Sreenivasa Institute of Technology and Management Studies

(Autonomous Approved by AICTE, New Delhi. Affiliated to JNTUA, Anantapuramu.)

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APPLIED CHEMISTRY
(23BSC111)

LECTURENOTES

I-B. TECH &II-SEM

Prepared by:

Mrs . K. RAMYA, Assistant Professor

Department of Humanities &Sciences

23 Regulations

HUMANITIES AND SCIENCES

Course Code	CHEMISTRY	L	T	P	C
23BSC111		3	0	0	3

Course Objectives:

- To familiarize engineering chemistry and its applications.
- To train the students on the principles and applications of electrochemistry and polymers.
- To introduce instrumental methods, molecular machines and switches

Course Outcomes (CO): After completion of the course, the student can able to

CO-1: Apply Schrodinger wave equation to hydrogen atom , Illustrate the molecular orbital energy level diagram of different molecular species , Explain the calculation of bond order of O_2 and Co molecules .

CO-2: Apply the principle of Band diagrams in application of conductors and semiconductors .

CO-3: Compare the materials of construction for battery and electrochemical sensors .

CO-4: Explain the preparation, properties, and applications of thermoplastics &thermosetting, elastomers& conducting polymers.

CO-5: Explain the principles of UV spectroscopy, and applications

Unit- I: Structure and Bonding Models:

Fundamentals of Quantum mechanics, Schrodinger Wave equation, significance of Ψ and Ψ2, particle in one dimensional box, molecular orbital theory – bonding in homo- and heteronuclear diatomic molecules – energy level diagrams of O_2 and CO, etc. π-molecular orbitals of butadiene and benzene, calculation of bond order

Unit-II: **Modern Engineering materials:**

Semiconductors, band diagram in solids, Semiconductor devices (p-n junction diode as rectifier and transistors)

Super conductors-Introduction basic concept, applications.

Supercapacitors: Introduction, Basic Concept-Classification – Applications.

Nano materials: Introduction, classification, properties and applications of Fullerenes, carbon Nano tubes and Graphine nanoparticles.

Unit-III: Electrochemistry

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

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, carbon fibres.

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), Polyl 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 spectroscopies, fundamental modes and selection rules, Instrumentation. Chromatography-Basic Principle, Classification-HPLC: Principle, Instrumentation and Applications.

Textbooks:

1. Jain and Jain, Engineering Chemistry, 16/e, Dhan Patrai, 2013. 2. Peter Atkins, Julio de Paula and James Keeler, Atkins' Physical Chemistry, 10/e, Oxford University Press, 2010

Reference Books:

1. G.V. Subba Reddy, K.N. Jayaveera and C. Ramachandra, Engineering Chemistry, Mc Graw Hill, 2020. 2. Skoog and West, Principles of Instrumental Analysis, 6/e, Thomson, 2007. 3. D. Lee, Concise Inorganic Chemistry, 5/e, Oxford University Press, 2008. 4. J.M. Lehn, Supra Molecular Chemistry, VCH Publications

UNIT-I: Structure and Bonding Models

Lecture notes

Planck's Quantum theory was proposed by Max Planck in1900.This theory explains the nature of black body radiation.

Black Body Radiation:- When solids are heated, they emit radiation over a wider range of wavelengths.

Definition: - "An ideal body which can emit and absorb radiation of all frequencies is called

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

Planck's Quantum Theory: -

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

The main points of quantum theory are:

- The emission and absorption of the energy by an atom occurs in the form of radiation is be not a continuous process.
- The emission and absorption of the energy by a body occurs in the form of pockets of energy is called quanta(or)photon.
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$E=h\nu$

Where v is the frequency of radiation and *h* is Planks ’ constant 6.626×10^{-27} erg. sec (or) 6.626×10^{34} J. sec. A body can radiate (or) absorb energy in whole number multiples of a quantum hv ,2hv, 3hv, nhv.

Where $\nu = \frac{C}{\lambda}$

$E = nhc / \lambda$

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

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

Dual nature of an electron

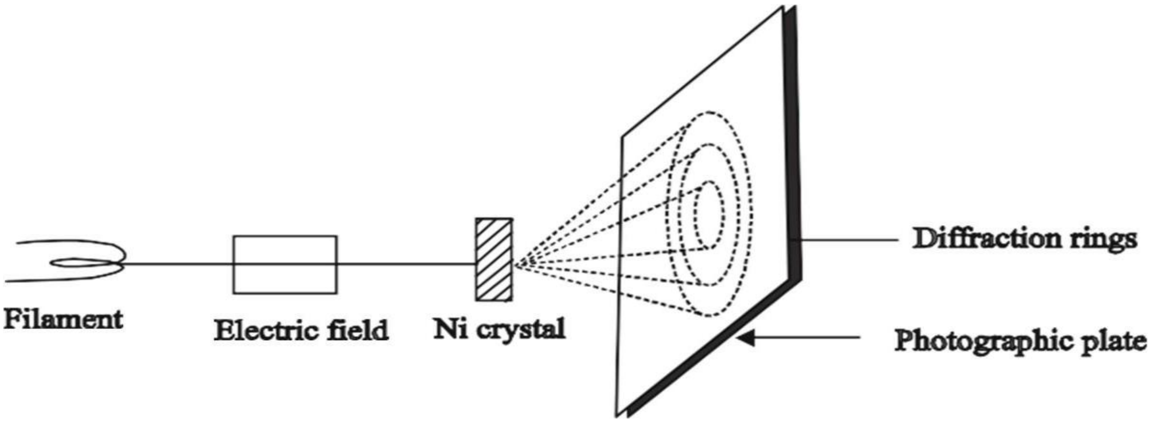
In case of light some phenomenon like diffraction and interference can be explained on the basis of its **wave character**. However, the other phenomenon such as black body radiation and photoelectric effect can be explained only on the basis of its **particle nature**. Thus, light is said to have a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

Particle character

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

Wave character

The wave character of microscopic particles such as an electron can be verified by the Division and Germer experiment. The experiment was originally suggested to verify the wave character of an electron. In this experiment, a beam of electrons obtained from a heated filament is allowed to strike in a nickel crystal. The nickel crystal operates like a natural grating and a characteristic diffraction pattern is observed on a photographic plate placed behind the crystal. This experiment confirms that the electron is capable of exhibiting diffraction, which is characteristic of a wave.



This is how it establishes the wave character of electrons.
Schrodinger Wave Equation and significance of ψ and ψ^2.

The Schrodinger wave equation can be derived from the classical wave equation as well as from the third postulate of quantum mechanics. Now though the two routes may appear completely different, the final result is just the same indicating the objectivity of the quantum mechanical system.

After the failure of the Bohr atomic model to comply with the Heisenberg's uncertainty principle and dual character proposed by Louis de Broglie in 1924, an Austrian physicist Erwin Schrodinger developed his legendary equation by making the use of wave-particle duality and classical wave equation. In order to understand the concept involved, consider a wave traveling in a string along the x-axis with velocity v.

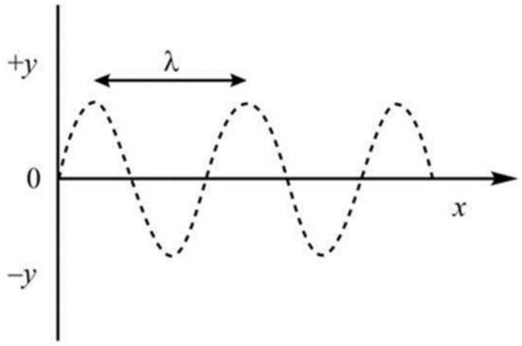


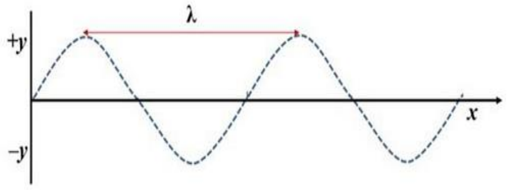
Figure 1. The wave motion in a string.

Schrodinger Time independent wave equation :

Whenever we want to understand how a system evolves, we need a law. Such laws are often called **equations of motion**. For *classical systems*, the fundamental equation of motion is called Newton's second law, F =ma, and for *relativistic systems*, it is the geodesic equation.

Similarly, for (non-relativistic) *quantum systems*, the equation that governs the evolution of the system is the Schrödinger equation. The full version of it is called the **time-dependent Schrödinger equation** (or TDSE for short):

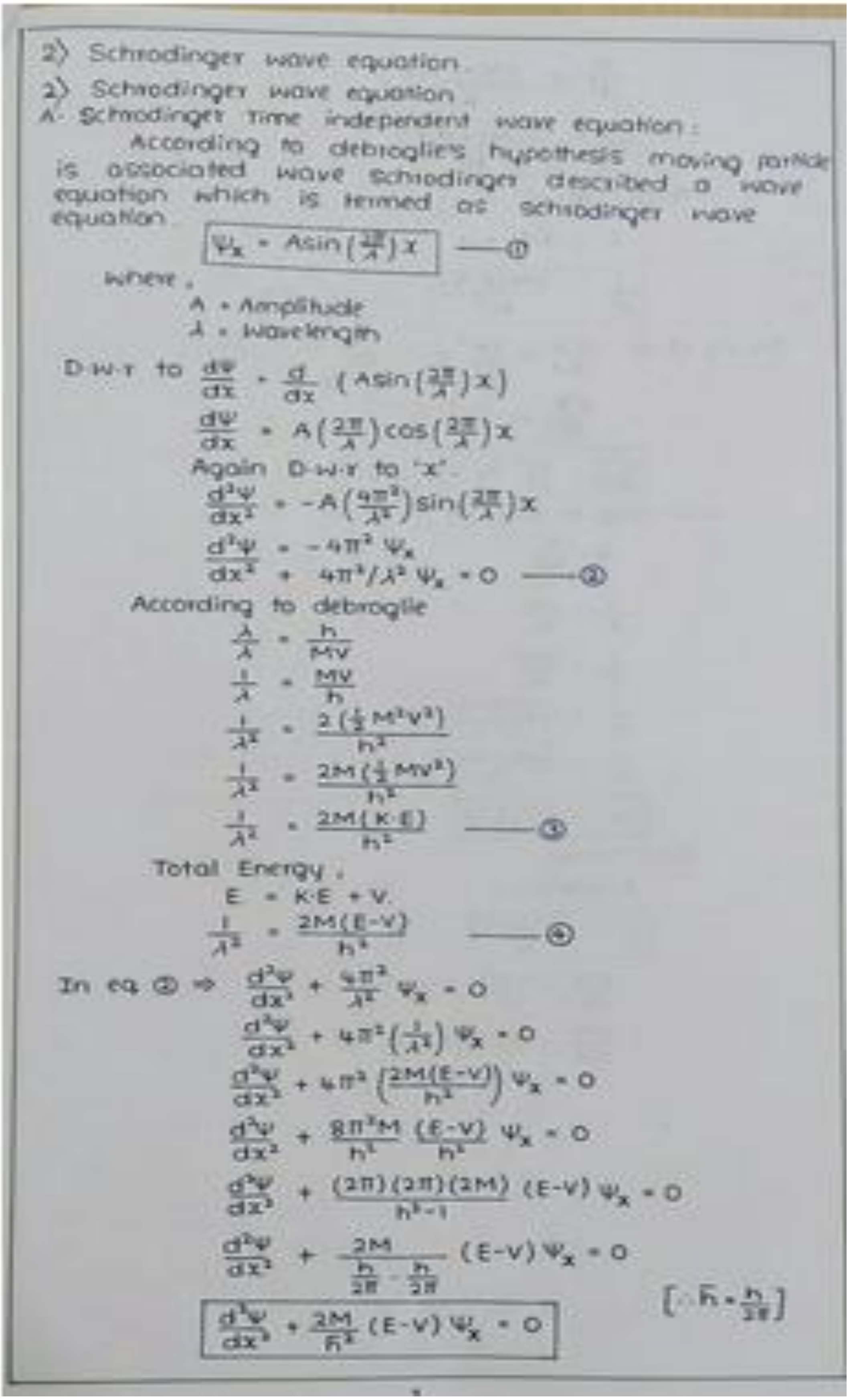
Time independent Schrodinger wave equation



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

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

Schrodinger equation :



2) Schrodinger wave equation

2) Schrodinger wave equation

A. Schrodinger Time independent wave equation :

According to debroglie's hypothesis moving particle is associated wave Schrodinger described a wave equation which is termed as Schrodinger wave equation

$$\boxed{\psi_x = A\sin\left(\frac{2\pi}{\lambda}\right)x} \quad \text{—— ①}$$

where,

A = Amplitude

λ = Wavelength

D.w.r to $\frac{d\psi}{dx} = \frac{d}{dx}\left(A\sin\left(\frac{2\pi}{\lambda}\right)x\right)$

$$\frac{d\psi}{dx} = A\left(\frac{2\pi}{\lambda}\right)\cos\left(\frac{2\pi}{\lambda}\right)x$$

Again D.w.r to "x".

$$\frac{d^2\psi}{dx^2} = -A\left(\frac{4\pi^2}{\lambda^2}\right)\sin\left(\frac{2\pi}{\lambda}\right)x$$

$$\frac{d^2\psi}{dx^2} = -4\pi^2\,\psi_x$$

$$\frac{d^2\psi}{dx^2} + 4\pi^2/\lambda^2\,\psi_x = 0 \quad \text{—— ②}$$

According to debroglie

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

$$\frac{1}{\lambda} = \frac{Mv}{h}$$

$$\frac{1}{\lambda^2} = \frac{2\left(\frac{1}{2}M^2v^2\right)}{h^2}$$

$$\frac{1}{\lambda^2} = \frac{2M\left(\frac{1}{2}Mv^2\right)}{h^2}$$

$$\frac{1}{\lambda^2} = \frac{2M(K.E)}{h^2} \quad \text{—— ③}$$

Total Energy :

$$E = K.E + V.$$

$$\frac{1}{\lambda^2} = \frac{2M(E-V)}{h^2} \quad \text{—— ④}$$

In eq ② ⇒ $\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi_x = 0$

$$\frac{d^2\psi}{dx^2} + 4\pi^2\left(\frac{1}{\lambda^2}\right)\psi_x = 0$$

$$\frac{d^2\psi}{dx^2} + 4\pi^2\left(\frac{2M(E-V)}{h^2}\right)\psi_x = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2M}{h^2}\,\frac{(E-V)}{h^2}\,\psi_x = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{(2\pi)(2\pi)(2M)}{h^{2-1}}(E-V)\,\psi_x = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\frac{h}{2\pi}\cdot\frac{h}{2\pi}}(E-V)\,\psi_x = 0$$

$$\left[\because \hbar = \frac{h}{2\pi}\right]$$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2}(E-V)\,\psi_x = 0}$$

Now differentiating equation (14) w.r.t. *x* only, we get

$$\frac{\partial y}{\partial x} = f'(t)\frac{\partial f(x)}{\partial x}$$

Differentiating again

$$\frac{\partial^2 y}{\partial x^2} = f'(t)\frac{\partial^2 f(x)}{\partial x^2}$$

Now put the value of equation (19) and (21) in equation (13), we get

$$f'(t)\frac{\partial^2 f(x)}{\partial x^2} = \left(\frac{1}{v^2}\right)[-4\pi^2\nu^2 f(x)\, f'(t)]$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{v^2} f(x)$$

The equation (23) is now time-independent; and therefore, shows the amplitude dependence only upon the coordinate *x*. Since *c* = *ν*λ (*ν* = *c*/λ), the velocity of the wave can also be replaced by the multiplication of frequency and wavelength i.e. v = *ν*λ.

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{\nu^2\lambda^2} f(x)$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x)$$

The symbol of the function *f(x)* is replaced by popular ψ(*x*) or simply the ψ.

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-4\pi^2}{\lambda^2}\psi$$

Also, as we know that λ=*h*/*m*v, the equation (26) becomes

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-4\pi^2 m^2 v^2}{h^2}\psi$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0$$

Furthermore, as the total energy (*E*) is simply the sum of the potential (*V*) and kinetic energy, we can say that

$$E = \frac{mv^2}{2} + \mathrm{v}$$

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

After putting the value of mv^2 from equation (30) in equation (28), we get

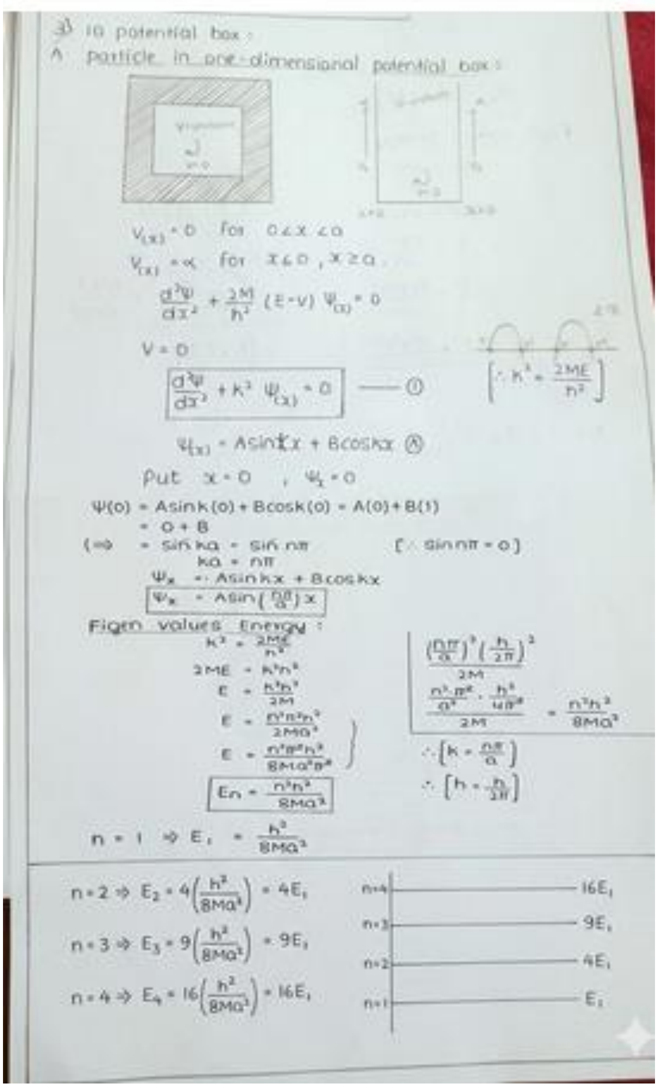
$$\frac{\partial^2\psi}{\partial x^2} - \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

For three-dimension i.e. $\psi(x, y, z)$, the above equation can be extended to following

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

The above-mentioned second order differential equation i.e. equation (32) is our popular form of the Schrodinger wave equation.

Particle in one dimensional potential box (1D Potential box)



3) 1D potential box :

A. particle in one-dimensional potential box :

$V_{(x)} = 0$ for $0 < x < a$

$V_{(x)} = \infty$ for $x \le 0,\ x \ge a$

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2}(E - V)\,\psi_{(x)} = 0$$

$V = 0$

$$\boxed{\frac{d^2\psi}{dx^2} + k^2\,\psi_{(x)} = 0} \quad \text{--- ①} \qquad \left[\because k^2 = \frac{2ME}{\hbar^2}\right]$$

$$\psi_{(x)} = A\sin kx + B\cos kx \quad Ⓐ$$

Put $x = 0$, $\psi_x = 0$

$$\psi(0) = A\sin k(0) + B\cos k(0) = A(0) + B(1)$$
$$= 0 + B$$
$$\Rightarrow\ = \sin ka = \sin n\pi \qquad [\because \sin n\pi = 0]$$
$$ka = n\pi$$
$$\psi_x = A\sin kx + B\cos kx$$
$$\boxed{\psi_x = A\sin\left(\frac{n\pi}{a}\right)x}$$

Eigen values Energy :

$$k^2 = \frac{2ME}{\hbar^2}$$
$$2ME = k^2\hbar^2$$
$$E = \frac{k^2\hbar^2}{2M}$$
$$E = \frac{n^2\pi^2\hbar^2}{2Ma^2}$$
$$E = \frac{n^2\pi^2 h^2}{8Ma^2\pi^2}$$
$$\boxed{E_n = \frac{n^2h^2}{8Ma^2}}$$

$$\frac{\left(\frac{n\pi}{a}\right)^2\left(\frac{h}{2\pi}\right)^2}{2M}$$
$$\frac{\frac{n^2\pi^2}{a^2}\cdot\frac{h^2}{4\pi^2}}{2M} = \frac{n^2h^2}{8Ma^2}$$
$$\therefore \left[k = \frac{n\pi}{a}\right]$$
$$\therefore \left[\hbar = \frac{h}{2\pi}\right]$$

$$n = 1 \Rightarrow E_1 = \frac{h^2}{8Ma^2}$$

$$n = 2 \Rightarrow E_2 = 4\left(\frac{h^2}{8Ma^2}\right) = 4E_1$$
$$n = 3 \Rightarrow E_3 = 9\left(\frac{h^2}{8Ma^2}\right) = 9E_1$$
$$n = 4 \Rightarrow E_4 = 16\left(\frac{h^2}{8Ma^2}\right) = 16E_1$$

significance of Ψ and Ψ2:

ψ is a wave function and refers to the amplitude of electron wave i.e. probability amplitude. It has got no physical significance. The wave function ψ may be positive, negative or imaginary.

[ψ]2 is known as probability density and determines the probability of finding an electron at a point within the atom. This means that if:

(i) is zero, the probability of finding an electron at that point is negligible.

(ii) [ψ]2 is high, the probability of finding an electron is high i.e. electron is present at that place for a long time.

(iii) [ψ]2 is low. the probability of finding an electron is low i.e. electron is present at that place for a shorter time.

Application of hydrogen atom in Schrodinger wave equation:

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

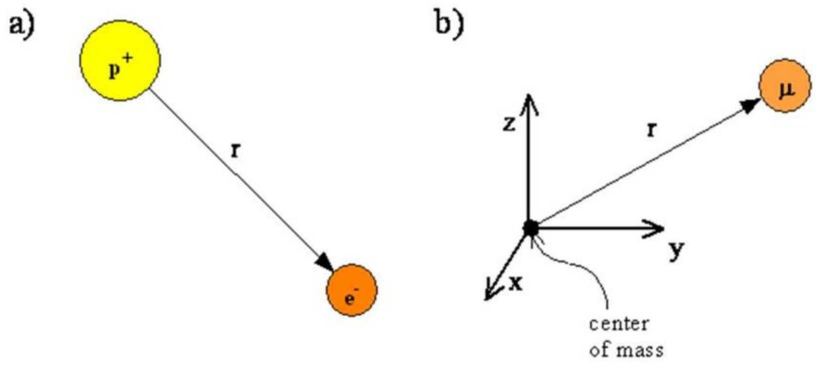


Figure 4.10.14.10.1: a) The proton (p+p+) and electron (e−e−) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The Schrödinger Equation for the hydrogen atom

H^(r,θ,φ)ψ(r,θ,φ)=Eψ(r,θ,φ)

employs the same kinetic energy operator, T^T^, written in spherical coordinates. For the hydrogen atom, however, the distance, r, between the two particles can vary, unlike the diatomic molecule where the bond length was fixed, and the rigid rotor model was used. The hydrogen atom Hamiltonian also contains a potential energy term, V^V^, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

V^(r)=−e24πϵ0r(4.10.2)(4.10.2)V^(r)=−e24πϵ0r

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential.

It is convenient to switch from Cartesian coordinates x,y,z to spherical coordinates in terms of a radius r, as well as angles ϕ, which is measured from the positive x axis in the xy plane and may be between 0 and 2π, and θ, which is measured from the positive z axis towards the xy plane and may be between 0 and π.

Pi molecular orbitals of butadiene : 1,3 butadiene :

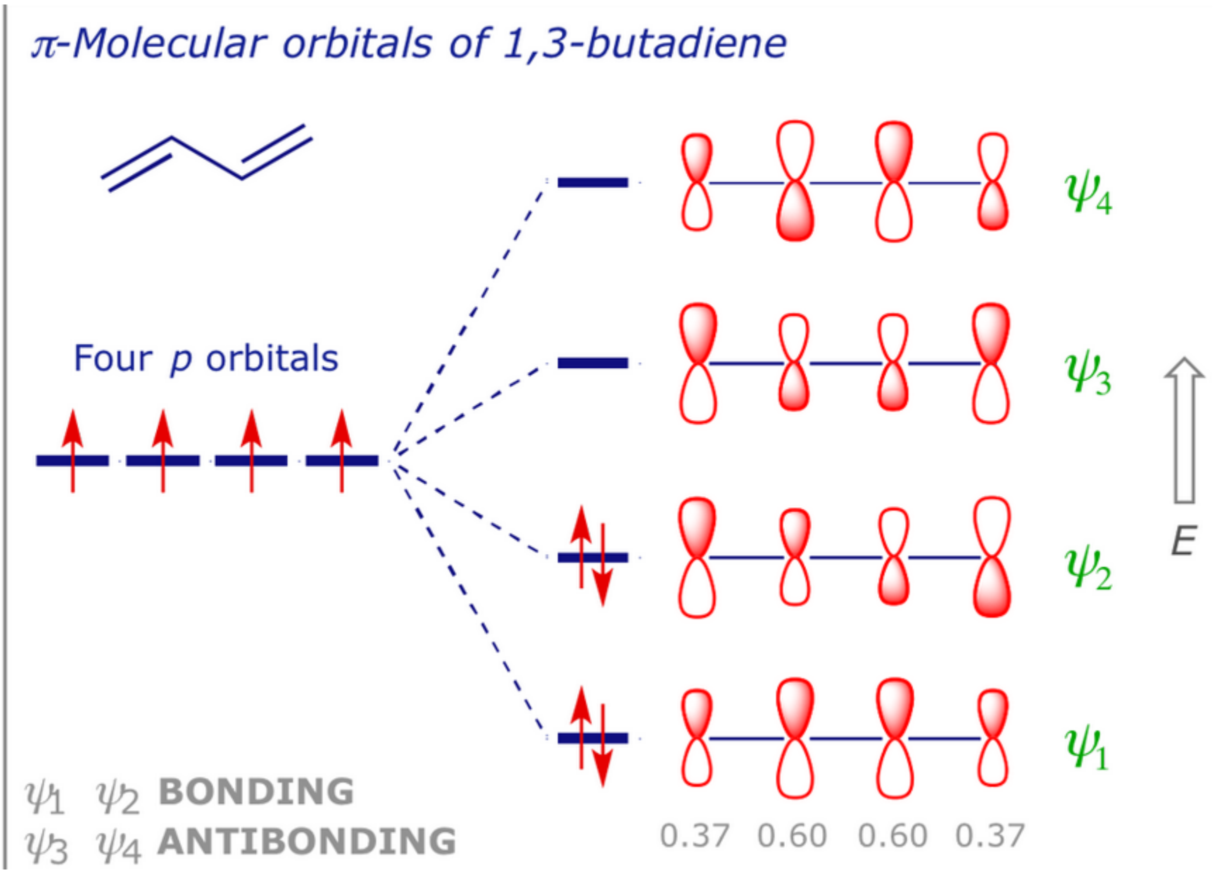
Butadiene is composed of 4 carbons with two adjacent Π bonds. These Π bonds are conjugated. All the four Pi orbitals are aligned with each other and buildup into a larger Π system. Since butadiene consists of 4 individual p orbitals, the Π system of butadiene will contain 4 Π molecular orbitals (containing4Πelectrons). During filling the lowest energy molecular orbitals get filled first as shown in the diagram.

The molecular orbital diagram of butadiene shows two molecular orbitals.

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

Bond order =The no of bonds between two atoms in all the structure/ Total no of resonating Structure.

BOND ORDER=1/2=0.5 .



1.

1. HOMO

HOMO is □2. It is the valence electrons of the □ system. They will be lost readily. If butadiene participates in a reaction, where It is the electron-donor (nucleophile), its electrons are going to come from that orbital.

2. LUMO

LUMO is □3. It is the lowest-energy unoccupied orbital. If butadiene participates in a reaction, where it is the electron acceptor(electrophile), the electrons will be donated to that orbital.

pi molecular orbital theory of Benzene :

Benzene □C6H6□ is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached. All carbon-carbon bonds have the same lengths having single and double bonds. There is a delocalized electrons above and below the plane of ring. There are six p-orbital electrons that form the stabilizing electron clouds below and above the aromatic ring. Molecular orbital description

We know that benzene has a planar hexagonal structure in which all the six carbon .

two carbon and one hydrogen atoms. The remaining cyclic array of six p- orbitals (one on each carbon) over lap to generate six molecular orbitals, three bonding and three anti-bonding.

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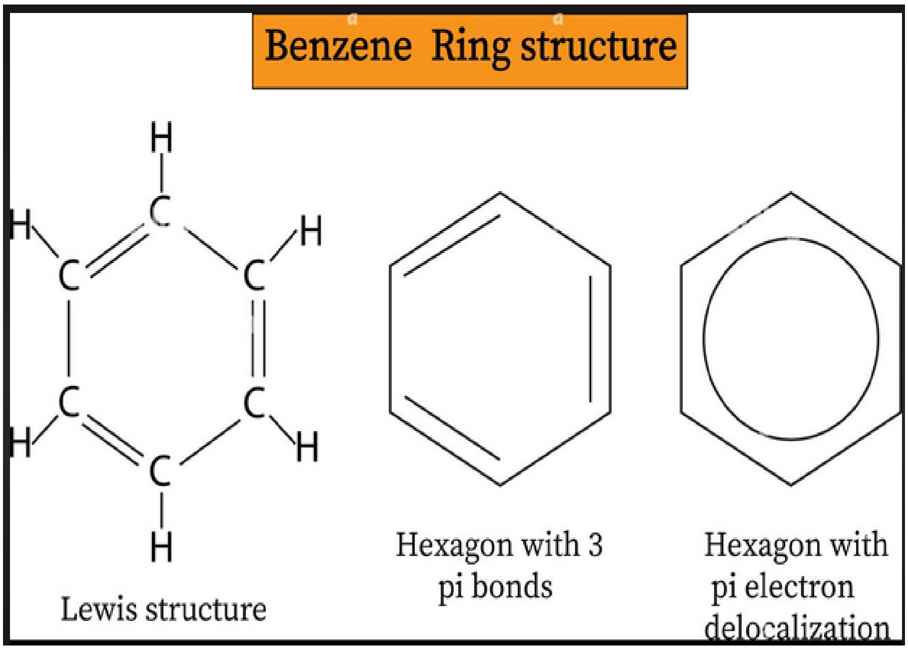
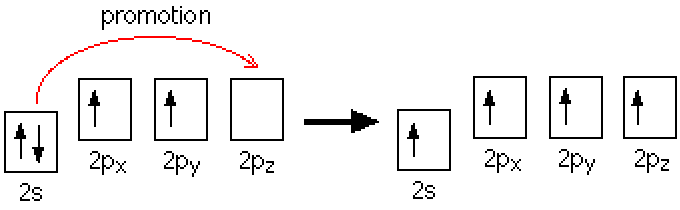
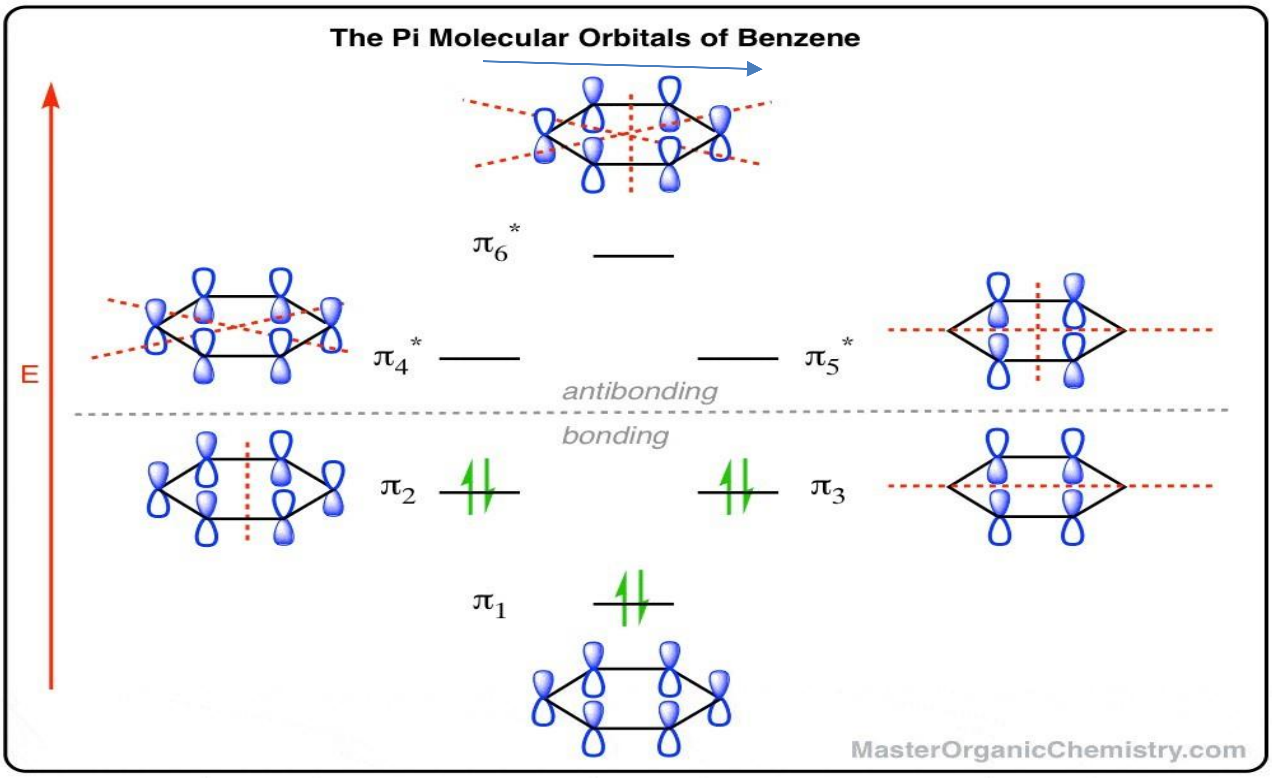


The plus [+]and minus[-] signs, shown in the diagram, do not represent electrostatic charge but refer to phase signs. When the phases, corresponds the orbitals, overlap to generate a common region of like phase, with those orbitals having greatest overlap(e.g.,▯1)being lowest in energy. The remaining carbon valence electrons then occupy these Molecular orbitals, in pairs, resulting in a fully occupied of bonding molecular orbital. BENZENE BOND ORDER= The no of bonds between two atoms in all the structure/ Total no of Resonating structure. B.D=3/2=1.5 ,Electronic configuration=$1S^2$ $2S^2$ $2P^2$[C6H6]

Electronic configuration : C6H6



$1S^2$ $2S^2$ $2P^2$



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De-Broglie’s equation:

The wavelength of the wave associated with any material particle was calculated by analogy with photon . According to the Planck’s quantum theory, If the photon has wave nature and its energy is given by,

$$E = hv \ldots (1)$$

Where, v is frequency of the wave and ‘*h*’ is Planck’s constant

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

$$E = mc^2 \ldots (2)$$

Where '*m*' is the mass of photon, '*c*' is the velocity of

light. From equation 1and2 we get,

$hv = mc^2$

But $v = c/\lambda$

$hc/\lambda = mc^2$ **(or)** $\lambda = h/mc$

The above equation is applicable to material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle.
Thus, for any material particle like electron
$\lambda = h/mv$ **(or)** $\lambda = h/p$

Where, *p* is the momentum of the particle

Heisenberg's Uncertainty Principle

Heisenberg's uncertainty principle states that for particles exhibiting both particle and wave nature, itwill not be possible to accurately determine both the position and velocity at the same time.The principle is named after German physicist, Werner Heisenberg who proposed the uncertainty principle in the year 1927. This principle was formulated when Heisenberg was in trying to build an intuitive model of quantum physics. He discovered that there were certain fundamental factors that limited our actions in knowing certain quantities. This principle basically highlights that simultaneous measurement of position and the velocity or momentum of microscopic matter waves will have an error such that the product of the error in measurement of position and momentum is equal or more than an integral multiple of a constant.,

a particle with a well-defined wavelength will show a definitive or precise velocity. All in all, if we get an accurate reading of one quantity it will only lead to large uncertainty in the measurement of the other.

If Δx is the error in position measurement and Δp is the error in the measurement of momentum, then

$$\Delta X \times \Delta p \geq h/4\pi$$

Since momentum, $p = mv$, Heisenberg's uncertainty principle formula can be alternatively written as- $\Delta X \times \Delta p \geq h/4\pi$

Or

$$\Delta X \times \Delta m \times \Delta v \geq h$$

$$/4\pi$$

Where, ΔV is the error in the measurement of velocity and assuming mass remaining constant during the experiment,

$$\Delta X \times \Delta V \geq h/4\pi m.$$

Accurate measurement of position or momentum automatically indicates rger uncertainty (error) in the measurement of the other quantity.Molecular orbital diagrams of Oxygen molecule (O2) and Nitrogen molecule (N2). Explain their magnetic nature and bond order:

Molecular orbital diagrams of Oxygen molecule (O2)

Oxygen molecule is formed from the combination of two O-atoms ($1s^2$, $2s^2$, $2p^2$, $2p^1$, $2p^1$).The outer shell of the O-atom

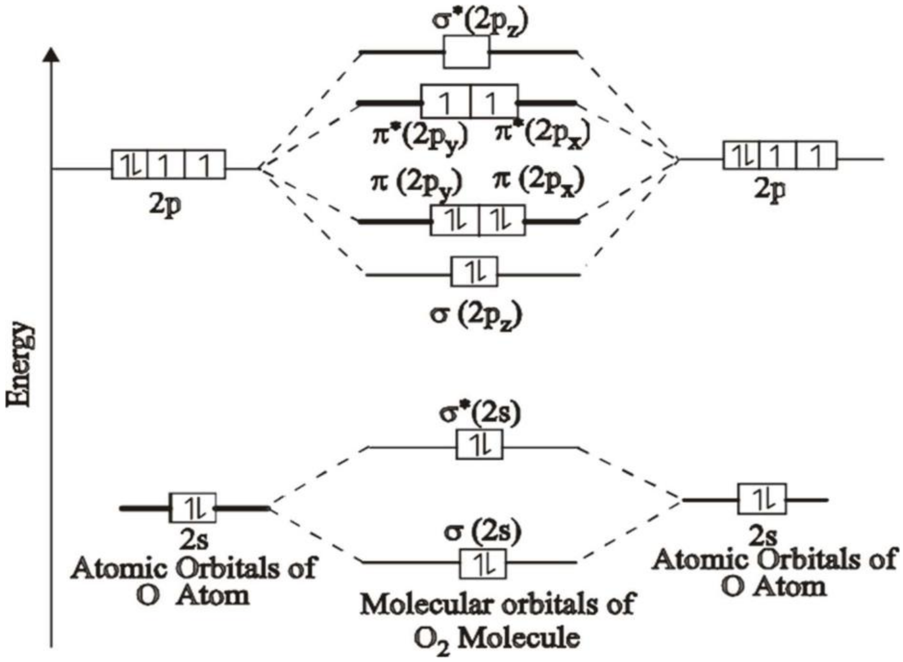


Fig: Molecular orbital diagram of O2 molecule

The bond order in O2:

Bond order = N_b-N_a/2 = 10 – 6 / 2 = 4/2 = 2

where
a = Number of electrons in bonding molecular orbitals.
b = Number of electrons in antibonding molecular orbitals.

Thus, the two oxygen atoms are bonded through **two bonds** (one σ and other π. The molecule is **stable** and **exists.**

(i) Magnetic properties

According to Hund’s rule, the last two electrons in π (2py) and π (2pz) orbitals remain unpaired. Therefore the molecule is **paramagnetic** due to the presence of two unpaired electrons.

