Code: 23BS1102

PVP 23

I B.Tech - I Semester – Regular/Supplementary Examinations
DECEMBER 2024

CHEMISTRY
(Common for EEE, ECE, CSE)

Duration: 3 hours Max. Marks: 70

Note: 1. This question paper contains two Parts A and B.
2. Part-A contains 10 short answer questions. Each Question carries 2 Marks.
3. Part-B contains 5 essay questions with an internal choice from each unit. Each Question carries 10 marks.
4. All parts of Question paper must be answered in one place.

BL – Blooms Level CO – Course Outcome

PART – A

		BL	CO
1.a)	What are Bonding molecular orbitals?	L1	CO1
1.b)	Calculate bond order and give magnetic behavior of Li_2.	L2	CO2
1.c)	List out the applications of semiconductors.	L1	CO2
1.d)	Define nano material.	L1	CO2
1.e)	Explain the advantages of the Conductometric titration.	L2	CO2
1.f)	Define the amperometric sensor.	L1	CO1
1.g)	What are thermoplastics?	L1	CO1
1.h)	Define conducting polymer.	L1	CO1
1.i)	What is the principle of Chromatography?	L2	CO3
1.j)	Explain any two selection rules of IR spectroscopy.	L2	CO3

PART – B

			BL	CO	Max. Marks
UNIT-I					
2	a)	Explain molecular energy level diagram of CO molecule.	L4	CO4	5 M
	b)	Derive Schrodinger wave equation.	L3	CO2	5 M
OR					
3	a)	Derive an equation for the energy of the particle in One Dimensional box.	L3	CO2	5 M
	b)	Explain the Postulates of Molecular Orbital Theory.	L4	CO4	5 M
UNIT-II					
4	a)	Choose any five applications of super conductors.	L3	CO2	5 M
	b)	Explain a detailed note on Carbon nano tubes.	L4	CO4	5 M
OR					
5	a)	Make use of neat diagram to explain intrinsic semiconductors.	L3	CO2	5 M
	b)	Classify Super capacitors.	L4	CO4	5 M
UNIT-III					
6	a)	Describe the construction and working of Electrochemical cell.	L3	CO2	5 M
	b)	Explain the construction and working of the PEMFC.	L4	CO4	5 M
OR					
7	a)	Derive Nernst equation.	L3	CO2	5 M
	b)	Explain the Potentiometric titration with suitable redox reaction.	L4	CO4	5 M
UNIT-IV					
8	a)	Explain the preparation and applications of the Bakelite.	L4	CO5	5 M
	b)	Discuss a detailed note on Carbon fibre reinforced plastics.	L3	CO3	5 M
OR					
9	a)	Describe the free radical mechanism of addition polymerization.	L3	CO3	5 M
	b)	Select the properties and applications of PVC and explain their preparation.	L4	CO5	5 M
UNIT-V					
10	a)	Explain the fundamental modes of vibrations.	L4	CO5	5 M
	b)	Describe the instrumentation of UV-Visible spectroscopy with neat sketch.	L3	CO3	5 M
OR					
11	a)	Derive Beer-Lamberts law and give its limitations.	L3	CO3	5 M
	b)	Analyze the applications and principle of HPLC.	L4	CO5	5 M

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(CSE, ECE,EEE)
SCHEME OF VALUTION

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PART -A

1a) what are Bonding molecular orbitals ? (2M)

Bonding molecular orbitals result from the constructive overlap of atomic orbitals, leading to a lowering of energy and the formation of a chemical bond between atoms. The electrons in these orbitals contribute to the stability of the molecule.

1b)Calculate bond order and magnetic behaviour of Li2 (2M)

Bond order of the lithium molecule is- 1

Diamagnetic in nature

Bond order- ½ (NO.of bonding electrons –NO. of anti bonding electrons)

1/2 (4-2)= 1

1c) list out the applications of semi conductor (2M)

1.Temperature sensors are made with semiconductor devices.

2.They are used in 3D printing machines

3.Used in microchips and self-driving cars

4.Used in calculators, solar plates, computers and other electronic devices.

5.The physical and chemical properties of semiconductors make them capable of designing technological wonders like microchips, transistors, LEDs, solar cells

1d) Define nano material (2M)

Any material that contains grains or clusters of the order of 1 to 100 nanometer, layers or filaments of that dimension is called as nanomaterials.Eg:fullerenes, quantum Dot

1e)Explain the advantages of the couductometric titration (2M)

1. **No indicator required**: Conductometric titration doesn't require an indicator, making it suitable for colored or turbid solutions

2. **2.Accurate endpoint**: The endpoint of a conductometric titration can be determined graphically with minimal error.

3.Works with dilute solutions: Conductometric titration can be used to titrate very dilute solutions down to 0.001 mol/L.

1f)Define the ampere metric sensor (2M)

Amperometric sensors are a type of electrochemical sensor that measure current generated by anelectroactive substance undergoing anelectrochemical reaction. The sensor measures the current at a constant working potential with respect to the referenceelectrode.

Ex: Glucometer

1g) what are thermo plastics? (2M)

plastics that soften when heated and solidify when cooled, and can be reshaped or remolded multiple times .eg: polyethylene

Ih) Define conducting polymer (2M)

Conducting polymers are organic polymers that can conduct electrons through their conjugated polymer chains. They are also known as organic conductors.Eg: polyacetylene

1i) what is the principle of chromatography? (2M)

Chromatography is based on the principle that components of a mixture are separated when the mixture which is a mobile phase is moved through a stationary phase, resulting in some components of the mixture being attached to the stationary phase material and the remaining mixture is passed along as the mobile phase

1j)Explain any two selection rules of IR spectroscopy (2M)

Dipole moment change

A vibration is only IR active if the molecular dipole moment changes during the vibration. The dipole moment is the separation of positive and negative charges within a molecule.

Frequency principle

The frequency of the incident light must equal the energy difference between electron orbits (molecule vibrations).

PART-B

UNIT-I

2a) Explain molecular energy level diagram of CO molecule (5M)

Diagram- 2M

Explanation-1M

Bond order & electronic configuration – 2M

(OR)

2b) Derive Schrodinger wave equation (5M)

Derivation-5M

3a) Derive an equation for the energy of the particle in one dimensaional box (5M)

Derivation-5M

3b) Explain the Postulates of Molecular orbital theory(5M)

Postulates-5M

UNIT-II

4a) Choose any of super conductors (5M)

Five applications -5M

4b) Explain a detailed note on carbon nano tubes (5M)

Classification-2M

Properties-1M

Applications -2M

(OR)

5a) Make use of neat diagram to explain intrinsic semiconductors (5M)

Explanation -3M

Diagram -2M

5b) Classify super capacitors (5M)

Classification – 5M

UNIT-III

6a) Describe the construction and working of electrochemical cell (5M)

Construction-2M

Working-2M

Diagram-1M

6b) Explain construction and working of the PEMFC (5M)

Construction-2M

Working-2M

Diagram-1M

(OR)

7a) Derive Nernst equation (5M)

Derivation- 5M

7b)Explain the potentiometric titration withsutable redox reaction (5M)

Explanation-3M

Reaction-2M

UNIT-IV

8a)Explain the preparation and applications of the Bakelite (5M)

Preparation-3M

Applications-2M

8b) Discuss a detailed note on carbon fibre reinforced plastics (5M)

Explanation-2M

Properties- 1M

Applications-1M

(OR)

9a) Describe the free radical mechanism of addition polymerization. (5M)

Chain initiation-2M

Propagation- 1M

Termination-1M

Explanation-1M

9b) Select the properties and applications of PVC and explain their preparation (5M)

Preparation-2M

Properties-1M

Applications-1M

UNIT-V

10a) Explain the fundamental modes of vibrations. (5M)

Strecteching vibrations - 2.5M

Bending vibrations-2.5M

10b) Describe the Instrumentation of UV- VISIBLE aspectroscopy with neat sketch(5M)

Instrumentation- 3M

Diagram-2M

(OR)

11a) Derive Beer-Lamberts law and give its limitations(5M)

Derivation-3M

Limitations-2M

11b) Analyze the applications and principle of HPLC (5M)

