ANNAMACHARYA UNIVERSITY::RAJAMPET
(ESTD UNDER AP PRIVATE UNIVERSITIES (ESTABLISHMENT AND REGULATION) ACT, 2016)
HUMANITES AND SCIENCES

CHEMISTRY
(24ACHE11T, 24ACHE21T)

I B.Tech. & I-Semester and II-Semester

Written by

Mrs. S. Reshma

Title of the Course:	Chemistry	
Category:	BS	
Semester:	I Semester	II Semester
Course Code:	24ACHE11T	24ACHE21T
Branch/es:	EEE, ECE, CSE(AI), AI&DS, CSE (ICB)	CSE, CSE(DS), CSE(AIML), AIML

Lecture Hours	Tutorial Hours	Practice Hours	Credits
3	-	-	3

Course Objectives: The course aims to familiarize students with the fundamentals of engineering chemistry and its practical applications. It provides training on key principles of electrochemistry and polymers, while also introducing students to various instrumental methods. Additionally, the course highlights the importance of green energy and e-waste management, emphasizing their relevance in modern engineering practices.

Course Outcomes:

At the end of the course, the student will be able to

1. discuss quantum mechanics and molecular orbital theory to interpret bonding, energy levels, and bond order in various molecules.
2. demonstrate the construction and functionality of various sensors, batteries, and fuel cells through practical examples.
3. summarize the preparation, characteristics, and applications of various polymers in real-world contexts.
4. utilize principles of various analytical techniques to evaluate nanomaterials effectively.
5. analyze sustainable energy solutions and develop strategies for effective e-waste management.

Unit 1 Structure and bonding models 9

Fundamentals of Quantum mechanics, Schrodinger wave equation, significance of Ψ and Ψ^2, 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 2 Electrochemistry and applications 8

Electrochemical cell, Nernst equation, cell potential calculations and numerical problems, types of electrodes - indictor and reference electrodes. Electrochemical sensors – potentiometric and amperometric sensors with examples.

Primary cells – Dry cell, secondary cells – Lithium-ion batteries - working of the batteries including cell reactions; Fuel cells, Hydrogen-Oxygen fuel cell – working of the cell.

Unit 3 Polymer chemistry 8

Introduction to polymers, functionality of monomers, Thermoplastics and Thermo-setting plastics, properties and applications of PVC and Bakelite.

Fibres - polyesters, mechanical requirements for fibres - crystallinity, stress strain curves. Biodegradable polymers - properties and applications of Poly Glycolic Acid (PGA), Polylactic Acid (PLA).

Elastomers – properties and applications of Buna-S, Buna-N, Thiokol.

Conducting polymers – Polyacetylene – mechanism of conduction and applications.

Unit 4 Nanomaterials and instrumental methods 9

Nanomaterials - Introduction, classification, synthesis of nanomaterial by Sol-gel method, properties and applications of carbon-based nanomaterials - CNT and Graphene.

Electromagnetic spectrum, absorption of radiation: Beer-Lambert's law. UV-Visible spectroscopy, principle, instrumentation and applications, IR spectroscopy – principle, instrumentation and applications, Potentiometry - potentiometric titrations (redox titrations), Conductometric titrations (acid-base titrations).

Unit 5 Alternative energy sources and e-waste management 8

Green Fuels: Introduction, construction and working of photovoltaic cell, applications, generation of green hydrogen energy by electrolysis of water and its advantages.

e-waste management: Introduction, sources of e-waste, composition and health hazards of toxic materials present in electronic and electrical e-waste, need for e-waste management, recycling and recovery; different approaches of recycling, extraction of Gold from e-Waste.

Prescribed Textbooks:

1. Jain, Jain. *Engineering Chemistry*. 16th Ed., Dhanpat Rai, 2013.
2. Atkins, Peter, Julio de Paula, and James Keeler. *Atkins' Physical Chemistry*. 10th Ed., Oxford University Press, 2010.
3. Jing, Dengwei. *Handbook of Hydrogen Energy*. 1st Ed., Wiley-VCH, 2023.
4. Fowler, Bruce A. *Electronic Waste: Toxicology and Public Health Issues*. 1st Ed., Academic Press, 2017.

Reference Books:

1. Skoog, Douglas A., F. James Holler, Stanley R. Crouch. *Principles of Instrumental Analysis*. 7th ed., Cengage Learning, 2016.
2. Lee, J.D. *Concise Inorganic Chemistry*. 5th ed., Wiley-Blackwell, 1999.
3. Billmayer, Fred W. Jr. *Textbook of Polymer Science*. 3rd ed., Wiley, 2007.
4. Sherif, S.A., D. Yogi Goswami, E.K. Stefanakos, A. Steinfeld. *Handbook of Hydrogen Energy*. CRC Press, 2014.

CO-PO Mapping:

Course outcomes	Engineering Knowledge	Problem Analysis	Design/Development of solutions	Conduct investigations of complex problems	Engineering tool usage	The engineer and the world	Ethics	Individual and collaborative teamwork	Communication	Project management and finance	Life-long learning
24ACHE11T/21T.1	2	2	1	1	-	-	-	-	-	-	1
24ACHE11T/21T.2	3	2	1	2	-	-	-	-	-	-	1
24ACHE11T/21T.3	3	2	1	2	-	-	-	-	-	-	1
24ACHE11T/21T.4	3	2	1	2	-	-	-	-	-	-	1
24ACHE11T/21T.5	3	3	2	2	-	-	-	-	-	-	1

UNIT-I

STRUCTURE AND BONDING MODELS

Fundamentals of Quantum mechanics, Schrodinger wave equation, Significance of ψ & ψ^2, particle in one-dimensional box, molecular orbital theory - bonding in homo & heteronuclear diatomic - molecules - energy level diagrams of O_2 & CO, etc. π- molecular orbitals of butadiene & benzene, calculation of bond-order.

① Fundamentals of Quantum mechanics:-

It is a fundamental theory in chemistry that describes the behavior of Matter & energy of the atomic & Subatomic particle.

Black Body Radiation:-

An ideal body which can emit & 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 black body is heated, it emits thermal radiation of different wavelengths (or) frequency

To explain these radiations, max planck's put forward a theory known as planck's Quantum theory.