Eg :- Molecular orbital diagrams of Nitrogen molecule (N2)

Electronic configuration of N2 (14 electrons) = $(\sigma1s)^2(\sigma^*1s)^2(\sigma2s)^2(\sigma^*2s)^2(\pi)^4(2pz)^2$

Electronic configuration of N2 (14 electrons) = $(\sigma1s)^2(\sigma^*1s)^2(\sigma2s)^2(\sigma^*2s)^2(\pi)^4(2pz)^2$

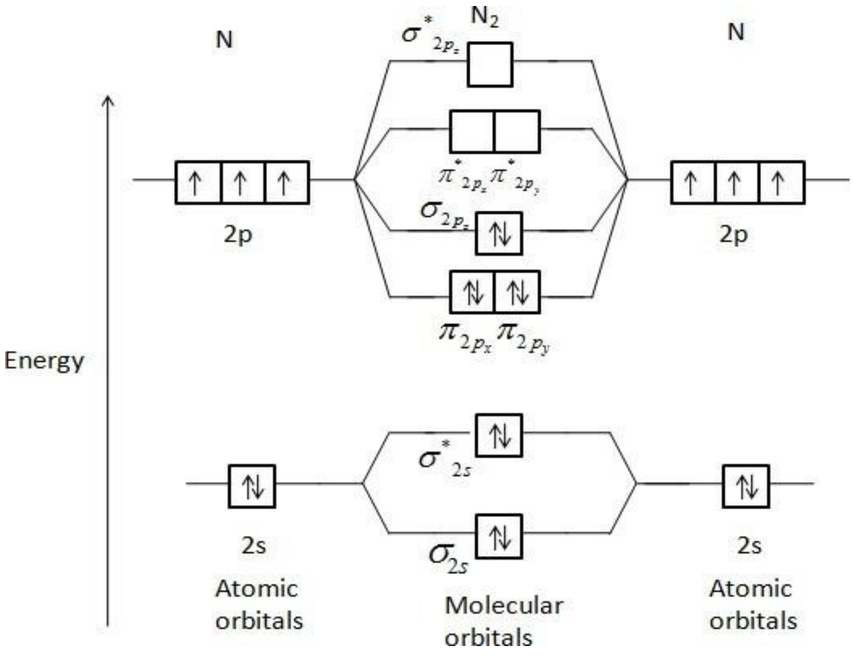


Fig: Molecular orbital diagram of N2 molecule

The bond order in N2

N (i) Bond order = N_b-N_a/2 = 10 – 4 / 2 = 6/2 = 3 where
a = Number of electrons in bonding molecular orbitals.
b = Number of electrons in antibonding molecular orbitals.

Thus, the two Nitrogen atoms are bonded through **three bonds** (one σ and other π). The molecule is **stable** and **exists.**

(ii) Magnetic properties

According to Hund's rule, all the electrons are paired Therefore the molecule is **diamagnetic**

due to the presence of paired electrons

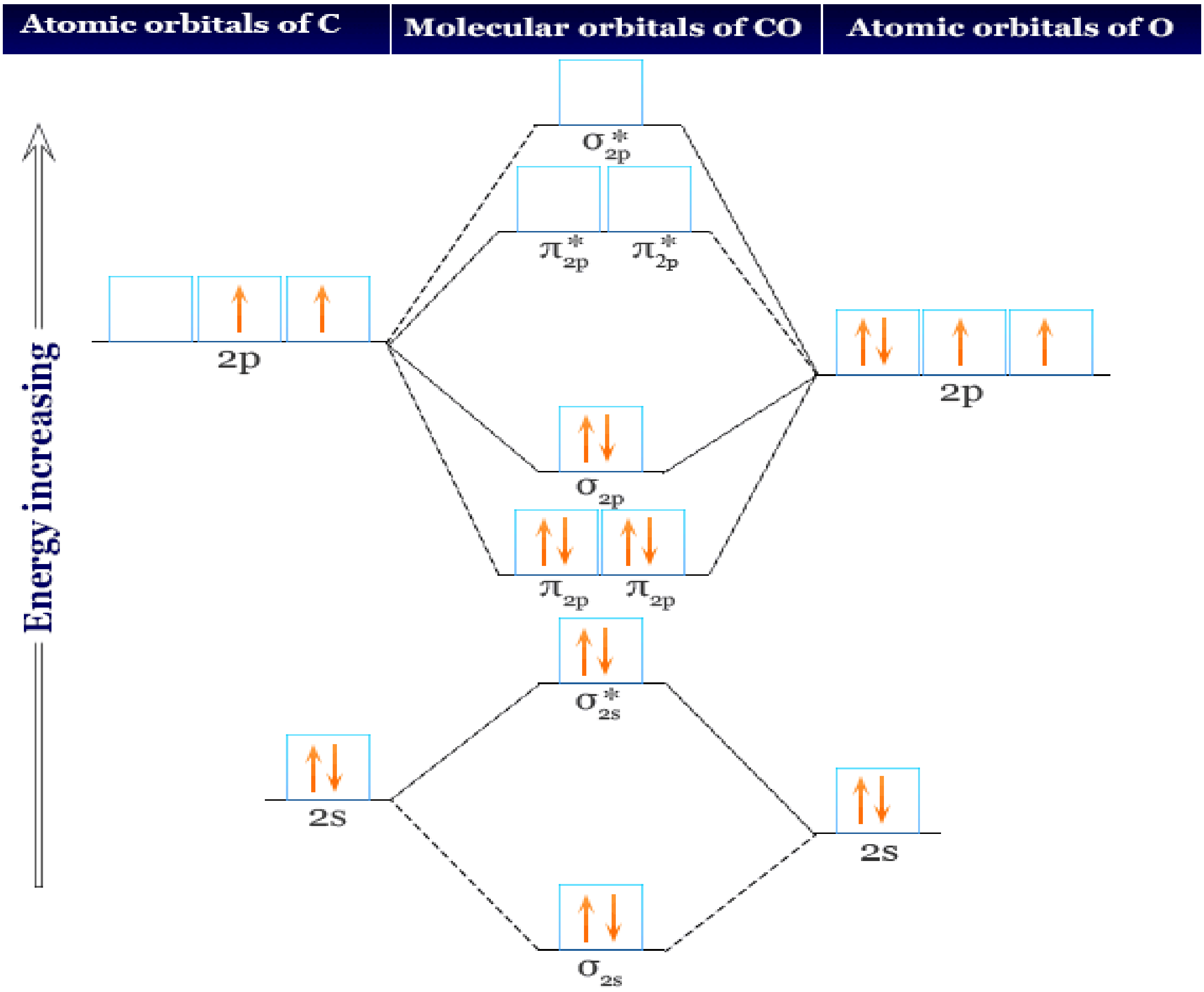
Energy level diagram of Carbon monoxide(CO) and (NO). Explain its magnetic

property and bond order.

Carbon monoxide is formed from the combination of one C–atom and one O–atom. The outer shell of the C–atom($1S^2$ $2s^2$, $2p^2$) contains 4 electrons and O–atom ($1S^2$ $2s^2$, $2p^4$) contains 6 electrons in the outer shell. Accordingly there are 1 electrons to be accommodated in the molecular orbitals of CO. The electronic configuration of CO molecule is represented by the equation.

$$CO: \sigma(2s)^2\sigma^*(2s)^2\pi(2p_y)^2\pi(2p_x)^2\sigma(2p_z)^2$$

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



The bond order in CO

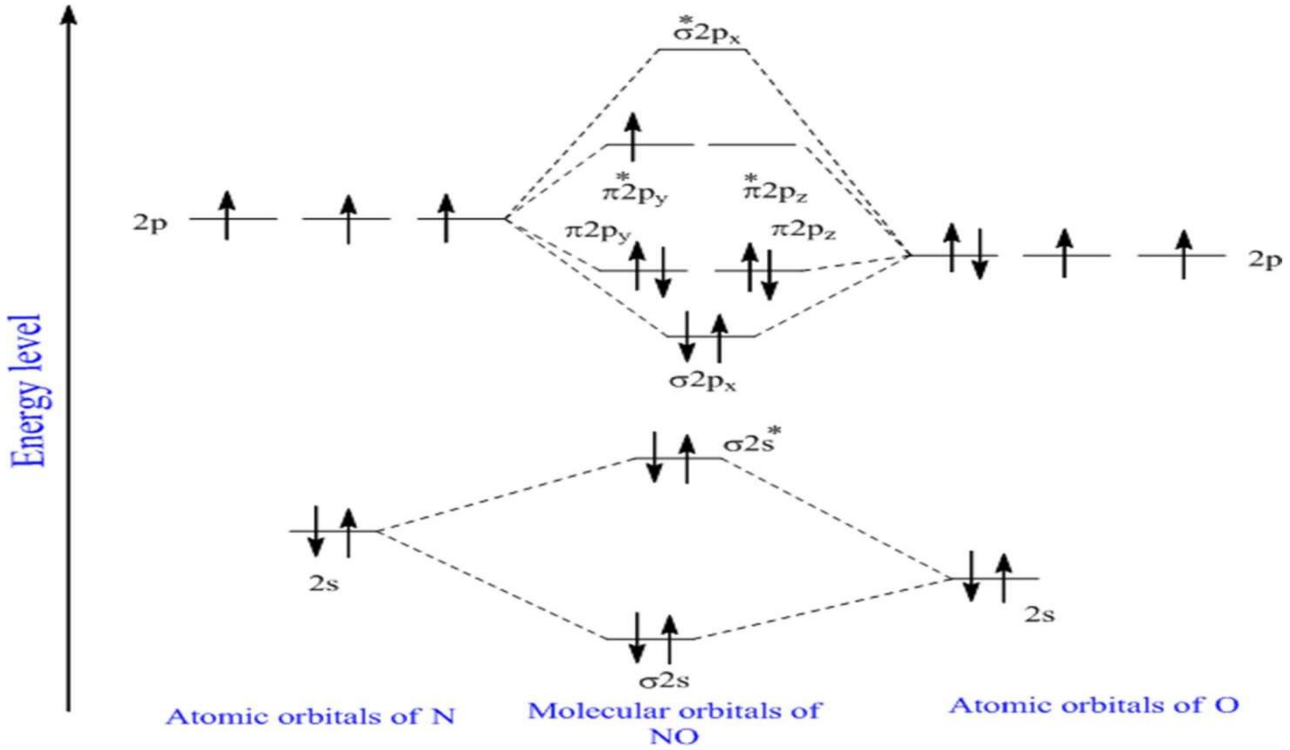
Bond order = Nb-Na/2 = 8 – 2 / 2 = 6/2 = 3

Thus, the C-atom and O-atom are bonded through three bonds (one □ and two□□.

(iii) Magnetic properties

Since noun paired electron is present in CO molecule. It is **diamagnetic**.

Eg:- Molecular energy level diagram of NO;



Eg:- Molecular energy level diagram of NO;

The molecular orbital energy level diagram for NO molecule is shown in fig.

(iv) The bond order in NO

Bond order = N_b-N_a/2 = 10 – 5 / 2 = 5/2 = 2.5

Thus, the N-atom and O-atom are bonded in ionic form.

(v) Magnetic properties

Since un paired electron is present in NO molecule. It is **Paramagnetic**.

Postulates of molecular orbital theory:

The Molecular Orbital Theory (often abbreviated to MOT) is a theory on chemical bonding developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. The valence-bond theory failed to adequately explain how certain molecules contain two or more equivalent bonds whose bond orders lie between that of a single bond and that of a double bond, such as the bonds in resonance-stabilized molecules. This is where the molecular orbital theory proved to be more powerful than the valence-bond theory (since the orbitals described by the MOT reflect the geometries of the molecules to which it is applied).

The key features of the molecular orbital theory are listed below.

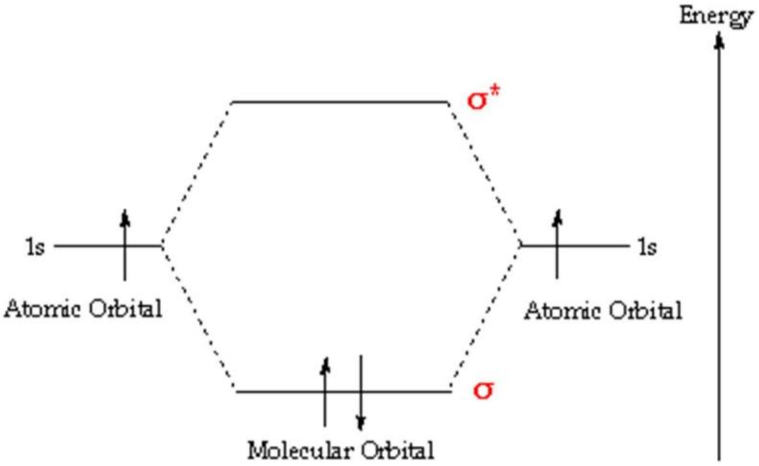
- The total number of molecular orbitals formed will always be equal to the total number of atomic orbitals offered by the bonding species.
- There exist different types of molecular orbitals viz; bonding molecular orbitals, anti-bonding molecular orbitals, and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
- The electrons are filled into molecular orbitals in the increasing order of orbital energy (from the orbital with the lowest energy to the orbital with the highest energy).
- The most effective combinations of atomic orbitals (for the formation of molecular orbitals) occur when the combining atomic orbitals have similar energies.

In simple terms, the molecular orbital theory states that each atom tends to combine

together and form molecular orbitals. As a result of such arrangement, electrons are found in various atomic orbitals and they are usually associated with different nuclei. In short

, an electron in a molecule can be present anywhere in the molecule.

Molecular orbital theory approximation of the molecular orbitals as linear combinations of atomic orbitals can be illustrated as follows.



Differences between bonding and anti-bonding:

Bonding molecular orbitals

- The molecular orbital formed by the constructive
- overlapping of atomic orbitals is called the bonding molecular orbital.
- In the bonding molecular orbitals, electrons
- density lies between the nuclei of bond atom.
- The bonding molecular orbitals represent the
- shape of molecule.

Antibonding molecular orbital

The molecular orbital formed by the destrcutive

- overlapping of atomic orbitals is called an antibonding molecular orbital.
- In the non bonding molecular orbitals, electrons
- density lies outside the nuclei of bonded atom.
- The non bonding molecular orbital does not
- contribute to shape of molecule.

THE-END

UNIT-II: MODERN ENGINEERING MATERIALS

Energy Bands

In the realm of materials science, the behaviour of substances regarding the flow of electric charge is categorised into three main types: conductors, insulators, and semiconductors. These distinctions are fundamental to various technological applications, ranging from basic circuitry to advanced electronics. To comprehend these concepts fully, it's crucial to delve into the underlying principles of electron behaviour within materials, particularly concerning valence bands, conduction bands, and bandgap in semiconductors

Conductors:

Conductors are materials that permit the flow of electrical current with little resistance. In conductors, electrons are loosely bound to their atoms, allowing them to move freely in response to an electric field.

Characteristics:

High Electrical Conductivity: Conductors possess a high number of free electrons available for conduction. Metals like copper and a Aluminium are classic examples of conductors due to their abundance of free electrons.

Low Resistivity: Conductors exhibit low resistance to the flow of electric current. This low resistance results from the ease with which electrons can move through the material.

External Influence: The conductivity of a conductor can be influenced by factors such as temperature, impurities, and mechanical stress.

Insulators:

Insulators are materials that inhibit the flow of electrical current. In insulators, electrons are tightly bound to their atoms, preventing their movement in response to an electric field.

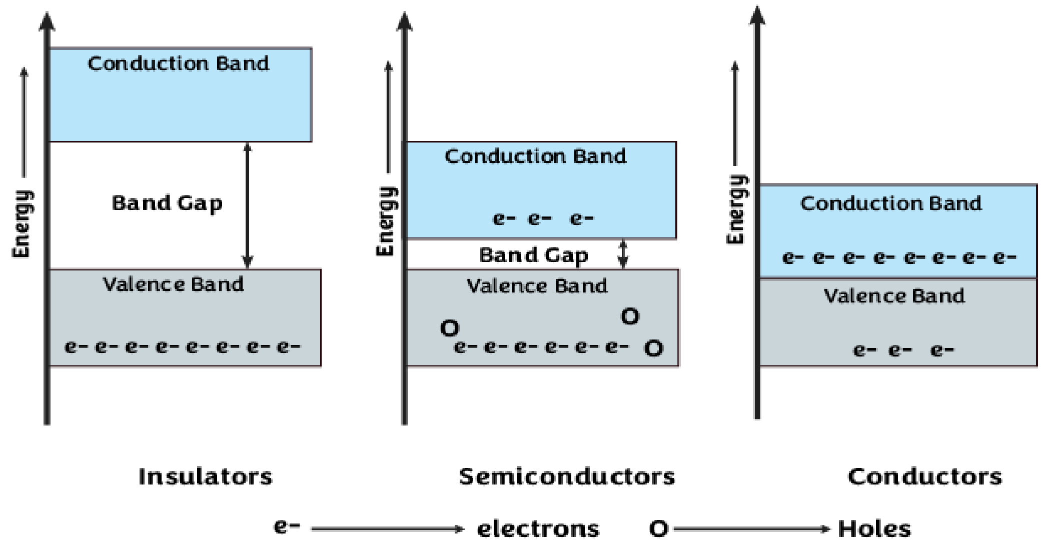
Characteristics:

High Electrical Resistivity: Insulators have very few free electrons available for conduction, resulting in high resistance to electric current flow.

Wide Bandgap: Insulators typically have a large energy gap between their valence and conduction bands, making it difficult for electrons to transition from the valence band to the conduction band.

Dielectric Properties: Insulators are often used as dielectric materials in capacitors and electrical insulation due to their ability to store electrical energy without conducting current.

Classification of solids on the basis of Band theory



Semiconductor

Semiconductors are materials with unique properties that allow them to conduct electricity under certain conditions. Their electrical conductivity lies between conductors, which conduct electricity easily, and insulators, which block electrical flow. This unique property makes them essential components in electronic devices and applications.

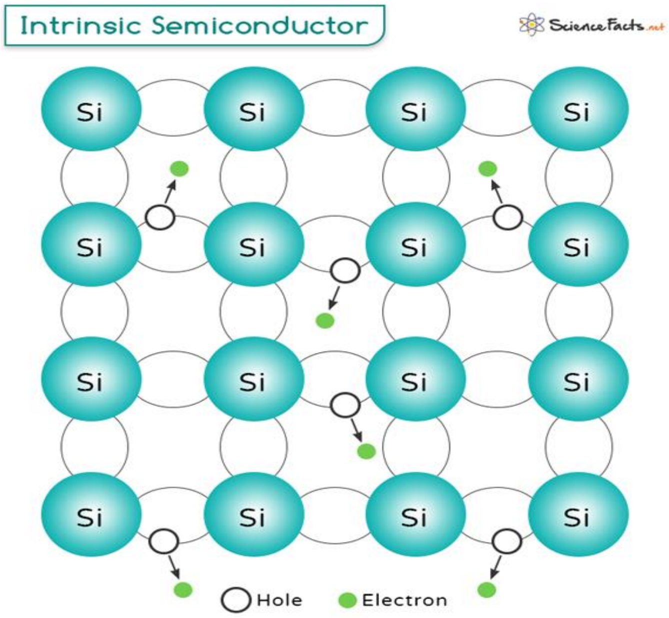
Examples of semiconductors include silicon (Si), germanium (Ge), gallium arsenide (GaAs), gallium nitride (GaN), indium phosphide (InP), and silicon carbide (SiC).

Doping: Adding impurities (trivalent or pentavalent atoms) to a semiconductor can change its electrical properties. N-type doping introduces more free electrons, while P-type doping creates more “holes”, which are positive charge carriers.

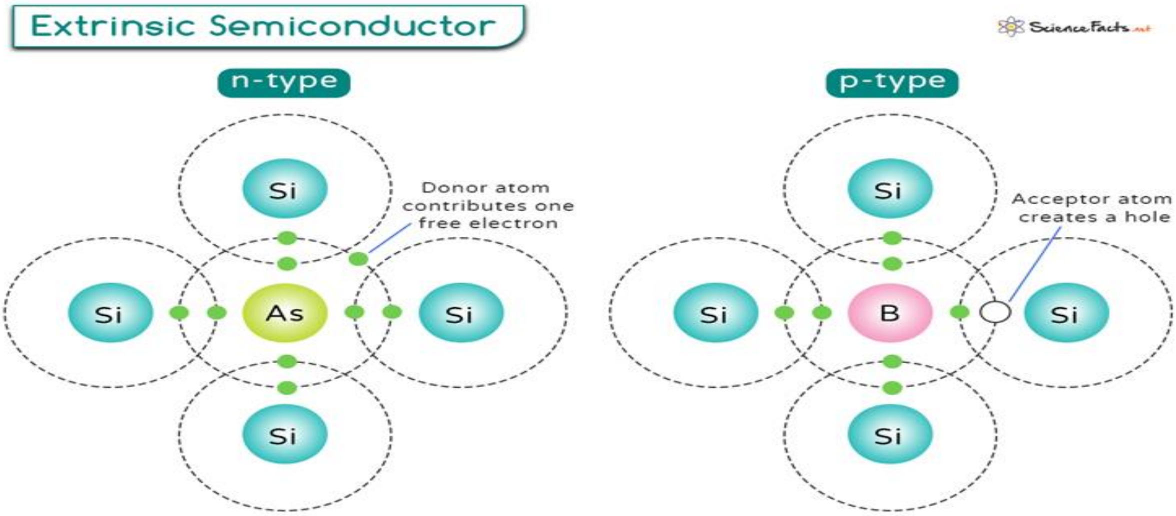
Energy Band Gap: Semiconductors have a well-defined energy band gap between the valence band, where electrons are bound to atoms, and the conduction band, where electrons can move freely. This gap determines how easily electrons can be excited to conduct electricity.

Types of Semiconductor

Intrinsic Semiconductors: They are pure semiconducting materials like silicon or germanium. Their electrical properties are determined by their structure. They have a limited number of charge carriers that can be easily excited by heat or electric field to conduct electricity.



Extrinsic Semiconductors: They are doped with impurities to enhance their conductivity. By adding specific atoms like phosphorus or boron to the crystal lattice of the semiconductor material, engineers can increase the number of charge carriers and modify its electrical properties. The next section discusses doping in extrinsic semiconductor properties. The next section discusses doping in extrinsic semiconductor section discusses doping in extrinsic semiconductor



This interplay between intrinsic properties and extrinsic modifications allows precise control over semiconductor behavior

Doping in Semiconductors

Doping is a crucial process in semiconductor technology that involves introducing impurities into a pure semiconductor material to alter its electrical properties. There are two main types of doping: N-type and P-type, each with distinct effects on the semiconductor's conductivity.

N-type: This doping type involves adding elements such as phosphorus or arsenic to a semiconductor material like silicon. These elements have one extra electron compared to silicon atoms, making them donors of electrons. When these donor atoms are introduced into the semiconductor crystal lattice, they release free electrons into the material, increasing its electron concentration. This excess of negatively charged electrons gives rise to an N-type semiconductor with high electron conductivity.

P-type: This doping type involves adding elements like boron or gallium to silicon. These elements have one less electron than silicon atoms, creating "holes" in the crystal lattice where an electron is missing. These "acceptor" atoms attract nearby electrons, creating spaces for new electrons to move in – effectively creating positively charged holes that behave as charge carriers. This results in a P-type semiconductor with increased hole concentration and enhanced hole conductivity.

APPLICATIONS OF SEMICONDUCTORS

Semiconductors are of enormous wide technological importance because of their special properties, which can be modified by doping. Some applications include:

Semiconductors are the foundation for modern electronics which includes radio, computers, and telephones.

Semiconductor-based electronics components employed in various applications including transistors, solar cells, light-emitting diodes (LEDs), and digital and analog integrated circuits.

The resistivity of semiconductors changes with temperature. On the basis of this, semiconductors enable to be used as thermometers.

Semiconductors are used in making of Hall Probes. These are measure magnetic field strengths with a small piece of semiconductor with known properties.

IR Sensors/Optoelectronic devices are made using semiconductors. Optoelectronic devices are capable of recognizing or responding to light of different wavelengths. This is called a phenomenon of photoconductivity

whereby a semiconductor can greatly increase its electrical conductivity if the

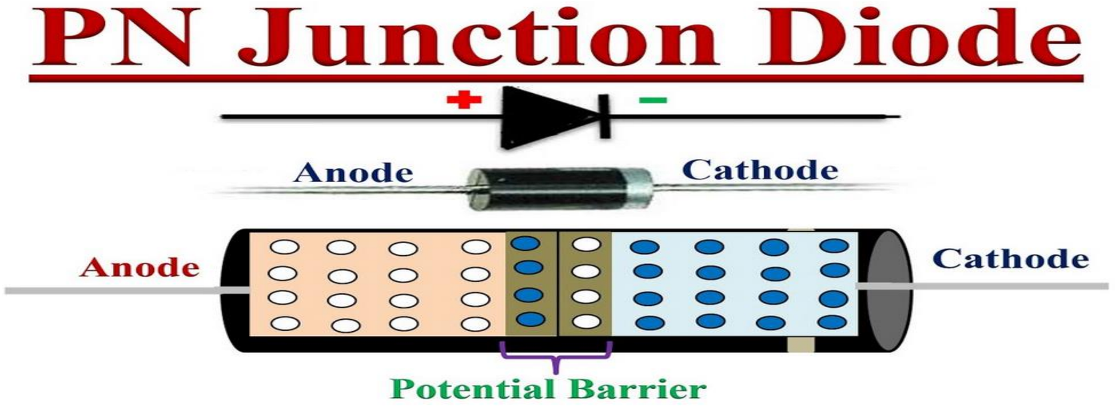
radiation energy has resonance with band gap energy can able to promote electrons across the band gap. Various semiconductors are available with different band gaps to suit particular applications.

P-N Junction diode as rectifier and transistors ;

When P-type and N-type semiconductors are placed in contact with one another, it forms a PN junction.

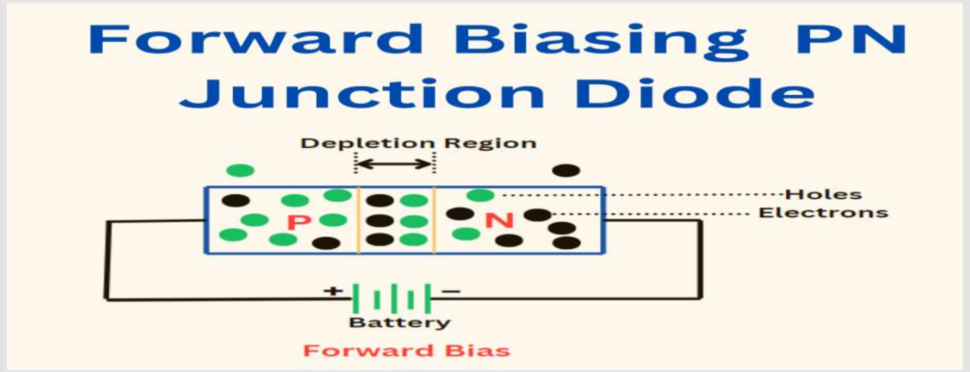
PN junction forms a popular semiconductor device called diode

A diode is a two terminal semiconductor device which conducts only in one direction offering a low resistance when forward biased and high resistance when reverse biased



Forward Biasing PN-Junction

PN Junction is said to be forward biased when the positive terminal of battery is connected to p-type and negative terminal of battery is connected to n-type as shown in fig.



If the applied voltage is less than the barrier potential, there will be no conduction

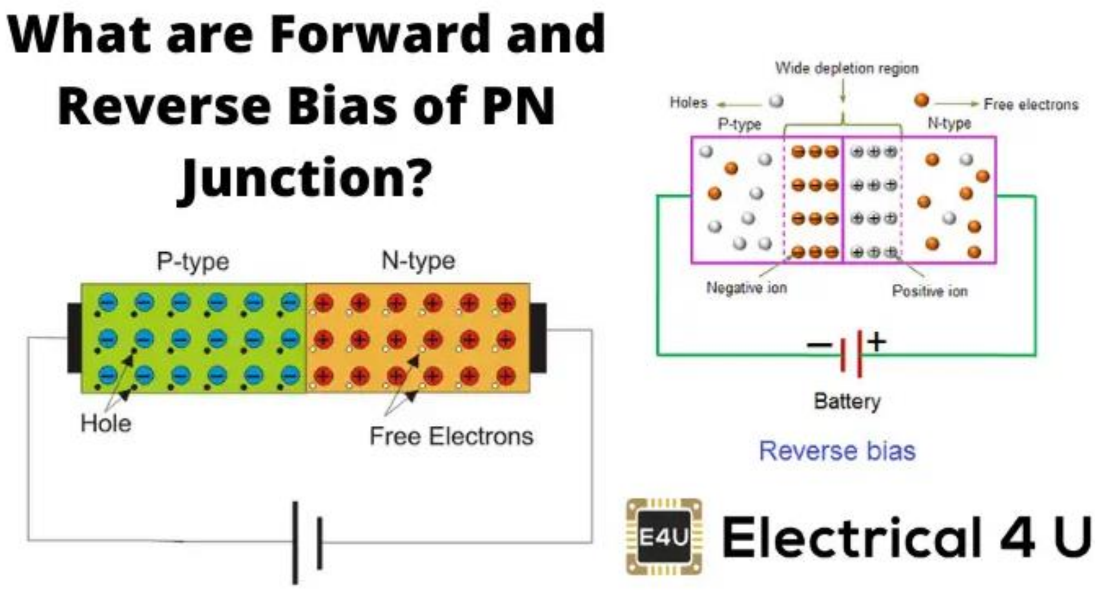
When the applied voltage is more than the barrier potential, then the holes on p-side which are positively charged gets repelled from positive terminal and driven towards junction.

Similarly the electrons on n-side which are negatively charged gets repelled from negative terminal and move towards the junction.

This result in the reduction of barrier potential, hence resulting large current known as forward current starts flowing as shown in fig.

Reverse Biasing PN-Junction

PN Junction is said to be reverse biased when the positive terminal of battery is connected to n-type and negative terminal of battery is connected to p-type as shown in fig.

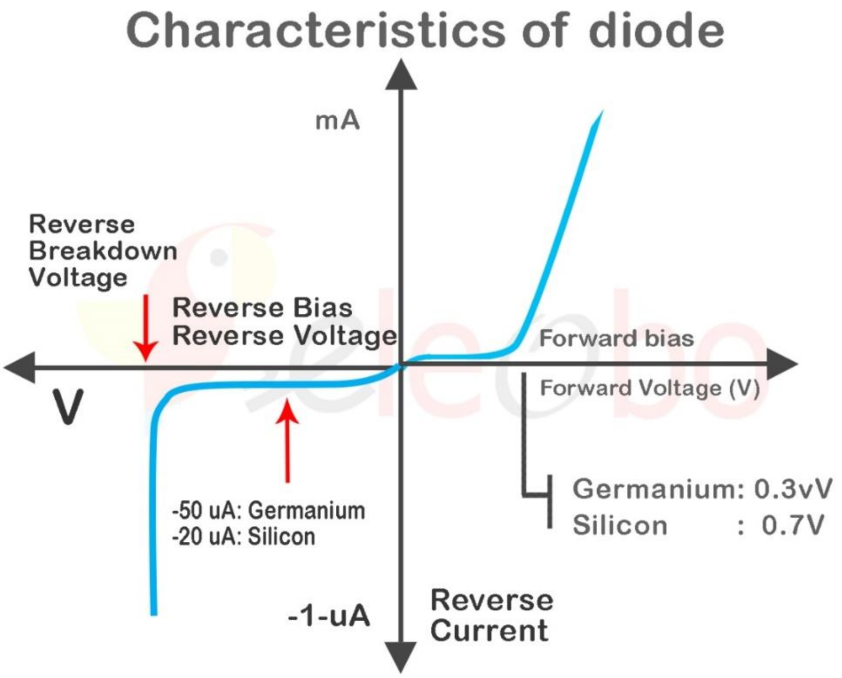


1. When PN junction is reverse biased, then the holes on p-side of junction are attracted
2. towards negative terminal and the electrons on n-side of junction are attracted towards
positive terminal of battery.

3 . Thus holes on p-side and electrons on n-side move away from the junction thereby increase
the barrier potential.

4. If the barrier voltage is increased, majority charged carriers cannot cross the junction and
there is no current flow across the junction.
Minority charge carriers cross the junction and leads to a small current flow called reverse
current as shown in fig

characteristics of diode:



Forward characteristics of diode

The positive terminal of battery is connected to p-type and negative terminal of battery is connected to n-type.

If supply voltage is less than the cut in voltage (0.7V for Si and 0.3V for Ge) of diode, then forward current very low.

If supply voltage is greater than the cut in voltage, then forward current increases linearly

Reverse characteristics of diode

The positive terminal of battery is connected to n-type and negative terminal of battery is connected to p-type.

Due to motion of minority carriers, a small reverse saturation current exists.

At point A, reverse breakdown of diode occurs and current increases sharply.

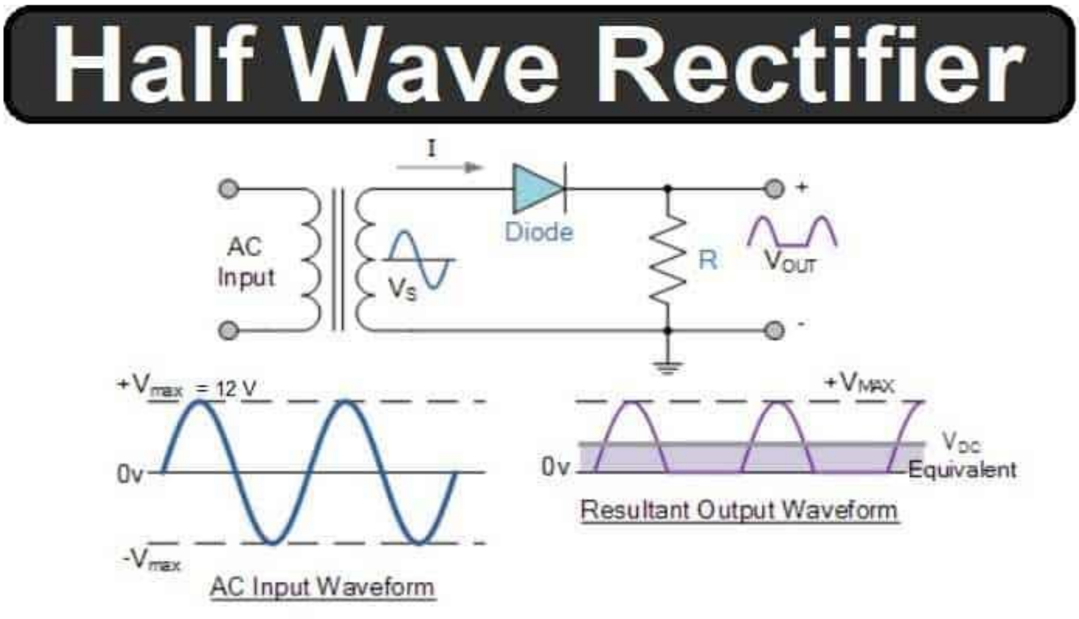
Rectifier

An electrical device used to convert ac voltage into pulsating dc voltage. Rectifiers are classified into 2 categories depending on period of condition.

1. Half wave rectifier
2. Full wave rectifier –which is further classified into
   a) Center tapped full wave rectifier
   b) Bridge rectifier

Half-wave rectifier

- Rectifiers which conducts current or voltage only during one half cycle of ac input is called half wave rectifier
- Fig shows half wave rectifier, which single diode acts as half wave rectifier.
- AC input supply to be rectified is applied through transformer to diode D and series load resistor RL



Operation:

- During positive half cycle of supply voltage, diode is said to be forward biased and acts as
  a short circuit and current flows through . Therefore V 0 = + V
- During negative half cycle of supply voltage, diode is said to be reverse biased and acts as
  an open circuit, no current flows through . Therefore V 0 = 0.

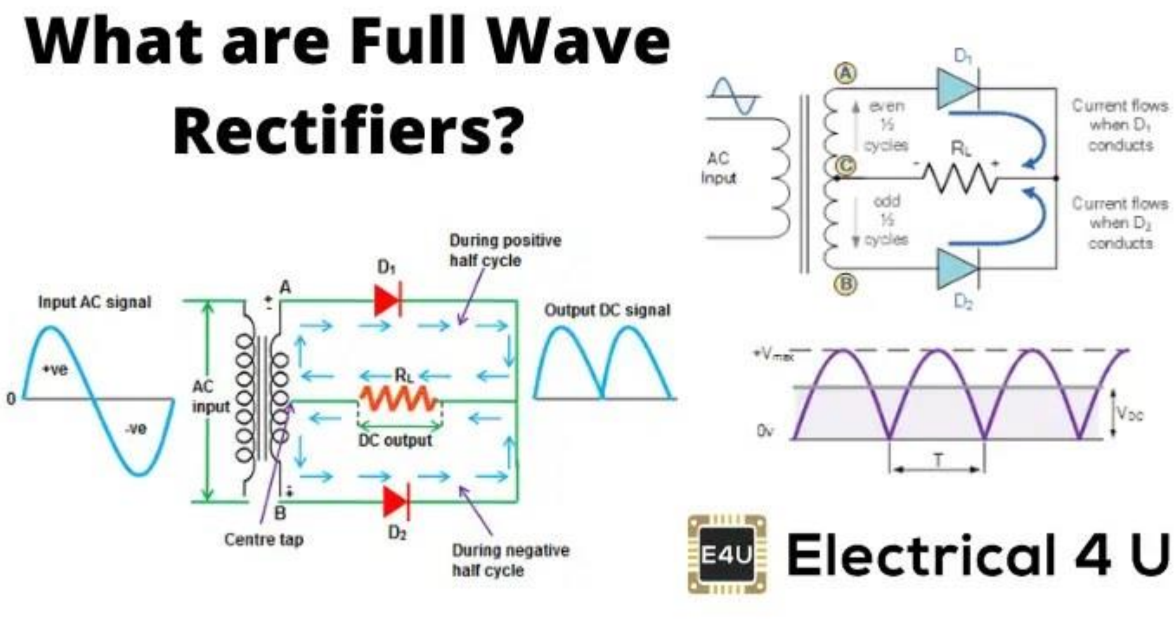
Full wave rectifier

- Full wave rectifier converts both the half cycles of input ac signal to pulsating dc
- It consists of two diodes as shown in figure
- Center tapping in the secondary of the transformer is done to obtain two equal voltages
  but of opposite phase

Operation:

During positive half cycle of supply voltage, terminal A is positive and terminal B is negative due to center tap transformer. Diode D1 will be forward biased and hen while D2 will be reverse biased and will not conduct. As D1 conducts, current flows through the path A-D1-C- -D. Therefore 0 = +v

During negative half cycle of supply voltage, terminal A is negative and terminal B is positive due to center tap transformer. Diode D1 will be reverse biased, while D2 will be forward biased and hence conduct. As D2 conducts, current flows through the path B-D2-C- -D. Thus current keeps on flowing through .