Principle of HPLC-3M

Applications -2M

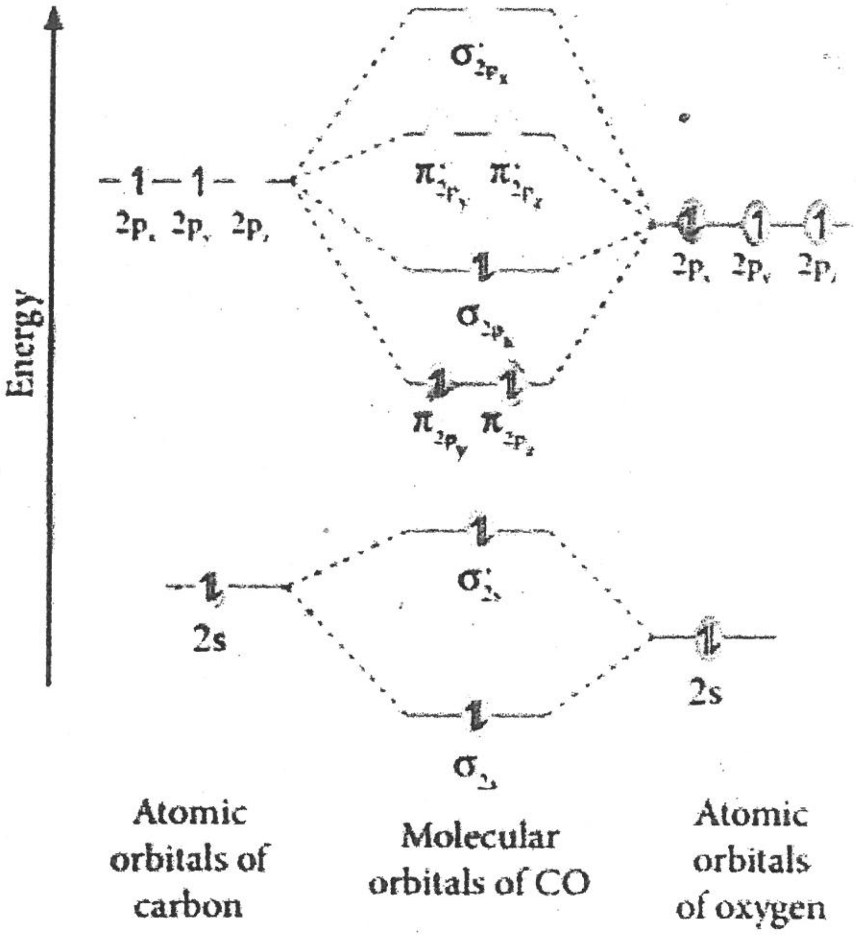
PART-B

UNIT-I

2a) Explain mecular energy level diagram of CO molecule

The electron configuration of oxygen is:$1s^2 2s^2 2p^4$

The electron configuration of carbon is:$1s^2 2s^2 2p^2$



E.C of CO = $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^2 = \pi 2p_z^2 \sigma 2p_x^2$

Bond Order= 1/2 (Number of electrons in bonding MOs−Number of electrons in antibonding MOs)

Bond Order= 1/2(8−2)=3

b) **Schrodinger wave equation:** The fundamental equation describing the behaviour of a smallparticlein terms ofwavemotion is

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

$$\Rightarrow \frac{1}{\lambda^2} = -\frac{d^2\psi}{dx^2}\times\frac{1}{4\pi^2\psi} \quad \text{----(1)}$$

where ψ =amplitude of the wave, x=displacement in a given direction and λ =wavelength. According to de Broglie equation,

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

$$\Rightarrow \frac{1}{\lambda^2} = \frac{m^2c^2}{h^2} \qquad \text{----(2)}$$

where m=mass of the particle, c=velocity of the particle and h=Planck's constant.
From eqs.(1) and (2),

$$\frac{m^2c^2}{h^2} = -\frac{d^2\psi}{dx^2} \times \frac{1}{4\pi^2\psi}$$

$$\Rightarrow m^2c^2 = -\frac{h^2}{4\pi^2\psi} \times \frac{d^2\psi}{dx^2} \qquad \text{----(3)}$$

For a particle of mass m moving with velocity c, the kinetic energy is given by,

$$K = \frac{1}{2}mc^2 \quad \text{or,} \quad K = \frac{m^2c^2}{2m}$$

$$\Rightarrow m^2c^2 = K \times 2m \qquad \text{----(4)}$$

From eqs.(3) and (4),

$$K \times 2m = -\frac{h^2}{4\pi^2\psi} \times \frac{d^2\psi}{dx^2}$$

$$\Rightarrow K = -\frac{h^2}{8\pi^2 m\psi} \times \frac{d^2\psi}{dx^2}$$

As the total energy E is the sum of kinetic energy K and potential energy V,

$$\mathrm{E} = \mathrm{K} + \mathrm{V}$$

$$\therefore E = \frac{h^2}{8\pi^2 m\psi} \times \frac{d^2\psi}{dx^2} + V$$

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

This is the Schrodinger wave equation in one dimension, X. If the motion of the particle is in three coordinates, X, Y and Z, then the equation becomes

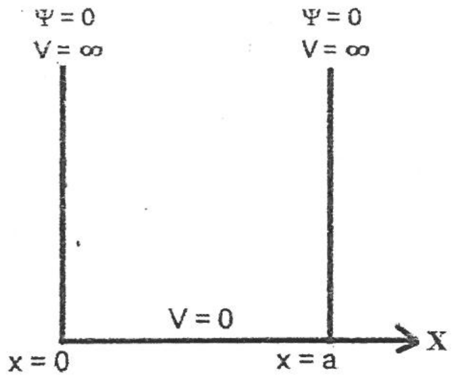
$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

3a) **Particle in one dimensional box:**

Consider a particle of mass 'm' confined to a one dimensional region (X–direction) between x=0andx=a.Theparticlebouncesbackandforthbetweenthewallsofthebox.Accordingtoquantum mechanics, potential of particle outside the box (0≤ x ≤ a) is infinite and inside the box,it is constant. For convenience, potential V is taken as zero inside the box. Since particle cannotpossessinfiniteenergy,itcannotexistoutsidethebox.Hence,wavefunctionΨ=0forx≤0andx≥ a. But when 0<x<a,Ψ≠0.

Schrodingerwaveequationis

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



SinceV=0

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}E\psi=0$$

$$\frac{d^2\psi}{dx^2}+k^2\psi=0 \qquad \text{-----(1)}$$

where $k=\frac{2\pi}{h}\cdot\sqrt{2mE}$

Onsolvingtheabovedifferentialequation,weget

$$\psi=A\sin(kx)+B\cos(kx) \qquad \text{-----(2)}$$

whereA=maximumamplitudefunctionofψ;B=constant

i) Applying ψ =0 at x=0, the second term on RHS of eq.(2) must be zero, i.e., B=0Now,eq. (2)is reduced to

ψ=Asin(kx)

ii) Onapplyinganotherboundaryconditionψ=0atx=a,

ψ=Asin(ka)=0

⇒sin(ka)=0 (∵A ≠ 0)

∴sin(ka)=0,ifka=π,2π,3π,etc.

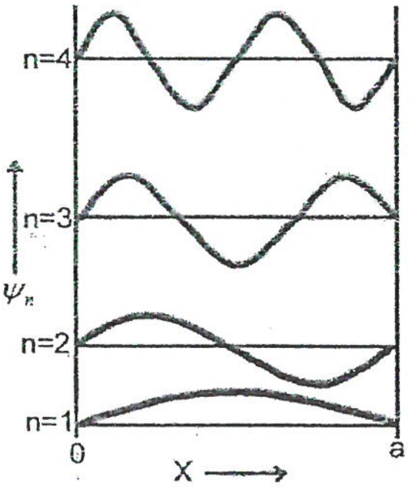
i.e.,sin(ka)=0,ifka=nπ,where n=1,2, 3,…

Each value of *n* gives a solution to Schrodinger equation. Since *k* depends on E and *k* depends on *n* value, it implies E depends on n.

Thus, each n value gives a different Eigen function and Eigen energy.

$$\psi_n = A\sin(kx) = A\sin(\frac{n\pi}{a}.x)$$

Graphically, it can be represented as below.



In order to normalize the wave function, let us impose normalization condition, i.e.,

$$\int_0^a |\psi_n|^2 .dx = 1$$

$$\int_0^a \left|A\sin\frac{n\pi}{a}x\right|^2 .dx = 1$$

$$A^2\int_0^a \sin^2(\frac{n\pi}{a}x).dx = 1$$

$$A^2.\frac{a}{2} = 1$$

$$\text{(or) } A = \sqrt{\frac{2}{a}}$$

Hence normalized wave functions of the particle are:

$$\psi_n = \sqrt{\frac{2}{a}}.\sin(\frac{n\pi x}{a})$$

With each 'n' value 1, 2, 3, etc. we get different wave functions, ψ_1, ψ_2, ψ_3, etc. Each of these wave functions is associated with Eigen energy.

Since, $k = \frac{2\pi}{h}\cdot\sqrt{2mE}$ and $k = \frac{n\pi}{a}$

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

Thus,

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

$$E_2 = \frac{4h^2}{8ma^2} = 4E_1$$

$$E_3 = \frac{9h^2}{8ma^2} = 9E_1$$

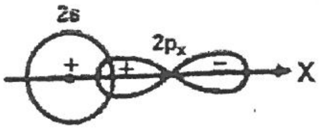
ψ_n values can be positive or negative, but $|\psi_n|^2$ values are always positive. Since ψ_n is normalized, $|\psi_n|^2$ at a given x gives the probability of finding of particle there. In case of the motion of particle in three dimensional box, the permitted energy levels are given by,

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

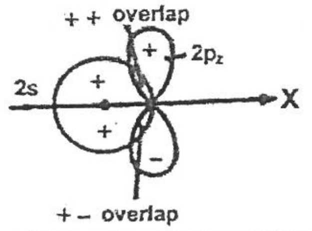
where a, b, c are the lengths of the sides of the box in x, y, z directions respectively.