The main points of Quantum theory:

- The emission & absorption of the energy by an atom occurs in the form of radiation & it is in continous process.
- The emission and absorption of the energy by a body occurs in the form of pockets of energy is called Quanta (or) photons.

$$\boxed{E = h\nu}$$

Where ν = frequency of radiation

h = planck's Quantum constant

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

* A body can radiate (or) absorb energy in whole Number multiples of a quantum $h\nu$, $2h\nu$, $3h\nu$, $nh\nu$.

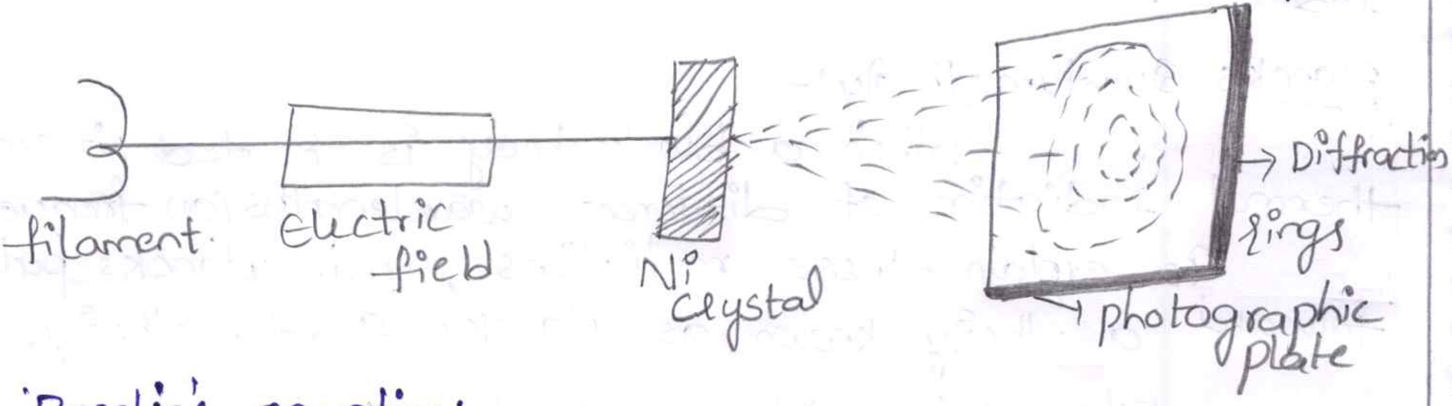
$\therefore \boxed{\nu = \frac{c}{\lambda}}$, $\epsilon = nhc/\lambda$

Dual nature of an electron:-

In case of light some phenomenon like diffraction & interference can be explained on the basis of its wave character.

However, the other phenomenon such as black body radiation & photoelectric effect can be explained by only on the basis of its particle nature. Thus, light is said to have a ~~black~~ dual character. Such studies are only made by Einstein in 1905.

Louis de-Broglie in 1924 extended the idea of photons to material particles such as electron & he proposed that matter also have a dual character as wave & as particle.



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 & its energy is given by

$\boxed{E = h\nu} \rightarrow ①$

ν = frequency

h = planck's constant.

According to Ginstein's Law of mass energy, equivalence. If the photon is supplied to have particle nature. its energy is given by

$$\boxed{E = mc^2} \rightarrow ②$$

Where m = mass of photon
C = velocity of Light

from ① & ② we get

$$h\nu = mc^2$$

But $\nu = c/\lambda$, $hc/\lambda = mc^2$

$$\boxed{\lambda = h/mc}$$

The above eq is applicable to material particle, if the mass & velocity of photon is replaced by the mass & momentum of material particle.

Thus for any material particle like electron

$$\boxed{\lambda = h/mv} \text{ (or) } \boxed{\lambda = h/p} \left(\because \text{mass} \times \text{velocity} = \text{momentum}\right)$$

Where p is the momentum of the particle.

Heisenberg's Uncertainity principle:-

Heisenberg's uncertainity principle states that for particles exhibiting both particle & wave nature it will not be possible to accurately determine both the position & velocity at the same time.

Note: "If an electron is exhibiting dual nature (Wave & particle) it is possible to know the exact position of the e⁻ in space at same given Instant".

Mathematically it can be written as

$$\boxed{\Delta p \times \Delta x \geq h/4\pi}$$

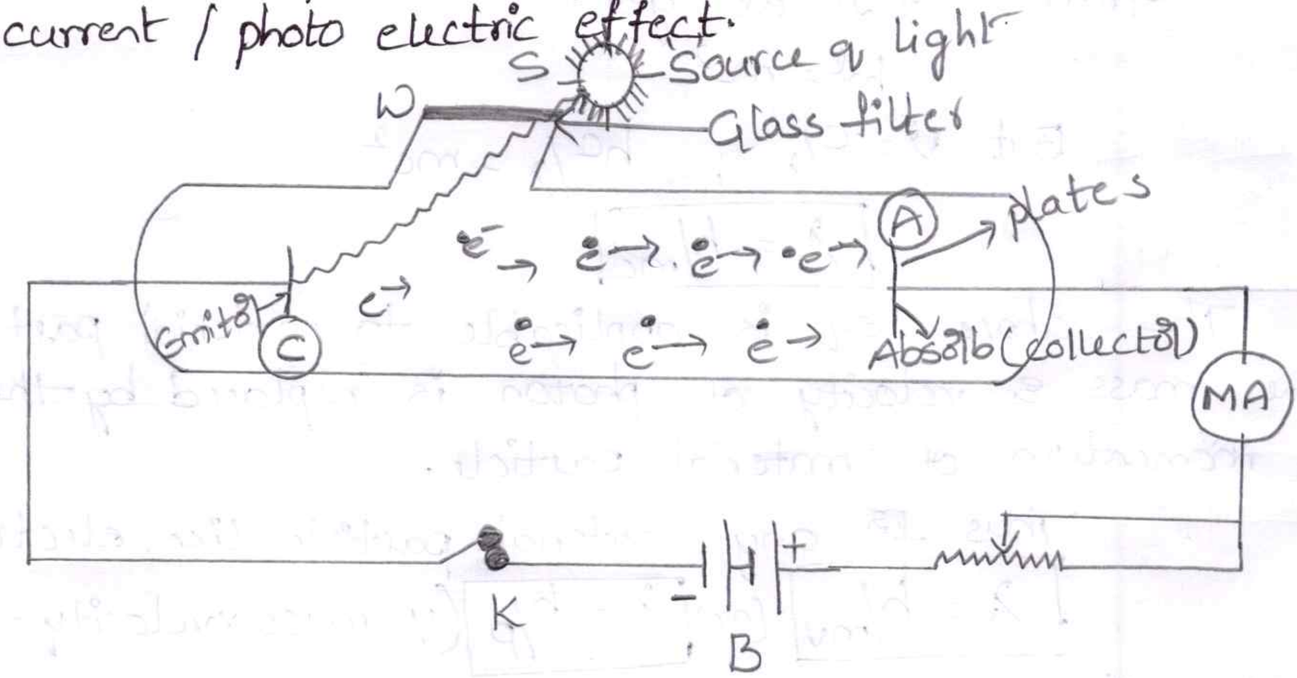
Where Δp is the uncertainity determination of the momentum
Δx is the uncertainity determination of the position.