SUPER CONDUCOR

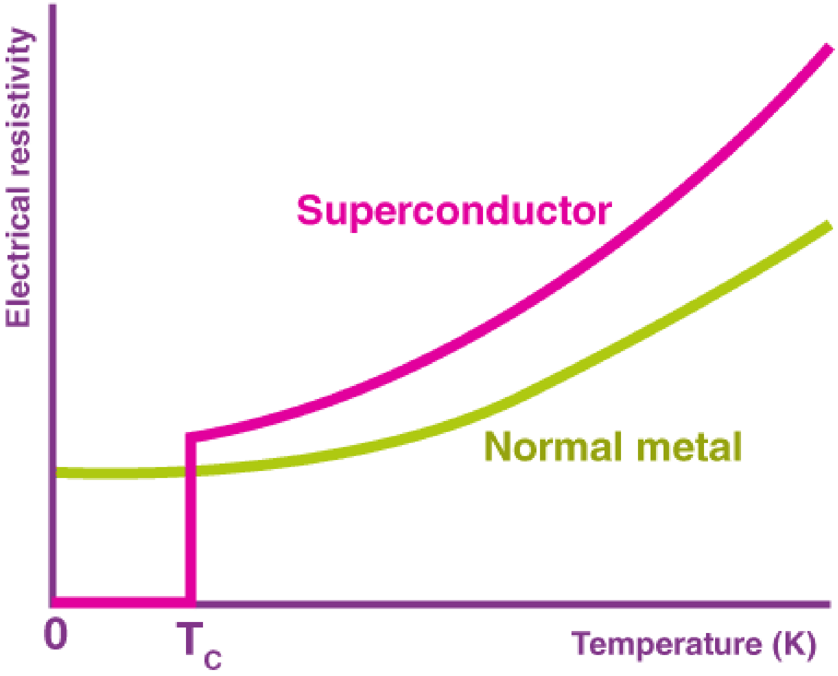
superconductivity, it was thought that the electrical resistivity of a material becomes zero only at absolute zero temperature.

It was found that in some materials, the electrical resistance suddenly falls to zero when they are sufficiently cooled below a certain low temperature, known as critical temperature TC.

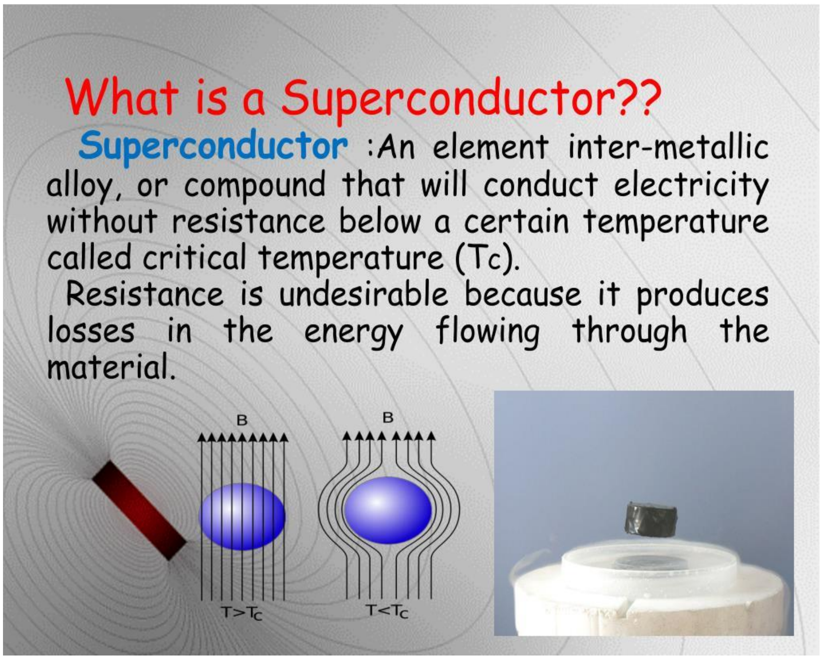
The variation of the electrical resistance with temperature for mercury is shown in fig. 4.1. It is found that the electrical resistance of pure mercury suddenly drops to zero when it is cooled below

Most of the conductors lose all of their electrical resistance when cooled to very low temperatures which is near to absolute zero or -273^{0}Celsius. Superconductors are materials that show almost zero electrical resistance at temperatures near 0 Kelvin. The threshold conductor for superconductor to switchover from normal conduction to superconductivity is called the **transition temperature**. Transition temperatures for classic superconductors are in the cryogenic range ie., near to absolute zero. Hundreds of materials are known to become superconductors at low temperatures. At low temperatures and low pressure, nearly 27 chemical elements, in which all of them metals are considered as superconductors with their normal crystallographic forms. Among these the common known metals are: Alluminium, tin, lead, and mercury and less common ones such as rhenium, lanthanum and protactinium. Further, 11 elements which are metals, semimetals and semiconductors are superconductors at low temperatures and high pressures. Examples of such elements are uranium, cerium, silicon, and selenium. Bismuth and five other elements are not superconducting with their normal crystallographic form, can be made superconducting in a highly disordered form, which is stable at extremely low temperatures. Most of the known superconductors are alloys or compounds. **Superconductivity is not exhibited by any of the magnetic material chromium, manganese, iron, cobalt and nickel**

Definition ; The phenomenon of sudden disappearance of electrical resistance in a material, when it is cooled below a certain temperature is known as superconductivity. the material is said to make a transition from normal conducting state to superconducting state. Superconductor or Superconducting materials A material which exhibits superconductivity is called superconductor or superconducting material. Transition temperature or critical temperature The temperature at which a material at normal conducting state changes into superconducting state is known as transition temperature or critical temperature



Transition temperatures of some superconducting elements



What is a Superconductor??

Superconductor :An element inter-metallic alloy, or compound that will conduct electricity without resistance below a certain temperature called critical temperature (Tc).

Resistance is undesirable because it produces losses in the energy flowing through the material.

Transition temperatures of some superconducting elements

S.No	Element	Critical temperature T_C (K)
1.	Indium (In)	3.40
2.	Tin (Sn)	3.72
3.	Mercury (Hg)	4.15
4.	Tantalum (Ta)	4.48
5.	Vanadium (V)	5.38
6.	Lanthanum (La)	6.00
7.	Lead (Pb)	7.19

Effect of magnetic field ;

Below transition temperature (TC) of a superconducting material, its superconductivity can be destroyed by the application of a strong magnetic field.

The minimum magnetic field strength required to destroy the superconducting property is known as critical magnetic field (HC).

The critical magnetic field (HC) depends upon the temperature of the superconducting material. The relation between critical magnetic field and temperature is given by.

$$H_C = H_o \left[1 - \left(\frac{T}{T_C} \right)^2 \right]$$

H_o → critical magnetic field at absolute zero temperature (0 K) of the material.

T_C → superconducting transition temperature of the material.

T → temperature below T_C of the superconducting material.

The critical magnetic field is zero at superconducting transition temperature, i.e., at $T = T_C$, $H_C = 0$. The variation of H_C with temperature T in a superconductor is shown in fig. 4.2.

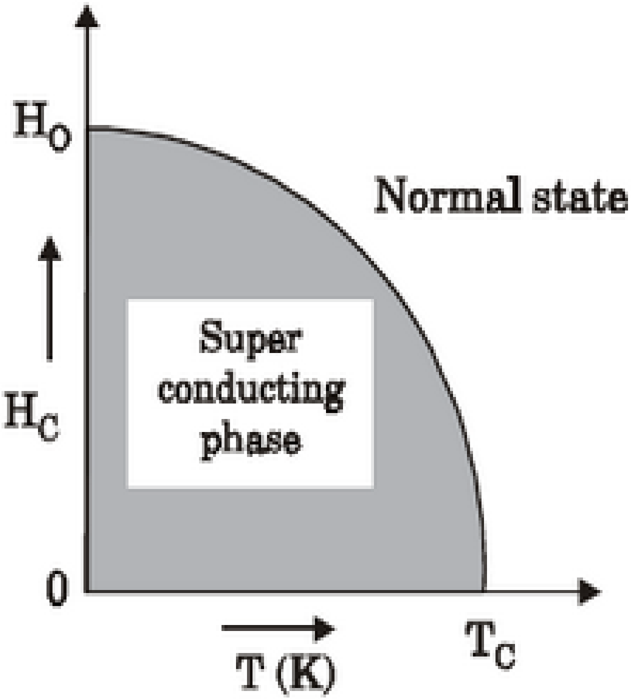
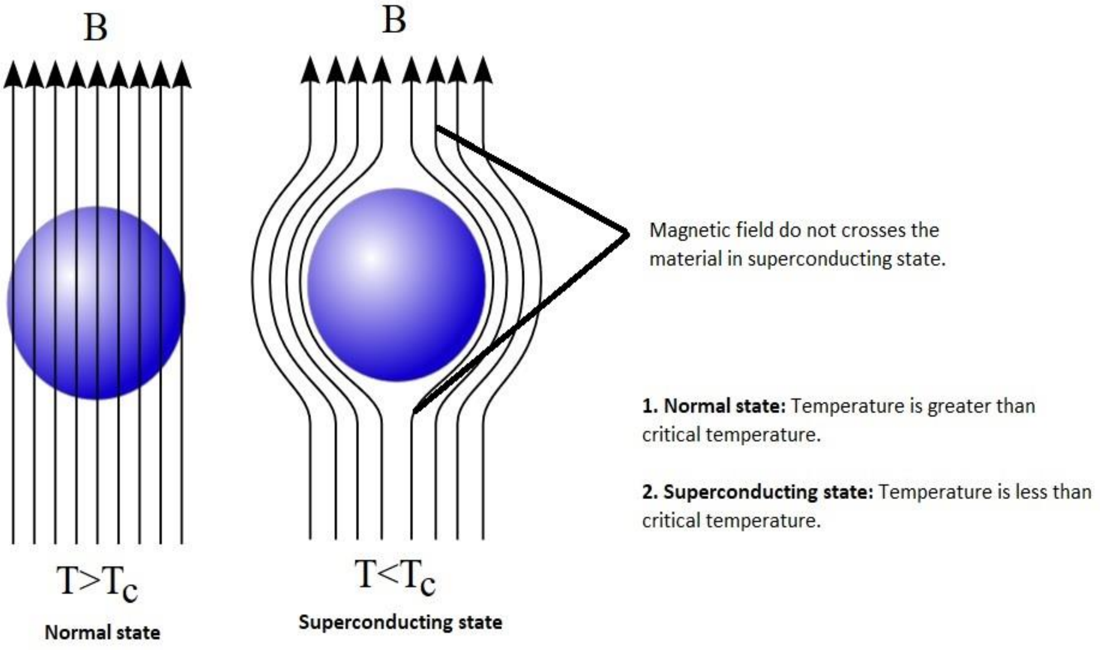


Fig. 4.2 Variation of H_C with T

It is noted that when the temperature of a material increases, the value of critical magnetic field decreases correspondingly. The value of critical magnetic fields at absolute zero temperature are different for different materials.

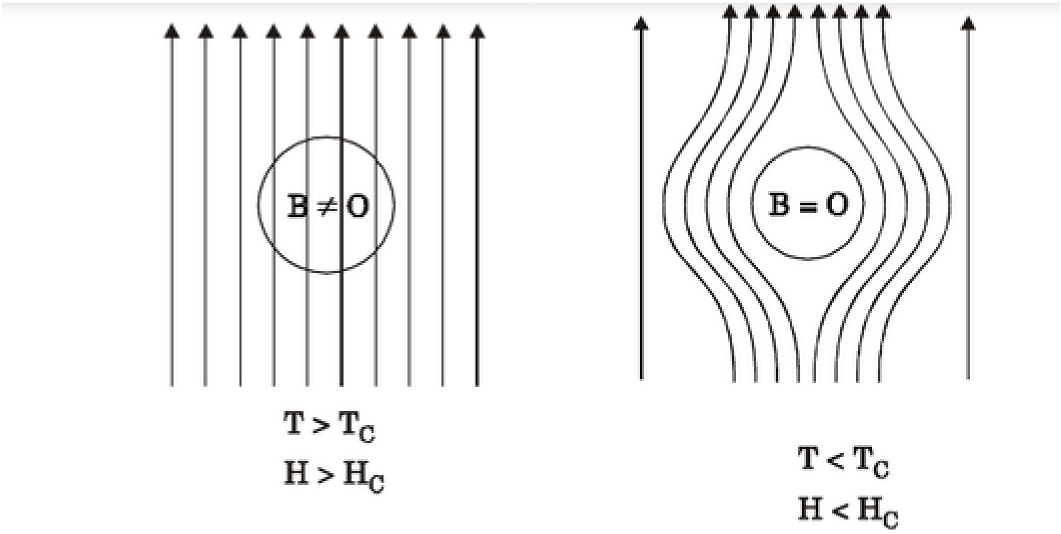
Meissner effect

When a super conducting material in its normal conducting state is placed in a uniform magnetic field of flux density B, the magnetic lines of force penetrates through the material as shown in fig. 4.5



Meissner Effect

www.elexexplorer.com



(a) Normal conducting state ***(b) Superconducting state***

Fig. 4.5

However, when the material is cooled below its transition temperature i.e., $T < T_C$, the magnetic flux ($H < H_C$) originally present in the specimen is pushed out from the specimen as shown in fig. 4.5 (b).

Thus, inside superconducting specimen, magnetic induction (B) is zero. This phenomenon is known as Meissner effect.

.This means that superconducting materials exhibit perfect diamagnetism

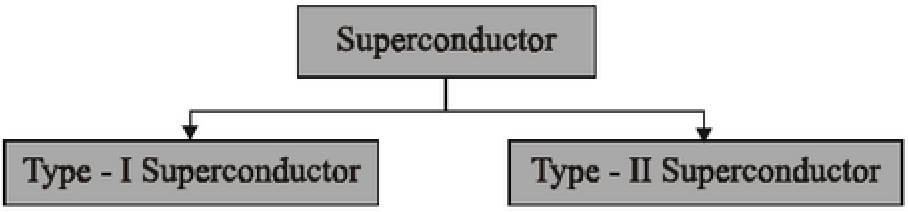
i.e., $\chi = -1$

TYPES OF SUPERCONDUCTORS

Based on the Magnetisation behaviour of super conductors in an external magnetic field, they are classified into two types.

(i) Type - I superconductors

(ii) Type - II superconductors



Type I - Superconductor

In this superconductor, the magnetic field is totally expelled from the interior of the material below the critical magnetising field H_C. At H_C, the material loses its superconductivity **abruptly and the magnetic field penetrates fully.**

The magnetisation curve for a type - I superconductor is shown in fig. 4.8.

-

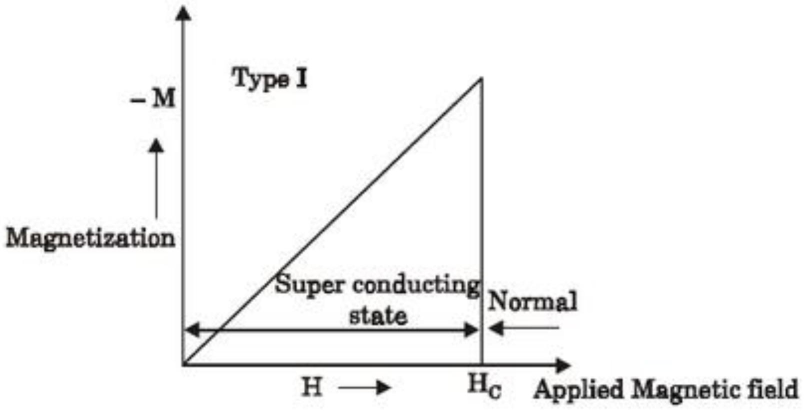


Fig. 4.8 Magnetisation curve for type - I superconductor

It is found that the transition from superconducting state to normal state in the presence of magnetic field occurs sharply at the critical magnetic field H_C.

Characteristics of type - I superconductors

- They exhibit complete Meissner effect i.e., they are completely diamagnetic.
- They have only one critical magnetic field. The value of the critical magnetic field HC is very low.
- The maximum known critical magnetic field for type-I superconductor is of the order of 0.1 Tesla.
- They are often called as soft superconductors because relatively low magnetic field can destroy Super conductor state.

.

- The magnatisation curve shows that transition at HC is reversible. This means that if the magnetic field is reduced below HC, the material acquires superconducting property again and the magnetic field is expelled

Below HC, the material behaves as a superconductor and above HC it behaves as a normal conductor.

Example:

Most of the elemental superconductors are type - I superconductors (except Niobium (Nb) and Vanadium (V)).

Disadvantages

Type-I superconductors have only a limited practical applications because they cannot carry high currents (as critical current is low).

(ii) Due to low value of HC these materials are not suitable for use in high-field superconducting magnets

Type - II Superconductor;

ype - II superconductor is one in which the material loses its magnetisation gradually rather than suddenly

The magnetisation curve for type-II superconductor is shown in fig. 4.9

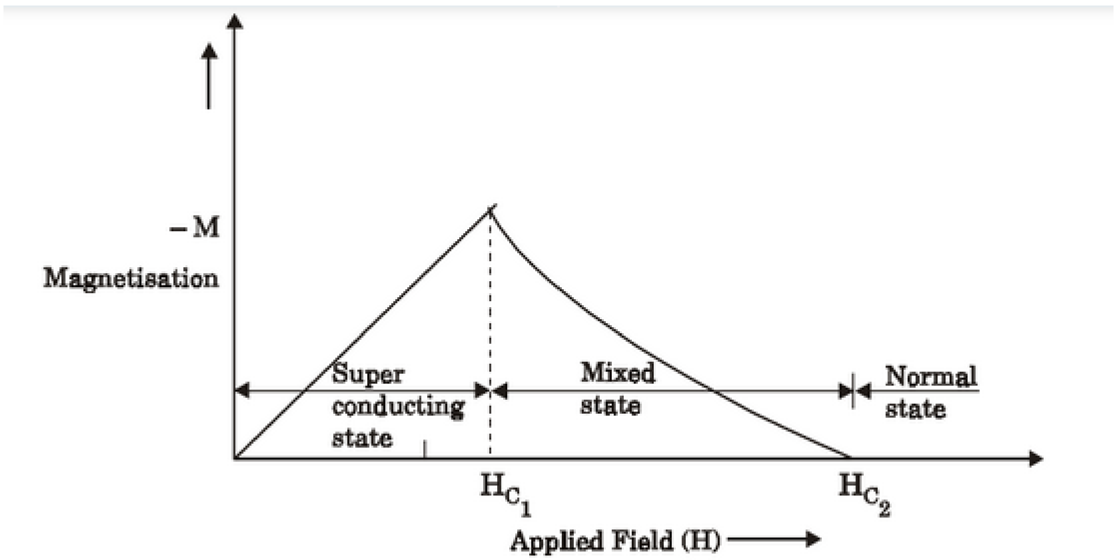


Fig. 4.9 Magnetisation curve for type II superconductor

The magnetisation curve for type-II superconductor is shown in fig. 4.9.

They have two critical fields: HC1 (lower critical field) and HC2 (upper critical field). The specimen is perfect diamagnetic below HC1, i.e., magnetic field is completely expelled below HC1.

At HC1, magnetic flux begins to penetrate the specimen and the penetration of flux continues until the upper critical field HC2 is reached.

At HC2 , magnetisation vanishes and the specimen returns to normal conducting state. (Fig.

Characteristics of type II superconductors

- They do not show complete Meissner effect.
- They are called as hard superconductors because they require a large amount of magnetic field to destroy superconducting state.

- They do not behave as perfect diamagnetic materials above HC1.
- Magnetization curve is reversible.

Examples

Typical type - II superconductors are Nb − Zr, Nb − Ti alloys and Va - Ga and Nb - Sn intermetallic compounds.

Applications of type - II superconductors

- They are of great practical interest because they can carry high current density.

They are used for power transmission without any loss.

- They are technically more useful than type - I superconductors due to toleration of high magnetic fields.

The differences between type - I and type - II superconductors are given in the table 4.4

Types of Superconductors based on their transition temperatures

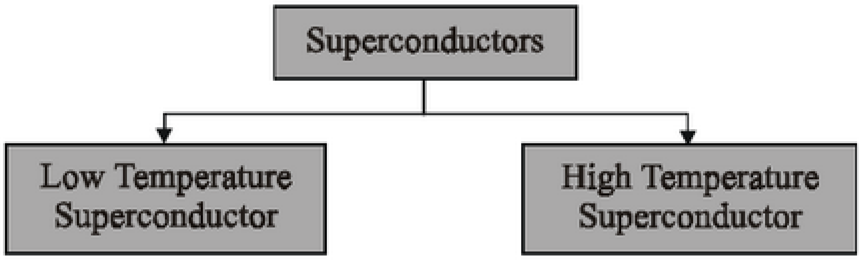
Based on the value of superconducting transition temperatures, the superconductors are classified into two types

Types of Superconductors based on their transition temperatures

Based on the value of superconducting transition temperatures, the superconductors are classified into two types:

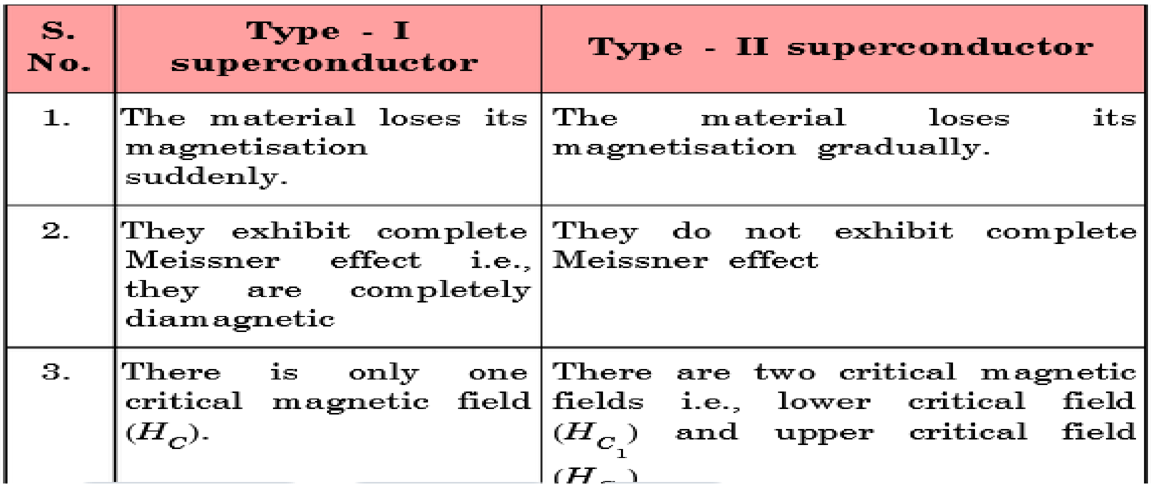
(i) **Low - temperature superconductor**

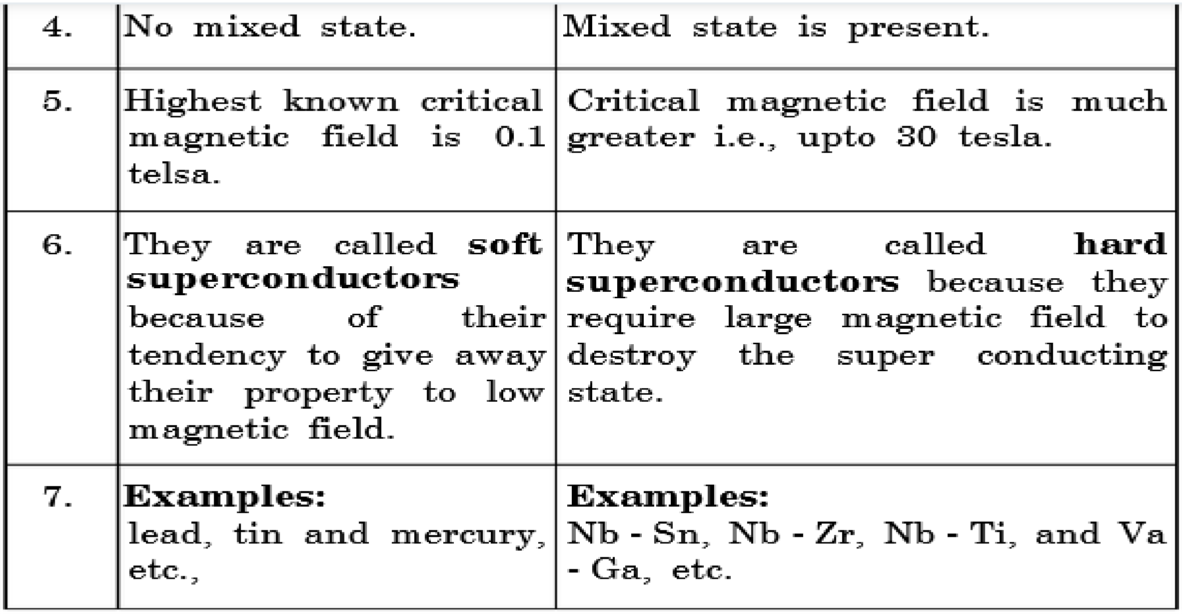
(ii) **High - temperature superconductor**



Low - temperature superconductor

If the transition temperature is low ie., less than 30 K such superconductors are called as **low - temperature superconductors**. They are also known as **elemental superconductors.**





S. No.	Type - I superconductor	Type - II superconductor
1.	The material loses its magnetisation suddenly.	The material loses its magnetisation gradually.
2.	They exhibit complete Meissner effect i.e., they are completely diamagnetic	They do not exhibit complete Meissner effect
3.	There is only one critical magnetic field (H_C).	There are two critical magnetic fields i.e., lower critical field (H_{C_1}) and upper critical field
4.	No mixed state.	Mixed state is present.
5.	Highest known critical magnetic field is 0.1 telsa.	Critical magnetic field is much greater i.e., upto 30 tesla.
6.	They are called **soft superconductors** because of their tendency to give away their property to low magnetic field.	They are called **hard superconductors** because they require large magnetic field to destroy the super conducting state.
7.	**Examples:** lead, tin and mercury, etc.,	**Examples:** Nb - Sn, Nb - Zr, Nb - Ti, and Va - Ga, etc.

APPLICATIONS OF SUPERCONDUCTORS

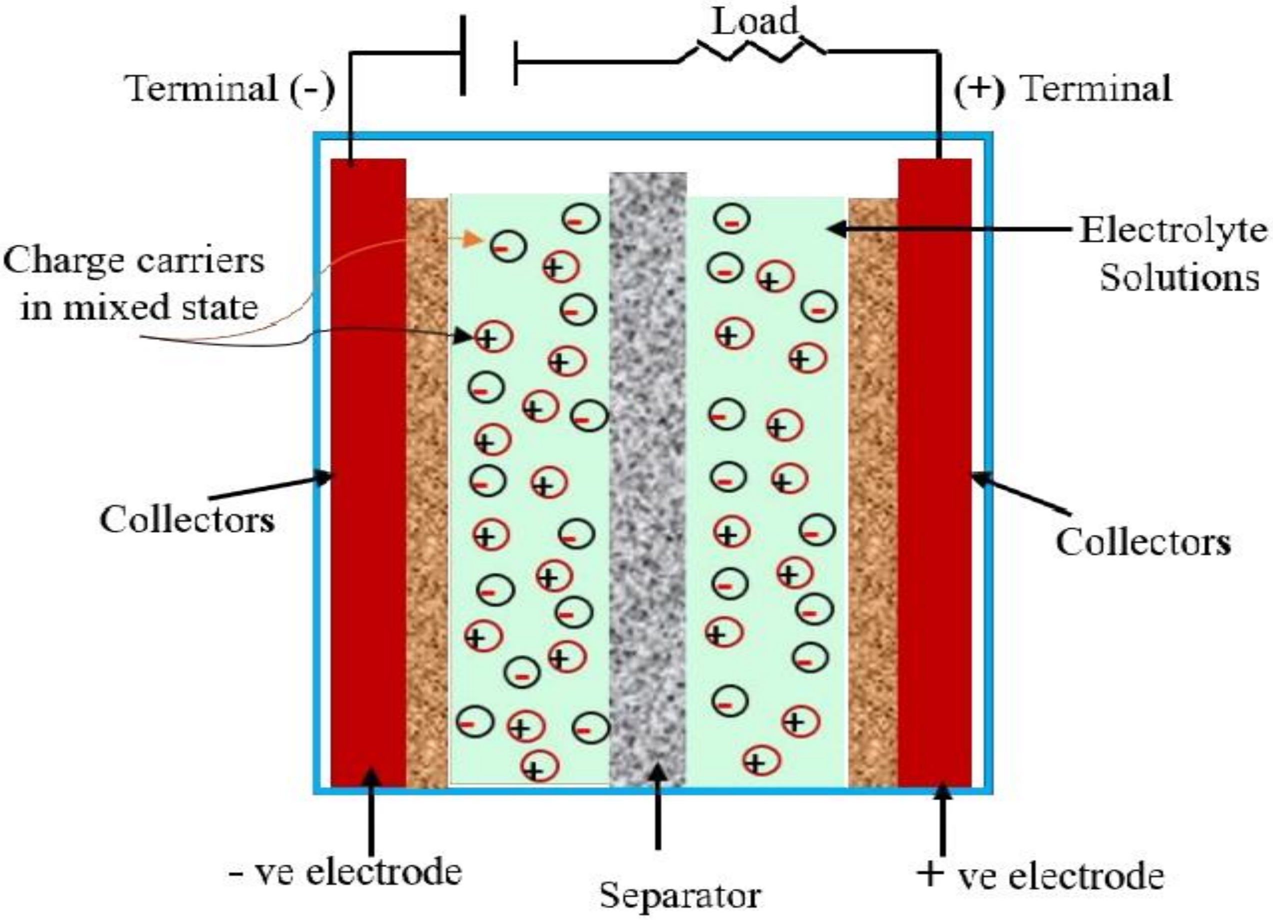
The following are important applications of superconducting materials:

1. A superconducting material widely used in the construction of electromagnetic materials is an alloy of niobium and titanium. Hence these materials may employ in a wide variety of applications, ranging from electric power transmission to high-speed computing.
2. High-temperature superconductors are many applications in metrology, electromagnetic sensing, and analog and digital circuits.
3. Superconductors are also able to maintain a current with no applied voltage. This property used in superconducting electromagnetic materials found in MRI machines. Experiments have illustrated that currents in superconducting coils can persist for many years without any noticeable degradation. Experiment evidence reveals that current lifetime or superconducting at least 100,000 years.
4. Niobium-titanium (Nb Ti) alloy used in industrially as superconductor wire for superconducting magnets, normally as Nb-Ti fibers in an aluminium or copper matrix.
5. Niobium superconducting alloys, also containing titanium and tin are widely used in the superconducting magnets of MR/NMRI scanners.
6. Niobium-titanium superconducting magnet coils under liquid helium cooled were built to be used in the Alpha Magnetic Spectrometer mission to be flown on the international space station.

SUPER CAPACTER

A **supercapacitor** (**SC**), also called an **ultracapacitor**, is a high-capacity capacitor with a capacitance value much higher than other capacitors, but with lower voltage limits, that bridges the gap

between electrolytic capacitors and rechargeable batteries. It typically stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerates many more charge and discharge cycles than rechargeable batteries.[2] Supercapacitors are used in applications requiring many rapid charge/discharge cycles, rather than long- term compact energy storage — in automobiles, buses, trains, cranes and elevators, where they are used for regenerative braking, short-term energy storage, or burst-mode power delivery.[3] Smaller units are used as power backup for static random-access memory (SRAM).



Unlike ordinary capacitors, supercapacitors do not use the conventional solid dielectric, but

rather, they Unlike ordinary capacitors, supercapacitors do not use the conventional solid dielectric, but rather,

use electrostatic double-layer capacitance and electrochemical pseudo capacitance,[4] both of which contribute to the total capacitance of the capacitor, with a few differences:

- **Electrostatic double-layer capacitors (EDLCs)**
-
- : use carbon electrodes or derivatives with much higher electrostatic double-layer capacitance than electrochemical pseudo capacitance, achieving separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. The separation of charge is of the order of a few ångströms (0.3–0.8 nm), much smaller than in a conventional capacitor.

- **Electrochemical pseudo capacitors** :
-
- use metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudo capacitar additional to the double-layer capacitance.
  Pseudo capacitance is achieved by Faradaic electron charge-transfer
  with redox reactions, intercalation or electro sorption.

- **Hybrid capacitors** :
- such as the lithium-ion capacitor, use electrodes with differing characteristics: one exhibiting mostly electrostatic capacitance and the other mostly electrochemical capacitance.
-

The electrolyte forms an ionic conductive connection between the two electrodes which distinguishes them from conventional electrolytic capacitors where a dielectric layer always exists, and the so-called electrolyte, *e.g.*, MnO_2 or conducting polymer, is in fact part of the second electrode (the cathode, or more correctly the positive electrode). Supercapacitors are polarized by design with asymmetric electrodes, or, for symmetric electrodes, by a potential applied during manufacturing.

Application of Supercapacitors:

Due to unique storage capability of supercapacitors, it has been widely used in various applications like electric drives, UPS, traction, electric vehicles, SSD's, LED flashlights etc. Let us discuss few of them. **Supercapacitors are used in the following:**

1. Electric cars
2. Wind turbines
3. Photographic flash
4. Flywheel in machines
5. MP3 players
6. Regenerative braking in the automotive industry
7. Static memories (SRAM)
8. Industrial electrical motors

Nanomaterials and Nano Technology , Nanopartical and Properties of Nanomaterials.

Properties of Nanomaterials.

The properties of Nanomaterials depends on size crystal structure and surface a characteristics

a) Size

Nano crystals have a large surface are a,size of crystal is important for available active surface area.

b) Catalytic Activity

Catalytic Activity of Nano particles in the form of colloids and Nano clusters have been investigated in a wide variety of reaction in homogeneous phase and heterogeneous phase .

Ex- Rhodium- hydrogenation of olefins.

Palladium –reduction of nitriles and nitro

arenes

c) Electrical properties

Nano materials show electrical properties vary between semiconducting to metallic depending upon the chirality and diameter.

Ex-Nanotubes of Mo S2,WS2.

d) Mechanical Properties

Nano materials possesses stiffness and strongest fibers known.

Optical properties

Nano materials that are provided large surface area exhibit better optical properties. Ex-Silicon Nano wires-Photo Allumini scence.

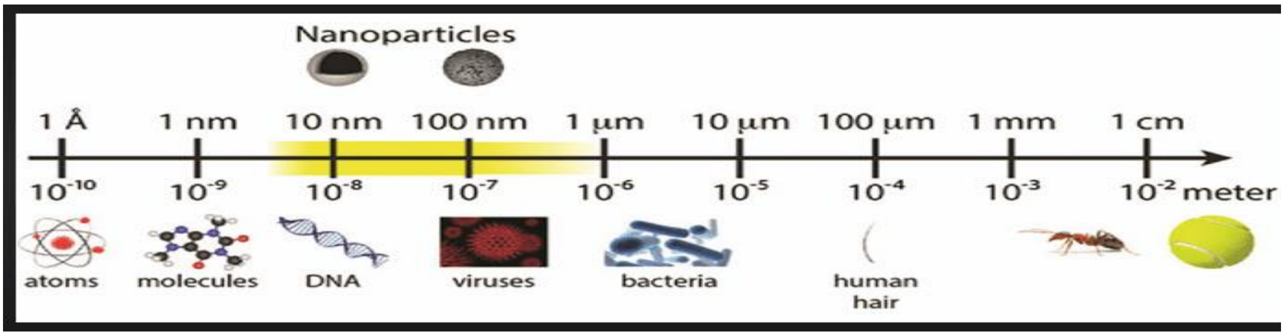
e) Semiconductors

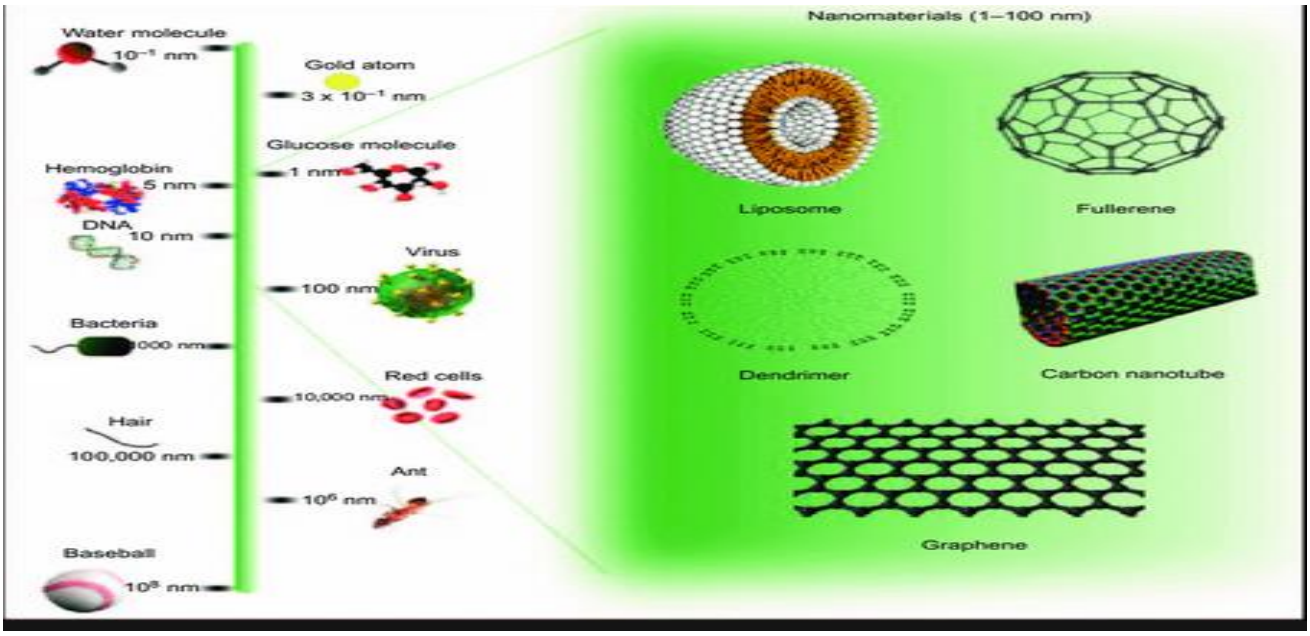
Most of the Nano materials exhibit semi conductivity properties Ex- carbon nanotubes and Nano wires.

f) Super conductors

There are some Nanomaterials which show superconductivity propertyEx- Nb Se2 becomes a super conductor at low temperature.

Nano scale ranges





Nanomaterials and classification of Nanomaterials:

Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale", with *nanoscale* defined as the "length range approximately from 1nm to 100 nm" Classification;

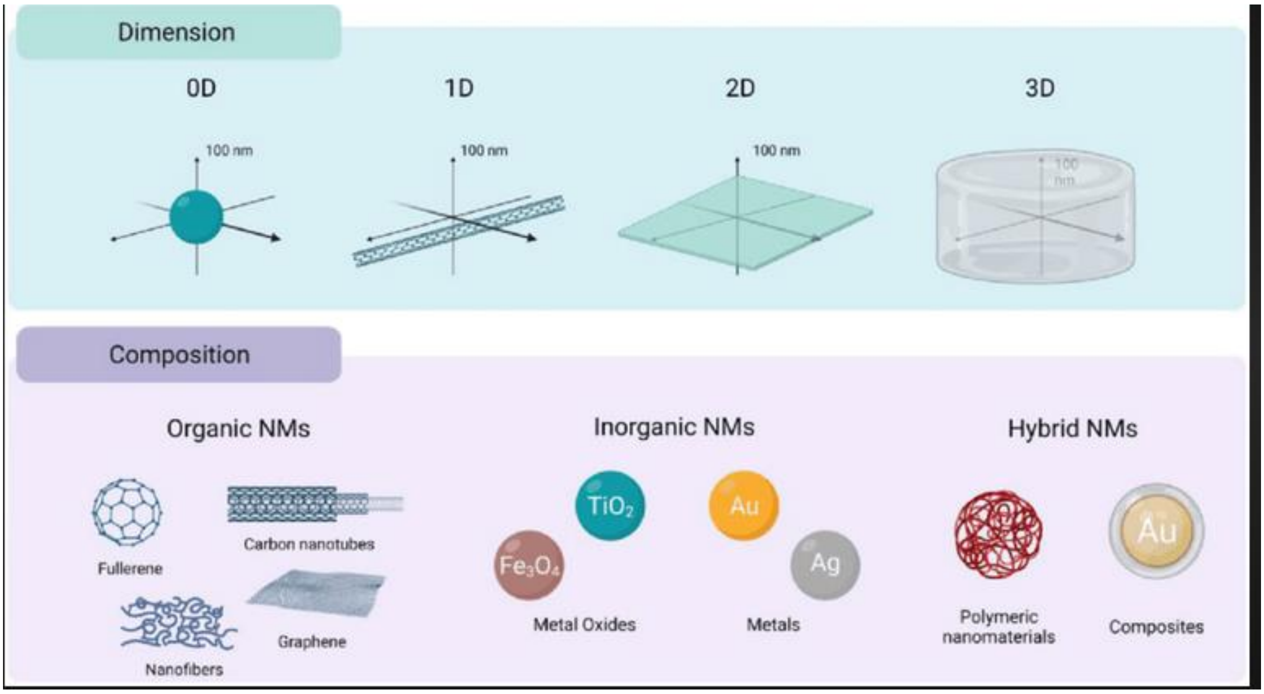
Nanomaterials are classified in to three types

one-dimensional **nanomaterials (1D)**-, materials with one dimension nanoscale. This classincludes nanotubes, nanorods, and nanowires.

