture with a stationary Phase and a Mobile phase in order to Separate the components .

Components are divided different levels of absorption to the stationary phase and Solubility in the Mobile phase.

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.

- Types of chromatography:-

### **Classification**

#### **Planar chromatography.....**

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

#### **Column chromatography**

The stationary phase is supported in a narrow tube through which the mobile phase is forced through a pressure

#### **Applications:-**

1. To identify and analyze 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

It is used for the trace level analysis of variety of compounds in a short time.

Principle:

The principle of separation is normal phase mode and reverse phase mode is adsorption. When a mixture of components is introduced into HPLC column, they travel according to their relative affinities towards the stationary phase. The component which has more affinity towards stationary phase travels slower and which has less affinity travel faster. No two components have the same affinity.

## Instrumentation:

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

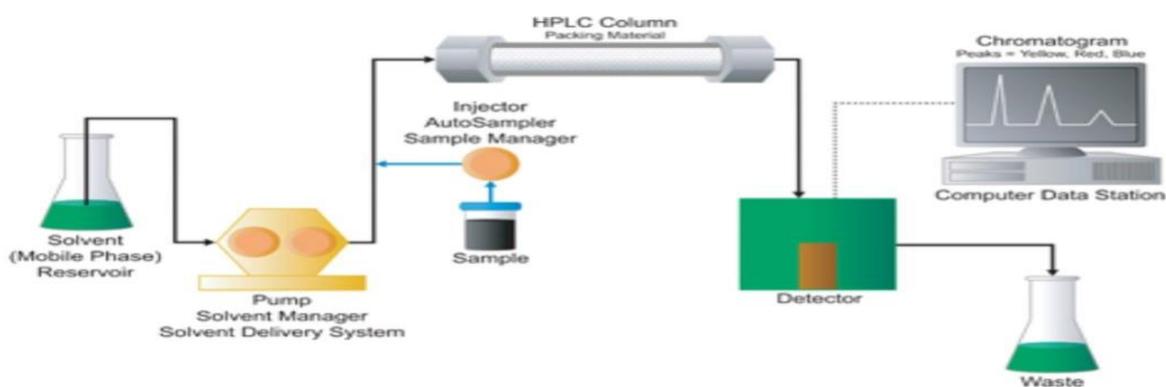
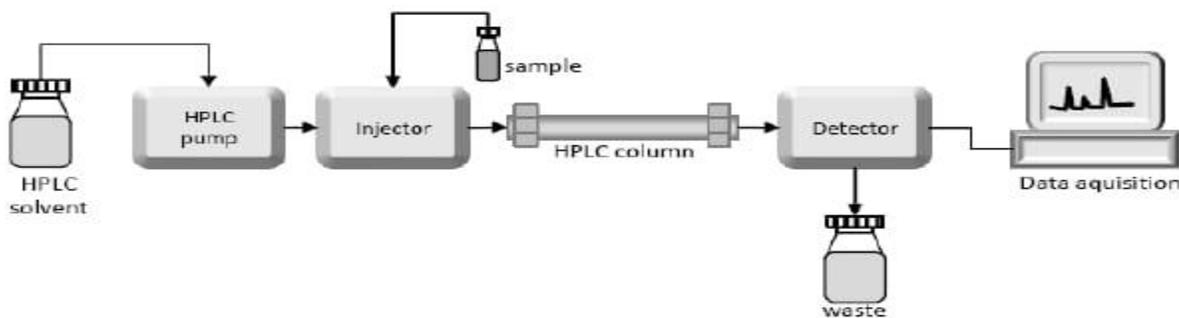


Figure E: High-Performance Liquid Chromatography [HPLC] System



## Detector

The UV, VIS, and PDA detectors are categorized as absorbance detectors. They provide good sensitivity for light absorbing compounds at ~pg level. They are easy to operate and provide good stability. UV detector is a very commonly used detector for HPLC

## Solvent Reservoir

Solvent reservoir, which contains the solvent used to carry the sample through the system. The solvent should be filtered with an inlet solvent filter to remove any particles that could potentially damage the system's sensitive components. It must contain volume enough for repetitive analysis. It must be inert solvent

## Pump

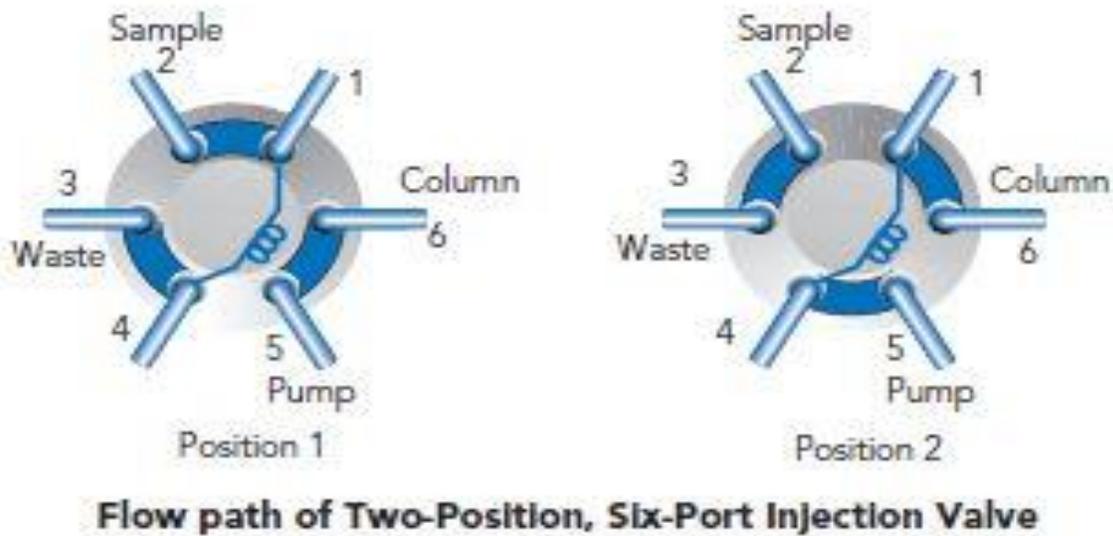
If one pump is used the composition of mobile phase is constant, It is called isocratic elution. If two or more pumps are used, the composition of mobile phase is variable is called gradient elution

## column

Columns are the main component in HPLC because the column is responsible for the separation of the sample components. The sample passes through the column with the mobile phase and separates in its components when it comes out from the column.

## Injectors:-

The most useful and widely used sampling device is the six port rheodyne valve. The sample is introduced into the sample loop using a special syringe. A clockwise rotation of the valve rotor places the sample filled loop into the mobile phase stream



## Data Collection Devices

Signals from the detector may be collected on chart recorders or electronic integrators that vary in complexity and in their ability to process, store and reprocess chromatographic data. The computer integrates the response of the detector to each component and places it into a chromatograph that is easy to read and interpret.

**Applications :**

1. Analysis of drugs
2. Analysis of synthetic polymers
3. Analysis of pollutants in environmental analytics
4. Determination of drugs in biological matrices
5. Isolation of valuable products
6. Product purity and quality control of industrial products and fine chemicals
7. Separation and purification of biopolymers such as enzymes or nucleic acids
8. Water purification
9. Pre-concentration of trace components
10. Ligand-exchange chromatography
11. Ion-exchange chromatography of proteins
- 12. High-pH anion-exchange chromatography of carbohydrates and oligosaccharides**