photo Electric Effect:-

The phenomenon of conveting Light energy into electrical energy is called photoelectric effect.

* The electron elected by photoelectric effect is called photo electron.

* The current produced by photoelectric effect is called photocurrent / photo electric effect.



Construction:-

(1) The experimental set up for the study of photoelectric effect is as shown in fig.

(2) `C' is a photosensitive plate which is called "emitter" & `A' is a metal plate is called collector.

3) A transparent window `w' is sealed on glass tube which can be converted with a filter for light of particular radiation. This will allow the light of particular wavelength to pass through it.

4) The plate `A' can be given desired ~~plates~~ positive (or) Negative potential with respect to plate `c' using the arrangement of battery & a micro ammeter is converted to measure the photo current in the circuit.

Working:-

When a monochromatic radiation of suitable frequency obtain from the source 's' of ka being filtered by filter fall on photosensitive plate 'c' & photo electrons are emitted from 'c' which can get accelerated towards the plate 'A'. The e's flow in the outer circuit & hence micro ammeter shows deflection.

Postulates of Quantum Mechanics:-

postulate - 1 (Wave function):-

Any dynamical physical state of a system is described as completely as possible by a wave-function (or state function), ψ which is a function of all the spatial co-ordinates & time.

$$\boxed{\psi = \psi(x,y,z,t)}$$

postulate - 2 (Time variability):-

For every system, the possible wave-functions $\psi(x,y,z,t)$ are obtained by solving the time-dependent schrodinger wave equation.

$$\left[\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)+V\,x,y,z,t\right]\psi = \frac{-\hbar}{i}\frac{d\psi}{dt}$$

Postulate - 3 (probability integration)

For the wave function $\psi(x,y,z,t)$ to be acceptable as a function representing the properties of a system, it must be continous, finite & single valued & must be quadratically integrable.

$$\boxed{\int_{-\infty}^{+\infty}\psi^*\psi\, d\tau = 1}$$

postulate-4: (observable & operator postulate)

To every observable in classical mechanics, there corresponds a linear Hermition operator in quantum mechanics

observable → experimentally measurable dynamical variable

variable	operator	Expression.
position(x)	$\hat{x}$	x
Momentum (p_x, p_y, p_z)	$\hat{p}_x, \hat{p}_y, \hat{p}_z$	$-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}$
Kinetic Energy	$\hat{T}_x$ (or) $\hat{E}_K$	$\frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

Postulates-5 (Eigen-value postulate)

The only values that can result from the measurement of an observable $\hat{A}$ will be the eigen values (a_i) satisfying the eigen value equation.

$$\boxed{\hat{A}\psi_i = a_i\psi_i}$$

postulate-6:-

The average value or expectation value of any observable which corresponds to an operator, when a large number of Measurements are involved is given by

$$\boxed{\langle A\rangle = \frac{\int\psi^*\hat{A}\psi\, d\tau}{\int\psi^*\psi\, d\tau}}$$

② Schrodinger Wave equation:-

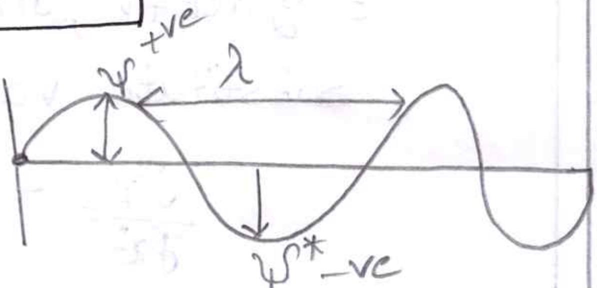
Erwin Schrodinger, in 1926 gave a wave equation to describe the behaviour of electron waves in atoms & molecules.

In Schrodinger wave model of an atom, the discrete energy levels or orbit proposed by Bohr are replaced by mathematical functions 'ψ' which are related to the probabilit of finding electrons at a various places around the nucleus.

Schrodinger derived an equation based on De-Broglie dual behaviour of electron & Heisenberg uncertainity principle.

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

Derivation:



The equation for a standing 'sin' wave of wavelength 'λ' is given by

$$\psi = A\sin\frac{2\pi}{\lambda}x \rightarrow ①$$

Where ψ = wave-function (Amplitude of the wave varying simutaniously along x)

A = maximum Amplitude.

Double differentiating eq ① with respect to 'x'

$$\frac{d\psi}{dx} = A\frac{2\pi}{\lambda}\cdot\cos\frac{2\pi}{\lambda}x$$

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

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2}\psi \rightarrow ② \left[\because \psi = A\sin\frac{2\pi}{\lambda}x\right]$$

According to de-Broglie relationship

$$\lambda = \frac{h}{mu} \text{ (or) } \lambda^2 = \frac{h^2}{m^2u^2} \rightarrow ③$$

Sub the value λ^2 of eq-②

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

The Kinetic energy of a moving particle of mass 'm' & velocity "u" is given by $K.E = \frac{1}{2}mu^2 \rightarrow ⑤$

Total Energy of a moving particle is given by

$$E = K.E + P.E \quad (\because \text{Where } V = \text{potential Energy})$$

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

$$E = \frac{1}{2}mu^2 + V \text{ (or) } mu^2 = 2(E-V) \text{ (or) } m^2u^2 = 2m(E-V) \rightarrow ⑥$$

Substitute value of m^2u^2 from eq ⑥ in eq ④.