3b) **Molecular orbital theory**: Molecular orbital theory was proposed by Mulliken in order to explain bonding and properties of molecules. The salient features of the theory are:

1. The atomic orbitals of the combining atoms overlap to form new orbitals, called molecular orbitals. Thus, atomic orbitals lose their identity after formation MO.
2. MO can be defined as a polycentric region in space, defined by its shape and size, associated with two or more atoms in a molecule. The electrons revolve in a MO in the field of more than one nucleus.
3. The number of MO formed is equal to the number of overlapping atomic orbitals. The shape of MO depends on the type of atomic orbitals combining.
4. Only those atomic orbitals can combine to form MO, which have comparable energies and proper orientations. For example, 1s orbital combines with 1s, 2s with 2s but not 1s with 2s. Similarly, 2s can combine with $2p_x$, $2p_x$ with $2p_x$, $2p_y$ with $2p_y$, $2p_z$ with $2p_z$, but not $2p_x$ with either $2p_y$ or $2p_z$.



2s orbital can overlap with 2px orbital



2s orbital cannot overlap with 2pz orbital

5. According to LCAO, linear combination of atomic orbitals can take place in two ways: i) by addition or constructive interaction, or ii) by subtraction or destructive interaction.
6. Molecular orbital obtained by addition of wave functions of atoms is called bonding molecular orbital, represented by σ, π, δ, etc.

   $\psi(MO) = \psi_A + \psi_B$

The energy of bonding MO is less than that of the corresponding atomic orbitals. The difference of energy is called stabilization energy. Thus, bonding MO stabilizes the molecule.

7. Molecular orbital obtained by subtraction of wave functions of atoms is called anti-bonding molecular orbital, represented by σ^*, π^*, δ^*, etc.

   $$\psi^*(MO) = \psi_A - \psi_B$$

   The energy of anti-bonding MO is more than that of the corresponding atomic orbitals. The difference of energy is called destabilization energy. Thus, anti-bonding MO destabilizes the molecule.
8. Probability of bonding MO formation (ψ^2) is greater than that of anti-bonding MO formation (ψ^{*2}).

   $$\begin{aligned}\psi^2 &= (\psi_A+\psi_B)^2 \\ &= \psi_A^2+\psi_B^2+2\psi_A\psi_B \\ &= (\psi_A^2+\psi_B^2-2\psi_A\psi_B)+4\psi_A\psi_B \\ &= (\psi_A-\psi_B)^2+4\psi_A\psi_B \\ &= (\psi^*)^2+4\psi_A\psi_B\end{aligned}$$
9. MO gives the electron probability distribution around a group of nuclei just as AO gives the electron probability distribution around a single nucleus.
10. The MO formed by overlapping of inner atomic orbitals are called non-bonding MO, and they do not participate in bonding.
11. Filling of electrons in MO follows the same rules just as in atomic orbitals.
    a) Aufbau principle: Filling of electron in the order of increasing energy.
    b) Pauli's exclusion principle: Maximum two electrons with opposite spin in any MO.
    c) Hund's rule: Pairing of electrons in degenerate MO does not occur, until each of them has one electron each.
12. If a molecule contains one or more unpaired electrons in its MO, it is paramagnetic, otherwise it is diamagnetic. Paramagnetic character is directly proportional to the no. of unpaired electrons in MO.

4a)Applications of Superconductors(any five applications): Magnetic Resonance Imaging (MRI): Superconducting magnets are widely used in MRI machines to generate strong, stable magnetic fields for medical imaging. The absence of electrical resistance and the Meissner effect contribute to the high-quality images produced by these machines.

Particle Accelerators: Superconducting magnets are essential components in particle accelerators like the Large Hadron Collider (LHC). They generate powerful magnetic fields to guide and accelerate particles.

Magnetic Levitation (Maglev): Superconducting materials are used in Maglev trains to create a magnetic cushion that allows the trains to hover above the tracks, eliminating friction and enabling high-speed, efficient transportation.

Energy Transmission: Superconductors can be used for high-capacity, low-loss electrical power transmission. While this technology is still in the experimental stage, it has the potential to significantly improve the efficiency of electrical grids.

Superconducting Quantum Devices: Superconductors are used in quantum computing and quantum sensing applications. They can be used to create qubits in quantum computers and enable extremely sensitive detectors for various scientific and industrial purposes.

Energy Storage: Superconducting magnetic energy storage (SMES) systems store energy in the form of a magnetic field and can release it when needed. These systems can be used for grid stabilization and as backup power sources.

Transportation: Beyond Maglev trains, superconductors have been explored for electric vehicle charging and propulsion systems, offering high efficiency and reduced energy loss.

Cryogenics: Superconductors require low temperatures to maintain their superconducting state, which has applications in cryogenics, such as cooling systems for scientific instruments and sensors.

Research and Experiments: Superconductors are used in various scientific experiments and research applications where precise control of magnetic fields and extremely low electrical losses are critical.

The field of superconductivity continues to evolve, and ongoing research seeks to discover new superconducting materials with higher critical temperatures, making them more practical for everyday applications.

4b) **Carbon Nanotubes** (CNTs):- Carbon nanotubes are allotropes of carbon with a nanostructurehaving length to diameter ratio greater than 1, 00,000. They can be considered as a sheet of graphite rolled in the form of a tube, with the ends of the sheet closed by bonds. Each carbon atom in carbon nano tube is covalently bonded to 3 other carbon atoms. Depending upon the way in which they are arranged, there are two types of CNTs.

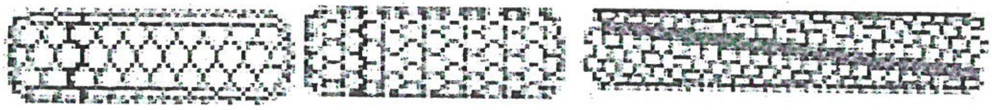
- Single walled nanotube (SWNTs)
- Multiwalled Nanotubes.(MWNTs)

Single Walled Nanotubes:-Most of the single walled nanotubes have a diameter of nearlyone nanometer and a length that can be many millions of times greater than the diameter. The structure of SWNT can be obtained by wrapping one atom thick layer of graphite called graphene into a seamless cylinder. There are 3 types of single walled nanotubes based on the way the graphene sheet is wrapped. The graphene sheet is represented by a pair of indices (n,m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in a crystal lattice of graphene.

If m=0 the nanotube is called zig-zag.

If n=m the nanotubes are called armchair. The lines of hexagons are parallel to the axis of the nanotube.

Otherwise they are called chiral. It has a twist or spiral around the nanotube



Arm chair Zig-zag Chiral

Types of SWNT

Types of SWNT

Multiwalled Nanotubes: - Multiwalled nanotubes consist of multiple layers (concentrictubes) of graphite. The inter layer distance in Multiwalled nanotubes is close to the distance between graphene layers in graphite. It is approximately 3.3 ^{0}A.

There are two models which can be used to describe the structure of Multiwalled nanotubes.

Graphite sheets can be arranged in concentric cylinders one around the other.

Single sheet of graphite can be rolled around itself resembling a scroll of parchment or a rolled newspaper.

Properties of carbon nanotubes:

Mechanical properties: Carbon nanotubes possess amazing mechanical properties. They arethe strongest and stiffest materials in terms of tensile strength and elastic modulus respectively. Their strength can be explained on the basis of sp^{2} carbon-carbon bonds between the individual atoms. Carbon nanotubes are softer in the radial direction than along the tube axis. These properties together with the lightness make the carbon nanotubes useful for their application in aerospace. It has been suggested that nanotubes can be used in space elevator, on earth to space cable.

Hardness:A super hard material could be synthesized by compressing SWNTs to above24Gpa at room temperature. The hardness of this material was measured by nanoindenter and was found to be 62-152 Gpa.

Electrical properties: Carbon nanotubes can be metallic or semiconducting depending upontheir structure. For a given nanotube with n=m, the nanotube is metallic. If n-m is a multiple of 3 then a nanotube is semiconducting and possesses a very small band gap. Otherwise a nano tube is a moderate semiconductor. Thus all arm chair nanotubes are metallic with conductivities higher than that of copper. Others behave more like silicon.

Vibration properties: Carbon nanotubes show two normal modes of vibration

A_1g mode: It involves in and out oscillation.

E_2g mode: It involves oscillation between sphere and an ellipse.

Engineering applications of carbon nanotubes:

Carbon nanotubes have high strength, small dimensions and remarkable physical properties. Due to this they find application in different fields.

- They find application in conductive composites, high strength composites, energy storage devices energy conversion devices, energy storage media, sensors, nanometer sized semi conductor devices etc. They are used as nanoprobes in biological and chemical investigations. They are the alternative and efficient tools for transporting and translocating therapeutic molecules.
- CNT can be functionalized with bio active peptides, proteins, nucleic acids, and drugs and can be used to deliver them to cells and organs.
- Functionalized CNTs possess low toxicity. Hence they are used in the fields of nanobiotechnology, and nano medicine.