Two-dimensional **nanomaterials (2D),-**materials with two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoatings.

Three-dimensional **nanomaterials (3D)** are materials that are not confined to the nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers

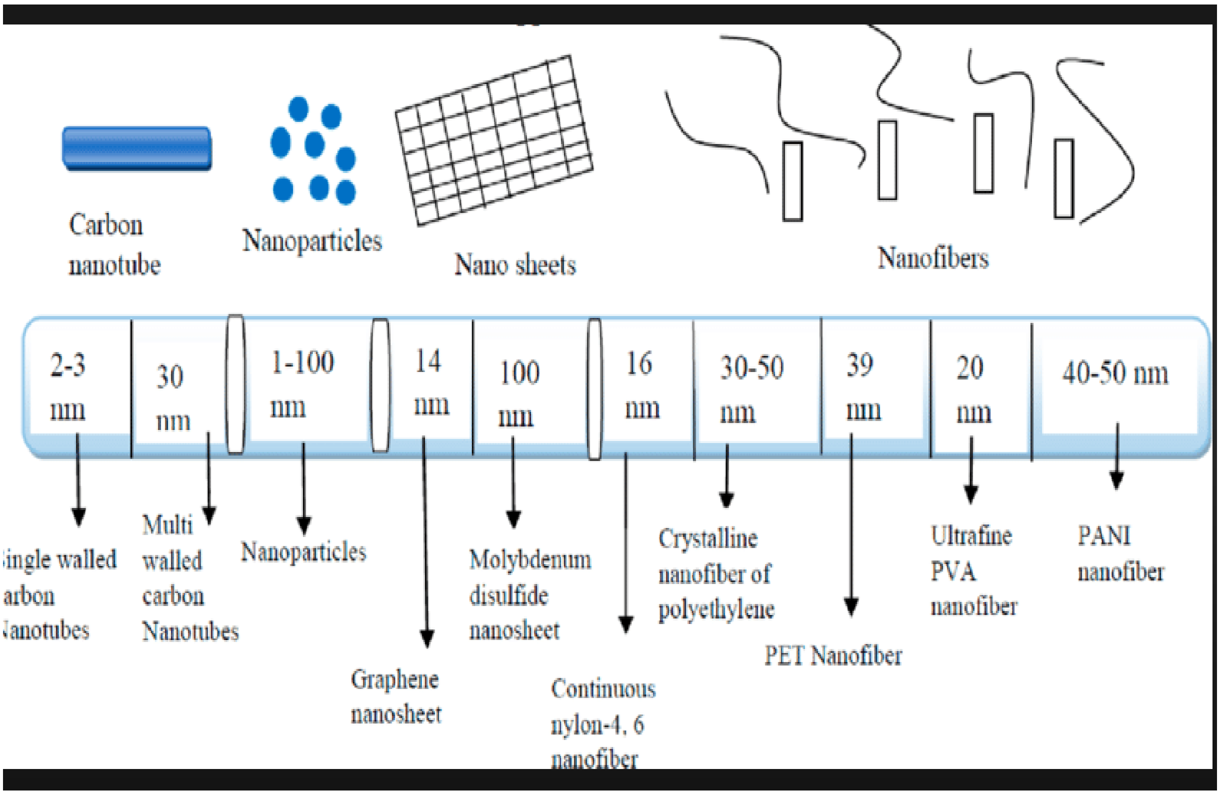
small molecule asymmetric catalysts, this article focuses primarily on large catalytic host molecules. Non-discrete and structurally poorly defined system such as micelle and dendrimers are not included.



Carbon nanotube (CNT) :

A carbon nanotube (CNT) is one of the most important nanomaterials. Before 1991, only two main allotropes of carbon were known. In 1991, a Japanese physicist, Sumio Lizima invented CNT (another allotrope of carbon). Let us discuss the carbon nanotubes definition, carbon nanotube is a hollow tube made up of carbon of nanoscale diameter. In short, it is represented as CNTs. Carbon nanotubes are also called buckytube.

Nanotubes are formed by folding or rolling two-dimensional graphite into a cylindrical shape structure. Nanotubes are hollow from inside. The diameter of the nanotube is around 1-3 nanometers. The length of the carbon nanotube is much higher than its diameter. Nano tube length generally goes to a few micrometers. In short, we can say that carbon nan (CNT) is a folded form of the two-dimensional graphene sheet. CNT (carbon nanotubes) exhibit extraordinary mechanical properties.



Types of Carbon Nanotubes

1. Single-walled Carbon nanotubes
2. Multi-walled Carbon nanotubes

Single-walled Carbon Nanotubes- it is represented as SWCNT. The Single-walled Carbon nanotubes exist in a 1-d structure. Some examples of Single-walled CNT are armchair and zig-zag Single-walled Carbon nanotubes

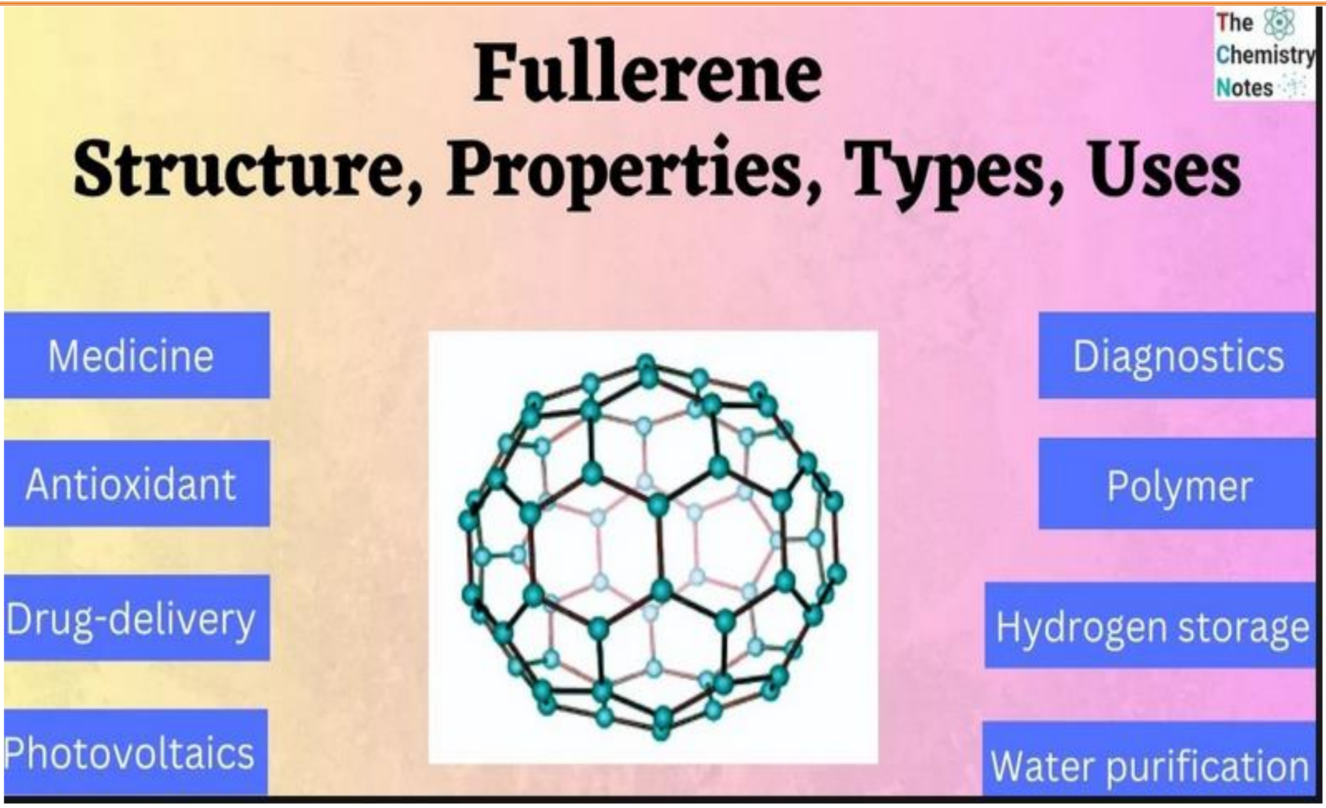
Properties of Single-walled Carbon Nanotubes are:

- The diameter of Single-walled Carbon nanotubes is 2nm.
- The length of Single-walled Carbon nanotubes is around 2 micrometres.
- They exist in a one-dimensional structure. Therefore, it is also known as a nanowire.
- Electronics can be miniaturized by using a Single-walled Carbon nanotube.
- Their band gap varies from 0-2 electron volts (eV).
- They show conductivity like a semiconductor. Therefore, they exhibit both metal
- lic andsemi conductivity behaviour.

Fullerenes:

Fullerene is one of the allotropic forms of the carbon. The other name of fullerene is buckminsterfullerene. In this allotropic form of carbon, the carbon molecules are arranged in a series and form a cage like structure. This structure of fullerene is hollow in nature.In this allotropic form when the carbon molecules are arranged in a cylindrical form, they form a tube like structure. These tube-like structures are known as carbon nanotubes.

Fullerene Structure



In nature, fullerenes, especially the C60 sphere, are highly symmetrical. Fullerenes have a similar structure to graphite, which is made up of a sheet of connected hexagonal rings, but they have pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. Buckyballs and buckytubes are terms used to describe them depending on their shape. Cylindrical fullerenes are referred to as nanotubes

C60 is the most common fullerene, with no two pentagons sharing anedge. A C60 molecule's average carbon-carbon bond length is 1.44 angstrom.

Properties of Fullerene

Physical Properties of Fullerene

- Fullerene shows variation in behaviour and structure on changing the temperature. At ahigher temperature the fullerene is converted into the C70 form.
- Fullerene shows change in structure under different pressures.
- The ionization enthalpy of fullerene is 7.61 electron volts.
- The electron affinity of fullerene is 2.6 to 2.8 electrons volts.

Chemical Properties of Fullerene

- Fullerene (C60) resembles an electrophile in the chemical reactions.
- Fullerene can act as an electron acceptor group. It can easily accept three electrons ormore. Therefore, it can behave as an oxidizing agent.
- Fullerenes are doped with the alkali or alkaline earth metals, so that it can exhibit superconductivity properties.
- Ferromagnetism is a property of fullerene.
- Carbon molecules abound in fullerene. As a result, it's very soluble in organic solvents.

Types of Fullerene

1. Buckminsterfullerene
2. Endohedral Fullerene
3. Herbal fullerenes
4. Bucky ball Clusters
5. Nanotubes
6. Mega tubes
7. Linked Bucky ball and chain Dimers
8. Herbal fullerenes

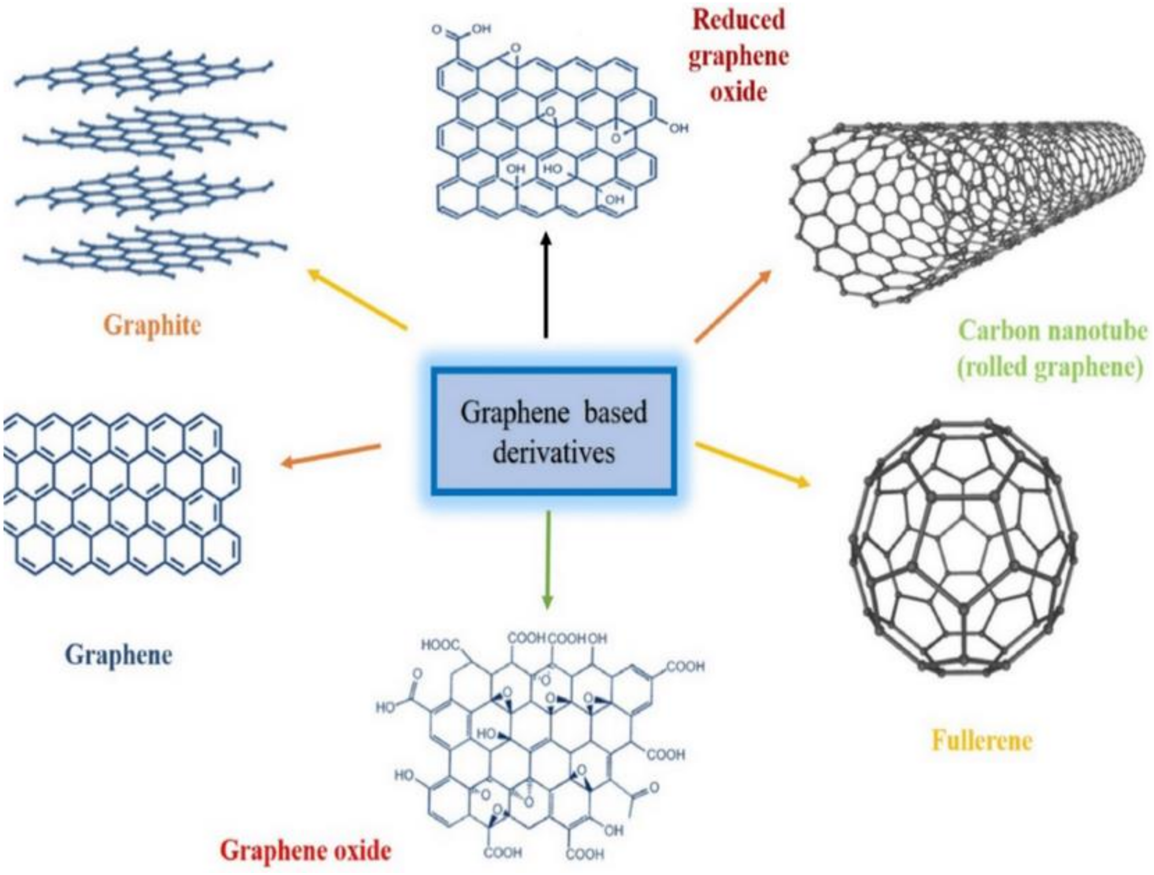
Buckminsterfullerene

Buckminsterfullerene is the most common form of the fullerene. It exists in C60 form. Graphene:

Graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice. It is the building- block of Graphite (which is used, among others things, in pencil tips), but graphene is a remarkable substance on its own - with a multitude of astonishing properties which repeatedly earn it the title â wonder material.

Graphene's

Structure of Graphene



Graphene is the thinnest material known to man at one atom thick, and also incredibly strong - about 200 times stronger than steel. On top of that, graphene is an excellent conductor of heat and electricity and has interesting light absorption abilities. It is truly a material that could change the world, with unlimited potential for integration in almost any industry.

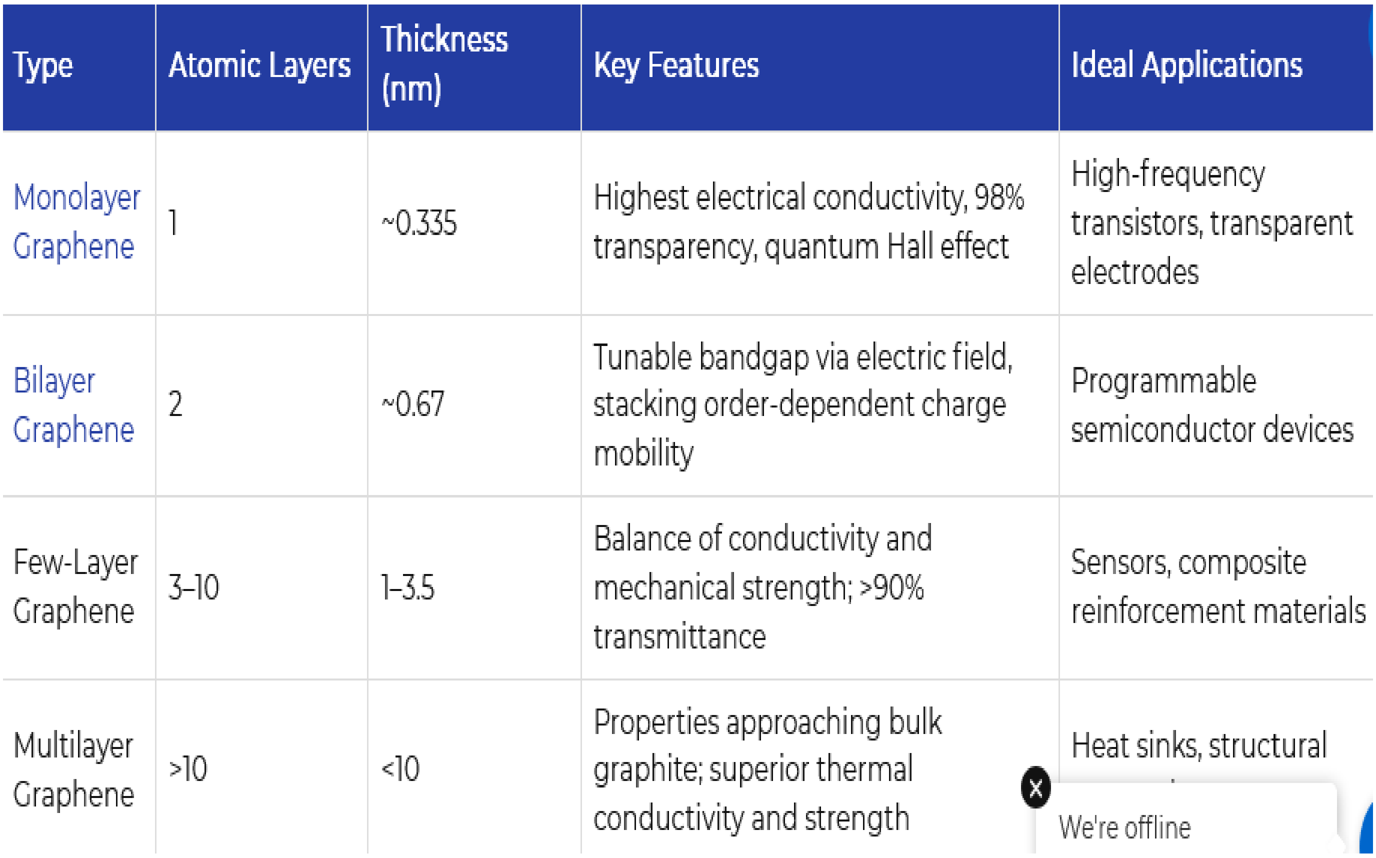
Graphene's applications

Graphene is an extremely diverse material, and can be combined with other elements (including gases and metals) to produce different materials with various superior properties. Researchers all over the world continue to constantly investigate and patent graphene to learn its various properties and possible applications, which include:

- batteries
- transistors
- computer chips

- energy generation
- supercapacitors
- DNA sequencing
- water filters
-
- antennas
- touchscreens (for LCD or OLED displays)
- solar cells
- Spintronics-related products
  do not use the conventional solid dielectric, but rather, they

Graphene's Properties



Type	Atomic Layers	Thickness (nm)	Key Features	Ideal Applications
Monolayer Graphene	1	~0.335	Highest electrical conductivity, 98% transparency, quantum Hall effect	High-frequency transistors, transparent electrodes
Bilayer Graphene	2	~0.67	Tunable bandgap via electric field, stacking order-dependent charge mobility	Programmable semiconductor devices
Few-Layer Graphene	3–10	1–3.5	Balance of conductivity and mechanical strength; >90% transmittance	Sensors, composite reinforcement materials
Multilayer Graphene	>10	<10	Properties approaching bulk graphite; superior thermal conductivity and strength	Heat sinks, structural

THE END

UNIT-III: Electrochemistry

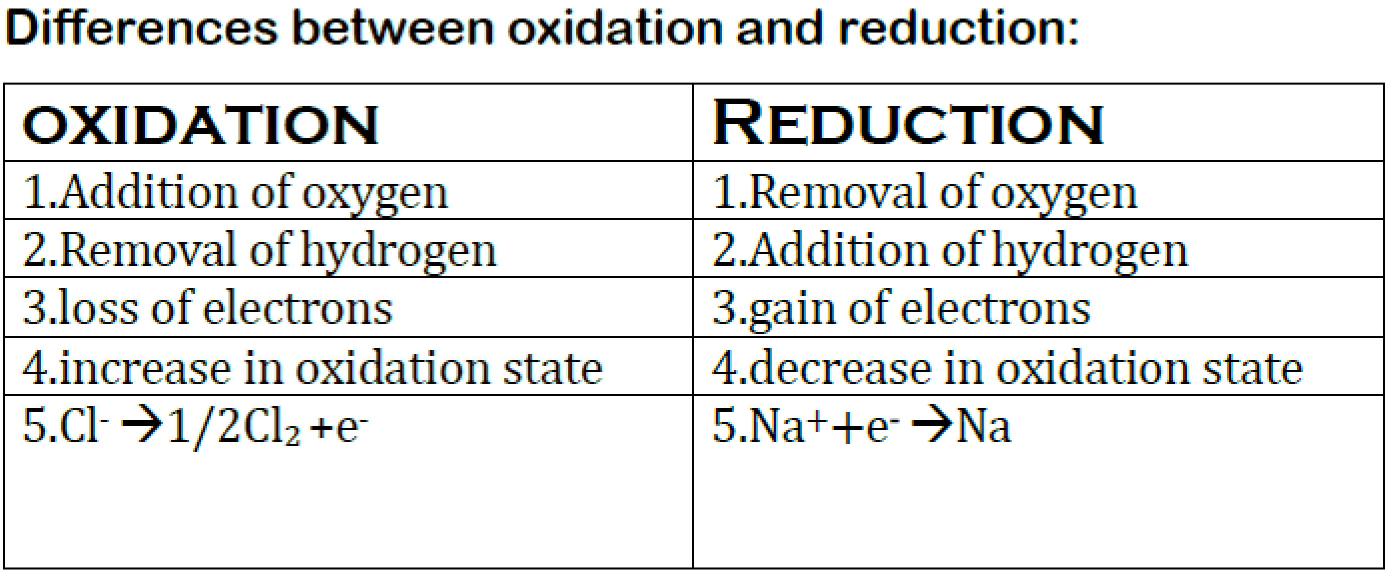
Lecture notes

Electrochemistry

“The branch of physical chemistry that deals with the inter-conversions of chemical energy and electrical energy is known as Electrochemistry.”

Electrochemistry is a science which deals with transformation of chemical energy into electrical energy (vice versa)

- An Electrochemical cell is a device which is used to convert chemical energy into electrical energy (or) electrical energy into chemical energy by redox reactions.
- The electrochemical cell which is used to convert chemical energy into electrical energy is called as Galvanic cell (or) Daniel cell (or) Voltaic cell.[anode -ve ,cathode +ve]
- The cell which is used to convert electrical energy into chemical energy is called as Electrolytic cell.[anode +ve ,cathode -ve]
- Redox reaction is a reaction which involves both reduction and oxidation



Differences between oxidation and reduction:

OXIDATION	REDUCTION
1.Addition of oxygen	1.Removal of oxygen
2.Removal of hydrogen	2.Addition of hydrogen
3.loss of electrons	3.gain of electrons
4.increase in oxidation state	4.decrease in oxidation state
5.$Cl^- \rightarrow 1/2Cl_2 + e^-$	5.$Na^+ + e^- \rightarrow Na$

Conductors:-

A substance which allows electric current or heat to pass through is called conductor.eg:- Metals, Aq. Solution of Salts, Acids & Bases.

Electric conductors are of two types.

i) ***Metallic conductors***:- The substance which conducts electricity by transfer of electrons without dissociation of it. eg:- Metals, $M(S)_{(aq)} \rightarrow M^{n+} + n\ e^-$

ii) ***Electrolytic conductor*** (Electrolytes):- When an electric current is passed through a substance

(electrolyte), it decomposes into ions. (Undergoes chemical changes) eg:- Acids, Bases, Salts, etc.

$ZnSO4 \leftrightarrow Zn^{2+} + SO4^{2-}$

—Electrolyte is a substance which conducts electricity by chemical decomposition in solution or fused state

Theory of Electrolytic dissociation:-

Electrolytes when dissolved in solvent dissociates into ions of one positive and other negative charge. $NaCl \dashrightarrow N^{a+} + Cl^-$

ii) When electric current is passed through the electrolytic solution (electrolyte dissolved in solvent), the positive ions moves towards cathode called cations and negative ions moves towards anode called anions.

Degree of ionisation:- The ratio of dissociated ions to the un-dissociated molecules is called degree of ionisation.

$$\alpha = \frac{No. of\ ions}{No. of\ un - dissociated\ molecules}$$

iii) The properties of ions depend on the properties of electrolytes.

Electrochemical cells:-

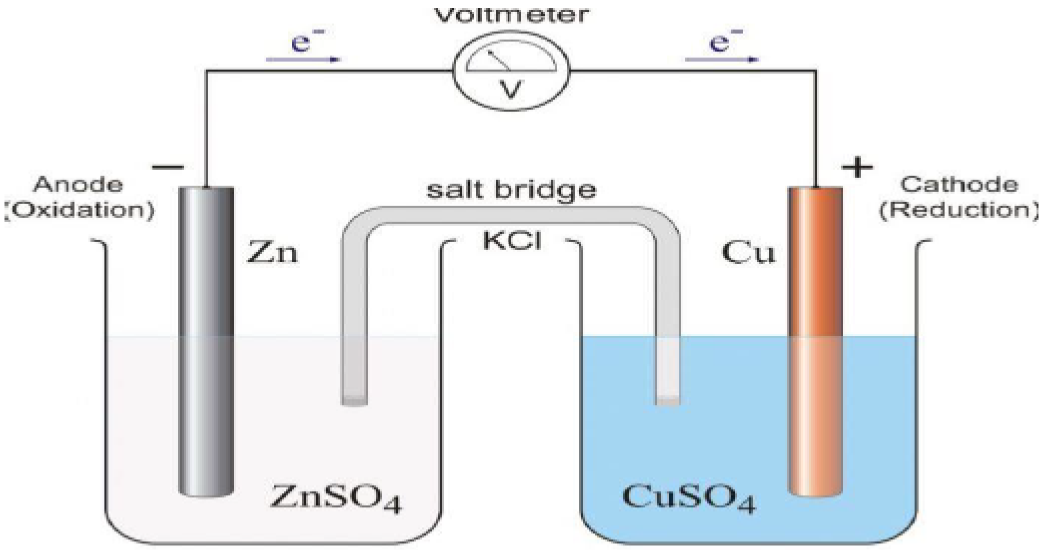
Electrochemical cell constitutes two electrodes and an electrolyte due to which electric current is produced as a result of chemical reactions and vice versa.

Electrochemical cell is used to i) convert chemical energy into electrical energy

ii) convert electrical energy into chemical energy

Construction of a cell:-(Galvanic cell)

➔ Chemical energy to Electrical energy



Half cell reaction:-

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (1) (oxidation reaction)

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (2) (reduction reaction)

Overall reaction: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

"Thus an electrochemical cell is a device in which redox reaction (oxidation and reduction) takes place which is utilised to get electrical energy." This is also known as voltaic cell or galvanic cell.

Redox reaction: Simultaneous oxidation and reduction, this produces electricity and so called electrochemical changes.

Eg: Respiration in human, Photosynthesis in plants, combustion of petroleum, Leaching of Stains.

Oxidation: Addition of O2 (or) Removal of H2 (or) Removal of electrons.

Reduction: Removal of O2 (or) Addition of H2 (or) Addition of electrons.

To explain consider an electrode (Zn) dissolved in electrolytic solution (CuSO4). The following reactions take place.

Oxidation Half Reaction (OHR)	**Reduction Half Reaction (RHR)**
$Zn(S) \text{----------}\rightarrow Zn^{2+}(aq) + 2\,e^-$	$Cu^{2+}(aq) + 2\,e\text{----} \rightarrow Cu(S)$

The overall reaction is as follows:

$Zn(S) + Cu^{2+}(aq)\text{--------}\rightarrow Zn^{2+}(aq) + Cu(S)$. Therefore Zn metal is oxidised by Cu.

Or

Working process

Copper on oxidation gives e^- s, which travels through outer circuit (external) and transferred to Ag^+ ions – due to it is reduced to Ag(s). The no. of e^- s released from one electrode is equal to no. of e^- s abstracted by other ions (another half side).

Note: The e^- s flows from anode to cathode, but electricity flows from cathode to anode.

<u>EMF</u> (Electro Motive Force):-

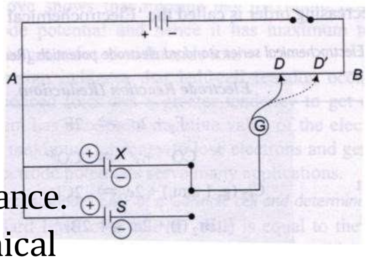
It is defined as potential difference between two electrodes which allows the current flow from one electrode to another. The current flows from higher potential to lower potential. ***measurement of EMF*****:- (Poggendoff's compensation method)**

Voltmeter is used for the EMF measurement and it can be measured by connecting two electrodes to the two terminals of voltmeter. This method is inaccurate due to two reasons.

i) Some current drawn from the cell by voltmeter, which causes alteration of the chemical equilibrium.

ii) While current flows, part of EMF is used to overcome internal resistance.

So to measure EMF accurately without disturbing chemical equilibrium and to avoid internal resistance, Poggendoff's compensation method is widely used. chnique, the EMF to be measured is balanced by equal and opposite EMF from another cell or battery and there is no net flow current in the circuit.



- The total assembly is known as Potentiometer.
- It consist of a uniform wire ‗AB‘ of high resistance and battery ‗C‘ is attached to the side wire AB through a Rheostat ‗R‘.
- The cell ‗x‘, whose EMF to be measured is included in another circuit by connecting to the end A of the wire through a press key (K1), Galvanometer (G) and a jockey (sliding contact D).
- The first circuit is completed by introducing key (K1).
- The jockey is slided along the wire till point D is reached and the galvanometer shows null deflection, the position D is noted.

- The second circuit is then completed through the stranded cell (S) of known EMF by introducing key (K2).
- The jockey is again moved along the wire ‗AB‘ till the point ‗E‘ is reached (when no deflection is observed) and it is noted.

Then EX α length ADES α length AE

Or EX/ES = length AD/ length AE EX= length AD/ length AE × ES Therefore AD, AE & ES are known

Note: AB is calibrated.

Nernest equation:-

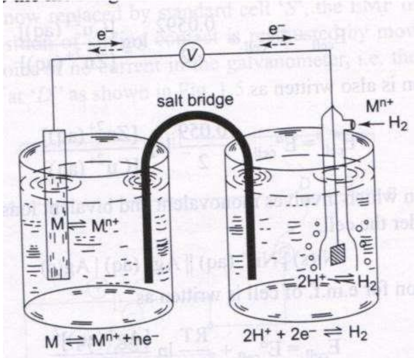
Electrode potential (cell potential)Consider an electrode reaction,

$M^{n+}_{(aq)}$ + ne ----→ $M_{(s)}$

The Nernst equation for the above reaction is given as follows:E

n+ = E^o $_{M}$ $_{/M}$ + RT$_M$/nf$_{/M}$× ln [M^{n+}]

n+



Where E $_{M/M}$ n+ = Electrode potential of given metal ion, E^o_M n+ = Standard electrode potential

R = Gas constant, 8314 J/K/mol/2KcalT = Temperature

n = no. of moles of electrons

f = Faraday (f = 96500 c/mol)

Nernest equation for cell potential

Consider Daniel cell and the electrodes and ions are denoted as follows:

$Zn(s)/Zn^{2+}(aq)||Cu^{2+}(aq)/Cu(s)$

OHR RHR

The electrode potential for RHR‘s written as

$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu}$ + RT/2f × ln [Cu^{2+}(aq)]The electrode potential for RHR‘s written as

$E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn}$ + RT/2f ×

ln [Zn^{2+}(aq)] Total cell potential

= RHR – OHR

Ecell = {$E^o Cu^{2+}/Cu$ + RT/2f × ln [Cu^{2+}(aq)]} – {$E^o Zn^{2+}/Zn$ + RT/2f × ln [Zn^{2+}(aq)]}

= ($E^o Cu^{2+}/Cu$ - $E^o Zn^{2+}/Zn$) + (RT/2f × ln [Cu^{2+}(aq)] - RT/2f × ln [Zn^{2+}(aq)])

= ($E^O Cu^{2+}/Cu$ - $E^O Zn^{2+}/Zn$) + RT/2f × ln [Cu^{2+}(aq)]/ [Zn^{2+}(aq)]

= E^0_{cell} + RT/2f × ln [$Cu^{2+}_{(aq)}$]/ [$Zn^{2+}_{(aq)}$] By

After converting natural logarithm into log, we get

= E^0cell + 0.0592/2 log [Cu^{2+}(aq)]/ [Zn^{2+}(aq)]

= E^0cell - 0.0592/2 log [Zn^{2+}(aq)]/ [Cu^{2+}(aq)]

eg: consider another following cell and whose cell reaction is written as follows

$Ni_{(s)}/Ni^{2+}_{(aq)}||Ag^{2+}_{(}$ $aq)/Ag_{(s)}$

Cell potential is written as

Ecell = E^0cell + 0.0592/2 log [Ag^{2+}(aq)]^2/ [Ni^{2+}(aq)] In general it is written as aA + bB → cC +dD _ 2.303 log $(C)^c\,(D)^d$

E

Relationship between chemical energy(heat energy) and electrical energy-

Electrical energy produced by an electrochemical cell is the product of quantity of electricity passed and emf of cell.

here, quantity of electricity passed-nf

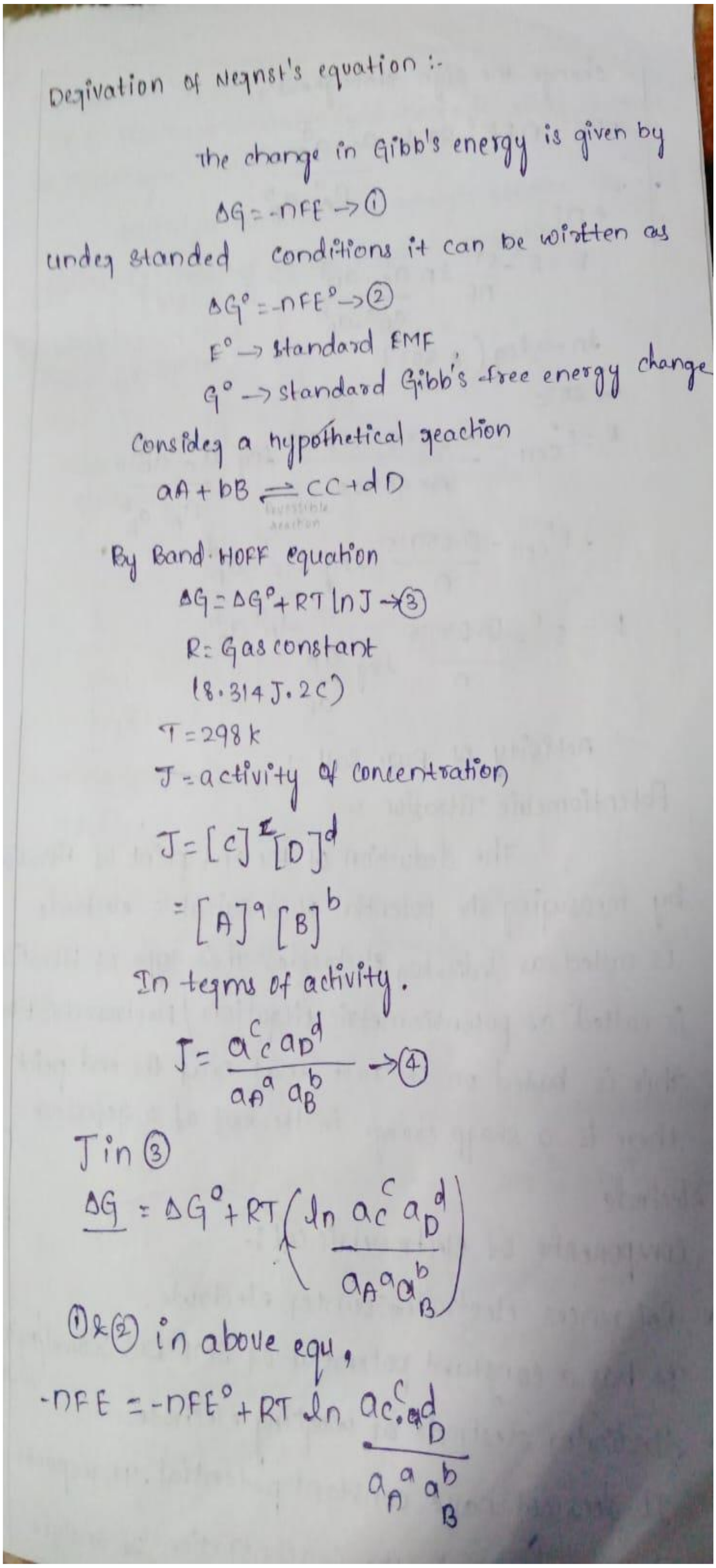
n= no. of electrons involved in the chemical reaction , F= Faraday(96500C)

The change in the gibbs free energy appears as electrical energy.

G = -nFE

E=Emf of the cell (in volts)

Derivation of Nernst equation



Derivation of Nernst's equation :-

The change in Gibb's energy is given by

$\Delta G = -nFE \rightarrow$ ①

under standed conditions it can be written as

$\Delta G^\circ = -nFE^\circ \rightarrow$ ②

$E^\circ \rightarrow$ standard EMF

$G^\circ \rightarrow$ standard Gibb's free energy change

Consider a hypothetical reaction

$aA + bB \underset{\text{reversible reaction}}{\rightleftharpoons} cC + dD$

By Band·HOFF equation

$\Delta G = \Delta G^\circ + RT \ln J \rightarrow$ ③

R: Gas constant

(8.314 J.2C)

T = 298 k

J = activity of concentration

$J = [C]^c [D]^d$

$= [A]^a [B]^b$

In terms of activity.

$J = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b} \rightarrow$ ④

J in ③

$\Delta G = \Delta G^\circ + RT\left(\ln \frac{a_C^c \, a_D^d}{a_A^a a_B^b}\right)$

①&② in above equ,

$-nFE = -nFE^\circ + RT \ln \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$

Potentiometric titration:

The detection of the end point of titration by measuring the potential of a suitable electrode is called as **Indicator electrode**.This type of titration is called as **Potentiometric titration / Electrometric titration.**This is based on the fact that near the end point there is a sharp change in the emf of a reference electrode.