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2 . 2m(E-V)}{h^2}\psi$$

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

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

eq ⑦ is called schrödinger equation (time dependent) for a particle in one dimension

for three dimensions schrodinger equation is

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

Where ψ = Wave function

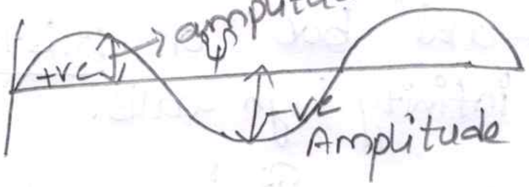
m = mass of electron

E = Total Energy
V = P.E with reference to nucleus.
h = planck's constant.

③ Significance of ψ & ψ^2 :-

(1) In schrodinger wave equation 'ψ', represent the wave function & refers to the amplitude of electron wave i.e, probability amplitude.

(2) It has no physical significance. The wave function may be +ve, −ve or Imaginary.



(3) ψ is a wave function that contains all the information about the electron

In water waves ⟶ height of water surface
In sound wave ⟶ pressure
In electromagnetic wave ⟶ Electric & Magnetic field
In matter wave ⟶ Wave function.

(4) ψ^2 is a probability density & determine the probability of finding an e^- at given point at given time within the atom. It means that

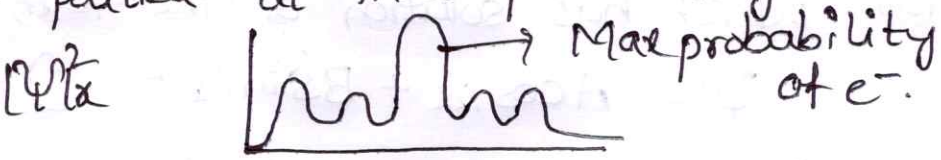
The wave function is in itself complex i.e,

$\psi = A + iB$ & its conjugate is $\psi^* = A - iB$

$$\psi\psi^* = |\psi|^2 = (A+iB)(A-iB)$$

$$\boxed{|\psi^2| = A^2 + B^2}$$ Real quantity.

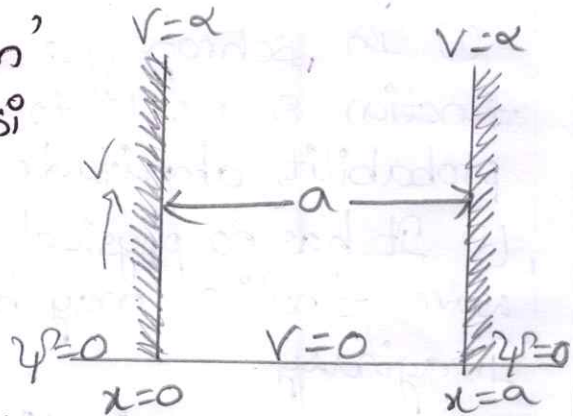
(5) A large value of ψ^2 means strong probability of finding the particle at that point of given time



(6) If $|\psi|^2$ is zero the probability of finding an electron at that point is negligible.

7) probability is always positive, hence ψ^2 is always +ve.

(4) Particle in One-dimensional Box:-



Consider a particle of mass 'm' is confined to move in a one dimensional box of width 'a', having the infinity high walls.

It is assumed, for the sake of simplicity, that the potential energy of the particle is zero anywhere inside the box, that is

$$V(x) = 0 \rightarrow ①$$

The schrodinger equation for one dimensional is

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

Thus inside the box the schrodinger equation

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

(or) $$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \rightarrow ③$$

Where K^2 is constant, independent of x

$$K^2 = \frac{8\pi^2 ME}{h^2} \rightarrow ④$$

Equation ③ is an ordinary second order differential equation which has solution of the form

$$\psi = A\cos Kx + B\sin Kx \rightarrow ⑤$$

Where A & B are constants.

- Outside the box, where $V(x)=\alpha$; the schrodinger eq is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-\alpha)\psi = 0 \rightarrow \textcircled{6}$$

The above eq ⑥ satisfied if ψ is zero everywhere outside the box. This is another way of saying that the particle cannot be fand outside the box, it is confined with in the box. This implies that ψ must be zero at the walls of the box, i.e at $x=0$ & at $x=a$.

Apply the bondary conditions to the solution equatio

Condition-1: At $x=0$, $\psi=0$

In Eq ⑤ $\psi = A\cos kx + B\sin kx$ $(\because \sin 0 = 0,\ \cos 0 = 1)$

$$0 = A\cos k0 + B\sin k0$$

$$0 = A + 0$$

$$\boxed{A=0}$$

Condition-2: At $x=a$, $\psi=0$

Eq ⑤ $\psi = A\cos kx + B\sin kx$

$$0 = 0 + B\sin ka$$

But since $B \neq 0$ $\qquad [\because \sin n\pi = 0]$

$$\sin ka = 0$$

$$\sin ka = \sin n\pi$$

$$ka = n\pi$$

$$k = \frac{n\pi}{a} \rightarrow \textcircled{7}$$

Squaring on both side to eq ⑦ changes to

$$k^2 = \frac{n^2\pi^2}{a^2}$$

Compare eq ④ & ⑦ the 'k^2' values

$$\frac{8\cancel{\pi^2} mE}{h^2} = \frac{n^2\cancel{\pi^2}}{a^2}$$

$$\boxed{E = E_n = \frac{n^2h^2}{8ma^2}} \rightarrow \textcircled{8}$$

E = Energy of the electron/particle
h = planck's constant
m = mass of electron/photon

In any atom which is regarded as a type of potential box there are several energy levels corresponding