Applications in fuel cells:

- Carbon nanotubes can be used to store hydrogen which in turn can be used for fuel cells.
- A new fuel electrode made-up of a network of single walled carbon nanotubes was created by a group of scientists .It is very thin and light in weight. This electrode can work as a conventional electrode. Use of this electrode makes the entire fuel cell much lighter.
- Carbon nanotubes can be applied as catalyst in fuel cells in place of platinum. It not only reduces the overall cost of the fuel cell but also provides resistance to corrosion.
- Carbon nanotube network can be used as diffusion electrode in fuel cells. It allows the gas and water vapor to pass through it to the catalyst layer. The catalyst layer consists of platinum particles, In this layer, protons and electrons of the gaseous reactant material (i.e. the fuel cell's fuel) are separated and the electrons become electricity.
- Electric power density produced using Pt/CNT electrodes are greater than that of Pt/carbon black. CNTs are thus found to be a good support of Pt particles.

5a)An **intrinsic semiconductor** is a pure semiconductor material without any significant impurity atoms. The most common examples are silicon (Si) and germanium (Ge). At absolute zero, intrinsic semiconductors behave as perfect insulators. However, as temperature increases, some covalent bonds break, and free electrons and holes are generated, enabling conductivity.

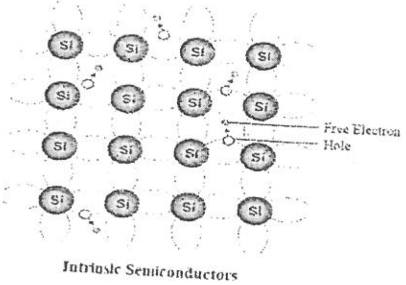
Imagine the structure of an intrinsic semiconductor (e.g., silicon crystal):

1. **Covalent Bonds**: Each silicon atom forms four covalent bonds with its neighboring silicon atoms.
2. **Valence and Conduction Band**:
   - **Valence Band**: Contains the electrons involved in bonding.
   - **Conduction Band**: Electrons in this band contribute to electrical conductivity.
3. **Electron-Hole Pair Formation**:
   - At room temperature or higher, thermal energy causes some electrons to break free from covalent bonds, leaving behind "hole

1. **Crystal Lattice**: Illustrates the arrangement of silicon atoms and their bonds.
2. **Energy Band Diagram**:
   - Shows the energy gap (EgE_gEg) between the valence band and the conduction band.
   - Depicts the thermal excitation of electrons across the gap

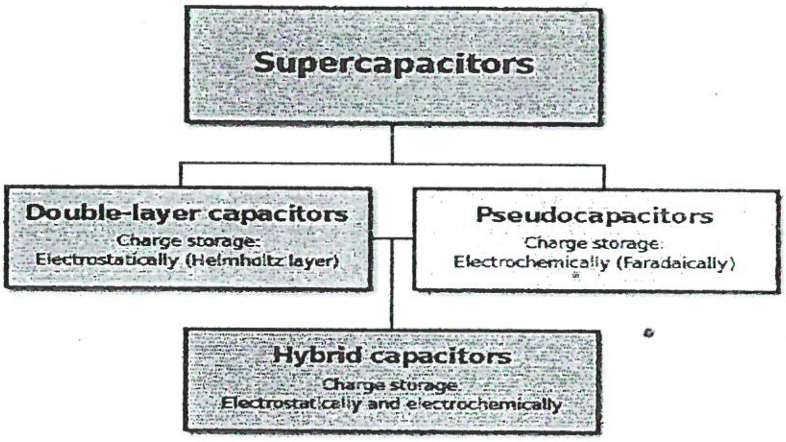
Electrical Conductivity:

- When a voltage is applied, electrons move toward the positive terminal.
- Holes appear to move in the opposite direction, acting as positive charge carriers.
- The conductivity of intrinsic semiconductors is relatively low and depends on temperature.

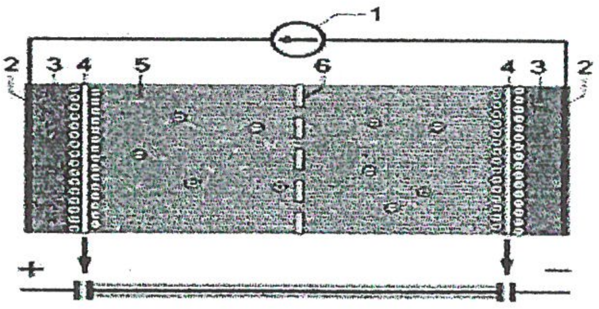


Intrinsic Semiconductors

5b)



- ➢ Double-layer capacitors
    - o (Store charge electrostatically)
- ➢ Pseudo-capacitors
    (Store charge electrochemically)
- ➢ Hybrid capacitors(store charge electrostatically & electrochemically)

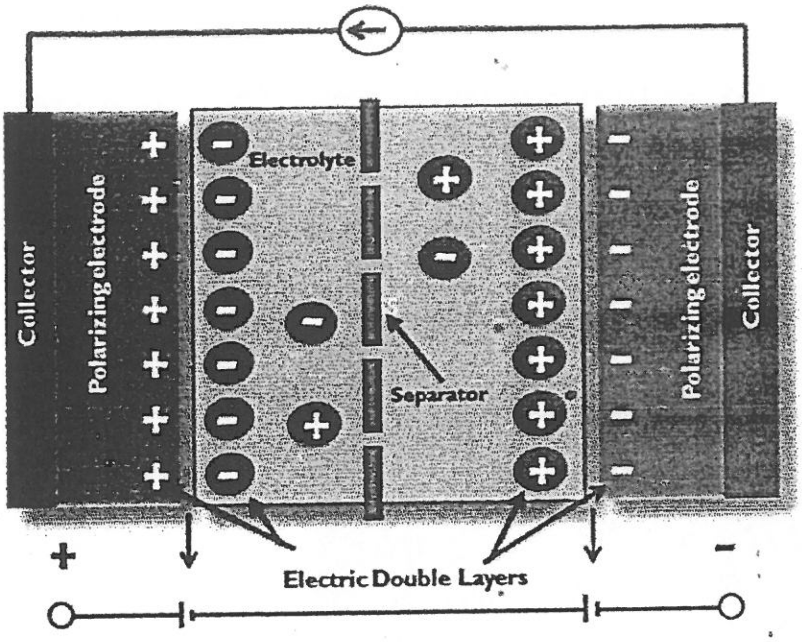


Typical construction of a supercapacitor:

(1)power source,
(2) collector,
(3) polarized electrode,
(4) Helmholtz double layer,
(5) electrolyte having positive and negative ions,
(6) separator

Electrical double-layer capacitance

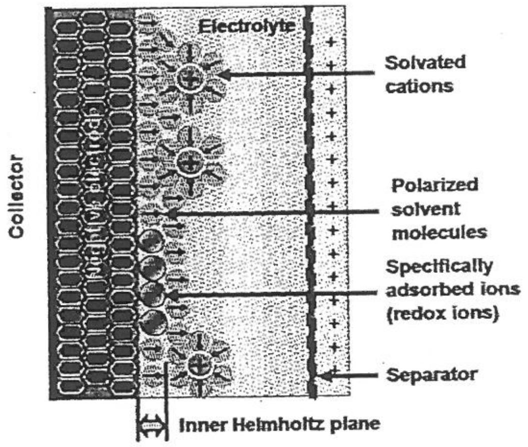
- Electrostatic Double Layer Capacitors comprises two **electrodes**, a separator, and an electrolyte.
- Electrolyte is a **mixture** comprising positive and negative **ions** dissolved in water.
- The two electrodes are separated from each other through a separator.
- The super capacitors use carbon electrodes with much higher electrostatic double-layer capacitance.
- The separation of charge in electrostatic double-layer capacitors is much less than in a conventional capacitor which ranges from 0.3–0.8 nm.



Electrochemical pseudo capacitance

- Pseudo Capacitors are also referred to as electrochemical pseudo-capacitors.
- They make use of metal oxide or conducting polymer electrodes that have a high amount of electrochemical pseudocapacitance.
- They store electrical energy by **electron** charge transfer between electrode and electrolyte.
- It is done through the **oxidation and reduction reaction** commonly known as a **redox reaction**.

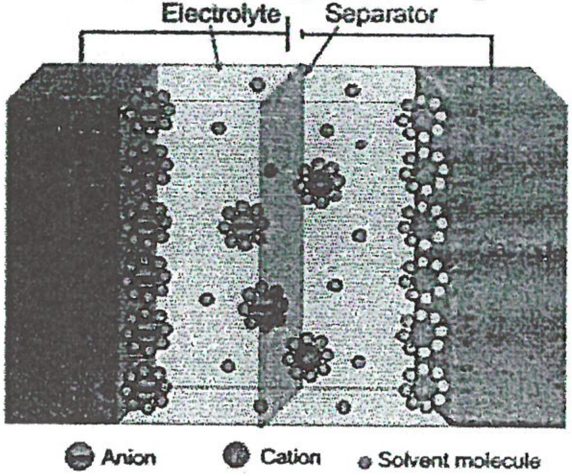
Pseudocapacitance with specifically adsorbed ions



Hybrid supercapacitor

- Hybrid Capacitors are made by using the techniques of double-layer capacitors and pseudo-capacitors.
- In these capacitors, electrodes with different characteristics are used.
- One electrode has the capacity to display electrostatic capacitance and the other electrode showcases electrochemical capacitance.