Components of Potentiometric cell:

1. Reference electrode or counter electrode- it has a constant potentiaal or emf

Eg; calomel/hydrogen electrode

2. Indicator electrode or working electrode- It does not have constant potential.It response to the change in the concentration of analyte solution.

Eg; platinum electrode, gold electrode ,silver electrode.

3. **Electrolyte**- Electrolyte contains the analyte solution and the end point is detected by the change in potential.

Analyte – FAS (Reducing agent) + Sulphuric acid
Titrant – $K_2Cr_2O_7$ (Oxidizing agent)
Reference electrode – saturated calomel electrode
Indicator electrode – platinum electrode

Reaction :-

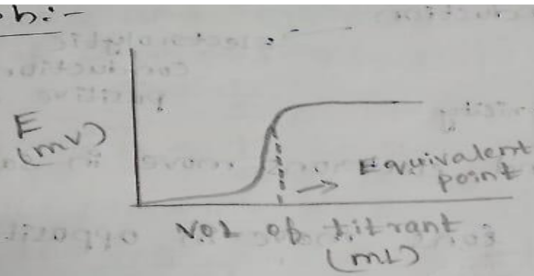
Oxidation: $Fe2+ \rightarrow Fe_{3++e\_}$ (1)
Reduction: $Cr_2O_{7-2} + 14H_{+} + e\_ \rightarrow 2Cr_{+3} + 7H_2O$ (2)
Overall reaction: $Cr_2O_{72-} + 6Fe_{2+} + 14H_{+}\ {}_{+3} + 7H_2O$

EMF:

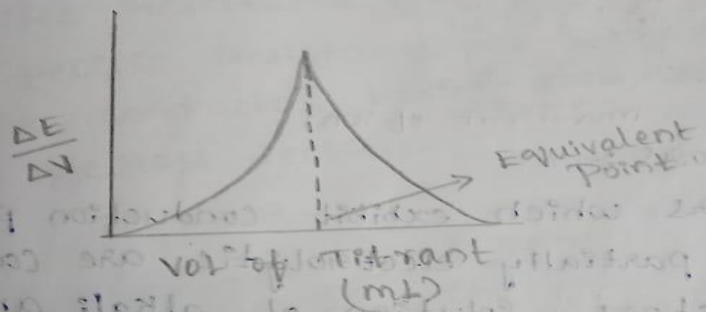
$E_{Cell} = E_{Ind} - E_{ref} + E_j$(liquid junction potential ,neglect as it is so small)

$E_{cell} = E_{Ind} - E_{ref}$
$= E_{Ind} – 0.05915/n \log (a_p/a_r)$
$= 0.77v – 0.05915/n \log (Fe_{3+}/Fe_{2+}) – 0.2422$

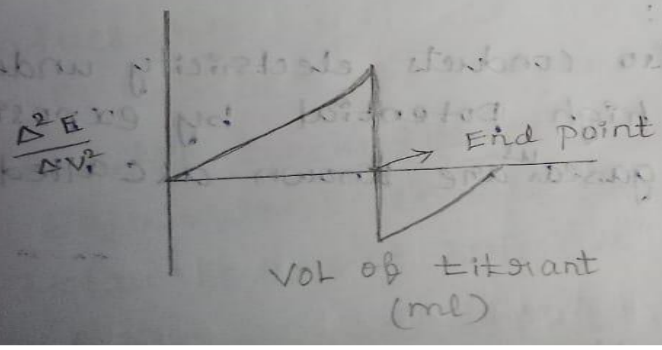
Graph:-



1st derivation curve



2nd derivation curve



Conductivity:-

1)conductance (I) – conductance always depends on number of ions and speed of ions.

2)conductor – The material which allows electric current to pass through it is called conductor. It is divided into two i.e **Electronic conduction**/ negative electricity and **Electrolytic conduction** or positive electricity.

- Current and electrons move in same direction.
- Whereas, current and ions move in opposite direction.

3)Mixed conductors- conductors which exhibit conduction partially electronic and partially electrolytic are called mixed conductors. Solution of alkali and alkaline earth metals in liquid ammonia

.

4) Gaseous conductors – gases can also conducts electricity under the influence of high potential by exposing it into the radiation. Such gases are known as **gaseous conductors.**

5) Resistance (R)- Resistance is the opposition that a substance offers to the flow of current.
Unit – ohm

Resistance of the conductor or material is directly proportional to length between two electrodes and inversely proportional to the area of the cross section.

$R \propto 1/I$ [l/a is cell constant]
$R \propto l/a$
$R= \rho l/$
$=> R = \rho$

6)specific resistance (ρ) –

Specific resistance is defined as the resistance of the conductor having unit length and unit area of cross section.

$\rho\, l = aR$
$\rho = aR/l = cm^2 * ohm / cm$
$=> \rho =$ ohmcm

Conductance:
It is divided into three types
1. Specific conductance (k)
2. Equivalent conductance (λ)
3. Molar conductance (μ)

- **Specific conductance (k)** – It is the reciprocal of specific conductance

kappa(k). It is defined as the conductance of the conductor having unit length and unit cross section. In case of a solution, kappa depends on the volume and number of ions present in the 1cc of the solution. Unit of kappa is **$ohm^{-1}cm^{-1}$**.

- **Equivalent conductance (λ) -** Equivalent conductance is defined as the conductance of the solution containing 1gm equivalent of solution. Equivalent conductance is the product of specific conductance and volume.

λ=k * V [V=1/c]
λ= k * 1/c [c= 1geq/cm^3]
= ($ohm^{-1}cm^{-1}$) / (geq/litre)
= ($ohm^{-1}cm^{-1}$) / (geq/cm^3)
= ohm-1cm2geq-1
Ohm^{-1} (or) mho =siemen(S)
=> Scm2geq-1

- **Molar conductance (μ) –** It is defined as the conductance of the solution containing 1 mole of the electrolyte

➚🖫 &✉ ✞
Unit : Sm^2gmol^{-1}

Conductometric titration :-

PRINCIPLE – conductivity of the solution depends on the number of ions and speed of ions**.**

Titrant = NaOH , Analyte = Hcl

MATERIALS REQUIRED / CONDITIONS FOR CONDUCTOMETRIC TITRATION –

✓Double distilled water
✓Electrodes must be freshly platinized(coating with platinum
✓Titrant must be 5-10 times stronger than the analytic solution.

ADVANTAGES –

➔Accurate results than volumetric titration
➔Need not use indicator.
➔No need to have an idea regarding the strength of acid or base.
➔Weak acid and Weak bases can be titrated easily
➔Precipitation titration can be done easily.
➔Mixture of acids can be titrated against the base.
➔Dark coloured solutions can be titrated.
➔Turbine solutions can be also titrated.

Type of ACID-BASE titration :-

1. Strong acid vs Strong base
2. Strong acid vs Weak base
3. Weak acid vs Strong base

4. Weak acid vs Weak base
5. Mixture of acids vs strong base

1 . Strong acid vs strong base :-
HCl vs NaOH
HCl + NaOH →NaCl + H_2O

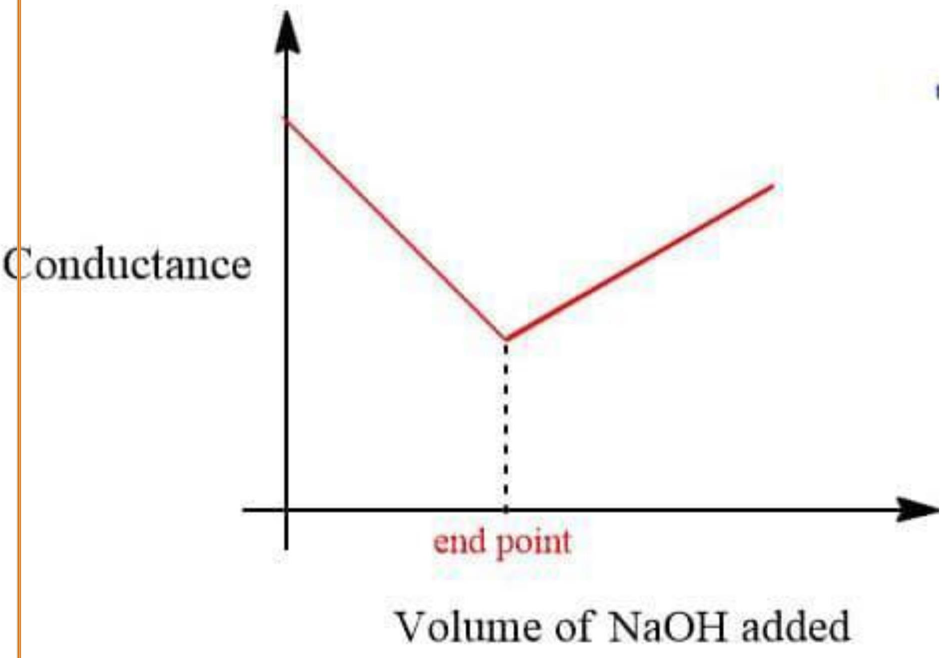
At point A, conductance is high since HCl has high degree of dissociation and H^+ ions are fast moving. On adding NaOH, curve decreases since fastly moving H^+ ions are replaced by slowly moving Na^+ ions ,the decrease occurs until the complete neutralization of acid.

On adding NaOH, the curve increases since NaOH has high degree of dissociation & fastly moving OH^- ions.

2.Strong acid vs Weak base :-

HCl vs NH4OH

HCl + NH4OH→NH_4Cl +H2O



At point A , conductance is high since HCl has high degree of dissociation and H^+ ions are fast moving.

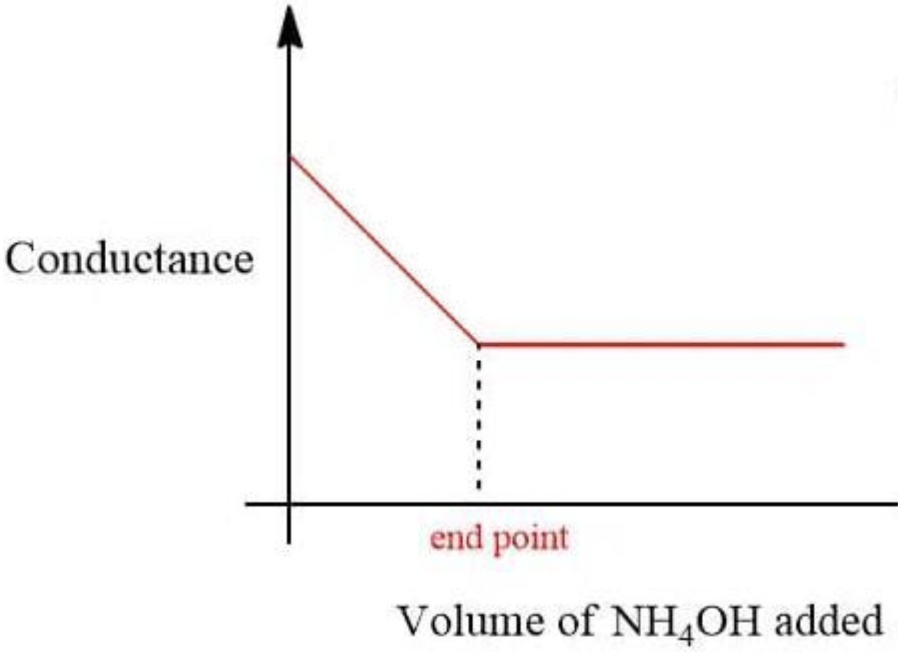
On adding NH_4OH, curve decreases since fastly moving H^+ ions are replaced by slowly moving NH_4^+ ions

. The decrease occurs until the complete neutralization. On adding NaOH , the curve does not change since NH_4OH has low degree of dissociation & slowly moving OH-ions

3 . Weak acid vs Strong base:-

CH_3COOH vs NaOH

CH_3COOH +NaOH →CH_3COONa +H2O.



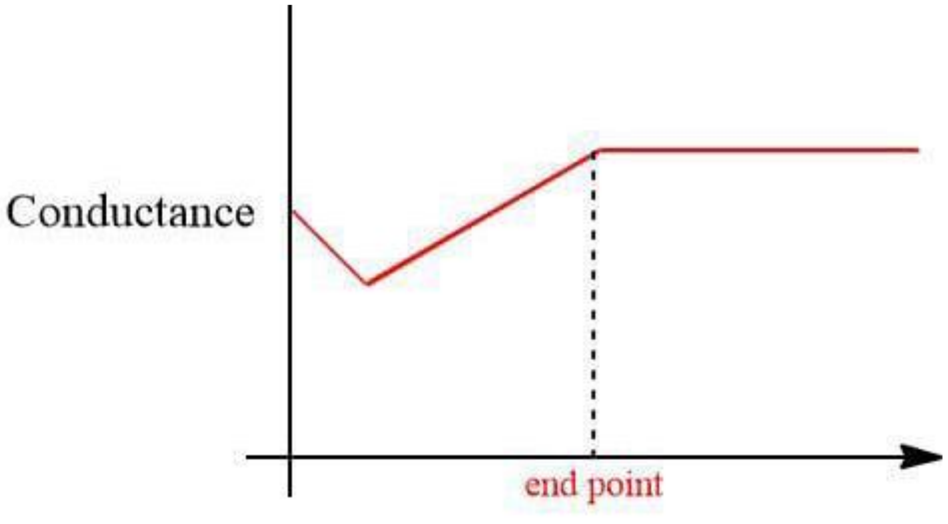
At point A , Conductance is low since acetic acid has poor degree of dissociation. On adding NaOH , highly ionised CH_3COONa is formed due to which curve increases from A to B. The increase

occurs until complete neutralization. Further, addition of NaOH increases the curve from B to C due to its high degree of dissociation and fast moving OH^- Ions.

4. Weak acid vs Weak base :-

CH_3COOH vs NH_4OH

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$



At point A, Conductance is low since CH_3COOH has poor dissociation . On adding NH_4OH , highly ionised sodium acetate is formed due to which curve increases from A to B . The increase occurs until complete neutralization.

Further, addition of NH_4OH the curve do not change from B to C .Due to its low degree of dissociation and slowly moving OH- ions . It does not change.

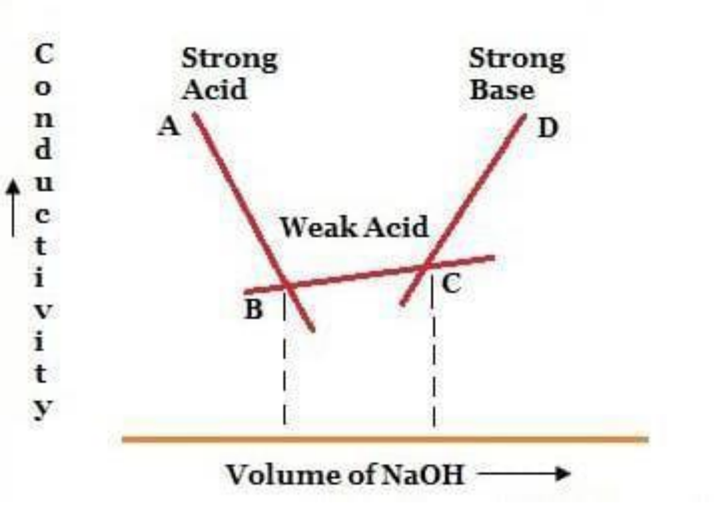
5. Mixture of acid vs Strong base :-

HCl / CH_3COOH vs NaOH

HCl + NaOH →Nacl +H_2O

CH_3COOH + NaOH→CH_3COONa + H_2O

At point A, conductance is high since Hcl has high degree of dissociation. A,B curve or conductance of AB curve decreases →H^+ ions are replaced by slowly moving Na^+ ions. Conductance of BC curve increases gradually due to the formation of highly ionized sodium acetate .Due to the further addition of NaOH the curve increases.



Fuel cell :-

Fuel cells are galvanic cells in which chemical energy of fuels are directly converted into electrical energy.

Fuel + oxidant →electrical energy

Types of fuel cells –

1) Low temperature fuel cells
2) High temperature fuel cells

1.low temperature fuel cells (60-250^{0}c) :

→solid polymer electrolyte fuel cell operating temperature is 80^{0}c.
→Alkaline fuel cell (90^{0}c)
→Phosphoric acid fuel cell (H_3PO_4) (200^{0}C)

2.High temperature fuel cell (600-1000^{0}c) :

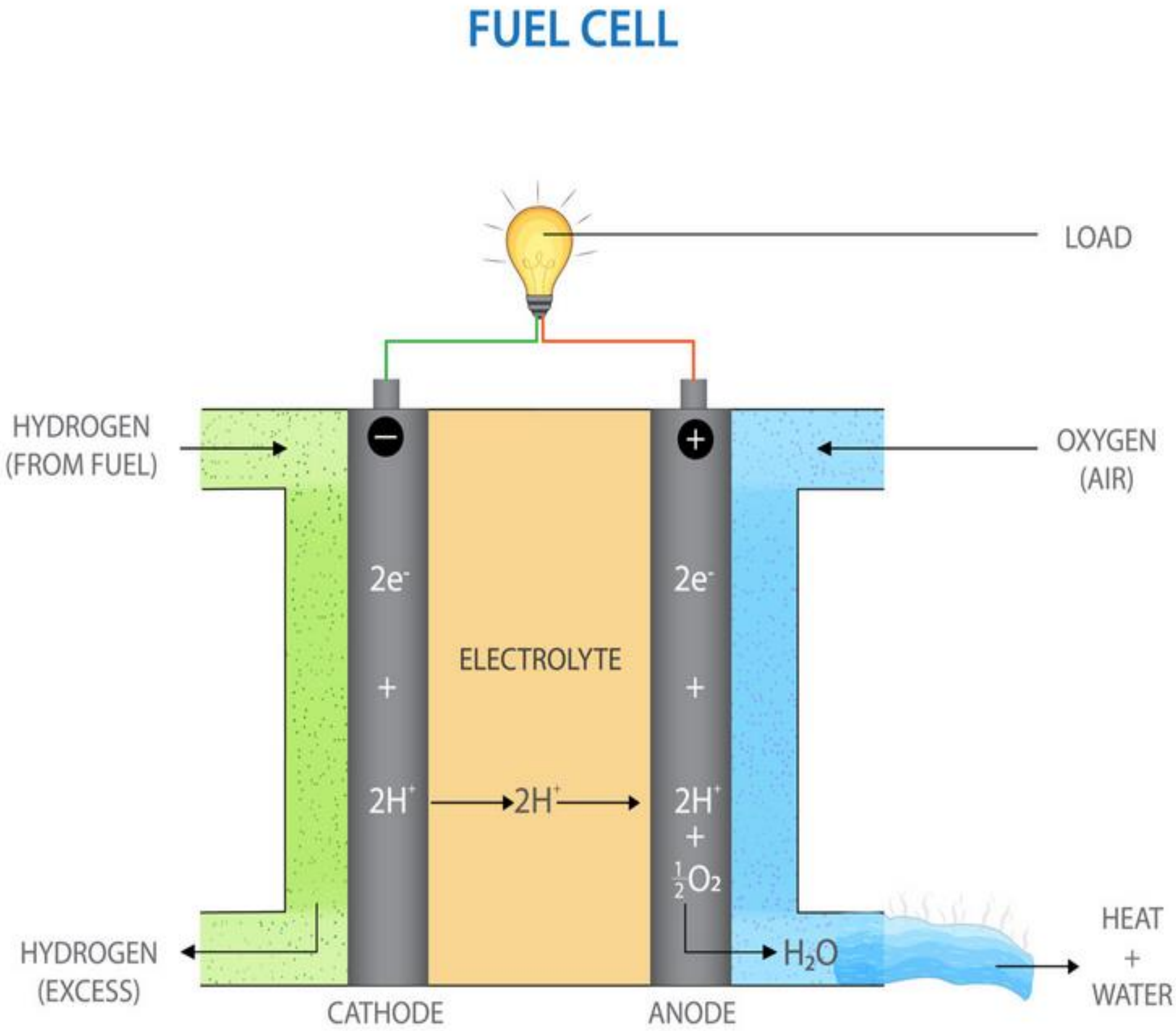
→Polycarbonate fuel cell – (600^{0}c)
→Mixed oxide fuel cell – (1000^{0}c)

Hydrogen-Oxygen fuel cell –

Fuel + oxidant →product + electricity

This cell is based on the combustion of hydrogen to form water. The operating temperature is around 100^{0}c .So, it is a low temperature fuel cell.
EMF = 1 volt

⇨Hydrogen-oxygen fuel cell is often referred to as simple as a hydrogen fuel cell ,is a type of fuel cell uses hydrogen as the fuel and O_2 as the oxidant. This type of fuel cell produces electricity, water and heat through an electrochemical reaction between H_2 and O_2 making it highly efficient and environmentally friendly.



Oxidation half cell reaction :

$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2OH^- \rightarrow 2H_2O$

$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \rightarrow (1)$

Eq (1)* 2

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \rightarrow (2)$

Reduction half cell reaction :

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \rightarrow (3)$

Eq (2) +(3),

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall reaction :

$2H_2 + O_2 \rightarrow 2H_2O$

DISADVANTAGES-

1. High cost
2. Hydrogen production
3. Storage and transportation
4. Energy efficiency
5. Recycling challenges

APPLICATIONS:

⇨Used in power vehicles like cars , buses etc
⇨Used in industrial process like ammonium production and oil factory.
⇨Used in storing excess energy from renewable sources.

⇨ H_2-O_2 fuel cells are used as auxiliary energy source in space vehicles, submarines or military vehicles.

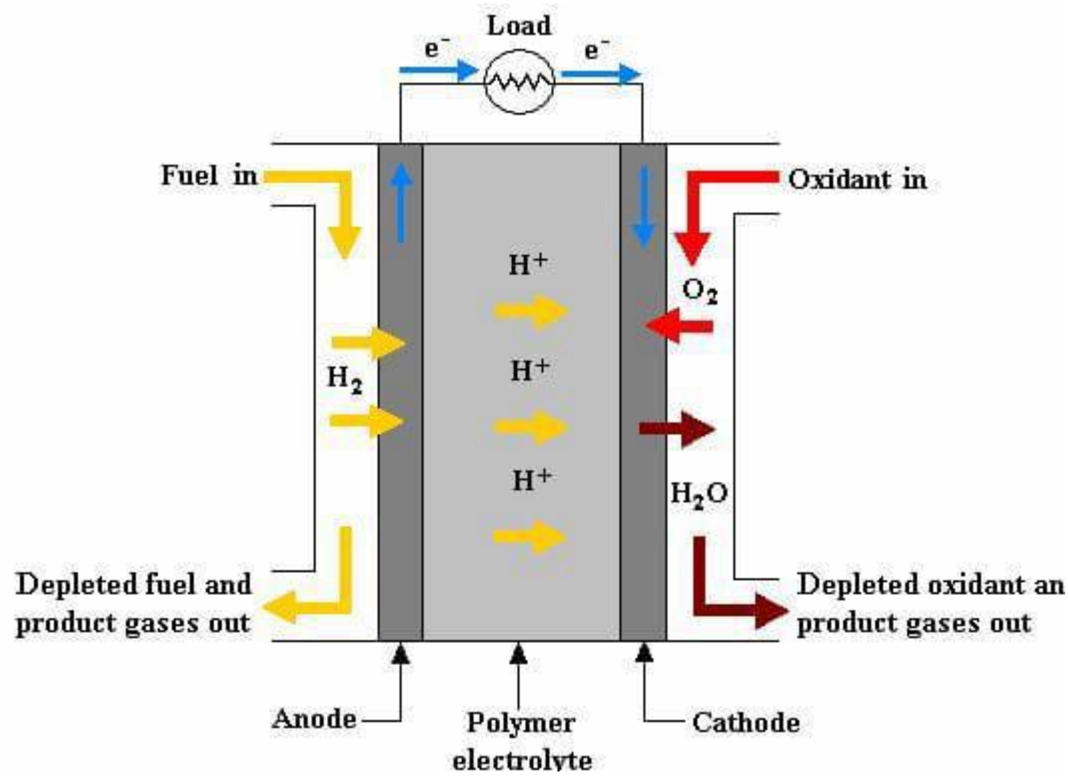
⇨ As the by-product is H_2O, used as fresh water for astronauts. For 15 days, weight required is 250 kg.

Polymer electrolyte membrane fuel cell :-(PEMFC)

It is also called as proton exchange fuel cell.

Anode, cathode →platinum based

Electrolyte →water based polymer membrane



At anode,

$H2 \rightarrow 2H_{+} + 2e\_$ (oxidation half cell reaction)

At cathode,

$\frac{1}{2} O_2 + 2H_{+} + 2e\_ \rightarrow H_2O$ (Reduction half cell reaction)
H_{+} is also exchanged so it is called as proton exchange membrane fuel cell

.

Overall reaction,

$H2 + 1/2\ O2 \rightarrow H_{2O}$
HT→PEMFC

Fuel →mineral based polymer membrane
Temperature →up to 200$_{0c}$

Batteries :-

A Cell is a single electrochemical unit consisting of cathode and anode. A battery is a series of several electrochemical cells connected together. Batteries are classified into two types

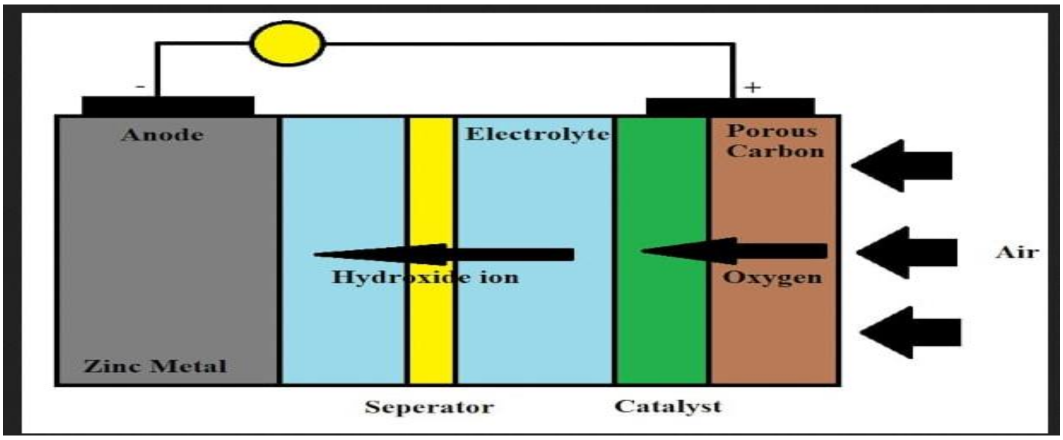
.

1) Primary cell or battery [cannot be recharged]
2) Secondary cell or battery [can be recharged]

Eg- mobile phones, laptops.

1) **PRIMARY CELL** – a primary cell is a cell that cannot be recharged with electricity and cannot be reused multiple times. these cells cannot be recharged because the redox reactions in the cell is in the single direction. Redox **REACTIONS IS NOT REVERSIBLE.**

ZINC-AIR BATTERY :



Anode :

$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O$

$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Cathode :

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Overall reaction :

$Zn + \frac{1}{2} O_2 \rightarrow ZnO$

EMF = 1.4V

Advantages –

1. High energy density
2. Inexpensive material
3. Environmental friendly
4. Long shelf life and light weight

Disadvantages –

1. Sensitive to cumin conditions.
2. After activation, chemicals tend to dry out and hence these batteries have to be used quickly .
3. Limited output.

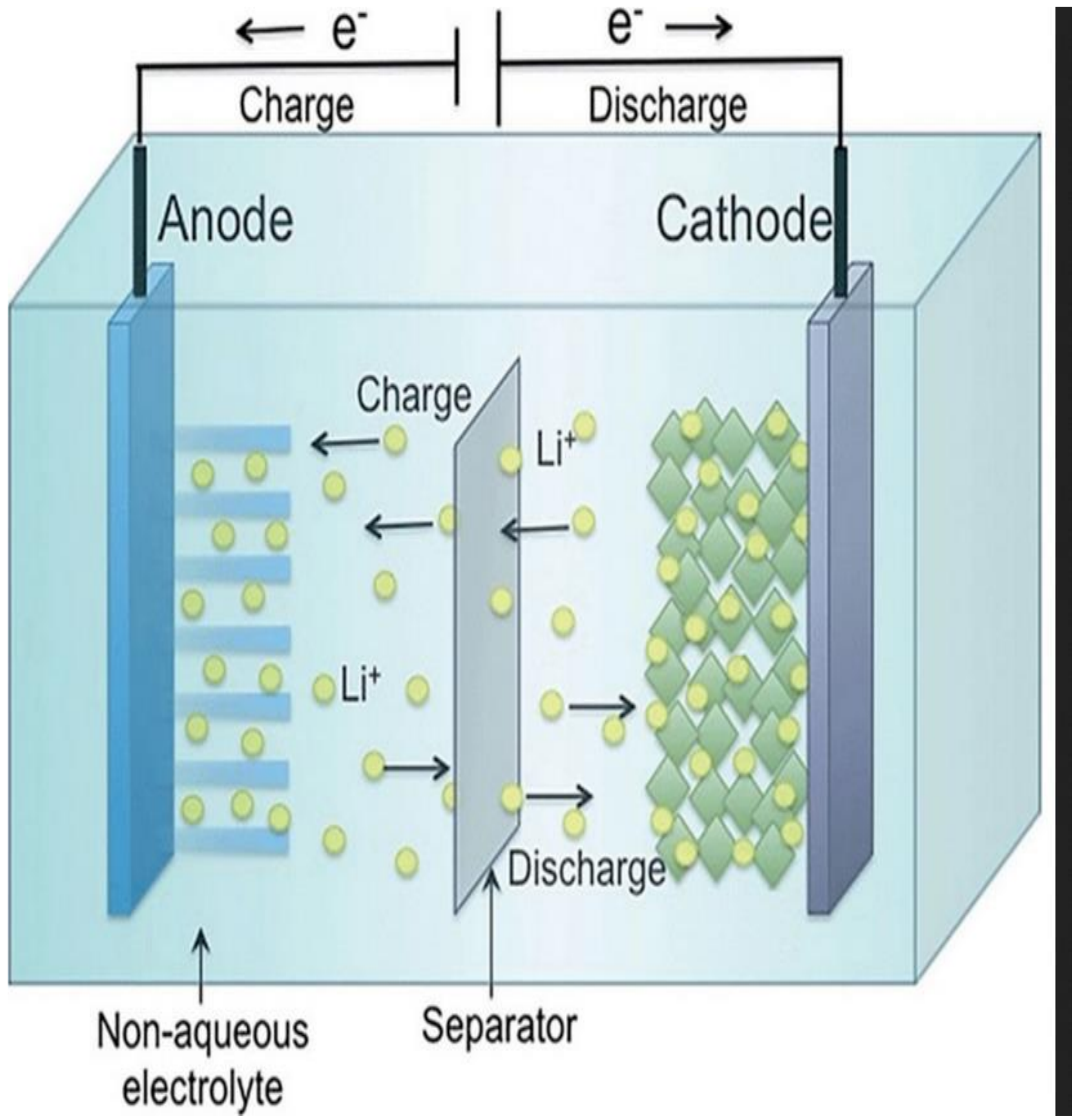
Applications –

1. Used in hearing devices.
2. Used in military transistors.
3. Used in voice transmitters.
4. Used in communication devices like pagers

2) Secondary cell –

A Secondary cell is a cell that can be recharged with electricity and reuse multiple times .These cell can be recharge because the redox reaction in the cell is largely reversible.

LITHIUM ION BATTERY :



Discharging cycle :

Anode : $LiC_6 \rightarrow Li^{+}+C_6+e^{-}$
(electron gets emitted , ion (anode → cathode)

Charging cycle :

$CoO_2 + Li^{+} + e \rightarrow LiCoO_2$ (lithium cobalt dioxide)
Electron gained , ion (cathode → anode)

Overall reaction :

$LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$

Swing batteries – since the reactions are reversible. These batteries are called as swing batteries.

Advantages –

1.High energy density
2.Fast charge
3 .Long cycle life
4.Wide temperature range operation.

Disadvantages –

1.Highly inflammable
2 .Limited performance
Heavily depends on imports

Applications –

1.Used in aerospace
2. Electric vehicles
3.Electronic industries

ELECTROCHEMICAL SENSORS :

- Sensor is a device that provides an output signal for the purpose of detecting a physical phenomenon.
- It converts the information associated with chemical reaction or chemical signal into an qualitative or quantitative signal of the sample under study.

Types of electrochemical sensor :-

1.potentiometric sensor (measures potential difference)
2. Amperometric sensor (measures the current flow)
3.conductometric sensor (measures the conductance)

POTENTIOMETRIC SENSOR

– It determines the analyte concentration by the measurement of potential difference between the indicator electrode and reference electrode.

. The tendency of an electrode to loss or gain e^-s when it is in contact with its own solution (eg:- Zn/ZnSO4) in standard conditions i.e., 25° C, 1 atm. pressure and 1M conc. Of solute is called electrode potential or Standard Reduction Potential (SRP).

Daniel cell comprises of two half cells i.e., OHR and RHR. So, one gets oxidized and gets reduced. The Standard Electrode Potential is obtained as follows:

E^o_{cell} = [Standard Reduction Potential (SRP)] – [Standard Reduction Potential (SRP)]of the substance reduced of the substance oxidised

E^o – Right E^o_L – Left

The Standard Electrode Potential of different electrodes is given in table.

The values of Standard Reduction Potentials are arranged in decreasing order known as ―Electrochemical series.‖

Eq.

The positive ion values of the electrodes are tendency to accept e^-s (reduced).

The negative ionvalues of the electrodes are tendency to donate e^-s (oxidised).

<u>Calculations</u>:- EMF – Galvanic.

i) E^oCell is given by $E^OCell = E^o_R - E^o_L$

ii) Notation of cell.

For right electrode Ion/Electrode {eg:- Cu^{2+}/Cu}For left electrode Electrode / Ion {eg:- Zn/ Zn^{2+}}i.e., $Cu^{2+}/Cu \parallel Zn/ Zn^{2+}$ (‗‖' is salt bridge)

Salt bridge:

iii) Complete cell reaction is the sum of two half cell

<u>Prediction of feasibility of reaction</u>

i) If the net EMF of the cell (i.e., from left and right) is positive (+), then the rection is spontaneous i.e., reaction takes place.

eg:- Zn/ Zn^{2+} ; Cu^{2+}/Cu

$E^oCell = E^oR - E^oL \{E^o(Cu^{2+}/Cu) – E^o(Zn/ Zn^{2+})\}$

$=0.34-(-0.76)$

$=0.34+0.76$

$+1.10V$

ii) If the net EMF of the cell (i.e., from left and right) is negative (-), then the reaction is non- spontaneousi.e., reaction does not takes place.

eg:- Fe^{2+}/ Fe ; Ni/Ni^{2+}

$E^oCell = E^oR - E^oL \{E^o(Fe^{2+}/ Fe) – E$

Electrochemical sensors:

—Sensor is a device, which provides information regarding sample continuously in the form of analytical assay and gives information in the discrete steps.||

There are different types of sensors:

i)	Electrochemical sensors	58%
ii)	Optical sensors	24%
iii)	Mass sensors	12%
iv)	Thermal	06%

- Electrochemical sensors are the largest group of sensors.
- In the Electrochemical sensors, the electro analytical devices which provide strong scientific base, chemical environment and growing need for reliable sources of information guarantees their future.
- The important application of electrochemical sensor is assay of blood glucose.
- Enzymatic glucose electrode is capable sensing the blood glucose level continuously. (Concentration changes continuously).
- It is clear that electrochemistry scope is to convert chemical information into electrical signal. No need of magnets (MRI, CT scans), light bulbs (endoscopy), vacuum pumps, etc.

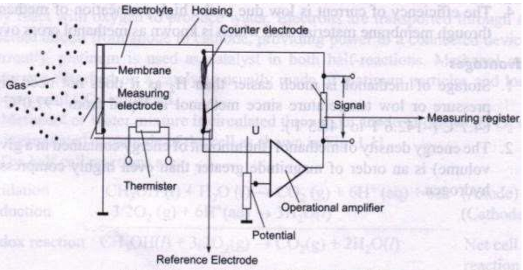


Fig. 1.12 *Block Diagram of Electrochemical sensor*

<u>Electrochemical sensors- Schematic representation</u>.

- It consists of outer frame with electrolytic gel and three electrodes.
- It has permeable membrane the top.
- The electrodes should have: -Large surface area
  -long life
  -highly sensitive
- Each cell consists of special filter electrodes & electrolytes with high specificity.
  - Even small amount of electrolyte is enough for large signal and gives immediate response. Fig.

Classification of Electrochemical sensors:

Based on electrical parameter, these are divided into three types. They are:

i) Potentiometric sensors – Parameter – potential (V)
ii) Amperometric/ Voltametric sensors – Parameter – current (A)
iii) Conductometric sensors or Chemical resistors – Parameter – Resistance

These three above sensors works based on ‗Ohms law' principle.

- The pd (potential difference) in a circuit is equal to product of current & resistance

V = i x R

- For all the three sensors, measurement is done with closed electrical circuit i.e., test charge can be passed through the electrical circuit and return to its origin.
- All the three sensors maintains electrical neutrality i.e., sum of positive charges are equal to sum of negative charges (this electrical neutrality is maintained as we divide solutions into smaller & smaller even.
- The chemical specificity (recognition) comes from the Ion Selective Electrodes (ISE's) and that is connected to amplifier.

Potentiometric sensors:

- Ion Selective Electrodes (ISE's) are used in Potentiometric sensors.
- ISE's depends on the concentration of ionic species in the test solution used for electro analysis.
- In ISE's, the recognition of H^+ ions is done by glass electrode sensing element. This is coupled with reference electrode.
- Now sensor results come from the pd between these two electrodes.
- Glass electrode is the mother of all ISE's, which is highly sensitive (selective) to H^+ ions and requires high input impedance.
- Glass electrode has high resistance, due to glass membrane and it is the oldest of all electrochemical sensors.
  - Glass electrode was introduced by Arnold Beckmann. Working Principle:

- ➢ The working principle is similar to glass electrode & common to all ISE's.
- ➢ The glass electrode is represented as follows Ag, AgCl / 1M HCl / H^+ (test solution)
- ➢ Potential of glass electrode depends on the conc. of H^+ ions.
- ➢ As a result of difference in conc. Of H+ ions on two sides of membrane potential difference is developed.

Ion Selective Electrode (ISE):

- ➢ ISE has a membrane which is sensitive to a particular chemical species.
- ➢ ISE respond to certain specific ions present in a mixture while ignoring others and develop potential.
- ➢ The potential developed is a measure of concentration of species of interest
- ➢ Glass electrode on its surface develops a thin gel like layer of H^+ ions (hydrated). So, partition is developed.

The Nernst eq. is given by

The potential = standard electrode potential + correction term for the deviation from the unit concentration of the reactant and product of the electro

Basic requirements of potentiometric sensors:

✓ It requires a stable & reproducible reference.

✓ Electrode has a well known & stable equilibrium electrode potential.

✓ It is used as reference point against which the potential of other electrodes can be measured. But few commonly used electrodes have potential independent of electrolyte used.
Eg: Ag-Cl electrode, calomel electrode (0.244v). / $H2$ electrode (0.0v).

✓ Exactly 50% of the information from the measurement comes from the reference electrode.

Glucose Potentiometric sensors*—(Estimation of glucose)*

- Glucose is an electrically neutral molecule. $C6H12O6$ cannot be divided into ions.
- So, without ions signals are not obtained.
- Hence glucose has to be converted into ions, which are selectively detected.

Oxidation of glucose

: Glucose is oxidised to gluconic acid with liberation of H^+ ions & e^-s. D-Glucose + $O2$ + $H2O$ ---------------→ D-Gluconic acid + $H2O$ ($2H^+ + O2 + 2e^-$)

- When Glucose Dehydrogenase (GDH) is used, the reactions are

D-Glucose + GDH(Oxidised) ------------→ δ-Glucolactone + GDH(Reduced)

Note: Glucose content in blood and urine sample are different. Because after the threshold level only in blood, then goes into the urine.