$n = 1, 2, 3 ----$

Where $n=1$ $E_1 = \frac{h^2}{8ma^2}$

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

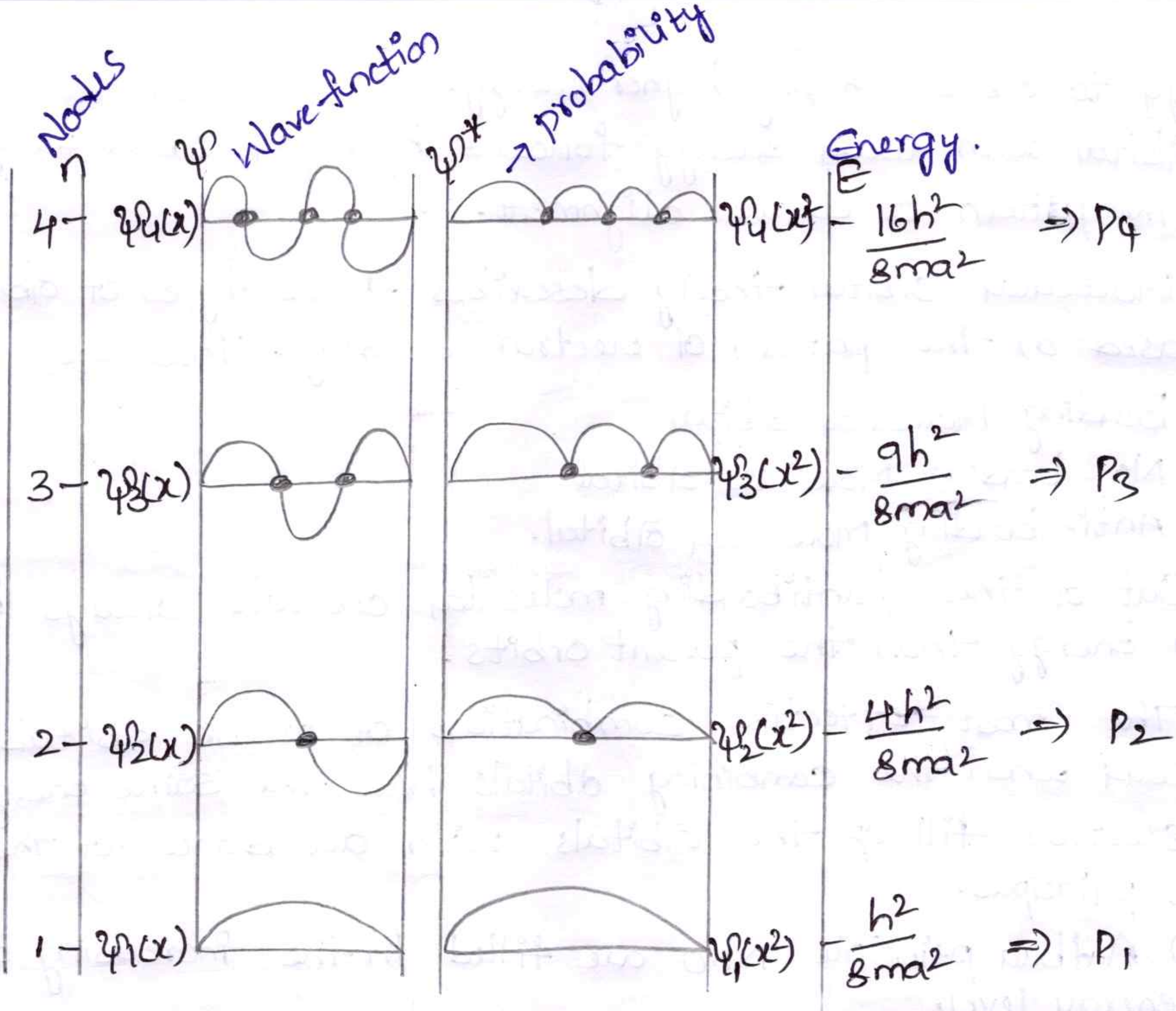
$n=3$ $E_3 = \frac{9h^2}{8ma^2}$

$E_2 - E_1 = \frac{3h^2}{8ma^2}$; $E_3 - E_2 = \frac{5h^2}{8ma^2}$ ------

This suggest that difference between consective energy levels is not constant.

- This energy levels, wave function (a), probability densities (P/ψ^2) for the particle in one dimensional box are given in fig.
- 'n' is the typical quantum number, which represents the nodes in the electron waves. As 'n' increases, the number of nodes varies in the following manners

$n=1$, no node
$n=2$ 1 node
$n=3$ 2 node
$n=4$ 3 node ---
⋮ ⋮



(5) MOLECULAR ORBITAL THEORY:-

The molecular orbital theory states that every atom tends to combine in order to form molecular orbitals. As a result of this arrangement, the electrons are found in different atomic orbitals and they are usually associated with different nuclei. Hence, in a molecule an electron can be present anywhere.

Postulates of Molecular orbital theory:-

(1) The total number of molecular orbitals formed is equal to the total No. of atomic orbitals offered by atomic Species.

(2) The electrons in the molecular orbital are filled in the increasing order of orbital energy (from orbital having lower

energy to orbital having higher energy.

(3) orbital with lower energy followed by higher orbital energy is the pattern of electron alignment.

(4) Molecular orbital theory describes three types of orbital based on the pattern of electron bonding - These are
Bonding Molecular orbital
Non-bonding Molecular orbital
Anti-bonding Molecular orbital.

(5) Out of these, antibonding molecular orbitals always have high energy than the parent orbits.

(6) The most effective combinations of atomic orbitals occur when the combining orbitals have the same energies

(7) electron fill up the orbitals with accordance of the 3 principles.

(a) Aufbau principle M.O are filled in the increasing order of energy level.

(b) pauli's exclusion principle: No two electrons can have the same set of four quantum numbers in an atom or a molecule.