An example of a hybrid capacitor is the **lithium**-ion capacitor



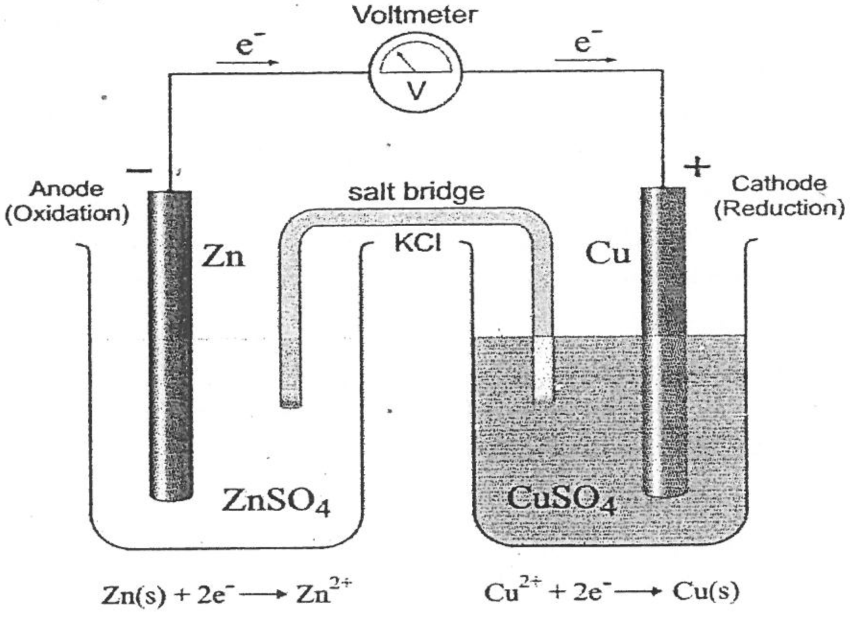
6a) **Electrochemical or Galvanic Cell**

"Electrochemical cell or Galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy i.e. electricity can be obtained with the help of oxidation and reduction reaction".

Construction and working of electrochemical cell: Following are the important characteristics of electrochemical cell,

i. Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.
ii. The two electrodes taken are made of different materials and usually set up in two separate vessels.
iii. The electrolytes are taken in the two different vessels called as half – cells
iv. The two vessels are connected by a salt bridge/porous pot.
v. The electrode on which oxidation takes place is called the anode (or – ve pole) and the electrode on which reduction takes place is called the cathode (or + ve pole).
vi. In electrochemical cell, ions are discharged only on the cathode.
vii. In electrochemical cell, electrons flow from anode to cathode and current flows from cathode to anode.
viii. For electrochemical cell,

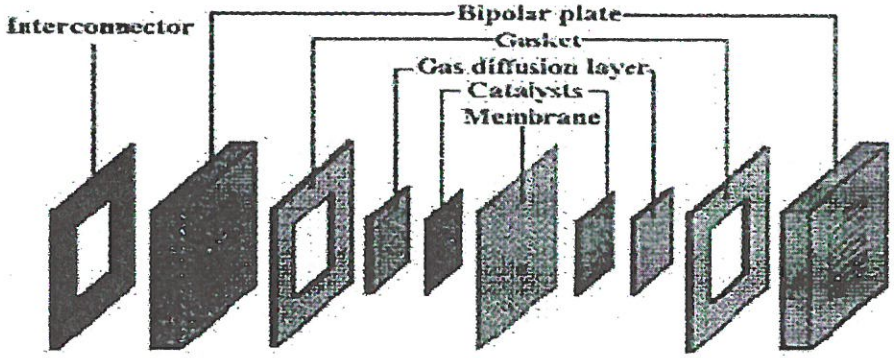
In a electrochemical cell, cell reaction is exothermic



$$\mathrm{Zn(s)}\mid \mathrm{ZnSO_4(aq)}\parallel \mathrm{CuSO_4(aq)}\mid \mathrm{Cu(s)}$$

Reactions of Daniel cell at cathode and anode are:
At cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)
At anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
During the chemical reactions the cell produces the potential of Ecell = 1.09 V

6b) Polymer Electrolyte Membrane Fuel Cells



Polymer Electrolyte Membrane Fuel cells (PEMFC): It offers an order of high powerdensity than any other fuel cells. A solid polymer membrane used as electrolyte. The thinsheetofporousgraphitepapersusedaselectrodes.Platinumblackcoatedonelectrodesused as catalyst. The poly styrene sulphonic acid used as electrolyte, allows only hydrogen ions.The electrolyte is then sandwiched between anode and cathode, and three components sealedtogether underheatand pressuretoproducemembraneand electrodeassembly.

Reactions:Hydrogengasisconsumedatanode,yieldingtheelectronsatanodeandproducing hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines withelectronsandhydrogenionstoproducewater.Thewaterrejected outfromthe cell.

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

Atthecathode:$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overallreaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $E^\circ_{cell} = 1.23V$

Advantagesofpolymerelectrolytemembrane:

- Highoperating temperature(50º–100ºC)
- Highionicconductivity
- Protonconductivity
- Chemicalstability
- Thermalstability
- Impermeabletowater
- Faststartup
- Flexibilityoffueltype

Reducedcorrosion,shielding,orleakingconcerns

7a) **Nernst Equation:**

Suppose the cell reaction involved in any reversible cell, which is represented by the given equation

$$aA + bB \rightarrow xX + yY$$

The free energy change of this reaction is given by the equation.

$$\Delta G = \Delta G^o + RT\ln\frac{aX^x . aY^y}{aA^a . aB^b} \quad \text{----------------} \quad 1$$

Where

ΔG^o = Standard free energy change

aA,bB,aX, &aY represents the activities of A,B,X,&Y respectively in any state.
If the cell reaction involves transference of 'n' moles of electrons, this corresponds to flow of 'nF' faradays of electricity.
If 'E' is the EMF of the cell, then the electrical energy produced in the cell = nFE
Since electrical energy produced is equal to the decrease in the free energy of the cell reaction, we have.

$$-\Delta G = nFE \quad \text{----------------} \quad 2$$

Similarly for the standard state, we will have

$$-\Delta G^o = nFE^o \quad \text{----------------} \quad 3$$

Where E^o is the standard EMF of the cell

Substituting the values of ΔG& ΔG^o from the equations 2&3 in 1 we get,

$$-nFE = -nFE^o + RT\ln\frac{aX^x . aY^y}{aA^a . aB^b} \quad \text{----------------} \quad 4$$

Divide the equation 4 with '$-nF$'

$$E = E^o - \frac{RT}{nF}\ln\frac{aX^x . aY^y}{aA^a . aB^b} \quad \text{----------------} \quad 5$$

Thus knowing the cell reaction and the standard EMF of the cell ' E^o ' ,the EMF of the cell for known activities of the various reactants and products can be calculated.
Equation '5' is known as "Nernst equation", which is useful for the calculation of EMF of the cell.
When the concentrations are very dilute, activities can be replaced by concentrations. Then, equations "5" becomes

$$E = E^o - \frac{RT}{nF}\ln\frac{[X]^x . [Y]^y}{[A]^a . [B]^b}$$

Where, R= 8.314 joule $joles. deg^{-} mole^{-}$
F = 96,500 coulombs
T = 298Kat25°
It must be born in mind that the activities or concentrations of the pure liquids or pure solids are taken as unity.

7b) **Potentiometric titrations:** Potentiometric titration is a chemical method used to determinethe quantity of a specific test substance. It is similar to direct titration, but it doesn't use anindicatorreagent,insteadofituses anelectrodeasanindicator.

Ex: Redoxtitrations

The redox titration is based on the oxidation-reduction reaction between the two solutions.Here the end point is detected using a potentiometer. From the Nernst equation, the potentialof a given reaction will depend on the relative concentration of oxidized /reduced from.During their titration, the solution potential changes due to the change in the concentration ofoxidized /reduced form. At one stage, where either of the form is absentat the end point,there is a sharp change in potential. Potassium dichromate is an oxidizing agent and in acidmedium; itfollowsthehalfreactiontogiveCr(III)asthe reductionproduct.