Ampherometric sensors: (*Voltametric sensors*)

Principle : This is a second kind in which it works based on the measurement of current between the working & counter electrode, which is initiated by Redox reaction at working electrode.

➢ The signal or response depends on the diffusion of current.

➢ But, the Diffusion of current α Conc. of species at the electrodes.

➢ The redox process at the electrode represent charge transfer reactions that can proceed in either direction (oxidation and reduction) with its own rate of reaction.

➢ Electrochemical reactions are of following types:

1. ***Reversible***:

- Very fast in both directions
- Charge transfer resistance is low
- Charge transfer capacity is high

2. ***Irreversible***:

- Very slow in rate of reaction
- Charge transfer resistance is high
- Charge transfer capacity is low

➢ Rate of electrode reactions depends on applied potential.

➢ At high negative potential: reduction is faster & charge transfer resistance is low.

➢ At high possitive potential: oxidation is faster & charge transfer resistance is low.

➢ Micro electrodes give best measurements, which are smaller than 20μm, because size of electrodes plays a key role in ampherometric sensors.

- Principle of operation: Glucose sensitive electrode (biocatalyst-glucose electrode).Uses of Amphrometric sensors:

- ✓ Oxygen sensors (or) clark electrode is used in estimation of DO in water
- ✓ These are used in gas analysis in food & beverage industry.
- ✓ Used in detection of hazardous materials like explosive gases.

Estimation of Uric Acid (UA):

- Uric acid is a major nitrogenous compound in urine.During the metabolism, purines are converted into uric acid in urine.
- Biological determination of uric acid comes from the electrochemical interference such as Ascorbic acid (AA), which has similar oxidation potential. This creates major problem in the determination of UA.
- UA is present at high conc. in biological system.
- Estimation of UA is done by two methods.

1. ***Enzymatic Method***: (two Process)

A) Uric acid is converted into Allatonin with the release of $CO2$ by uricase enzyme.Uric acid + $O2$ + $H2O$ ------------→ Allatonin + $H2O2$ + $CO2$

B) Uric acid is converted into Allatonin by e- transfer mediators.

Uric acid + Mediator(Oxidised) + $H2O$-→ Allatonin + Mediator(Reduced) + $CO2$ + $2H^+$ + $2e^-$

2. ***Non-enzymatic method***:

Differential pulse voltammeter is used to detect uric acid in the presence of AA. Peak currents of UA & AA could be separated in this method and current correlated with conc. of both.

Advantages of Electrochemical sensors:

- ✓ When the analyte is optically inactive, in such condition electrochemical sensors are used.
- ✓ Electrochemical sensors are used in the analysis of more inorganic ions.
- ✓ Electrochemically inactive ions are also determined with the help of polymer modified electrodes.
- ✓ Oxygen and toxic gases like (N_zO_y), (S_xO_y), (C_xO_y) & $H2S$.
- ✓ Environmental pollutants are monitored.
- ✓ To estimate the conc. of ions in blood, urine and other biological samples
- ✓ To check the conc. levels of fertilizers, pesticides, drugs and pharmaceuticals, etc.

THE END

UNIT-IV: Polymers Chemistry

Lecture notes

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: It is defined as a high molecular weight compound (macro molecule) made by linking together a large number of small molecules called **monomers.**

Ex: PVC, Polyethylene, Starch, Poly styrene, Proteins, DNA etc

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.

$$\text{Degree of polymerization (D.P)} = \frac{\text{Mol.wt of polymer}}{\text{Mol.wt of monomer}}$$

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

Classification of Polymers:

1. Based on degree of polymerization:

- Polymers having high DP (having of more number of monomers) are called **High polymers**. Their molecular weight range is about 10,000 to 10,00,000 Daltons.
- Polymers with low DP are called **Oligopolymers**. Their molecular weight ranges from 5,000 to 2,00,000 Daltons.

2. Based on occurrence:

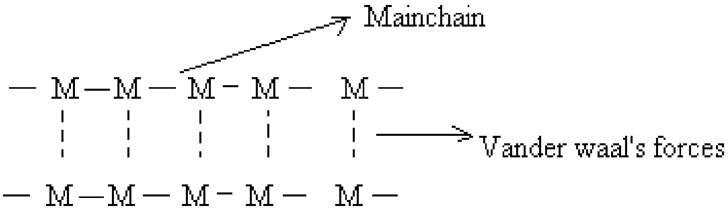
- Polymers may be either **Natural** (natural rubber, proteins, cellulose, starch etc) (or) **Synthetic** (PVC, PE, PS, Teflon, Nylon, Bakelite etc…..).

Basic Concepts:

1) Functionality:

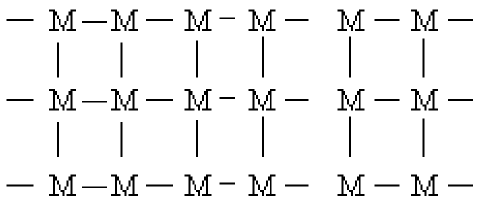
- The number of bonding sites (or) reactive sites present in a monomer is called as functionality.
- Each monomer should have minimum two bonding sides for polymerization.

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

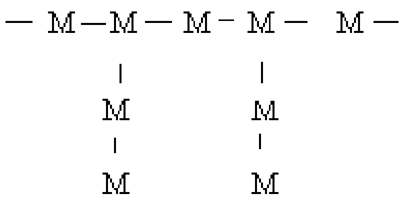


b) If the functionality of monomer is three (trifunctional), Cross linked three dimensional polymers are obtained.

Ex: Bakelite.



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



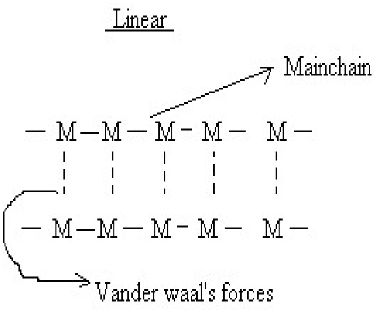
2) Nomenclature: polymers are given names based on two properties

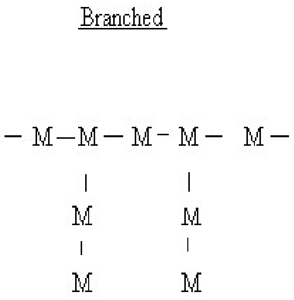
1. Type of monomers present
2. Type of atoms present in back bone chain

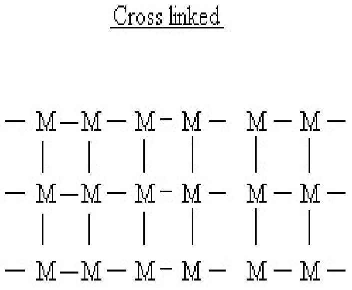
(i) Type of monomers:

a) Homo polymer: If a polymer consists of identical monomers, then that polymers are called homo polymers. They may be linear, branched (or) Cross – linked.

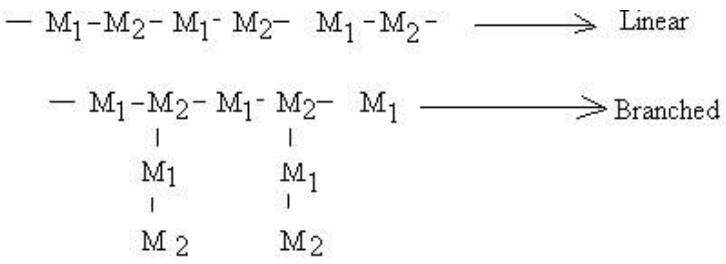
Ex: PVC, Polythene, Teflon etc………..







b) Hetero or Co–polymers: If a polymer is composed of different types of monomers, then it is called Hetero / co – polymers. They may be generally **linear (or) Branched**.



(ii) Type of atoms present in back bone chain:

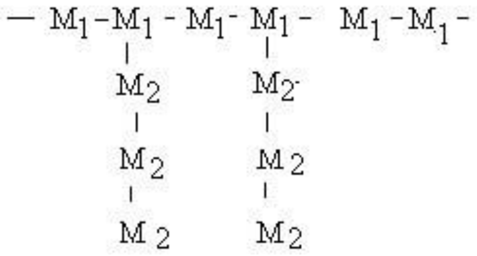
a) Homo chain polymer: If the main chain is mode up of same species of atoms is called homo chain polymer.

– C – C – C – C – C –

b) Hetero chain polymer: If main chain is composed of different atoms is said to be Hetero chain polymer

– C – O – C – O – C – O –

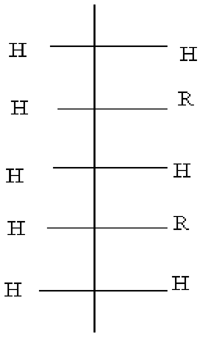
e) Graft co-polymers: These polymers are branched structures in which the monomer units on the branches and back bone differ.



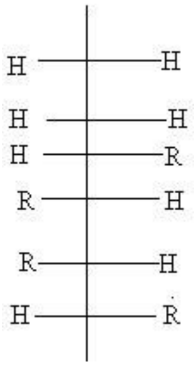
Tacticity: The orientation of functional groups in polymer is called as configuration. The difference in configuration of polymers because of the difference in arrangement of functional grouund main chain is called as Tacticity. Based on tacticity, polymers

Hetero or Co–polymers: If a polymer is composed of different types of

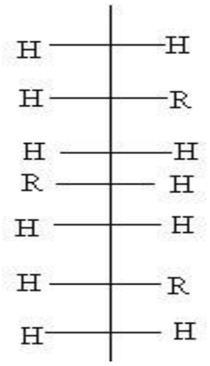
a) **Isotactic:** If all the functional groups are arranged on the same side of the chain, the polymer is called Isotactic polymer.



b. **Atactic:** If all the functional are arranged randomly around the main chain, the polymer is called Atactic polymer.



c. Syndiotactic: If all the functional groups are arranged alternately with respect to the main chain, the polymer is called syndiotactic polymer.



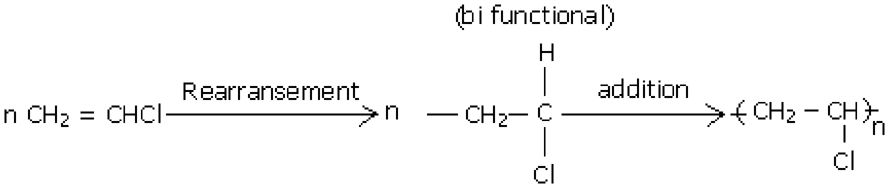
Polymerization:

1) Addition Polymerization:

- This polymerization takes place between monomers that are bifunctional and contains double bonds in its structure.
- This can be defined as binding of several bifunctional monomers to form polymers without elimination of by products by addition reactions.
- This polymerization results in the formation of linear polymers.
- The produced polymer has same chemical composition as that of monomers.
- The molecular weight of polymer is an integral multiple of the monomer.

Examples:

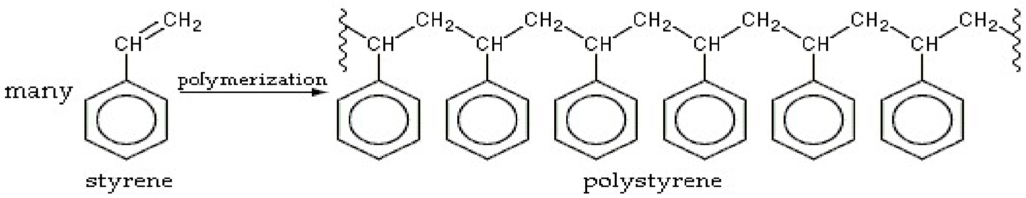
1. Formation of PVC:



2. Polymerization of ethylene:

$n\ CH_2 = CH_2 \longrightarrow n\ [= CH_2 - CH_2 -] - \longrightarrow (CH_2 - CH_2)_n$

3. Polymerization of Styrene:



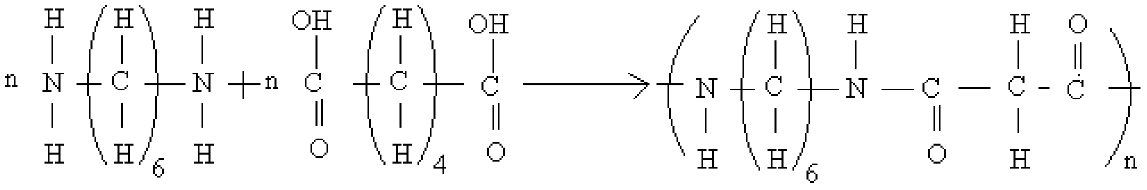
Condensation Polymerization:

- This is also called Step-wise polymerization.
- This occurs between monomers that contain polar side groups.

- A reaction occurring between the same (or) different polar groups containing monomers with elimination of small molecules like ammonia, water, HCl etc….. and forms linear(or) Cross – linked polymers is called condensation polymerization.
-
-
- The molecular weight of polymer is not an integral multiple of the mol-wt of monomer.
- The molecular weight of polymer is not an integral multiple of the mol-wt of monomer
-
- The chemical composition of monomer and polymer are different.
-
- It results in the formation of linear or cross linked polymers.

Example:

1. **Formation of Nylon-6,6**: Formed by the condensation of Hexamethylenediamine with adipic acid (Tetra methylene dicarboxylic acid)



Hexamethylene diamine Adipic acid Nylon-6,6

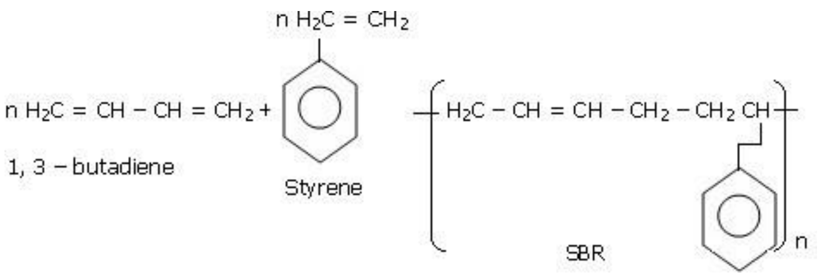
2. **Formation of Polyester**: Formed by the condensation between ethylene glycol and Terephthalic acid $\mathrm{OH{-}CH_2{-}CH_2{-}OH}$ + $\mathrm{COOH{-}C_6H_4{-}COOH}$ $\longrightarrow$ $\mathrm{({-}{-}{-}{-}{-}O{-}CH_2{-}CH_2{-}CO{-}C_6H_4{-}CO\ )_n}$

Ethylene glycol Terephthalic acid Polyester

2) Co-polymerization:

- When two (or) more different types of monomers undergo simultaneous polymerization then it is called Co-Polymerization.
- The properties of co-polymer are different from those of individual monomers.
- The copolymers may be alternating, random, block and graft polymers.

Ex: Styrene butadiene rubber (SBR)



Plastics:

An organic substance with high molecular weight, which can be moulded in to any desired form when subjected to heat (or) pressure in the presence of catalyst is called as plastic.

The term plastic must be differentiated from resins.

Resins are basic binding materials, which from a major part of the plastic and which actually undergo polymerization and condensation reactions during their preparations

However, the term resin and plastic are considered as synonyms.

Advantages:

Now a days, plastics play a important role in daily life because of their certain unique properties.

- Light in weight
- Transparent
- Low maintenance cost
- Chemically inert
- Corrosion resistance
- Insect resistance
- Easy transportability
- Easy workability
- Impermeable to water
- High resistance to abrasion

Disadvantages:

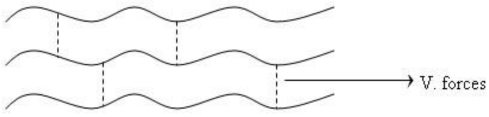
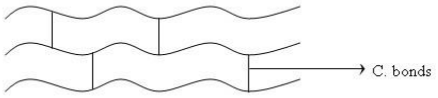
- Low heat resistance, so combustible
- High softness
- Poor ductility
- Major pollutant not degraded by soil

Uses:

- For Making many house hold articles
- For making furniture
- For making electric goods
-

Types of Plastics: Plastics are classified in to two types

- Thermo plastics
- Thermo setting plastics.

THERMOPLASTICS	THERMO SETING PLASTICS
• They are formed by addition reactions. (some times formed by condensation r/n) • They become softened on heating & hardened on cooling • They are soft, weak and less – brittle. • Adjacent polymer chains are held together by weak Vanderwaal's forces  • They have either linear (or) branched structures • The chemical nature is not altered during heating & cooling. • They can be remoulded, reshaped & reused so they can be reclaimed from waste. • Low molecular weight thermoplastics are soluble in suitable organic solvents **Ex:** PE, PVS, PS, Nylon Teflon etc…	• Formed by condensation reactions. • They become soft on initial heating and hard on cooling. On reheating they become more hard. • They are hard, strong and more – brittle. • Adjacent polymer chins are held together by strong covalent bonds.  • Due to strong bonds, they exhibit cross-linked 3D-structure. • Chemical changes takes place during moulding process. • They cannot be remoulded and reused so they cannot be reclaimed from the waste. • Due to strong bonds and cross links, they are not soluble in almost all organic solvents. **Ex:** Bakelite, amino resins, poly ester resins, poly orethones epoxy resins etc……..

Important plastics: Polythene, PVC, Polystyrene, Teflon, Nylon, Bakelite

1. **Poly Vinyl Chloride (PVC):**
2.

Preparation: Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at $100-150^0C$ in the presence of metal salt catalyst.

$$CH \equiv CH + HCl \longrightarrow CH2 = CH2+HCL$$

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

n(CH2 = CH)   (–CH2 – CH–)n ⟶
I   I
Cl Cl

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.

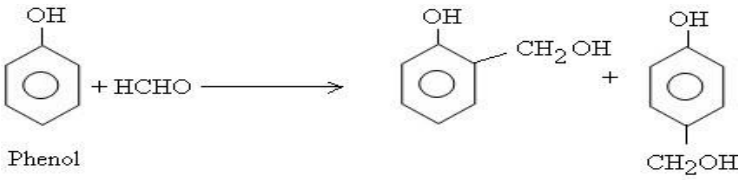
Uses:

- 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.

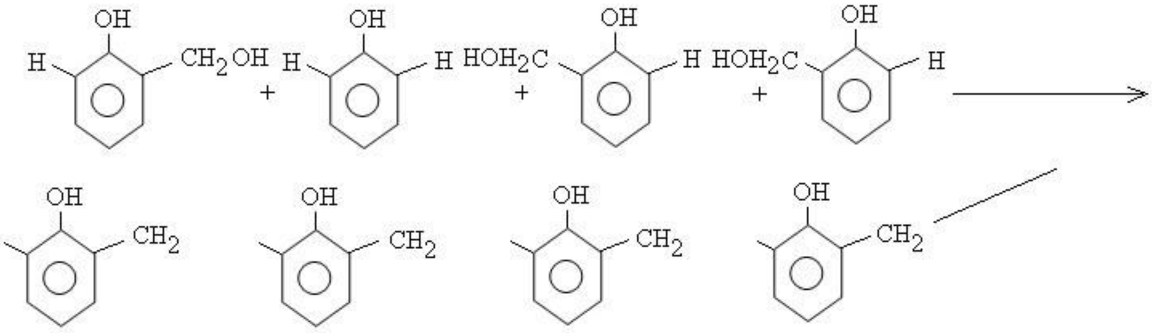
BAKELITE: (Phenol formaldehyde resin / phenolic resin / phenoplasts)

- Bakelite is a important thermosetting resin named after the scientist Bakeland, who synthesized this resin in they year 1909.
- It is prepared by the step polymerization of phenol with formaldehyde in presence of an acid (or) Alkali as a catalyst.
- This polymerization takes place in three steps:

Step I: Phenol can condense with formaldehyde to produce O – hydroxy methyl phenol and P – hydroxy methyl phenol

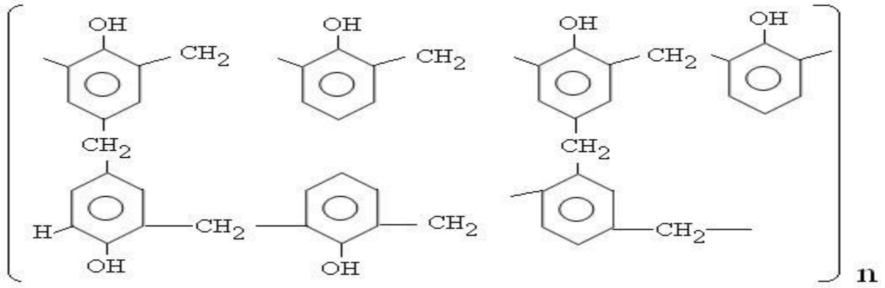


Step II: condensation takes place between O – hydroxy methyl phenol and phenol to give linear polymer called Novalac



Novalac

Step III: During molding, Hexa methylene tetraamine ((CH2)6 N4) is added, it produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible Novalac in to a hard infusible and insoluble solid of cross – linked structure called Bakelite, whereas NH3 neutralizes the acid.



Properties:

Bakelite are rigid, hard, scratch resistant, infusible, water resistant, solid substance.
* Resistant to acids, salts and most organic solvents but attacked by alkali due to the presence of hydroxyl groups.
* Good electrical insulator

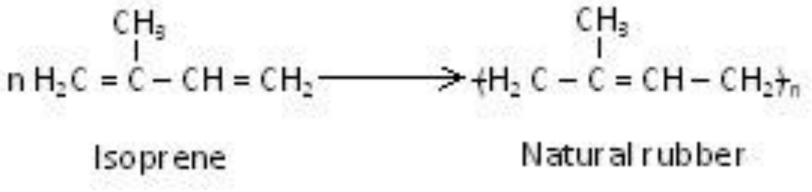
Applications:

* For making electric insulator parts like switches, plugs, holders, switch boards, heater etc……….
* For making moulded article like telephone parts, cabinets for radio and T.V.
* Used in paints and varnishes
* as adhesives for grinding and wheels.
* In the product of ion exchange resin
* For making bearings used in propeller shops, for paper industry and Rolling mills.

RUBBER (ELASTOMERS):

- The polymers which possess the property of elasticity are called as rubber.
- Rubbers are high polymers, which have elastic properties in excess of 300%.
- The molecular weight of raw rubber is about 1,00,000 to 1,50,000 Daltons.
- Most of the Indian production comes from kerala state.

Natural rubber: It is a high polymer of polyisoprene, which are arranged in Cis – Configuration (functional groups are arranged on the same side).



$$n\,H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2 \longrightarrow \left[H_2C - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]_n$$

Natural rubber is mainly produced from the milk of the rubber tree “Have a brasiliensis”. Small quantities of natural rubber is also produced from the milk of a shrub known as “guayule”.

Processing of natural rubber:

- The milk of rubber tree is called latex.
- It is a colloidal emulsion consists a 25 – 45% of rubber and the reminder are protein and resinous materials
- The Latex was collected by cutting the bark of rubber trees.
- There after the Latex is diluted with water and filtered to eliminate dirt present in it. The Latex then coagulates by the addition of acetic acid (or) formic acid.
- The coagulated rubber is called as crude rubber. It is then made (or) rolled out in to sheets.
- The rubber sheets are dried under sunlight or mild heat and then subjected to further processing of rubber.

a) Crepe rubber: To the crude rubber, a small amount of sodium bi-sulphite is added to bleach the colour and passed into rollers which produce one mm or more thickness sheets which are dried in air about 40 to 50^0C. The dried thin sheet of rubber are known as crepe rubber.

b) Smoked rubber: The crepe rubber sheets are placed inside smoke rooms maintaining a temperature 40 to 50^0C for 4 days. The dried rubber sheets are called smoked rubber, which are sent to rubber factories for further processing.

Milk of rubber latex

↓

Diluted & filtered to remove

dirt Coagulation CH3

COOH / HCOOH Crude rubber

(coagulation)

Passed in to roller

↓

Rolled sheet dried at 40^0 –

50^0C

Crepe rubber
40^0 – 50^0C / 4
days

↓

Smoked rubber

Draw backs of crude rubber (or) raw rubber

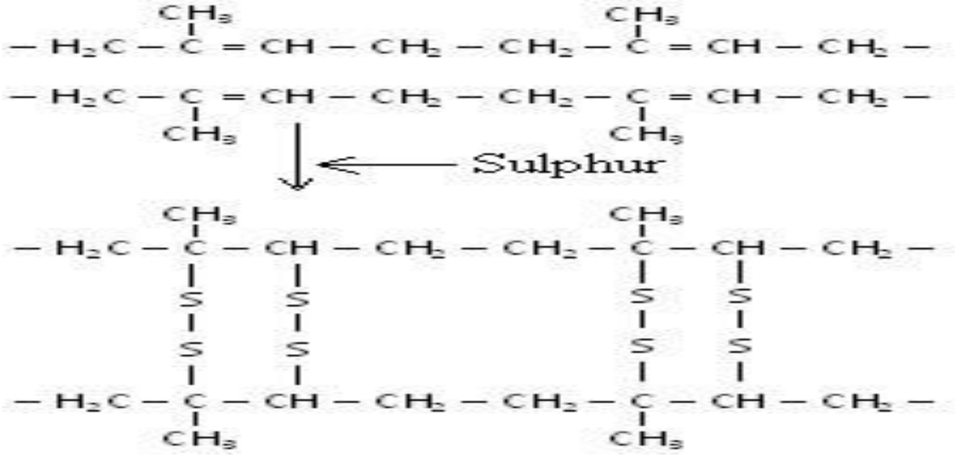
: Crude rubber has following drawbacks.

1. Soft at high temperature and brittle at low temp.
2. It shows large water capacity
3. Shows little durability
4. Shows high elasticity
5. Attacks easily by oxidizing agents
6. Swells in organic solvents
7. Possess tackiness
8. Show low tensile strength.

The draw backs can be crude are rectified by the process of vulcanization.

Vulcanization:

- This was discovered by “Charles Good year” in 1839.
- The process of addition of sulphur at 110-140^{0}C to natural rubber to improve its properties is called as “Vulcanization”.
- The added sulphur combines at the double bonds of rubber chains and cross – links of the linear polymer chains, resulting in a three dimensional network structure.
- Thus the rubber loses plastic state and acquires elastic state.
- The stiffness of vulcanized rubber depends on the amount of the sulphur added.
- A flexible tyre rubber contains about 3 – 5% if sulphur whereas hard rubber contains 32% of sulphur.



Advantages of Vulcanization:

Vulcanization process brings excellent changes in the properties of rubber.
A Vulcanized rubber has

(i) Low water absorption tendency
(ii) Higher resistance to oxidation
(iii) High stiffness
(iv) Slight tackiness
(v) Good durability
(vi) Good resistant to changing temperature
(vii) Resistance to swelling in organic solvents etc………..

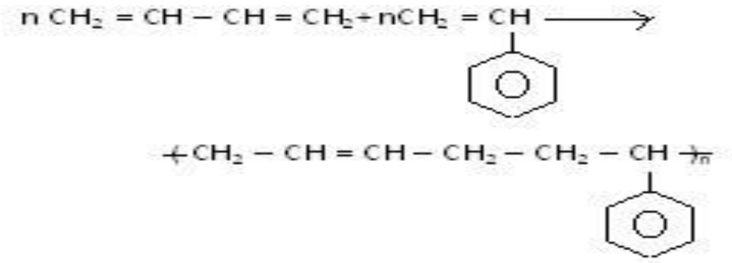
SYNTHETIC RUBBER: (ELASTOMERS):

The following rubbers are considered as synthetic rubbers.

1. Buna – S - Rubber
2. Buna – N – Rubber
3. Polyurethane rubber
4. Silicone rubbe

1. Buna – S / Styrene / GR – S rubber:

Preparation: It is prepared by copolymerization of 1, 3 – butadiene and styrene.



Properties:

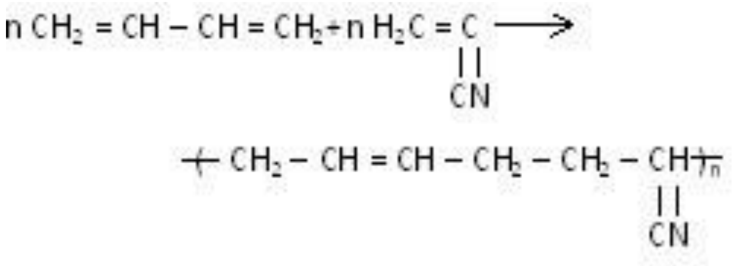
a) It has high abrasion resistance and high load barring capacity
b) Easily oxidized in presence of ozone
c) It swell in oils and organic solvents
d) Its Vulcanization process is similar to natural rubber.

Applications / Uses:

1. It is mainly used for manufacture of tyres.
2. It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, Tank linings etc…………

2. Buna – N / Nitrile rubber: / GR – A rubber:

It is formed by copolymerization of 1, 3 but a – diene an Acrylo Nitrile.



$$n\,CH_2 = CH - CH = CH_2 + n\,H_2C = \underset{\overset{||}{CN}}{C} \longrightarrow +\!\!\!\!-\, CH_2 - CH = CH - CH_2 - CH_2 - \underset{\overset{||}{CN}}{CH} \,-\!\!\!\!+_n$$

Properties:

Properties:

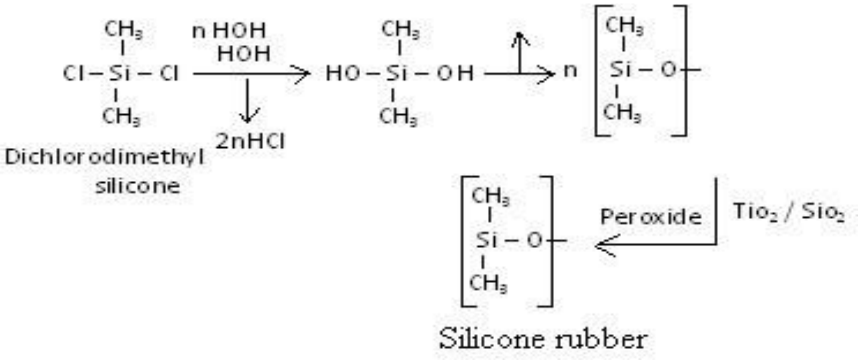
- It can be vulcanized in same way as natural rubber.
- It has good oil resistance, heat resistance and abrasion resistance
- It is attacked by alkalis, due to presence of cyno groups.

Uses: making air craft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts etc.

3. Silicone rubber:

Preparation: It is formed by the polymerization of dihydroxy dimethyl silicon, which is formed by dichlorodi methyl silicon. This step requires water molecules and HCL elimination takes place.

Dihydroxy dimethyl silicon forms an unstable silicon rubber by dehydration which yields silicon rubber in the presence of peroxide and in organic fillers like TiO2, SiO2 etc. by the polymerization.



Properties:

- It has good resistant to Oils, dilute acids, alkalis and sunlight.
- It retains rubber properties at elevated temperatures.
- It is also resistant to air and ozone at high temperature.

Uses:

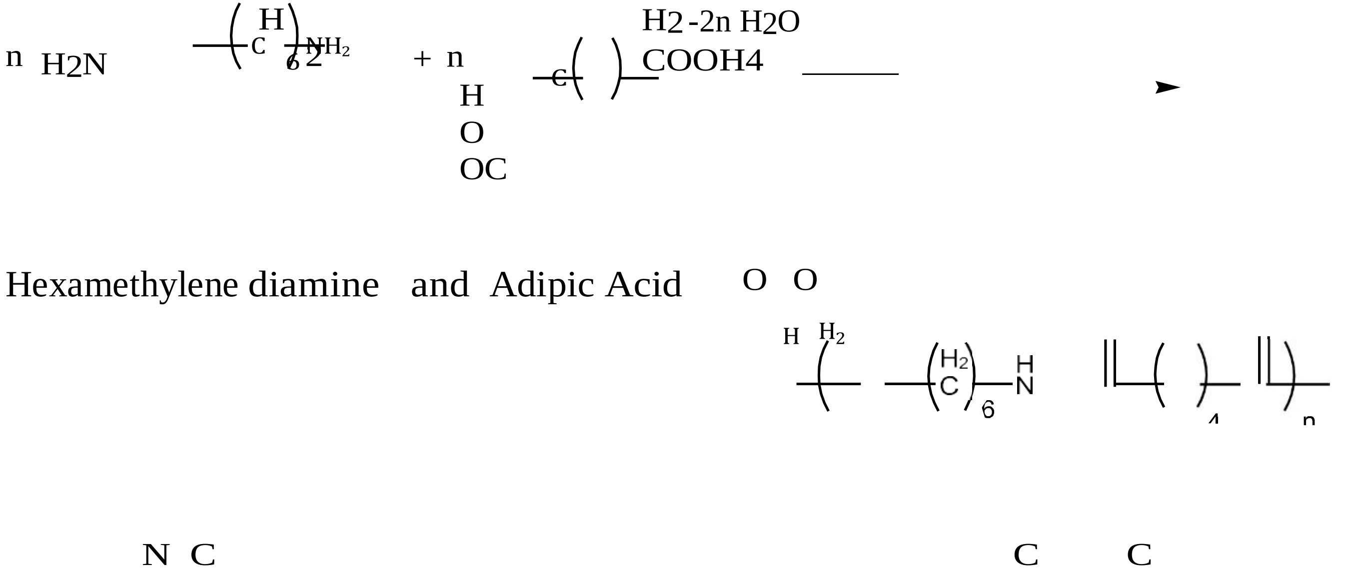
- It is mainly used in making lubricants, paints etc ………..
- For making artificial heart valves, transfusion tubings, for special boots to be used at low temperature.

Nylon (Polyamide):-

The aliphatic amides are known as **'NYLON'** which are synthetic fibre forming materials. These components contain –CO–NH– linkage. They are usually obtained from condensation of dibasic acids and diamines. Commercially Nylon–6,6 , Nylon–6 , Nylon– 11 are important.

(a) Nylon-6,6

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



Nylon-6,6

Properties:-

1. They are translucent, whitish, horny, high melting points (160–264^{0}C) polymers.
2. They possess high temperature stability and good abrasion–resistance.
3. They are insoluble in common organic solvents like methylated spirit, benzene and acetone.
4. They are soluble in phenol and formic acid.

Uses:-

1. Nylon–6,6 is primarily used for fibres in making socks under–garments, dress, carpets, etc.
2. They are also used for making filaments for ropes, bristles for tooth–brushes and films, tyre –cords etc,.
3. Nylon bearings and gears work quietly without any lubrication.

Carbon Fibers:

Carbon fibers or carbon fibres are fibers about 5–10 micrometer in diameter and composed mostly of carbon atoms. Carbon fibers have several advantages including 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, along with other competition sports. However, they are relatively expensive when compared with similar fibers, such as glass fibers or plastic fibers.

Classification and types

Based on modulus, strength, and final heat treatment temperature, carbon fibers can be classified into the following categories:

Based on carbon fiber properties, carbon fibers can be grouped into:

- Ultra-high-modulus, type UHM (modulus >450Gpa)
- High-modulus, type HM (modulus between 350-450Gpa)
- Intermediate-modulus, type IM (modulus between 200-350Gpa)
- Low modulus and high-tensile, type HT (modulus < 100Gpa, tensile strength > 3.0Gpa)
- Super high-tensile, type SHT (tensile strength > 4.5Gpa)

Based on precursor fiber materials, carbon fibers are classified into:

- PAN-based carbon fibers
- Pitch-based carbon fibers
- Mesophase pitch-based carbon fibers
- Isotropic pitch-based carbon fibers
- Rayon-based carbon fibers
- Gas-phase-grown carbon fibers

Based on final heat treatment temperature, carbon fibers are classified into:

- Type-I, high-heat-treatment carbon fibers (HTT), where final heat treatment temperature should be above 2000°C and can be associated with high-modulus type fiber.
- Type-II, intermediate-heat-treatment carbon fibers (IHT), where final heat treatment temperature should be around or above 1500°C and can be associated with high-strength type fiber.
- Type-III, low-heat-treatment carbon fibers, where final heat treatment temperatures not greater than 1000°C. These are low modulus and low strength materials.

Manufacturing Process

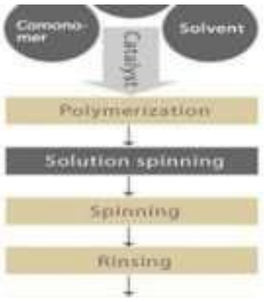
Carbon fibers from polyacrylonitrile (PAN):

Raw Materials

The raw material used to make carbon fiber is called the precursor. About 90% of the carbon fibers produced are made from polyacrylonitrile. The remaining 10% are made from rayon or petroleum pitch. All of these materials are organic polymers, characterized by long strings of molecules bound together by carbon atoms. The exact composition of each precursor varies from one company to another and is generally considered a trade secret. During the manufacturing process, a variety of gases and liquids are used. Some of these materials are designed to react with the fiber to achieve a specific effect. Other materials are designed not to react or to prevent certain reactions with the fiber. As with the precursors, the exact compositions of many of these process materials are considered trade secrets.

The Manufacturing Process

PAN Figure 1



Click on image to enlarge

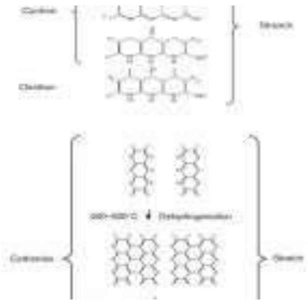
Spinning

- Acrylonitrile plastic powder is mixed with another plastic, like methyl acrylate or methyl methacrylate, and is reacted with a catalyst in a conventional suspension or solution polymerization process to form a polyacrylonitrile plastic.
- The plastic is then spun into fibers using one of several different methods. In some methods, the plastic is mixed with certain chemicals and pumped through tiny jets into a chemical bath or quench chamber where the plastic coagulates and solidifies into fibers. This is similar to the process used to form polyacrylic textile fibers. In other methods, the plastic mixture is heated and pumped through tiny jets into a chamber where the solvents evaporate, leaving a solid fiber. The spinning step is important because the internal atomic structure of the fiber is formed during this process.
- The fibers are then washed and stretched to the desired fiber diameter. The stretching helps align the molecules within the fiber and provide the basis for the formation of the tightly bonded carbon crystals after carbonization.
- Stabilizing
  Before the fibers are carbonized, they need to be chemically altered to convert their linear atomic bonding to a more thermally stable ladder bonding. This is accomplished by heating the fibers in air to about 390- 590° F (200-300° C) for 30-120 minutes. This causes the fibers to pick up oxygen molecules from the air and rearrange their atomic bonding pattern. The stabilizing chemical reactions are complex and involve several steps, some of which occur simultaneously. They also generate their own heat, which must be controlled to avoid overheating the fibers. Commercially, the stabilization process uses a variety of equipment and techniques. In some processes, the fibers are drawn through a series of heated chambers. In others, the fibers pass over hot rollers and through beds of loose materials held in suspension by a flow of hot air. Some processes use heated air mixed with certain gases that chemically accelerate the stabilization.

Carbonizing

Once the fibers are stabilized, they are heated to a temperature of about 1,830-5,500° F (1,000-3,000° C) for several minutes in a furnace filled with a gas mixture that does not contain oxygen. The lack of oxygen prevents the fibers from burning in the very high temperatures. The gas pressure inside the furnace is kept higher than the outside air pressure and the points where the fibers enter and exit the furnace are sealed to keep oxygen from entering. As the fibers are heated, they begin to lose their non-carbon atoms, plus a few carbon atoms, in the form of various gases including water vapor, ammonia, carbon monoxide, carbon dioxide, hydrogen, nitrogen, and others. As the non-carbon atoms are expelled, the remaining carbon atoms form tightly bonded carbon crystals that are aligned more or less parallel to the long axis of the fiber. In some processes, two furnaces operating at two different temperatures are used to better control the rate de heating during carbonization.