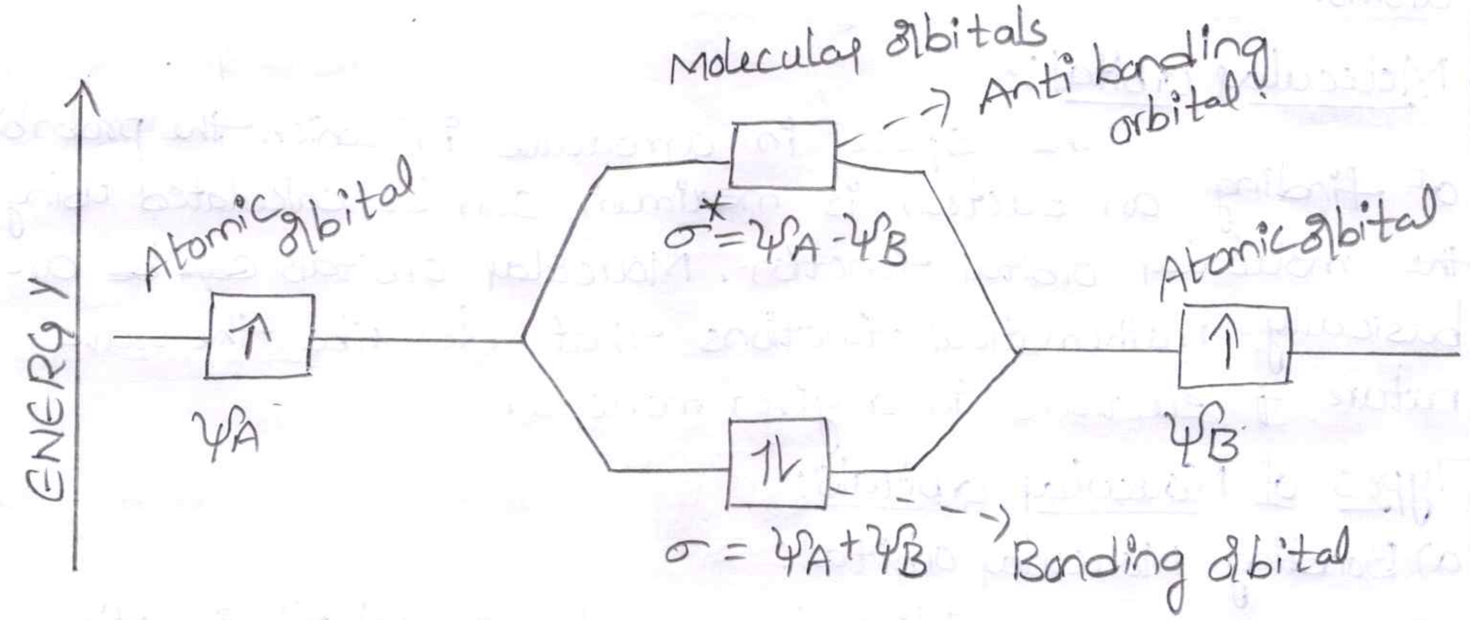
(c) Hund's rule of maximum multiplicity: pairing of electrons doesn't take place until all the atomic (or) molecular orbitals are singly occupied.

(8) If a molecule contains one or more unpaired electrons It is paramagnetic in nature, otherwise diamagnetic nature.

Linear Combination of Atomic orbitals (LCAO):-

Molecular orbital theory is expressed through a linear combination of Atomic orbitals (LCAO), These LCAO's are useful to estimate the formation of these orbitals are bonding b/w the two atoms of a molecule.

The schrodinger equation that is based to describe the behaviour of electrons for the molecular orbitals can be written in a method as the atomic orbitals.



Conditions for LCAO method:-

Three main conditions for linear combination of atomic orbitals (LCAO)

1) Same Energy of combining orbitals:-

The combining atomic orbitals must have the same or approximately the same energy.

This means that the 2p orbital of an atom can combine with another 2p orbital of another atom only. but not with 1s & 2s.

2) Same Symmetry about molecular axis:-

The combining atoms should have the same symmetry around the molecular axis for proper combination.

Eg:- The sub-orbitals of 2p have the same energy but still, the $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom. It cannot combine with $2p_x$ & $2p_y$ because they have diff symmetry

(3) proper overlapping between atomic orbitals:-

The two atomic orbitals will combine to form a molecular orbital only if the overlap is proper the greater the extent of overlap of orbitals, the greater will be the nuclear density between the nuclei of the two atoms.

Molecular Orbital:-

The space in a molecule in which the probability of finding an electron is maximum can be calculated using the molecular orbital function. Molecular orbitals ~~can be~~ are basically mathematical functions that describe the wave nature of electrons in a given molecule.

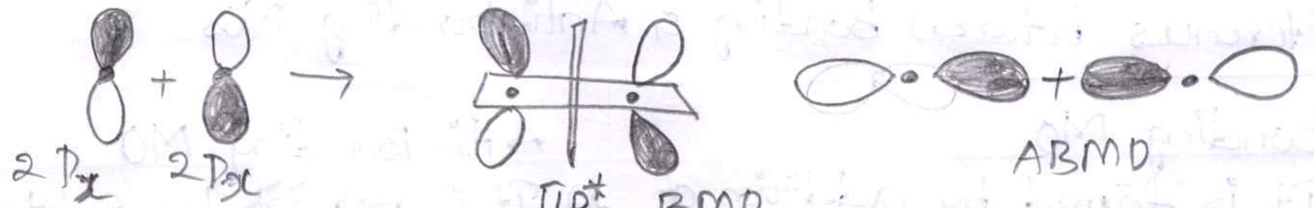
Types of Molecular orbitals:

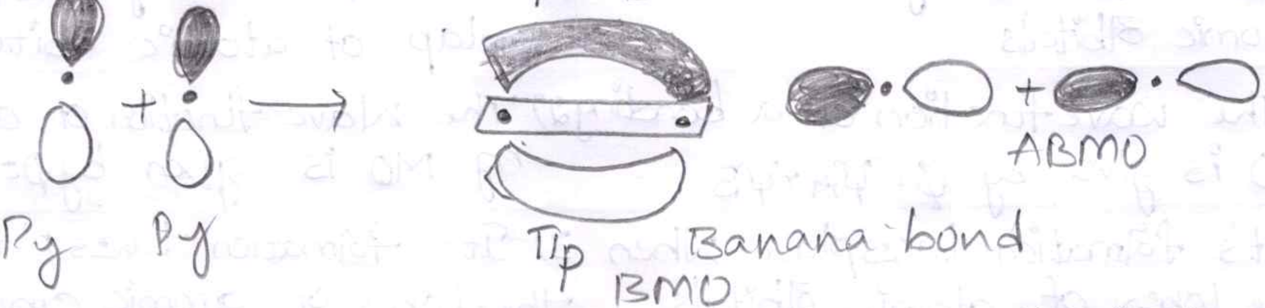
a) Bonding Molecular orbital:

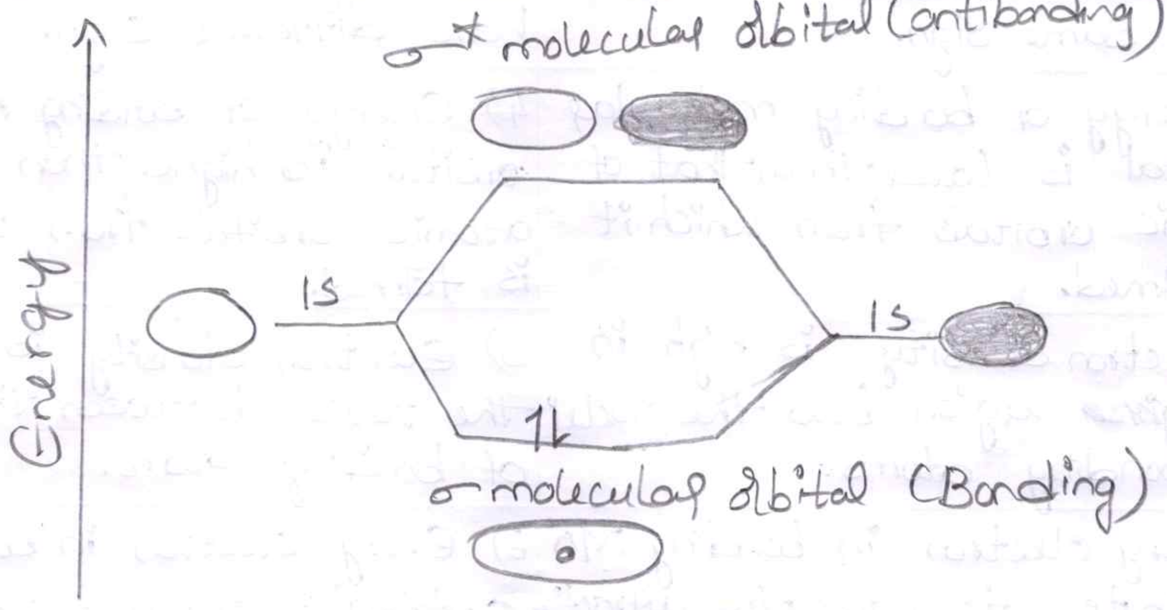
According to molecular orbital theory, the molecular orbital which is formed by the addition of overlapping of atomic orbital is called Bonding molecular orbital. This is because the electrons in the orbital are attracted by the nuclei.

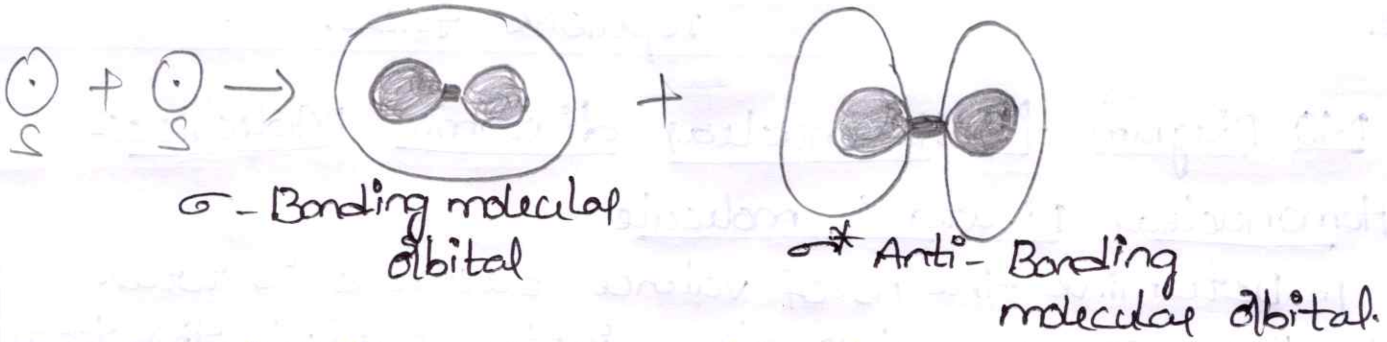
b) Anti-Bonding Molecular orbitals:

In the anti-bonding molecular orbitals, the density of electron is concentrated behind the nuclei of two-atoms. This means that two atoms are being pulled away from each other. Hence it results in the weakening of the bond between them.









c) Non-bonding Molecular orbital:-

Due to the lack of symmetry in two bonding atomic orbitals, the molecular orbital formed from their interaction has no negative or positive interactions with each other. This doesn't affect the bond between them.

Differences between Bonding & Anti-bonding MOs

Bonding MO	Anti-Bonding MO
1) It is formed by addition of atomic orbitals	1) It is formed by Subtraction overlap of atomic orbitals.
2) The wave function of a bonding MO is given by $\phi = \psi_A + \psi_B$	2) The wave function of anti-bonding MO is given by $\phi = \psi_A - \psi_B$
3) It's formation takes place when the lobes of atomic orbitals have same sign.	3) It's formation takes place when the lobes of atomic orbitals have different sign.
4) Energy of bonding molecular orbital is lower than that of atomic orbitals from which it is formed.	4) Energy of bonding molecular orbital is higher than that of atomic orbitals from which it is formed.
5) Electron density is high in the ~~given~~ region b/w the nuclei of bonding atoms.	5) Electron density is low in the region between the nuclei of bonding atoms.
6) Every electron in bonding MO contributes towards the attractive force.	6) Every electron in bonding MO contributes towards the repulsive forces.