$Cr_2O_7^{2-}+14H^{+}+6e^{-}\rightleftharpoons 2Cr^{3+}+7H_2O$...(1)

While Fe^{2+} which is used to titrate $K_2Cr_2O_7$ gets oxidized to Fe^{3+} as per the reaction

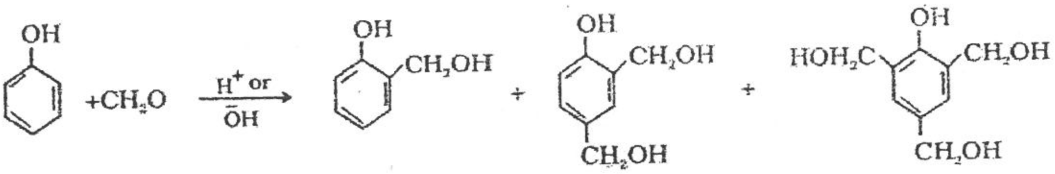
of$Fe^{2+}\rightleftharpoons Fe^{3+}+e^{-}$...(2)

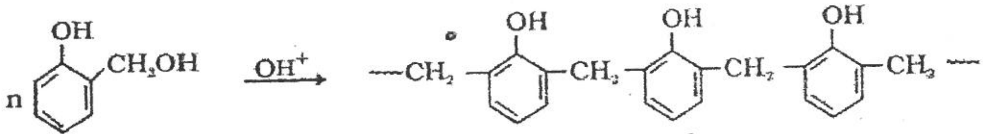
The overall ionic equation of this titration can be obtained by adding the above two

equations$Cr_2O_7^{2-}+6Fe^{2+}+14H^{+}\rightarrow 6Fe^{3+}+2Cr^{3+}+7H_2O$...(3)

Phenolformaldehyderesins:Bakelite Preparation:

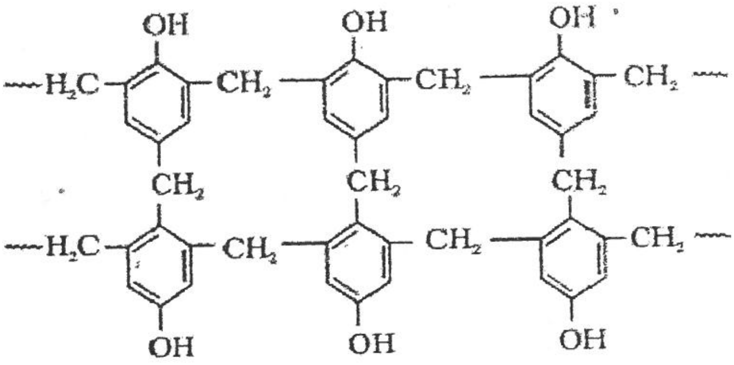
- Theseareformedbythepolycondensationbetweenphenolandformaldehyde.
- Thereaction is catalysedbyacid orbase.
- The initialproduct isNovolac(linearproduct).





Novolac

- Novalaconheatingwithformaldehydeformsbakelite.



Bakelite

Uses: Usedforthepreparationof Electrical insulator parts like

- Switches
- Plugs
- Handles

Mouldedarticleslike

- Telephoneparts
- Cabinets forT.V
- Cabinets forradio

8b)**Carbon Fiber Reinforced Plastics (CFRP)** are composite materials made by combining a polymer matrix with carbon fibers. The carbon fibers provide strength and stiffness, while the polymer matrix holds the fibers in place and transfers loads between them. CFRP is widely used in industries requiring lightweight and high-strength materials.

Composition:

1. **Carbon Fibers**:
    - High tensile strength and modulus.
    - Lightweight and resistant to high temperatures.
    - Manufactured through the pyrolysis of organic precursors like polyacrylonitrile (PAN) or pitch.
2. **Polymer Matrix**:
    - Typically made of thermosetting resins (like epoxy, polyester, or vinyl ester) or thermoplastics.
    - Provides shape and protects the fibers from environmental damage.

Properties:

1. **High Strength-to-Weight Ratio**:
    - CFRPs are significantly lighter than metals but stronger, making them ideal for aerospace and automotive applications.
2. **Corrosion Resistance**:
    - Resistant to environmental degradation, such as rust.
3. **Fatigue Resistance**:
    - Exhibits excellent fatigue life compared to metals.
4. **Thermal Conductivity**:
    - Carbon fibers have good thermal conductivity, though the polymer matrix might limit it.
5. **Low Thermal Expansion**:
    - Maintains dimensional stability across temperature changes.

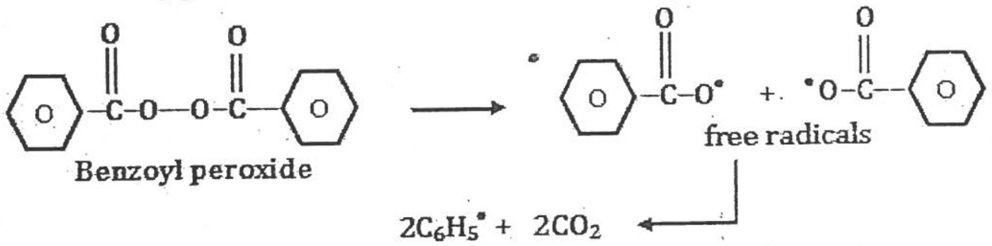
Applications:

1. **Aerospace**:
    - Aircraft structures, satellites, and space vehicles due to weight reduction and strength.
2. **Automotive**:
    - High-performance vehicles, lightweight body panels, and structural components.
3. **Sports Equipment**:
    - Tennis rackets, bicycles, golf clubs, and skis.
4. **Wind Energy**:
    - Wind turbine blades for durability and light weight.
5. **Construction**:
    - Strengthening and retrofitting of concrete structures.

9a) MechanismofpolymerizationFree radical polymerization

Inthistypeofpolymerizationmonomerisactivatedtofreeradicalbyanyoneofthe following methods.

a) Photochemicalinitiation:-Byexposingto sunlightfree radicalsare generated.
b) Thermalinitiation:-Byheatingfreeradicalsare generated.
c) Radiationinitiation:-Byexposingtoα,βory-raysfree radicalsare generated.
d) Chemical initiation:- By using initiators like peroxides free radicals are generated. Benzoyl peroxide or Azobisisobutyronitrile, persulphatesetc are used as chemical initiators. They produce free radicals as



Mechanismof freeradicalpolymerization involves threesteps.

1. Chaininitiation:-

Itinvolvestwosteps.

a) Formationof freeradicalsfrom theinitiator.

$$\text{Initiator} \longrightarrow 2\,R^{\bullet}\ \text{free radicals}$$

b) Additionoffreeradicalstomonomertoforma freeradical intermediate.

$$R^{\bullet} + CH_2{=}\underset{X}{CH} \longrightarrow R{-}CH_2{-}\underset{X}{CH^{\bullet}}$$

Free radical Intermediate

X = substituent group

2.Chainpropagation:-

Here addition of monomer molecules to the intermediate takes place one byone leads to the formation of macro-radicals.

$$R{-}CH_2{-}\underset{X}{CH^{\bullet}} + n\,CH_2{=}\underset{X}{CH} \longrightarrow R{-}\left[CH_2{-}\underset{X}{CH}\right]_n{-}CH_2{-}\underset{X}{CH^{\bullet}}$$

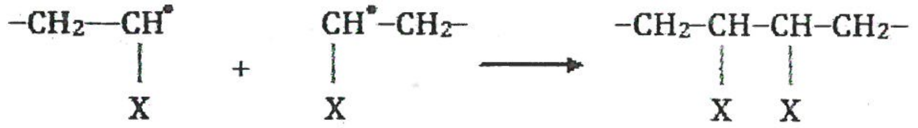
Macro radical

3.Chaintermination:-

Thegrowingpolymerchainis terminated bymanyways.

c) Recombination:-

Combinationoftwo freeradicals leads totermination.



$$\mathrm{-CH_2-\underset{X}{\underset{|}{CH^{\bullet}}}} + \mathrm{\underset{X}{\underset{|}{CH^{\bullet}}}-CH_2-} \longrightarrow \mathrm{-CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_2-}$$

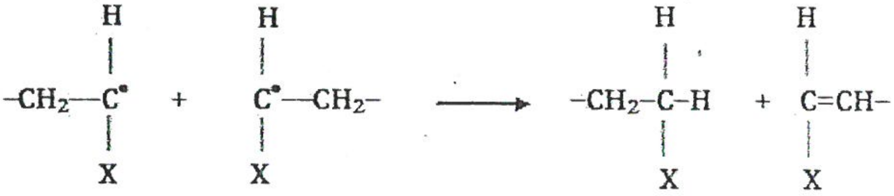
(or)

$$\mathrm{-CH_2-\underset{X}{\underset{|}{CH^{\bullet}}}} + \mathrm{R^{\bullet}} \longrightarrow \mathrm{-CH_2-\underset{X}{\underset{|}{CH}}-R}$$

At60°C polystyreneor Acrylonitrilechainsterminate mainlybyrecombination.

d) Disproportionation:-

Transfer of 'H' atom from one radical to another leads to formation of two macro molecules, one of them with a double bond.