Figure 2



Click on image to enlarge

Treating the surface

After carbonizing, the fibers have a surface that does not bond well with the epoxies and other materials used in composite materials. To give the fibers better bonding properties, their surface is slightly oxidized. The addition of oxygen atoms to the surface provides better chemical bonding properties and also etches and roughens the surface for better mechanical bonding properties. Oxidation can be achieved by immersing the fibers in various gases such as air, carbon dioxide, or ozone; or in various liquids such as sodium hypochlorite or nitric acid. The fibers can also be coated electrolytically by making the fibers the positive terminal in a bath filled with various electrically conductive materials. The surface treatment process must be carefully controlled to avoid forming tiny surface defects, such as pits, which could cause fiber failure.

Sizing

After the surface treatment, the fibers are coated to protect them from damage during winding or weaving. This process is called sizing. Coating materials are chosen to be compatible with the adhesive used to form composite materials. Typical coating materials include epoxy, polyester, nylon, urethane, and others.

- 8 The coated fibers are wound onto cylinders called bobbins. The bobbins are loaded into a spinning machine and the fibers are twisted into yarns of various sizes.

Properties

Carbon Fiber has High Strength to Weight Ratio (also known as specific strength)
Strength of a material is the force per unit area at failure, divided by its density. Any material that is strong AND light has a favourable Strength/weight ratio. Materials such as Aluminium, titanium, magnesium, Carbon and glass fiber, high strength steel alloys all have good strength to weight ratios.

Carbon Fiber is very Rigid

Rigidity or stiffness of a material is measured by its Young Modulus and measures how much a material deflects under stress. Carbon fiber reinforced plastic is over 4 times stiffer than Glass reinforced plastic, almost 20 times more than pine, 2.5 times greater than aluminium.

Carbon fiber is Corrosion Resistant and Chemically Stable

Although carbon fiber themselves do not deteriorate, Epoxy is sensitive to sunlight and needs to be protected. Other matrices (whatever the carbon fiber is imbedded in) might also be reactive.

Carbon fiber is Electrically Conductive

This feature can be useful and be a nuisance. In Boat building It has to be taken into account just as Aluminium conductivity comes into play. Carbon fiber conductivity can facilitate Galvanic Corrosion in fittings. Careful installation can reduce this problem.

Fatigue Resistance is good

Resistance to Fatigue in Carbon Fiber Composites is good. However when carbon fiber fails it usually fails catastrophically without much to announce its imminent break. Damage in tensile fatigue is seen as reduction in stiffness with larger numbers of stress cycles, (unless the temperature is hight) Test have shown that failure is unlikely to be a problem when cyclic stresses coincide with the fiber orientation.
Carbon fiber is superior to E glass in fatigue and static strength as well as stiffness.

Carbon Fiber has good Tensile Strength

Tensile strength or ultimate strength, is the maximum stress that a material can withstand while being stretched or pulled before necking, or failing. Necking is when the sample cross-section starts to significantly contract. If you take a strip of plastic bag, it will stretch and at one point will start getting narrow. This is necking. It is measured in Force per Unit area. Brittle materials such as carbon fiber does not always fail at the same stress level because of internal flaws. They fail at small strains.

Testing involves taking a sample with a fixed cross-section area, and then pulling it gradually increasing the force until the sample changes shape or breaks. Fibers, such as carbon fibers, being only 2/10,000th of an inch in diameter, are made into composites of appropriate shapes in order to test.

Fire Resistance/Non Flamable

Depending upon the manufacturing process and the precursor material, carbon fiber can be quite soft
and can be made into or more often integrated into protective clothing for firefighting. Nickel coated fiber

is an example. Because carbon fiber is also chemically very inert, it can be used where there is fire combined with corrosive agents. Carbon Fiber Fire Blanket excuse the typos.

Thermal Conductivity of Carbon Fiber

Thermal conductivity is the quantity of heat transmitted through a unit thickness, in a direction normal to a surface of unit area, because of a unit temperature gradient, under steady conditions. In other words its a measure of how easily heat flows through a material.

Because there are many variations on the theme of carbon fiber it is not possible to pinpoint exactly the thermal conductivity. Special types of Carbon Fiber have been specifically designed for high or low thermal conductivity. There are also efforts to Enhance this feature.

Low Coefficient of Thermal Expansion

This is a measure of how much a material expands and contracts when the temperature goes up or down. Units are in Inch / inch degree F, as in other tables, the units are not so important as the comparison. In a high enough mast differences in Coefficients of thermal expansion of various materials can slightly modify the rig tensions. Low Coefficient of Thermal expansion makes carbon fiber suitable for applications where small movements can be critical. Telescope and other optical machinery is one such application.

Non Poisonous, Biologically Inert, X-Ray Permeable

These qualities make Carbon fiber useful in Medical applications. Prosthesis use, implants and tendon repair, x-ray accessories surgical instruments, are all in development. Although not poisonous, the carbon fibers can be quite irritating and long term unprotected exposure needs to be limited. The matrix either epoxy or polyester, can however be toxic and proper care needs to be exercised.

Carbon Fiber is Relatively Expensive

Although it offers exceptional advantages of Strength, Rigidity and Weight reduction, cost is a deterrent. Unless the weight advantage is exceptionally important, such as in aeronautics applications or racing, it often is not worth the extra cost. The low maintenance requirement of carbon fiber is a further advantage.

It is difficult to quantify cool and fashionable. Carbon fiber has an aura and reputation which makes consumers willing to pay more for the cachet of having it. You might need less of it compared to fiberglass and this might be a saving.

Carbon Fibers are brittle

The layers in the fibers are formed by strong covalent bonds. The sheet-like aggregations readily allow the propagation of cracks. When the fibers bend they fails at very low strain.

Applications

Characteristics and Applications of Carbon Fibers

1. Physical strength, specific toughness, light weight	Aerospace, road and marine transport, sporting goods
2. High dimensional stability, low coefficient of thermal expansion, and low abrasion	Missiles, aircraft brakes, aerospace antenna and support structure, large telescopes, optical benches, waveguides for stable high-frequency (GHz) precision measurement frames
3. Good vibration damping, strength, and toughness	Audio equipment, loudspeakers for Hi-fi equipment, pickup arms, robot arms
4. Electrical conductivity	Automobile hoods, novel tooling, casings and bases for electronic equipments, EMI and RF shielding, brushes
5. Biological inertness and x-ray permeability	Medical applications in prostheses, surgery and x-ray equipment, implants, tendon/ligament repair
6. Fatigue resistance, self- lubrication, high damping	Textile machinery, genera engineering
7. Chemical inertness, high corrosion resistance	Chemical industry; nuclear field; valves, seals, and pump components in process plants
8. Electromagnetic properties	Large generator retaining rings, radiological equipment

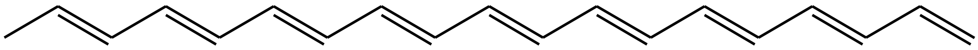
Conducting Polymer:-

Polymers are poor conductors of electricity and generally used as electrical insulators and dielectric materials. However, there are polymers with improved electrical conductivity prepared by the addition of some additives such as conducting metals like copper and silver or other materials.

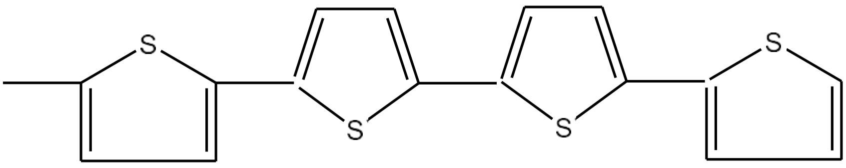
‘An organic polymer with highly delocalised Pi-electron system, having electrical conductance on par with metallic conductor is called a conducting polymer.’

For example: Polyacetylene, Polythiophene, Polyphenylene, Polyaniline.

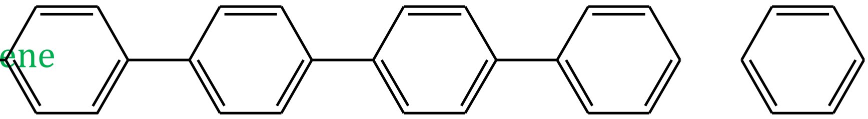
Chemical structure:-



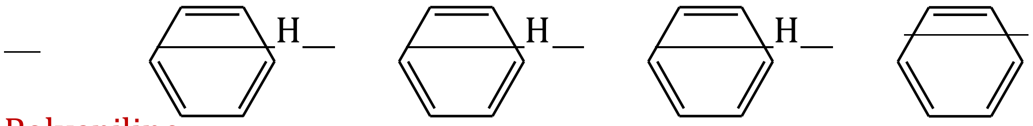
Polyacetylene



Polythiophene



Polyphenylene



Polyaniline

Classification:-

1. Pi-electrons conducting polymers: The polymer whose backbone is made up of molecules that contain conjugated Pi-electrons which extend the entire polymer andmade it conducting.
2. Conducting element filled polymer: Polymer filled with conducting elements such as carbon black, metallic fibres, metal oxides, etc. In this, the polymer acts as a binder to hold the conducting elements together in the solid entity.
3. Doped conducting polymer: It is obtained by exposing a polymer to a charge transfer agent in either gas phase or in solution.
4. Blended conducting polymer: It is obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change.

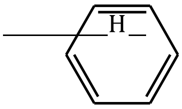
5. Inorganic or Coordination conducting polymer: It is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentateligand.

Synthesis:-

The conducting polymers like poly acetate and polyaniline can be synthesised by doping, in which charged species are introduced in organic polymers having Pi-electron backbone.

i. **p-doping:** In this process, an intrinsically conducting polymer or conjugated Pi-electron conducting polymer is treating with Lewis acid. There by, oxidation takes place and creates positively charged sites on polymer backbone, which are current, carries for conduction. Some of the general P-dopant used are I_2, Br_2, AsF_3. etc.

→ +



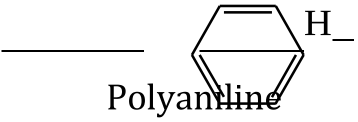
-

(a) $(C_2H_2)_n$ + $2FeCl_3$ $(C_2H_2)_n$ $FeCl_4$ +

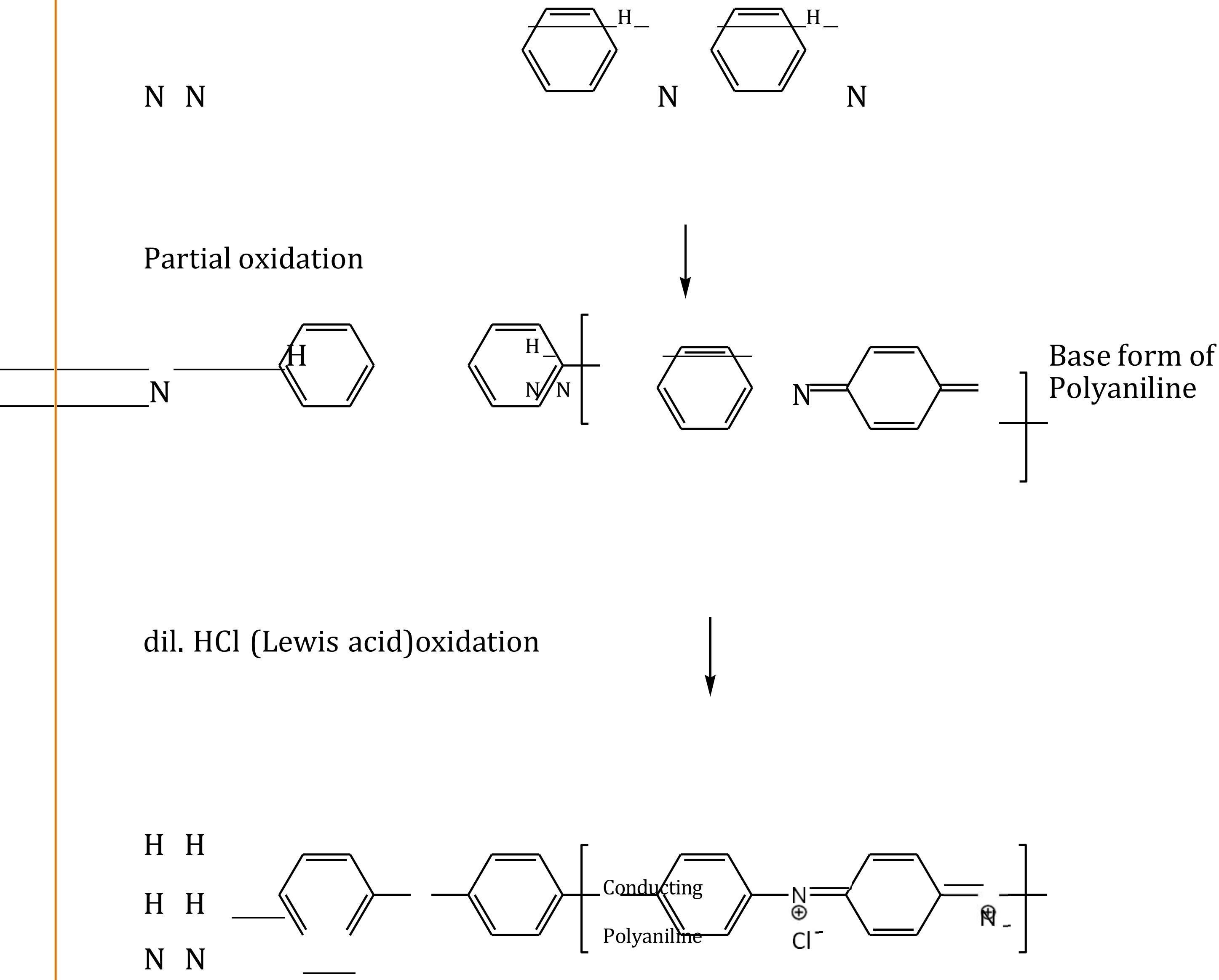
$FeCl_2$ Polyacetylene $2(C_2H_2)_n$ + $3I_2$ 2 $(C_2H_2)_n$ I_3

→ [+ -]

(b)

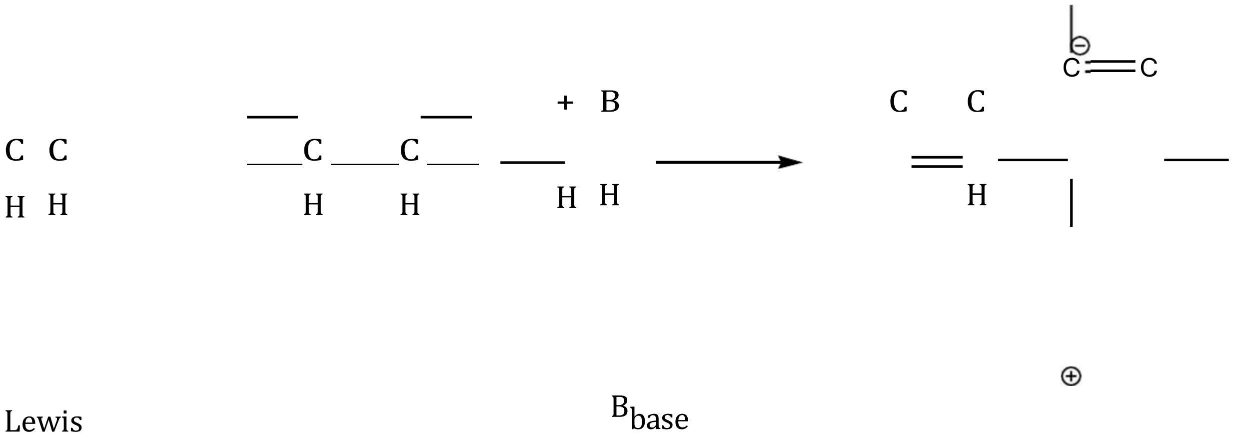


Polyaniline

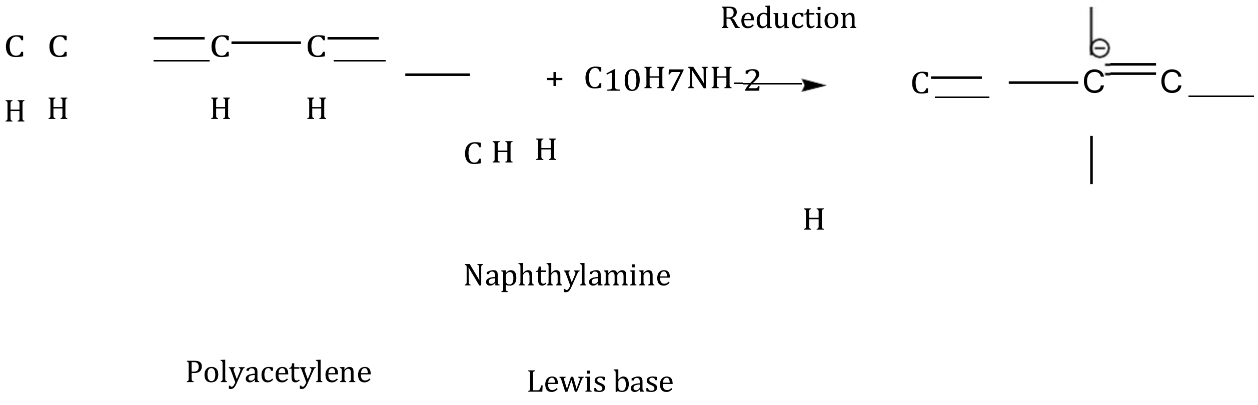

N N
H
H
N
N
Partial oxidation
H
N
H
N N
N
Base form of Polyaniline
dil. HCl (Lewis acid)oxidation
H H
H H
N N
Conducting
Polyaniline
N
⊕
Cl⁻
N
⊕

ii. **n-doping:** In this process, conjugated Pi-electrons are treated with Lewis base. There by, reduction takes place and creates negatively charged sites on polymer backbone, which are responsible for the conduction. Some of thegeneral n-dopant used are Li, Na, Ca and tetrabutyl ammonium.

H



H



Application:-

Some of the important applications of conducting polymers are:

i. In solar cells.

ii. In photovoltaic devices.

iii. In non-linear optical materials.

iv. In telecommunication systems.

v. As electrode material for commercial rechargeable batteries.

vi. In antistatic coatings for clothing.

Naphthalene

UNIT-V

INSTRUMENTAL METHODS AND APPLICATIONS

Beer-Lambert's Law.

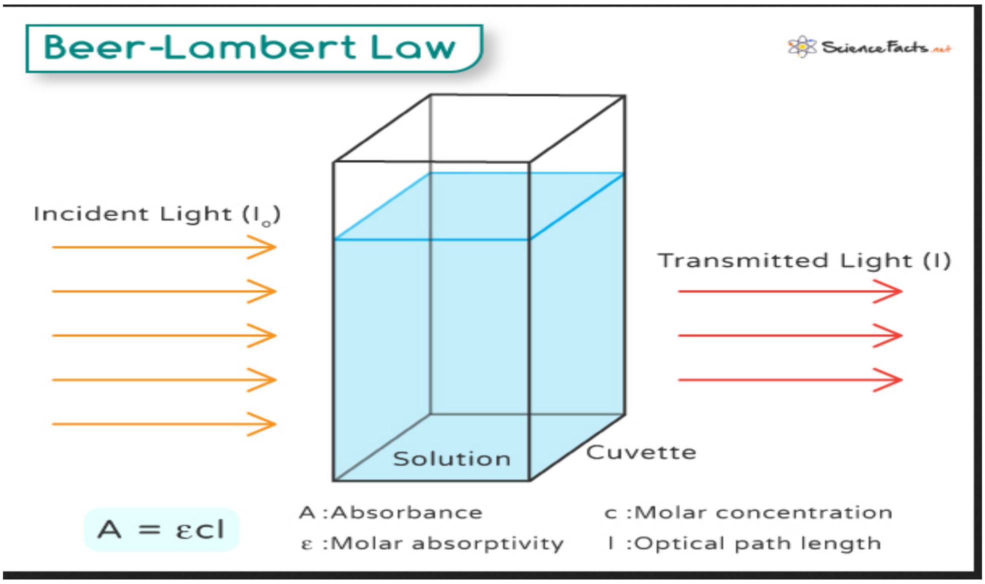
The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

A = a(ʎ) * b * c where A is the measured absorbance, a(ʎ) is a wavelength-dependent absorption coefficient, b is the path length, and c is the analyze concentration. When working in concentration units of molarities, the Beer-Lambert law is written as:

A = ε* b * c

Where ε is the wavelength-dependent molar absorption coefficient with units of M-1 cm-1

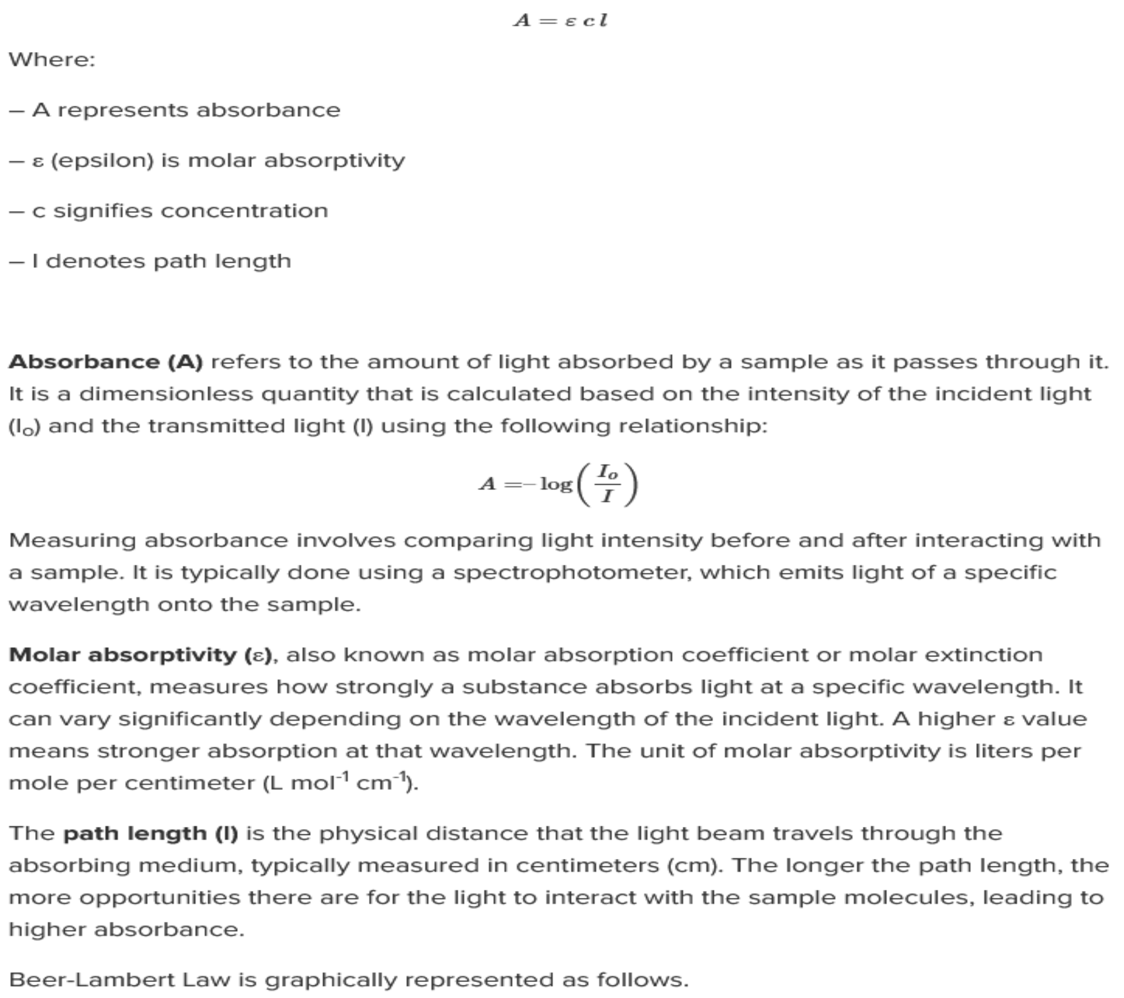
Statement: "The amount of light absorbed by a substance is directly proportional to the substance's concentration and the path length of light."



Equation

Let us consider a sample solution with concentration c and path length l. When light passes through this solution, it is absorbed by particles or molecules in the sample. The amount of light absorbed is directly proportional to the concentration and path length.

According to Beer-Lambert Law, we can express this relationship mathematically as:



$$A = \varepsilon c l$$

Where:

– A represents absorbance

– ε (epsilon) is molar absorptivity

– c signifies concentration

– l denotes path length

Absorbance (A) refers to the amount of light absorbed by a sample as it passes through it. It is a dimensionless quantity that is calculated based on the intensity of the incident light (I_O) and the transmitted light (I) using the following relationship:

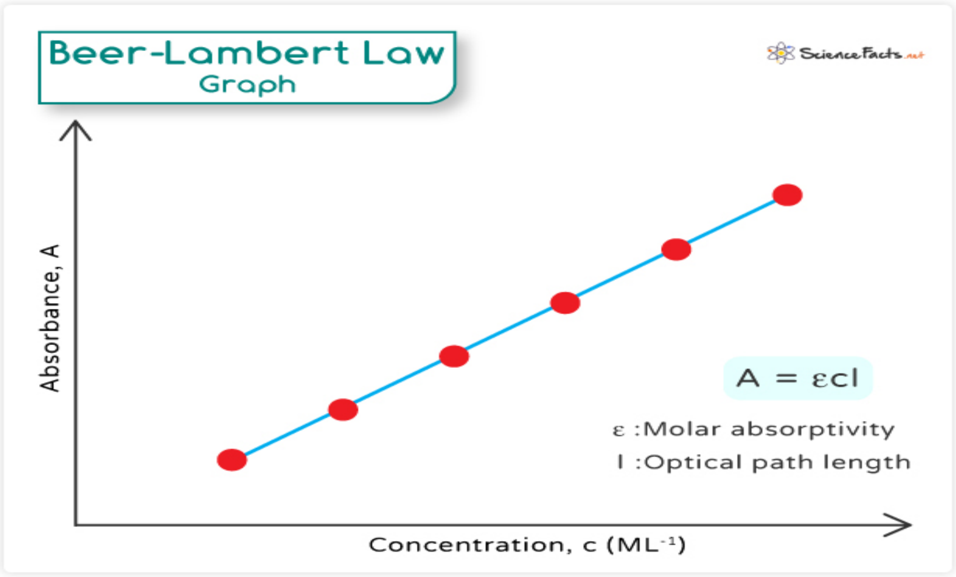
$$A = -\log\left(\frac{I_o}{I}\right)$$

Measuring absorbance involves comparing light intensity before and after interacting with a sample. It is typically done using a spectrophotometer, which emits light of a specific wavelength onto the sample.

Molar absorptivity (ε), also known as molar absorption coefficient or molar extinction coefficient, measures how strongly a substance absorbs light at a specific wavelength. It can vary significantly depending on the wavelength of the incident light. A higher ε value means stronger absorption at that wavelength. The unit of molar absorptivity is liters per mole per centimeter (L mol^{-1} cm^{-1}).

The **path length (l)** is the physical distance that the light beam travels through the absorbing medium, typically measured in centimeters (cm). The longer the path length, the more opportunities there are for the light to interact with the sample molecules, leading to higher absorbance.

Beer-Lambert Law is graphically represented as follows.



Derivation

When an object is exposed to radiation, some of the incident radiation is absorbed, some are scattered, and some are transmitted. As a result of absorption, the intensity of the substance that transmits light, i.e, the Intensity of transmitted light. The absorption part of the incident light depends on the thickness of the absorption medium. Lambert deriveda quantitative relationship between the decrease in the intensity of monochromatic light passing through a homogeneous medium of thickness dx and the light intensity I. This law is known as Lambert's Law and can be given as. The decrease in light intensity due to the thickness of the absorbing medium at any point is directly proportional to the light intensity.

$$-dI / dx a I \qquad —— (1)$$

ere dI is the slight decrease in light intensity when passing a small distance dx, and I is the intensity of monochromatic light just before entering the medium.

$$-dI / dx = aI \qquad —— (2)$$

Where –dI/dx is the rate of decrease in strength with thickness dx, and a is called the absorption coefficient.

By the integral of Eq. (2) after dislocation,

$$-\ln I = ax + C \qquad —— (3)$$

Where C is the constant of integration. At $x = 0$, $I = I_0$. Therefore, $C = -\ln I_0$.Substituting this into equation (3) yields:

$$\ln I/ I_0 = -ax \qquad —- \qquad (4)$$

Equation (4) can also be

written as, $I = I_0 e^{-ax}$ —

- (5) Equation (5) can also be

written as,

$\log I/I_0 = -a/2.303\ x$ ——

(6) or,

$\log I/I_0 = -a'\ x$ —— (7)

Where a’ (= a / 2.303) is the extinction coefficient and -ln I / I_0 is the absorbance of the medium. Absorbance is represented by A.

Absorbance is a dimensionless quantity that depends on the optical path length, the concentration of the absorbing substance, and the wavelength of the light. Lambert-Beer’s law shows that when light passes through a solution of a certain thickness, the rate at which incident light is absorbed depends not only on the intensity I of the light but also on the concentration c of the solution. Extended by Beer. This is known as Lambert-Beer’s Law.

$-dI / dx a\ c$ —— **(8)**

Combining the two laws $-dI / dx a\ b \times I \times c$ —— **(9)**

When expressed, b is called the molar absorption coefficient.

As with Lambert’s Law, equation (9) can be transformed as follows:

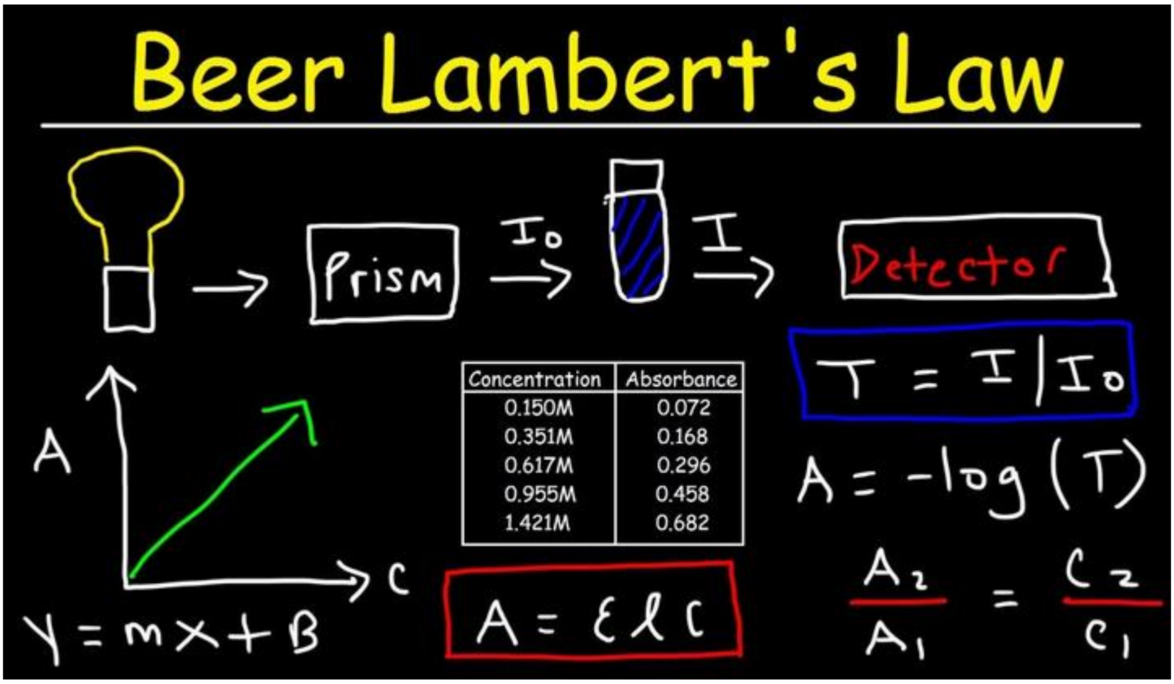
$\log I / I_0 = -b / 2.303 \times c \times x$ ——

(10) $\log I$

$/ I_0 = -\varepsilon \times c \times x$ ——— **(11)**

Here, ε (= a / 2.303) is called the molar extinction coefficient and is expressed in L /mol/cm.

Molar extinction coefficient: It measures the probability of electronic transitions. The higher the molar extinction coefficient, the higher the likelihood of electronic transitions. Molar extinction coefficient ε depends on the type of solute to be absorbed and the wavelength of the incident light used. Equation 11 is known as Beer-Lambert’s Law.



Concentration	Absorbance
0.150M	0.072
0.351M	0.168
0.617M	0.296
0.955M	0.458
1.421M	0.682

Applications

Spectroscopy: It is used to determine concentrations of various compounds in solutions or identify unknown substances based on their absorption spectra.

Blood Analysis: It can determine the concentrations of various biomolecules, such as glucose, cholesterol, and hemoglobin, in blood samples.

Environmental Monitoring: This involves monitoring pollutant levels in water bodies and the atmosphere. Pollutants like nitrates, phosphates, and heavy metals can be determined in water using UV-visible spectrophotometry.

Food Analysis: It analyzes the concentration of various components in food and beverages. For example, the concentration of caffeine in coffee, sugar in soft drinks, and color additives in food products can be determined spectrophotometrically.

Drug Analysis: The concentration of active pharmaceutical ingredients (APIs) and impurities is often measured using spectrophotometric techniques, ensuring the efficacy and safety of pharmaceutical products.

Limitation of Beer-Lambert’s law

1. Applicable only for dilute solutions.
2. Monochromatic radiation must be used.
3. The solute should not dissociate or associate in solution.
4. Not applicable to suspensions.
5. Solution should not contain impurities.

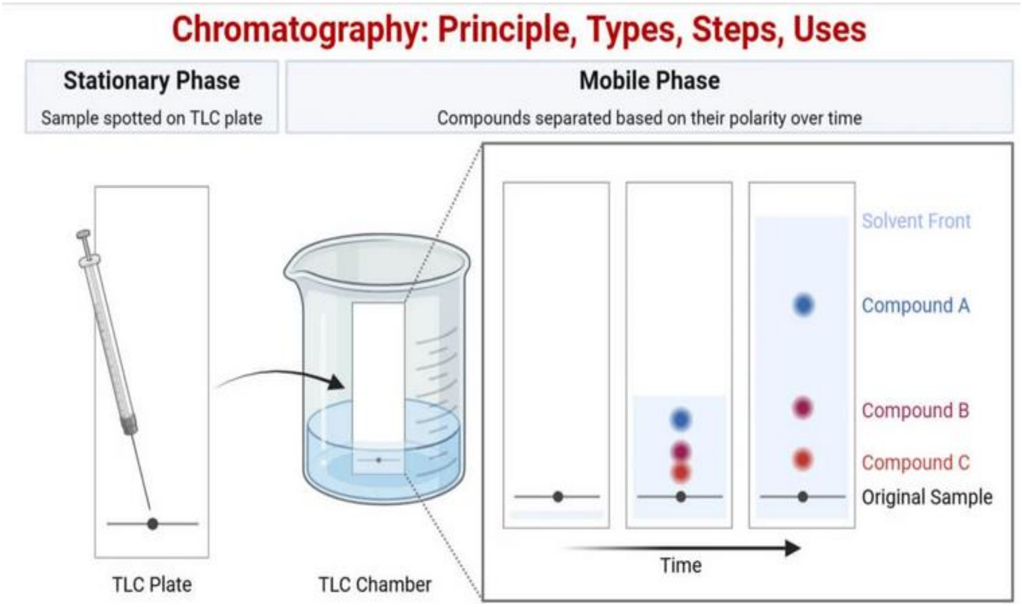
Principle, and applications of chromatography

Chromatography is a method used to separate the individual components of a mixture on the basis of their interactions with a stationary and a mobile phase. Each component interacts differently with the two phases which causes them to move at different speeds and separate.

It was first developed by Russian botanist Mikhail Tswett in 1906 when experimenting with plant pigments.

Tswett poured a plant pigment solution on top of a column with an adsorptive material and added a solvent to wash it through the column. As the solution moved down, the pigments separated into bands of different colors.

Over time, chromatography has advanced to different types which allow separation from small molecules to complex biomolecules.



Principle of Chromatography

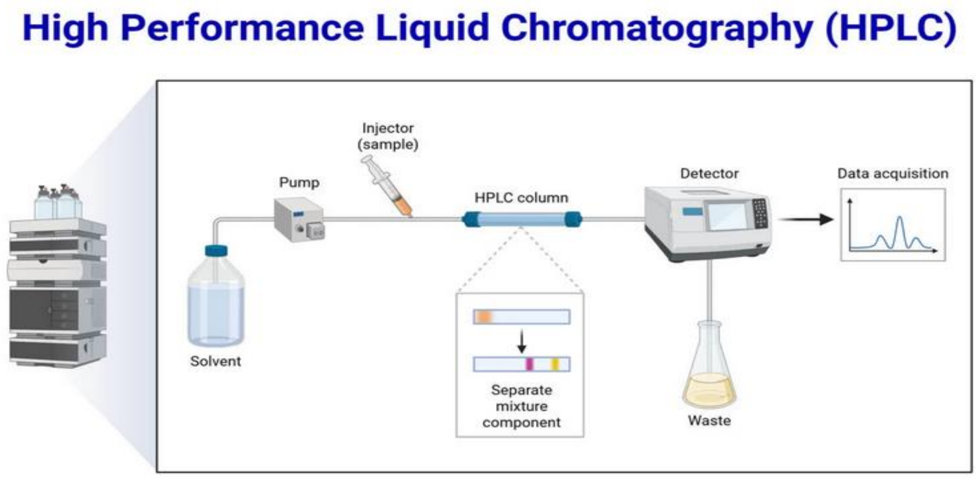
The main principle of chromatography is that different substances interact differently with the stationary and mobile phases and this difference in interaction separates the compounds. As the mobile phase moves with the sample through the fixed stationary phase, each compound moves at a different speed based on its properties like size, charge, or affinity to the stationary phase resulting in separation. The separated components are represented as peaks on a chromatogram and identified by its retention time which is the time a compound takes to move through the system. Types of Chromatography

Adsorption Chromatography

1. Anion exchange chromatography
2. Column chromatography
3. Gas chromatography (GS)
4. Gel-permeation (molecular sieve) chromatography
5. High performance liquid chromatography (HPLC)
6. Paper chromatography

7 . Partition Chromatograph

Column Chromatography: Here, the stationary phase is packed inside a vertical column and compounds are separated as they move with the solvent at different rates through the column. Examples: Gas chromatography and HPLC



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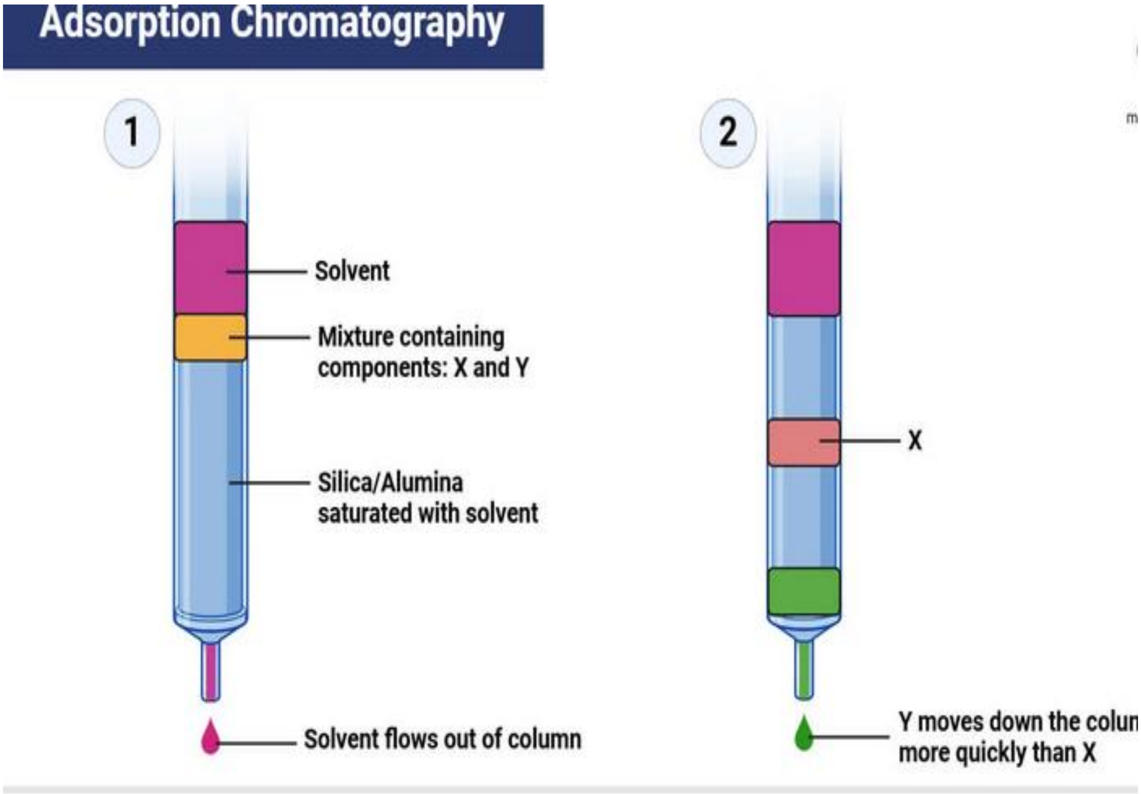
Adsorption Chromatography separates compounds based on how strongly they are adsorbed to the stationary phase. Components with weaker adsorption to the stationary phase move faster and those with stronger binding move slower.