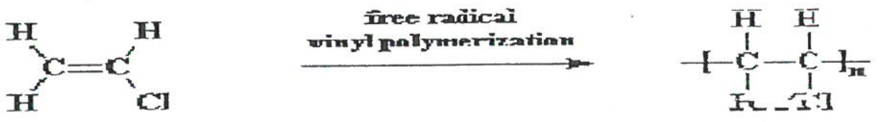


$$\mathrm{-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\bullet}}}}}} + \mathrm{\overset{H}{\overset{|}{\underset{X}{\underset{|}{C^{\bullet}}}}}-CH_2-} \longrightarrow \mathrm{-CH_2-\overset{H}{\overset{|}{\underset{X}{\underset{|}{C}}}}-H} + \mathrm{\overset{H}{\overset{|}{\underset{X}{\underset{|}{C}}}}=CH-}$$

9b) **Polyvinyl chloride:**

Preparation:

Polyvinylchlorideispreparedbyheatingawateremulsionofvinyl chloridein presenceofbenzyl peroxideorhydrogenperoxideinautoclaveunderpressure.



vinyl chloride

poly(vinyl chloride)

Properties: Polyvinyl chloride is

- Colourless
- Odourless
- Non-inflammable
- Chemicallyinert
- Solubleinhotethylchloride

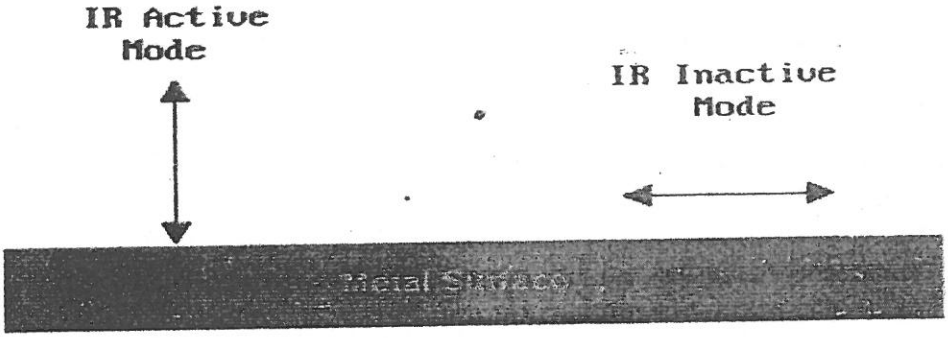
Uses: Used forthe preparation of

- Safetyhelmets
- Lightfittings
- Tyres,cycles
- Refrigeratorcomponents

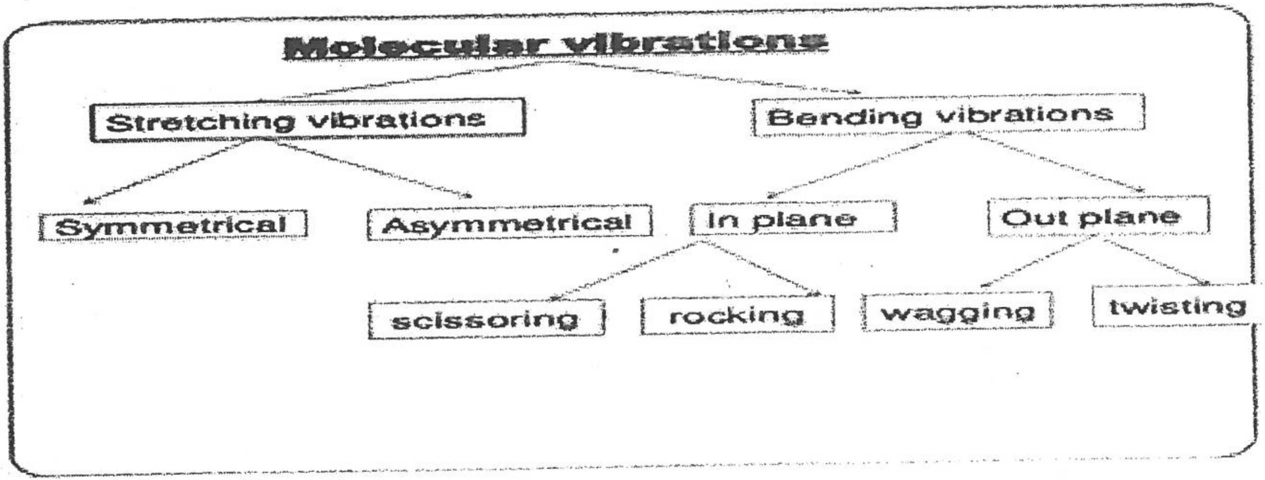
oa)

Fundamental modes of vibrations

- The observation of vibrational modes of adsorbates on metallic substrates is subject to the surface dipole selection rule.
- This states that only those vibrational modes which give rise to an oscillating dipole perpendicular (normal) to the surface are IR active and give rise to an observable absorption band.



Vibration Modes and Their Significance



Stretching vibrations:

- This involves the alternating compression and elongation of bond lengths.
- Here distance between two atoms increases or decreases but the atoms remain in same bond axis.
- Symmetrical molecules like O=C=O are not IR active because no change in dipole moment is observed upon stretching vibrations.

Stretching vibrations are of two types:

- a. Symmetrical stretching: When two bonds increase or decrease in length.
- b. Asymmetrical stretching: When one bond length increased, the other decreases.

Bending vibrations:

- This type results in a change of bond angles.

- However, not all molecular vibrations induce an absorption of IR radiation.
- For a vibration to be IR-active, it must cause a change in the molecule's dipole moment.
- Hence, symmetrical molecules like O2 show no IR absorption.
- Involve movement of atoms which are attached to a common central atom, such that there is change in bond axis & bond angle of each individual atom without change in their bond lengths.
- Bending vibrations requires less energy & occur at longer wavelength than stretching vibrations.
- Also called deformation vibrations.

Types of bending vibrations

- A. In plane vibrations

a) Scissoringb) Rocking

- B. Out plane vibrations

a) Waggingb) Twisting

A. In-plane vibration:

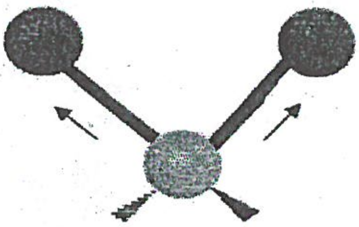
a) Rocking: In plane bending of atoms occurs wherein they swing back & froth with respect to the central atom.

b) Scissoring: 2 atoms connected to central atom move towards and away from each other

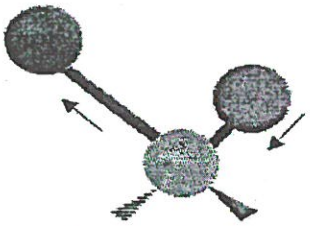
B. Out plane vibrations:

a) Wagging: two atoms oscillate up and below the plane with respect to the central atom.

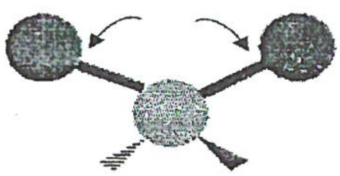
b) Twisting: one of atom moved up the plane while other down the plane with respect to central atom.



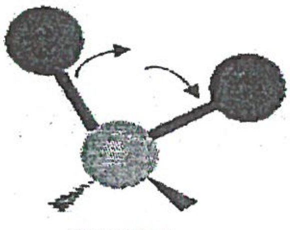
Symmetric stretching



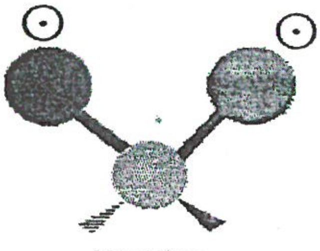
Antisymmetric stretching



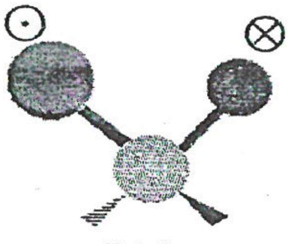
Scissoring



Rocking



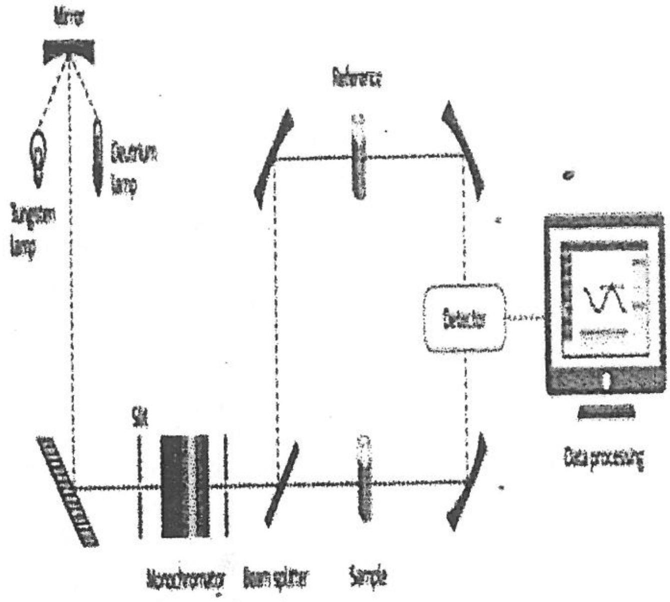
Wagging



Twisting

- U.V-Visible spectroscopy is absorption spectroscopy that deals with the recording of the absorption of electromagnetic radiation of the U.V and Visible regions of the electromagnetic spectrum.
- The U.V-region ranges from 200-400 nm whereas the visible region ranges from 400 to 800 nm.
- So, we can say that U.V-Visible spectroscopy utilises a 200-800 nm range for working.
- This technique is widely used for detecting the presence and elucidating the nature of the conjugated multiple bonds and aromatic rings.

Instrumentation of UV-Visible Spectroscopy



1.Radiation source

- Hydrogen-discharge lamp is the most commonly used source of radiation in the U.V region (200-400 nm) whereas a deuterium-discharge lamp is used when more intensity (3-5 times) is desired.
- A tungsten-filament lamp is used when absorption in the Visible region (400-800 nm) is to be determined.

2. Monochromator

- It helps to separate the radiations into separate wavelengths that are only allowed to pass a specific wavelength through it.
- Monochromators are generally made up of prism or grating which is made up of quartz.
- This is so because quartz does not absorb the radiations thus ensuring no loss of intensity and precise results.

3. Beam separator

- As the name suggests, beam separators help to separate the single radiation into two different paths/chambers : the reference chamber and the sample chamber.
- The former is called the reference beam and the latter is known as the sample beam.

4. Detectors
    - Detectors have photocells or photomultiplier tubes that generate a voltage proportional to the radiation energy that strikes them.
5. Amplifier
    - The spectrophotometer has a balancing electronic amplifier that subtracts the absorption of the solvent from that of the solution electronically.
6. Recorder
    - A recorder automatically records the spectrum as a plot of the wavelengths of absorbed radiations against absorbance (A) or molar absorptivity (e).

Working of U.V-Visible spectroscopy

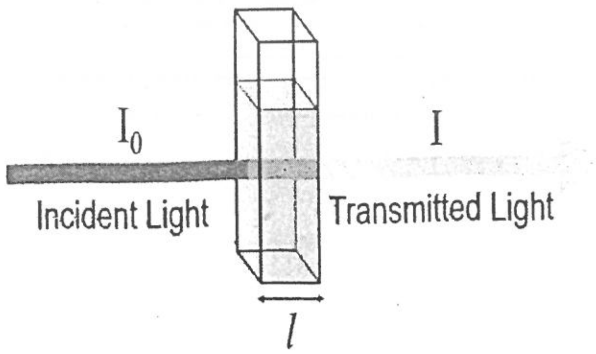
- When the U.V-Visible range electromagnetic radiation is emitted by the source, it passes through a monochromator which separates the electromagnetic radiations into separate radiations of different wavelengths.
- Then the desired wavelength electromagnetic radiation components are passed through a beam separator which divides the radiations into two chambers: a reference chamber containing a reference sample and sample chamber containing actual sample which is to be analysed.
- Then, the radiations penetrate both the samples, and some radiations are absorbed by the sample while some different wavelength is transmitted without any absorbance.
- These transmitted radiations fall on the amplifier which subtracts the absorption of the solvent from that of the solution.
- Then finally, the transmitted electromagnetic radiation falls on the detector then recorded by a recorder.
- The most important thing is that the U.V-Visible spectrometer does not plot the graph between the transmittance and wavelength instead it plots the graph between absorbance and the wavelength because it is easy for the expert to analyse the graph as it is linear and not inverted.
- This is done by taking the log value to transmitted light and incident light as stated by the beers-lambert law that is

$$A = \varepsilon c l$$

A	Absorbance	
ε	Molar absorption coefficient	$M^{-1}cm^{-1}$
c	Molar concentration	M
l	optical path length	cm

1/a)

Beer-Lambert Law



- **The Beer-Lambert Law (also called Beer's Law) is a relationship between the attenuation of light through a substance and the properties of that substance.**
- **In this article, the definitions of transmittance and absorbance of light by a substance are first introduced followed by an explanation of the Beer-Lambert Law.**

- The transmittance, T, of the solution is defined as the ratio of the transmitted intensity, I, over the incident intensity, I0 and takes values between 0 and 1.

Beer Lambert Law Equation: $T = \frac{I}{I_0}$

However, it is more commonly expressed as a percentage transmittance:

$$T(\%) = 100\frac{I}{I_0}$$

The absorbance, A, of the solution is related to the transmittance and incident and transmitted intensities through the following relations:

$$A = \log_{10}\frac{I_0}{I}$$
$$A = -\log_{10} T$$

- The absorbance has a logarithmic relationship to the transmittance; with an absorbance of 0 corresponding to a transmittance of 100% and an absorbance of 1 corresponding to 10% transmittance.
- Additional values of transmittance and absorbance pairings are given in Table 1.
- A visual demonstration of the effect that the absorbance of a solution has on the attenuation light passing through it is shown Figure 2, where a 510 nm laser is passed through three solutions of Rhodamine 6G with different absorbance.

Absorbance	Transmittance
0	100%
1	10%

The Beer-Lambert law is a linear relationship between the absorbance and the concentration, molar absorption coefficient and optical path length of a solution:

$$A = \varepsilon c l$$

A	Absorbance	
ε	Molar absorption coefficient	$M^{-1}cm^{-1}$
c	Molar concentration	M
l	optical path length	cm

Limitations of Beer-Lambert law

- The linearity of the Beer-Lambert law is limited by chemical and instrumental factors.

\# Causes of non-linearity of the law occur in the following conditions:

- deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- scattering of light due to particulates in the sample
- fluorescence or phosphorescence of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimised by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band

High Performance Liquid Chromatography

b)

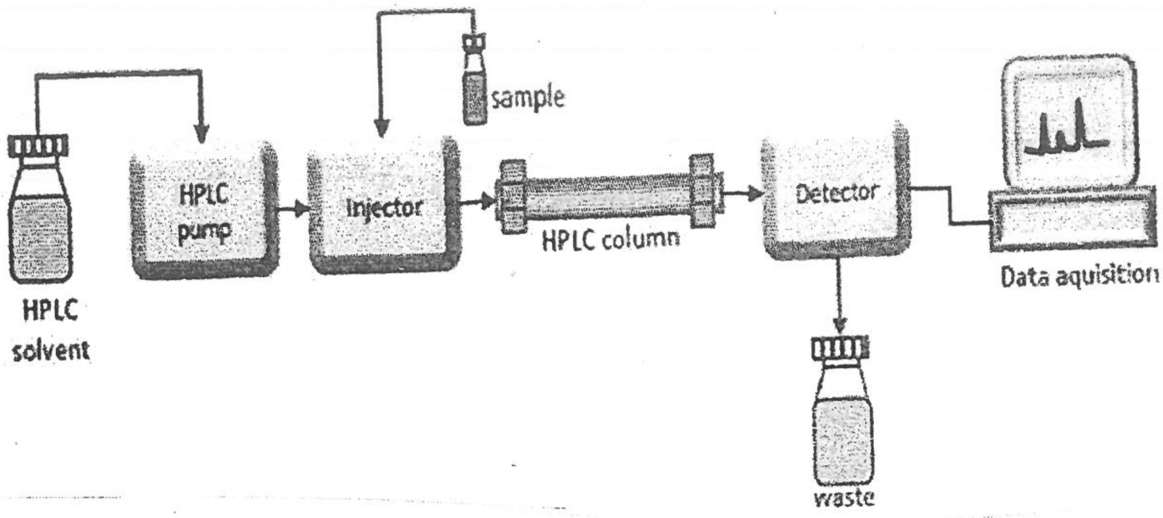
- HPLC stands for High Performance Liquid Chromatography.
- "Chromatography" is a separation technique, "chromatogram" is the chromatography result, and "chromatograph" is the chromatography

1b

b)

Principle of HPLC

- A separation column separates the stationary and mobile phases during purification.
- In a separation column, the stationary phase is a granular substance with very small porous particles.
- The mobile phase is a solvent or solvent combination that is pushed through the separation column under high pressure.
- The sample is loaded into the mobile flow regime from the pump to the separation column using a syringe through a valve with a linked sample loop, i.e. a tiny tube or capillary made of stainless steel.
- A chromatogram is generated in the HPLC software at the conclusion of this operation/run.
- The chromatogram allows the various compounds to be identified and quantified.
- As a result, owing to interactions with the stationary phase, the constituent components of a mixture migrate through the column at different speeds.
- Individual compounds are identified by an appropriate detector after exiting the column and transmitted as a signal to the computer's HPLC



Uses of HPLC

- Purification of water.
- Impurity detection in the pharmaceutical industry.
- Trace components are pre-concentrated.
- Chromatography based on ligand exchange.
- Protein chromatography via ion exchange.
- Carbohydrate and anion-exchange chromatography at high pH.
- Drug evaluation
- Synthetic polymer analysis
- Pollution analysis in environmental analytics
- Drug determination in biological matrices
- Isolation of high-value goods

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