Partition Chromatography separates compounds based on their solubility properties or differential partitioning between the liquid mobile phase and stationary phas

Ion Exchange Chromatography **(IEC)** is used to separate molecules by their net charge. This method separates charged ions or biomolecule



Thin Layer Chromatography Procedure

Before starting with the Thin Layer Chromatography Experiment, let us understand the different components required to conduct the procedure along with the phases involved.

Thin Layer Chromatography Plates – ready-made plates are used which are chemically inert and stable. The stationary phase is applied on its surface in

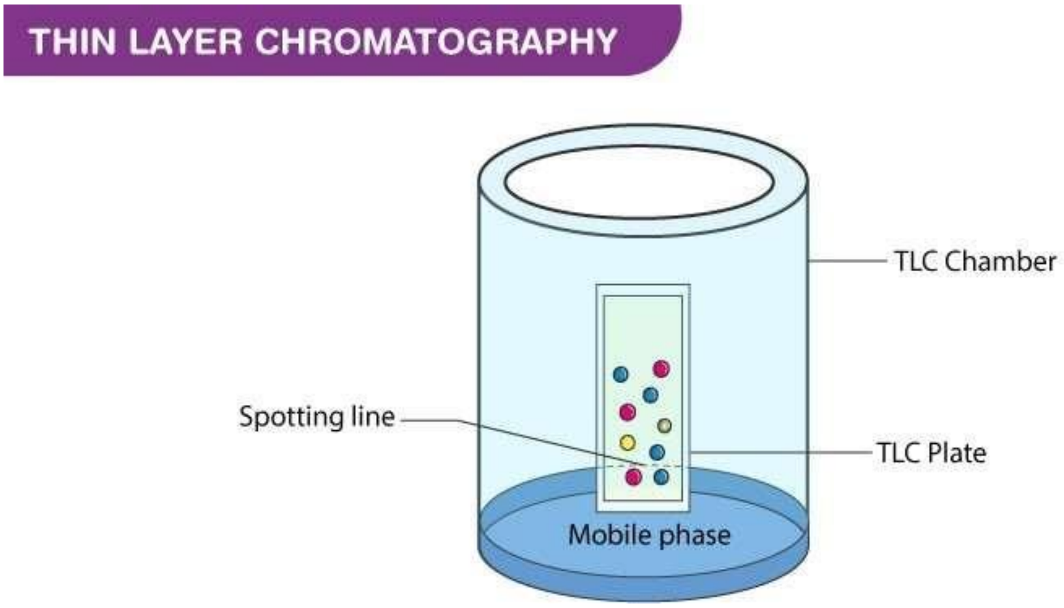


Diagram of Thin Layer Chromatography

Advantages of Chromatography

- It can separate all the component of a mixture with little to no prior information about the sample composition.
- It is a versatile method as it is compatible with a wide range of substances.
- It is accurate and can handle complex mixtures.
- It is highly sensitive and can detect substances in extremely small amounts

Recent Advances and Innovations in Chromatography

- Compact and portable chromatographic devices using microfluidics systems are being developed which allow onsite analysis and reduces sample consumption.
- Innovations in stationary phase materials such as development of monolithic columns and nanoparticle-based phases.
- Chromatographic methods are combined with other analytical methods like Mass Spectrometry that improves separation.
- Artificial intelligence (AI) can be used to predict retention, analyze complex data, and improve accuracy.
- Sustainable practices are being adopted such as minimizing wastes and using natural solvents

IR spectroscopy (infra red)

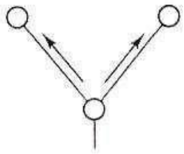
1. Principle and instrumentation of IR spectroscopy:

There are two types of fundamental vibrations in a molecule.

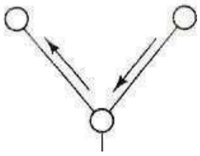
1) Stretching vibration

In this vibration ,the bonds are longated and compressed. But the bond angle remains unchanged. There are two kinds of stretching vibrations:

i) Symmetric stretching



ii) Asymmetric stretching

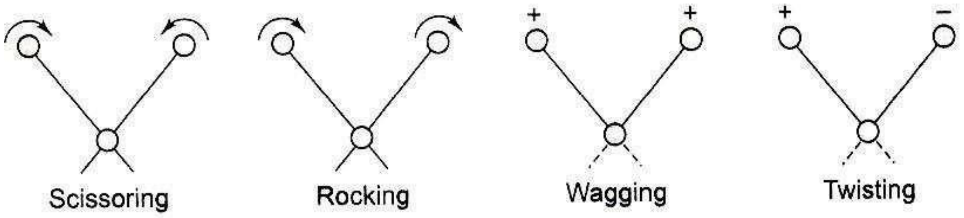


2) Bending or deformation vibrations

In this vibration, the bond angle increases and decreases but the bond length does not change.

Bending vibrations are of two kinds.

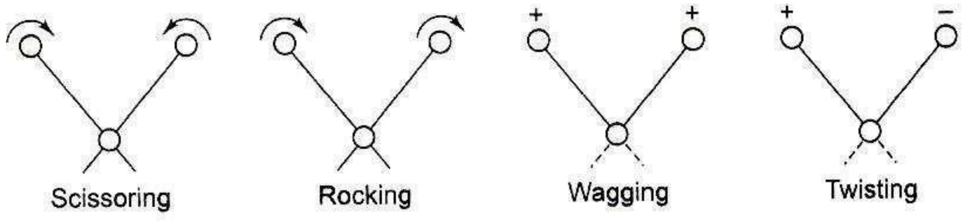
i) In plane bending vibrations: Here all the atoms are in the same plane during vibration.



ii) Out of plane bending vibration : Here the atoms go out of plane during vibrations

iii) In plane bending vibrations: Here all the atoms are in the same plane during vibration.

iv) Out of plane bending vibration : Here the atoms go out of plane during vibration.



In plane bending Out of plane

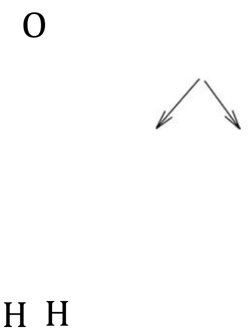
bending Number of modes of vibrations linear molecule 3n-5)

fundamental vibrational modes .n=number of atoms in ay are shown

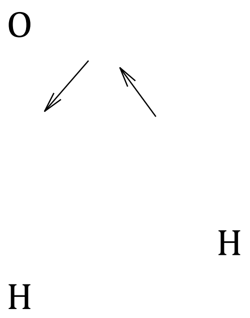
above.

i) A non-linear molecule has (3n-6) fundamental vibrational modes. n=number of atoms in the molecule.

(e.g.) Water (H_2O) is a non-linear molecule. It has (3n-6) = 3 x 3 - 6 = 3vibrational modes. They are shown below.

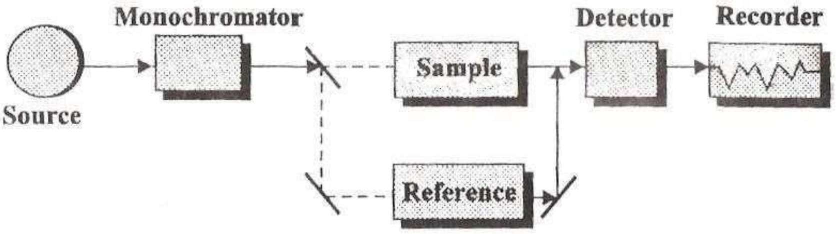


symmetric stretching



Assymetric stretching

Instrumentation of IR Spectrometer



Block diagram of double beam IR spectrophotometer.

Components

I) Radiation Source

Nichrome wire and Nernst glower are the main sources of IR radiation. Nernst glower is filament made of oxides of Zr, Th and Ce held together using a binder.

i) Monochromator

It permits only radiation of desired wavelength to pass through and absorbs other wave lengths.

ii) Cell

ThecellholdingthesamplesolutionshouldbetransparenttoIRr adiation. NaCl cells are used.

iii) Detector

The IR radiation falling on the detector is converted into an electric signal. Some detectors are:

i) Thermocouple
ii) Poly electric detectors

iv) Recorder

Theelectricalsignalfromthedetectorisrecordedaspercentagetransmittanceagainstwavelength.

Working

The radiation rom the source is split into two beams of equal intensity. One beam pass es through the sample and the other through the reference.

When the sample absorbs, the two emerging beams will have different intensities. This produces an oscillating signal to be measured by the detector.

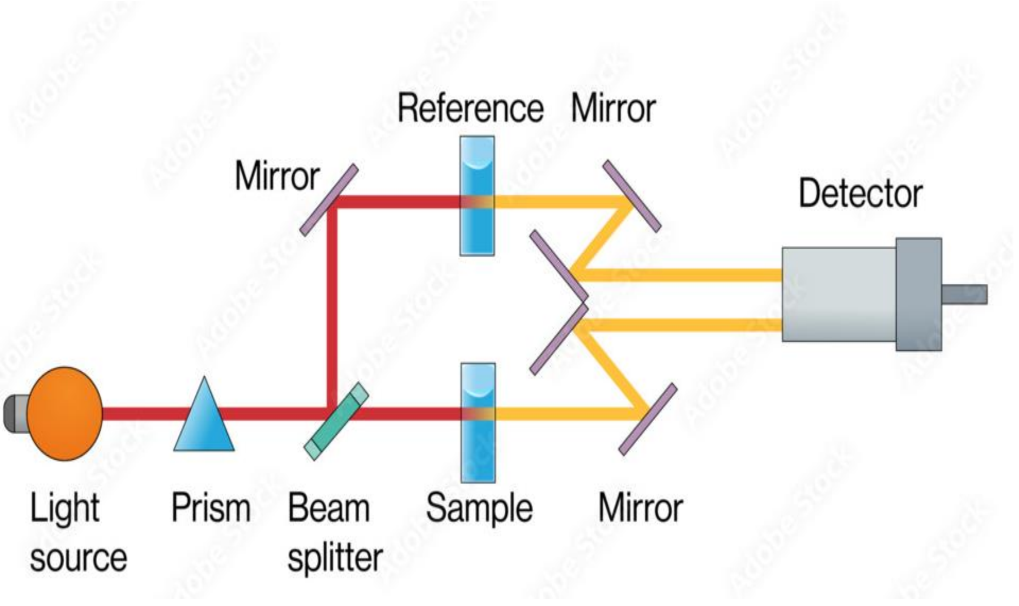
The signal from detector get sample field and goes to there corder which gives aprintoutordisplay.

UV-visible spectroscopy (ultra violet)

Principle & instrumentation of UV-visible spectroscopy with neat diagram. Principle

UV-Visible spectroscopy involves transition of valence electrons of moleculesor ions from the ground electronic state E_0 to a higher electronic state E_1. The ultraviolet region is 100 to 400 nm. The visible region is 400 to 800 nm. The amount of energy required for the transitionis,

$$DE = h\upsilon = E_1 - E_0$$



UV-Vis Spectroscopy, an important analytical tool, relies on several key components to function effectively. Here's an overview of these components:

1. **Light Source:** The light source is crucial in a UV-Vis spectrophotometer, as it emits a broad range of wavelengths covering both UV and visible light. Typically, two types of lamps are used: a deuterium lamp for UV light and a halogen or tungsten lamp for visible light. These lamps ensure a strong and consistent light output. The spectrometer switches between these two lamps, usually around the wavelength range of 300-350 nm, to ensure smooth transition and consistent light emission in both UV and visible ranges.
2. **Wavelength Selector:** This component is responsible for selecting the appropriate wavelength of light from the source to be used in analyzing the sample. The most common type of wavelength selector in a UV-Vis spectrometer is a monochromator. It works by separating the incoming light into narrow bands of wavelengths using a prism, which bends the light and produces a spectrum. Only light of a specific wavelength is allowed to pass through the exit slit of the monochromator and reach the sample.
3. **Sample Container:** The sample container or cuvette holds the sample through which the light passes. There are two types of spectrophotometers based on how they handle the light beam: single-beam and double-beam. In a single-beam spectrophotometer, all light passes through the sample, while in a double-beam spectrophotometer, the light is split into two paths – one passes through the sample and the other through a reference. This setup helps to measure the absorbance of the sample more accurately by comparing it with the reference. The cuvettes are usually made of materials like fused silica or quartz, especially for UV and visible light.
4. **Detector:** The detector's role is to convert the light that has passed through the sample into an electrical signal. This signal is proportional to the light's intensity. Detectors are designed to be sensitive and produce low noise, ensuring accurate measurements. They vary in their wavelength range and sensitivity.

The working of the spectrophotometer can be understood through the Beer-Lambert Law. This law relates the absorbance of light to the properties of the material through which the light is passing. The absorbance (A) is calculated using the equation A = -log(T) = -log(I/Io), where 'I' is the intensity of light that passes through the sample, and 'Io' is the intensity of the incident light. The transmittance (T), which is I/Io, represents the fraction of light that has passed through the sample. This relationship helps in determining the concentration of the substance in the sample

Applications of UV-Vis spectroscopy

1. **Identification of Species**:
   - UV-Vis spectroscopy plays a pivotal role in identifying both organic and inorganic species present in a solution.
2. **Concentration Determination**:
   - This technique is adept at determining the concentration of unknown solutions, providing valuable insights into sample composition.
3. **Structural Elucidation**:
   - UV-Vis spectroscopy aids in the determination of molecular structures. It provides data on bands and intensities associated with specific functional groups, facilitating a deeper understanding of molecular configurations.
   - It is instrumental in detecting the presence or absence of unsaturation and heteroatoms in organic molecules.

4. **Chemical Kinetics**:
    - The study of chemical kinetics, specifically the appearance and disappearance of functional groups during reactions, is enhanced using UV-Vis spectroscopy. By passing UV radiation through a reaction cell, absorbance changes can be meticulously observed.
5. **Isomer Study**:
    - In the realm of geometric isomerism, UV-Vis spectroscopy offers insights into species differentiation. For instance, trans-species, which absorb at higher wavelengths, exhibit larger molar absorptivity values compared to their cis counterparts.
6. **Detection of Conjugation**:
    - The technique is proficient in detecting the presence of conjugation in molecules, further elucidating molecular behavior.
7. **Impurity Detection**:
    - UV-Vis spectroscopy stands out as an optimal method for impurity determination in organic molecules. By comparing the sample's absorption spectrum with that of a standard raw material, impurities can be identified.
8. **Functional Group Analysis**:
    - The presence or absence of specific functional groups in compounds can be ascertained using this technique. The absence of a specific band at a designated wavelength serves as evidence of the absence of a particular group.
9. **Pharmaceutical Applications**:
    - In the pharmaceutical domain, many drugs, whether in raw material form or as formulations, can be assayed. This is achieved by preparing a suitable solution of the drug and measuring its absorbance at specific wavelengths.
10. **Molecular Weight Determination**:
    - By preparing suitable derivatives of compounds, their molecular weights can be determined spectrophotometrically.

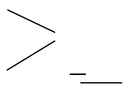
11. **High-Performance Liquid Chromatography (HPLC)**:
    - UV spectrophotometers can be employed as detectors in HPLC, enhancing the precision of chromatographic analys

Type of transitions involved n organic molecules

There are three types of electrons in organic molecules - s bonded electrons, p bonded electrons and non-bonded electrons (n). All the three types of electrons are present in formaldehyde:

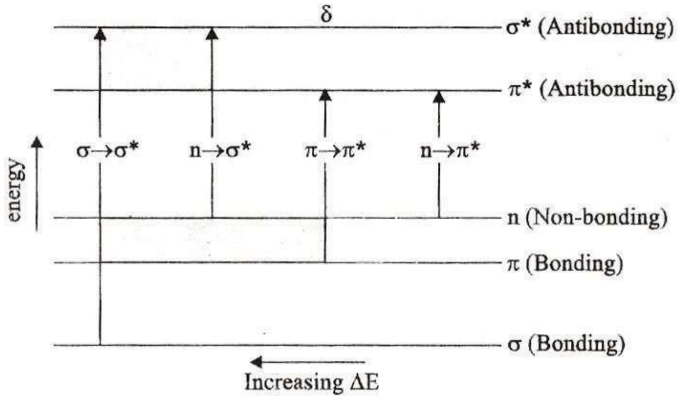
Hs

C Ö :n



H P

The types of transitions and their order of energy is are:



Energy level diagram

1. n®P*transitions

These are shown by unsaturated molecules with heteroatoms like N,O, S and halogen.They are due to the excitation of an electron from non-bonding lone pair(n) to an empty anti-bonding P*orbital.

Example:

Acetaldehyde and acetone

n®P*transition occurs at 270 to 300nm. An electron from the non-bonding orbital of oxygen atom is excited to aP*orbital.

2. P®P*transitions

These are shown by molecules with P electrons. (e.g.) olefins, aromaticcompounds. They are due to the excitation of an electron from P bonding orbital to anti- bondingP*orbital.

Example :Ethylene CH2=CH2

A P®P*transitionoccursat200 nm.

3. n®s*transitions

These are shown by saturated compounds containing a lone pair of electrons. They are due to the excitation of an electron from non-bonding orbital (n) to a s*anti- bonding orbital.

Example

:Trimethylamine(CH3)3N: transition occurs at 227 nm. An electron from the non-bonding orbital of 'N' atom is excited to a s* orbital.

3.s®s*transitions

These are shown byall saturated compounds .They are due to the excitation of an elect ron froms bonding orbital to as*anti-bonding orbital.

Example: CH_4

s®s*transition occursat 122nm.s®s* are high energy transitions.
They are weak in ,and usually no to observed.

Principle and instrumentation of HPLC spectroscopy:

High-Performance Liquid Chromatography (HPLC) is a sophisticated analytical technique used extensively in various scientific fields to separate, identify, and quantify the components of a mixture. This technique, originally known as high-pressure liquid chromatography, has evolved significantly since its inception.

- HPLC operates on the principle of column chromatography but utilizes advanced technology to enhance its performance. Unlike traditional column chromatography, where gravity slowly drives the solvent through the column, HPLC employs high-pressure pumps to force the solvent, or mobile phase, through the system. This increased pressure allows for faster and more efficient separation of compounds.
- The core components of an HPLC system include the high-pressure pumps, the column, and the detector. The column, a key element in the system, is packed with adsorbent material—typically granular particles such as silica or polymer beads. The sample mixture, dissolved in a suitable solvent, is injected into the column where its components interact with the adsorbent material.

Principle of HPLC (High-performance liquid chromatography)

Initially, the mixture is introduced into the HPLC system via a sample loop connected to a valve. This valve directs the sample into the mobile phase, a solvent or a mixture of solvents that is propelled through the system under high pressure by the pumps. The role of the mobile phase is to carry the sample through the separation column.

The separation column is packed with a stationary phase, which consists of granular materials with porous particles. These particles, typically made from substances such as silica, are designed to interact with the sample components to varying degrees. As the mobile phase flows through the column, different components of the sample are retained by the stationary phase to different extents, causing them to migrate at different rates.

The varying retention times of the components result in their separation as they exit the column. Once the components have been separated, they are detected by an appropriate detector, such as a UV detector. The detector generates a signal that is processed by the HPLC software on a computer.

- The output of this process is a chromatogram, a graphical representation of the detector’s response over time. Each peak in the chromatogram corresponds to a different component of the sample, with the position and area of the peak providing information about the component’s identity and concentration.
- Therefore, the principle of HPLC involves the precise manipulation of the interactions between the sample, stationary phase, and mobile phase to achieve effective separation and analysis of the sample components. This process allows for detailed identification and quantification of substances within complex mixtures.

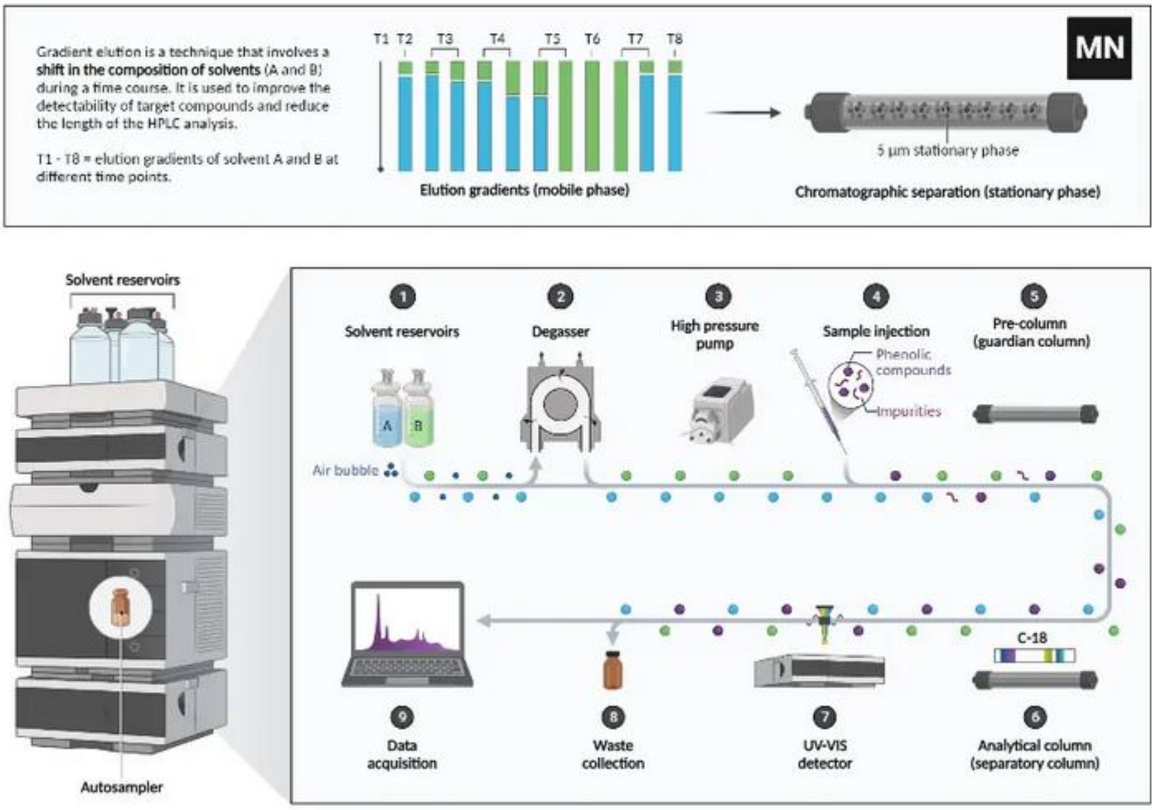
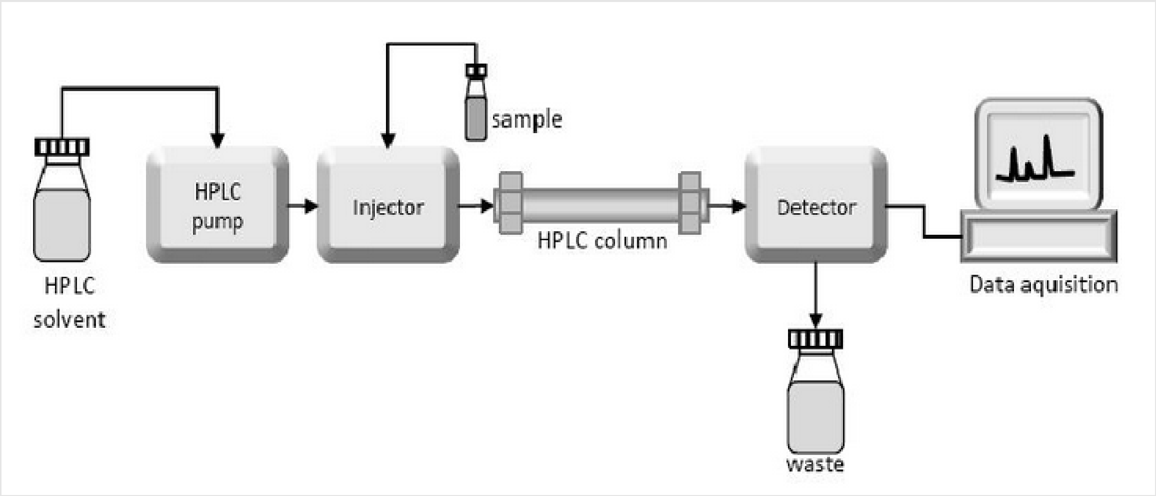


Fig: Components and Steps of High-performance Liquid Chromatography (HPLC) Analysis

Instrumentation of HPLC

High-Performance Liquid Chromatography (HPLC) is a sophisticated analytical technique that relies on a precise set of instruments to achieve effective separation, detection, and analysis of chemical compounds. The key components of an HPLC system include the mobile phase reservoir, solvent delivery system, pump, injector, column, detector, computer, degasser, and column heater. Each plays a crucial role in the chromatography process. Here is a detailed examination of each component



Instrumentation of High-Performance Liquid Chromatography (HPLC)

2. Mobile Phase/Solvent Reservoir

- Function: The mobile phase or solvent reservoir holds the liquid that will be used to carry the sample through the chromatographic system.
- Description: Typically, this is a glass bottle that stores the HPLC solvent. Some advanced systems, such as those by Agilent, feature specialized compartments for multiple reservoirs. These compartments may include additional features for degassing the solvent and preventing exposure to air, which helps in maintaining the consistency of the mobile phase

Solvent Delivery System

Function: This system is responsible for delivering the mobile phase to the chromatograph with a continuous, pulse-free flow.

Description: It ensures a steady and precise flow rate of the mobile phase, despite variations in system back pressure. This consistent delivery is crucial for reproducibility and accuracy in chromatographic analyses.

3. Pump

Function: The pump propels the mobile phase through the chromatograph at a controlled flow rate, typically measured in milliliters per minute (mL/min).

Description: Pumps in HPLC systems can generate pressures up to 6000-9000 psi (400-600 bar). They can be configured to deliver a constant mobile phase composition (isocratic mode) or to gradually change the composition (gradient mode). The pump's ability to maintain consistent pressure and flow rate is critical for effective separation.

4. Injector

Function: The injector introduces the sample into the flow of the mobile phase.

Description: Samples are generally introduced in volumes ranging from 5 to 20 microliters (µL). Injectors must withstand the high pressures present in the system. Automated versions, known as autosamplers, allow for high-throughput analysis by scheduling multiple injections.

4. Column

Function: The column is the central component where separation of the sample components occurs.

Description: The stationary phase within the column interacts with the sample, leading to separation based on various physical and chemical properties. Columns are typically housed in stainless steel to withstand high pressures and chemical interactions. The packing material, often silica or polymer gels, contributes to the separation efficiency.

6. Detector

Function: The detector measures and quantifies the analytes as they elute from the column.

Description: Detectors provide signals based on the presence and concentration of analytes. These signals are converted into chromatograms, which graphically represent the detector response over time. Various types of detectors are used depending on the nature of the sample and the analysis required.

7.Computer/Data System

Function: The computer controls the HPLC system and processes the data from the detector.

Description: It manages all system modules and interprets the detector signals to determine both the retention times and quantities of sample components. Modern systems use sophisticated software for data acquisition, peak analysis, and quantitative calculations, enhancing the accuracy and efficiency of chromatographic analysis

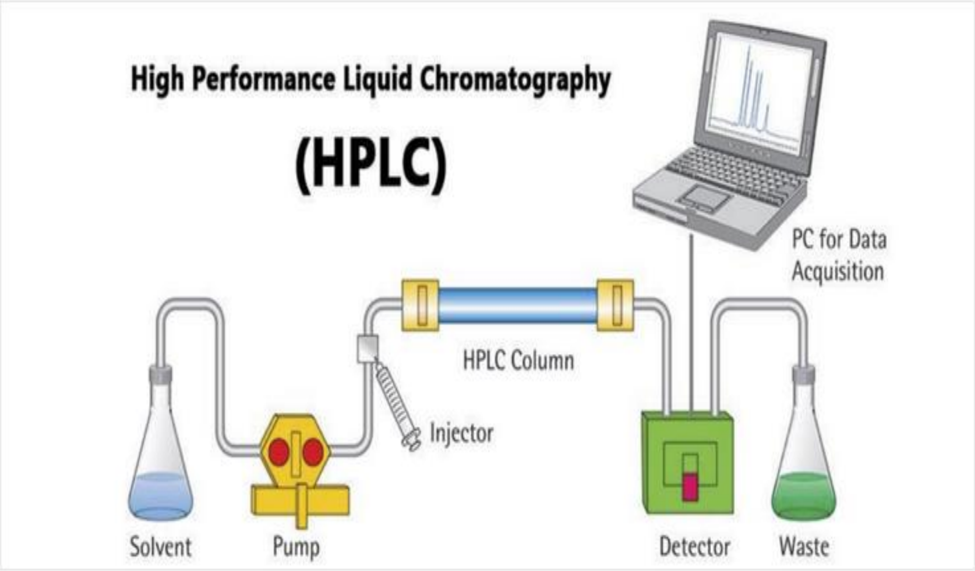
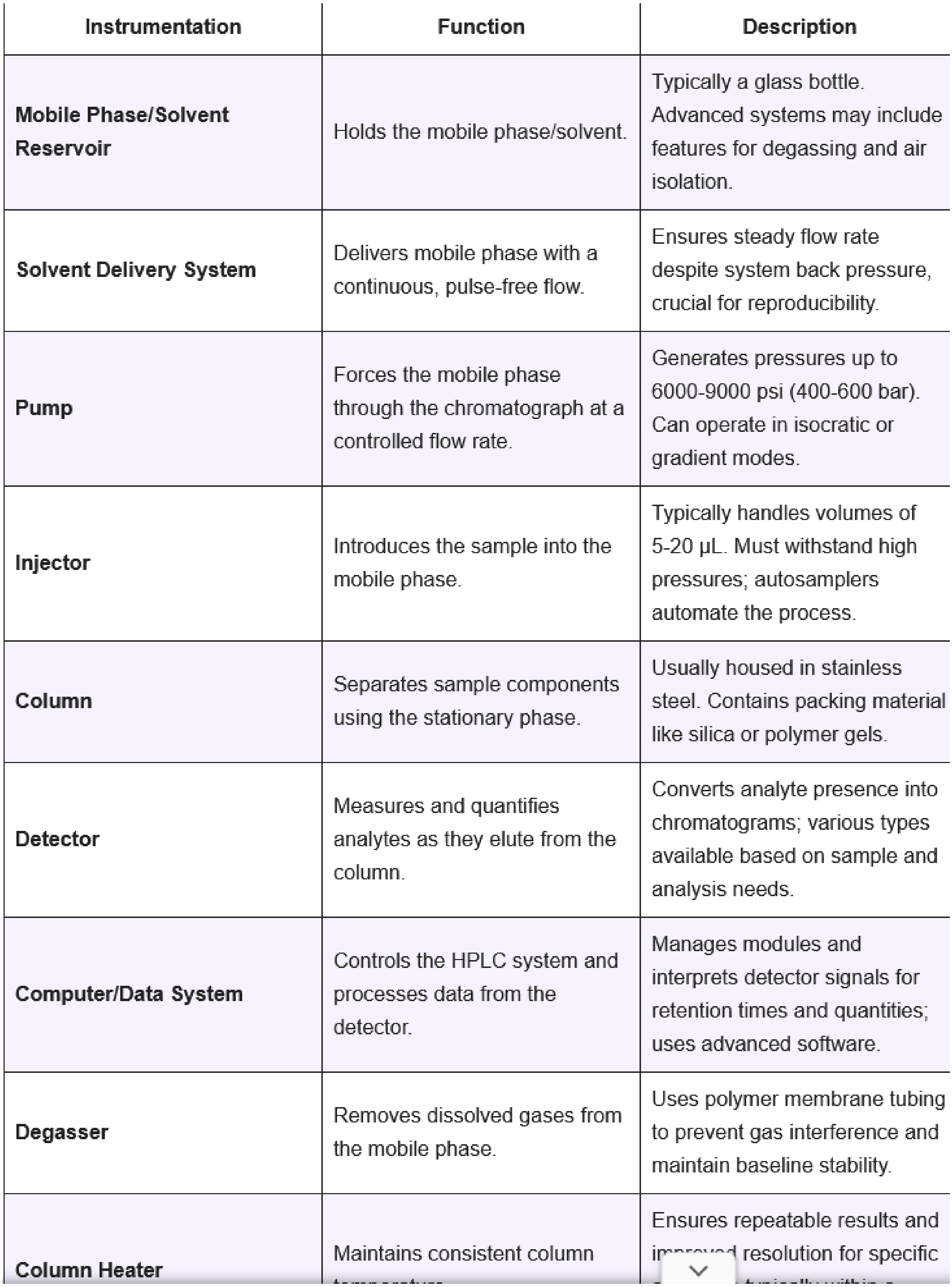


Fig: Instrumentation of HPLC



Instrumentation	Function	Description
Mobile Phase/Solvent Reservoir	Holds the mobile phase/solvent.	Typically a glass bottle. Advanced systems may include features for degassing and air isolation.
Solvent Delivery System	Delivers mobile phase with a continuous, pulse-free flow.	Ensures steady flow rate despite system back pressure, crucial for reproducibility.
Pump	Forces the mobile phase through the chromatograph at a controlled flow rate.	Generates pressures up to 6000-9000 psi (400-600 bar). Can operate in isocratic or gradient modes.
Injector	Introduces the sample into the mobile phase.	Typically handles volumes of 5-20 µL. Must withstand high pressures; autosamplers automate the process.
Column	Separates sample components using the stationary phase.	Usually housed in stainless steel. Contains packing material like silica or polymer gels.
Detector	Measures and quantifies analytes as they elute from the column.	Converts analyte presence into chromatograms; various types available based on sample and analysis needs.
Computer/Data System	Controls the HPLC system and processes data from the detector.	Manages modules and interprets detector signals for retention times and quantities; uses advanced software.
Degasser	Removes dissolved gases from the mobile phase.	Uses polymer membrane tubing to prevent gas interference and maintain baseline stability.
Column Heater	Maintains consistent column	Ensures repeatable results and improved resolution for specific

Applications of HPLC

High-Performance Liquid Chromatography (HPLC) has become an indispensable analytical technique across various scientific fields due to its versatility and precision. The following outlines the diverse applications of HPLC, emphasizing its role in different sectors:

Pharmaceutical Industry

Drug Analysis:

Identification and Quantification: HPLC is utilized to identify and quantify active pharmaceutical ingredients and metabolites in drug formulations. This ensures that the correct dosage is administered and that the drug is effective.

Electromagnetic Spectrum

The **electromagnetic spectrum** is the complete range of electromagnetic radiation arranged according to wavelength or frequency. All electromagnetic waves travel at the speed of light ($c = 3 \times 10^8$ m/s) in vacuum.

Electromagnetic radiation shows **wave–particle dual nature** (photons).

c=λνc = \lambda \nuc=λν

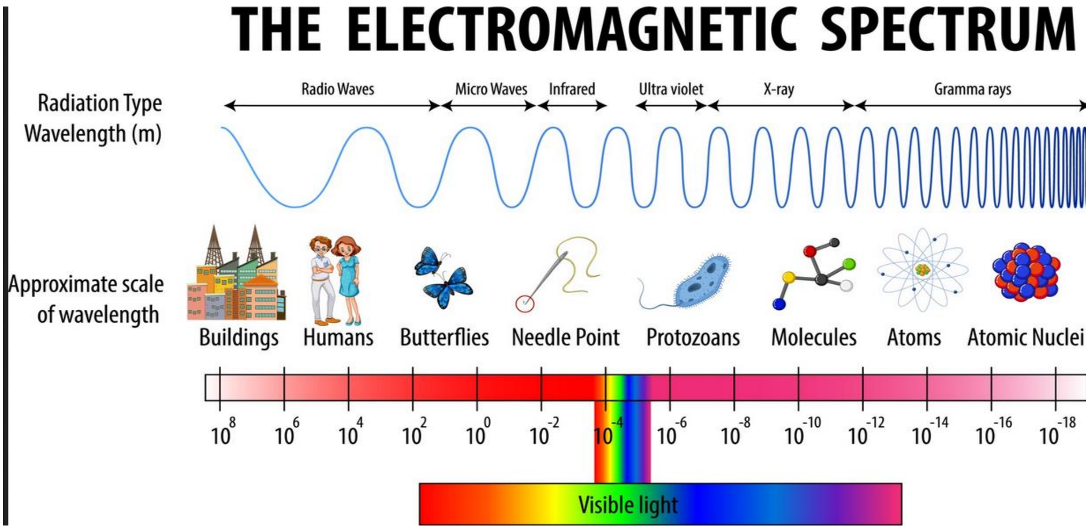
Where:

ccc = speed of light

λ\lambdaλ = wavelength

ν\nuν = frequency

Regions of the Electromagnetic Spectrum



Radio Waves

Longest wavelength (km to m)

Used in communication (TV, radio)

Microwaves

Used in radar and microwave ovens

Cause molecular rotation in water

Infrared (IR)

Heat radiation
Causes molecular vibrations

Visible Light
Only part visible to human eye (400–700 nm)

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Heat radiation
Causes molecular vibrations

Visible Light
Only part visible to human eye (400–700 nm)

bsorption of Radiation

Absorption occurs when matter takes in electromagnetic radiation and converts it into internal energy.

When radiation strikes matter:
It may be **absorbed**
It may be **reflected**
It may be **transmitted**

Mechanism of Absorption

When a molecule absorbs radiation:
Electron moves from lower energy level (E_1) to higher energy level (E_2).
Energy absorbed:
ΔE=hν\Delta E = h\nuΔE=hν
Where hhh = Planck’s constant.
Absorption occurs only when:
E2−E1=hνE_2 - E_1 = h\nuE2−E1=hν
This is called **quantized energy absorption**.

THE END

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