⑥ MO Diagram for Homonuclear diatomic Molecules:-

Homonuclear Di-atomic molecule:-

1. Determine the no. of valence electrons is total. Since there are now two atoms in the molecule, the total no. of valence electron is double that of the atomic species.
2. Determine the number of e's in each s & p orbital
3. Fill in the electrons in the correct MO diagram's molecular orbitals

4) All the orbital filling principles (Hund's Rule, Pauli Exclusion principle, Aufbau principle) still apply when filling in molecular orbitals.

i) The pauli Exclusion principle states that each molecular orbital can hold two electrons

ii) The Aufbau principle states that electrons will always fill orbitals from bottom to top.

iii) Hund's Rule states that orbitals on the same energy Level fill singly before doubly. This applies primarily to the π & π^* orbitals, where one electron will enter into each orbital before filling in the second.

5) predict the molecule's properties using the diagram. For example, bond order, bond angle, paramagnetism etc.

MO Diagram of O_2 molecule is:-

1) Oxygen (O_2) molecule has 16 e^-s

2) Oxygen atom has electronic configuration

$$O_8 = 1s^2\,2s^2\,2p^4 \text{ (or) } 1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$$

3) Complete O_2 molecule has 16 e^-s.

4) The MO electronic configuration of O_2 is

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < [\pi 2p_x^2 = \pi 2p_y]^2 <$$
$$[\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z^0$$

5) Bond order: It may be defined as the half of difference between the No. of e^-s present in bonding orbitals & No. of e^-s present in the anti-bonding orbitals.

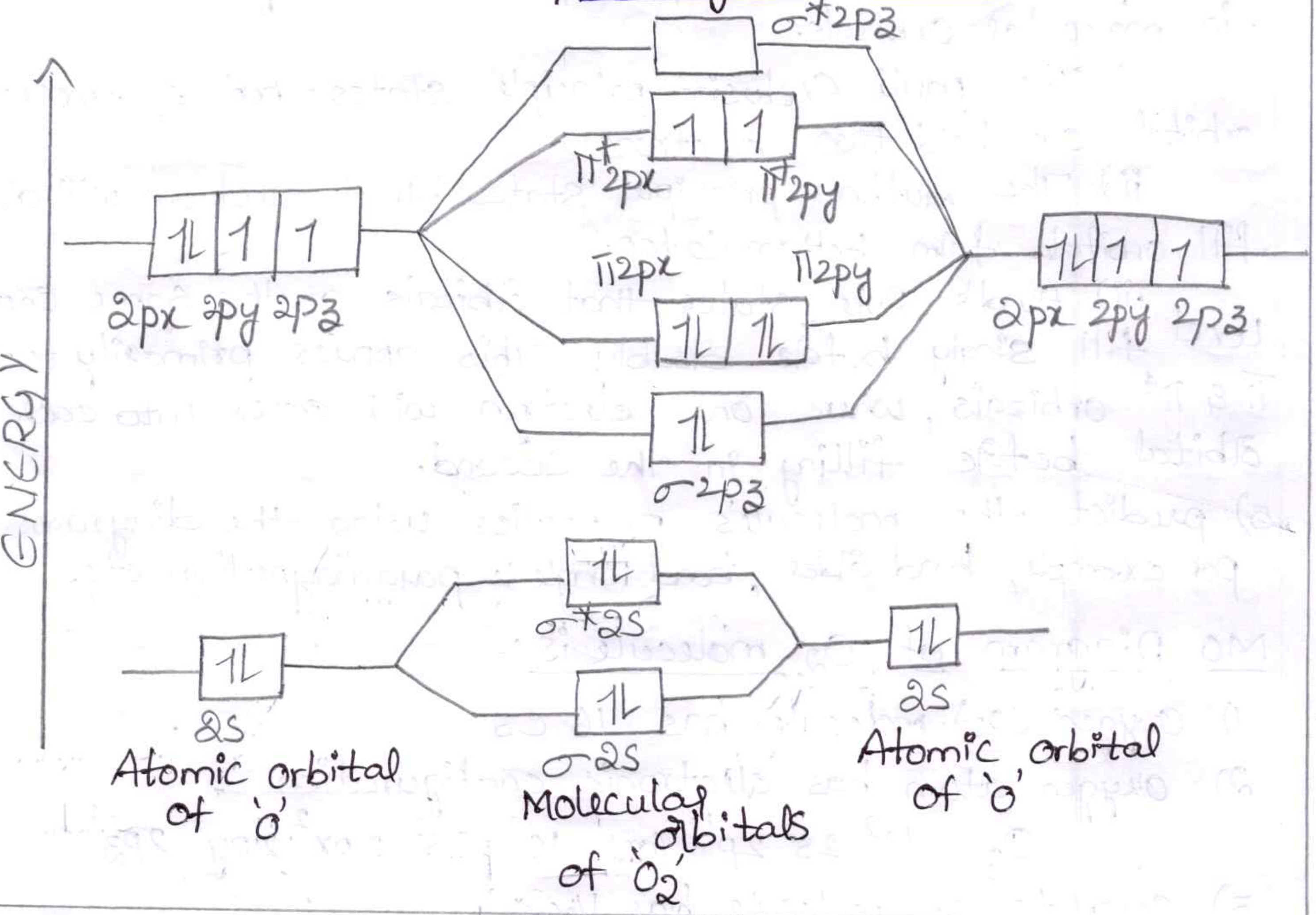
B.O O_2 :

$$B.O = \frac{\text{No. of Bonding orbitals} - \text{No. of Antibonding orbitals}}{2}$$

$$= \frac{10-6}{2} = 4/2 = 2$$

$$O_2 = \boxed{O=O}$$

6) Due to the presence of unpaired electrons in the O_2 molecule it exhibits in "paramagnetic nature."



Note:- In diatomic molecules 'O_2' through Ne_2, ($\sigma2pz$) is at lower level than [($\pi2px = \pi2py$)]

⑦ Molecular orbital Energy level diagram of 'CO' molecule:

1) 'CO': carbon monoxide is formed from the combination of one carbon atom & O-atom. The outershell E.C of the carbon atom is ($2s^2, 2p^2$) & O-atom ($2s^2 2p^4$).

2) 'C' contains 4 e's, & 'O' atom contains 6 es in the outermost shell.

3) 'C' Electronic configuration : $1s^2 2s^2 2px^1 2py^1 2pz^0$
'O' Electronic configuration : $1s^2 2s^2 2px^2 2py^1 2pz^1$

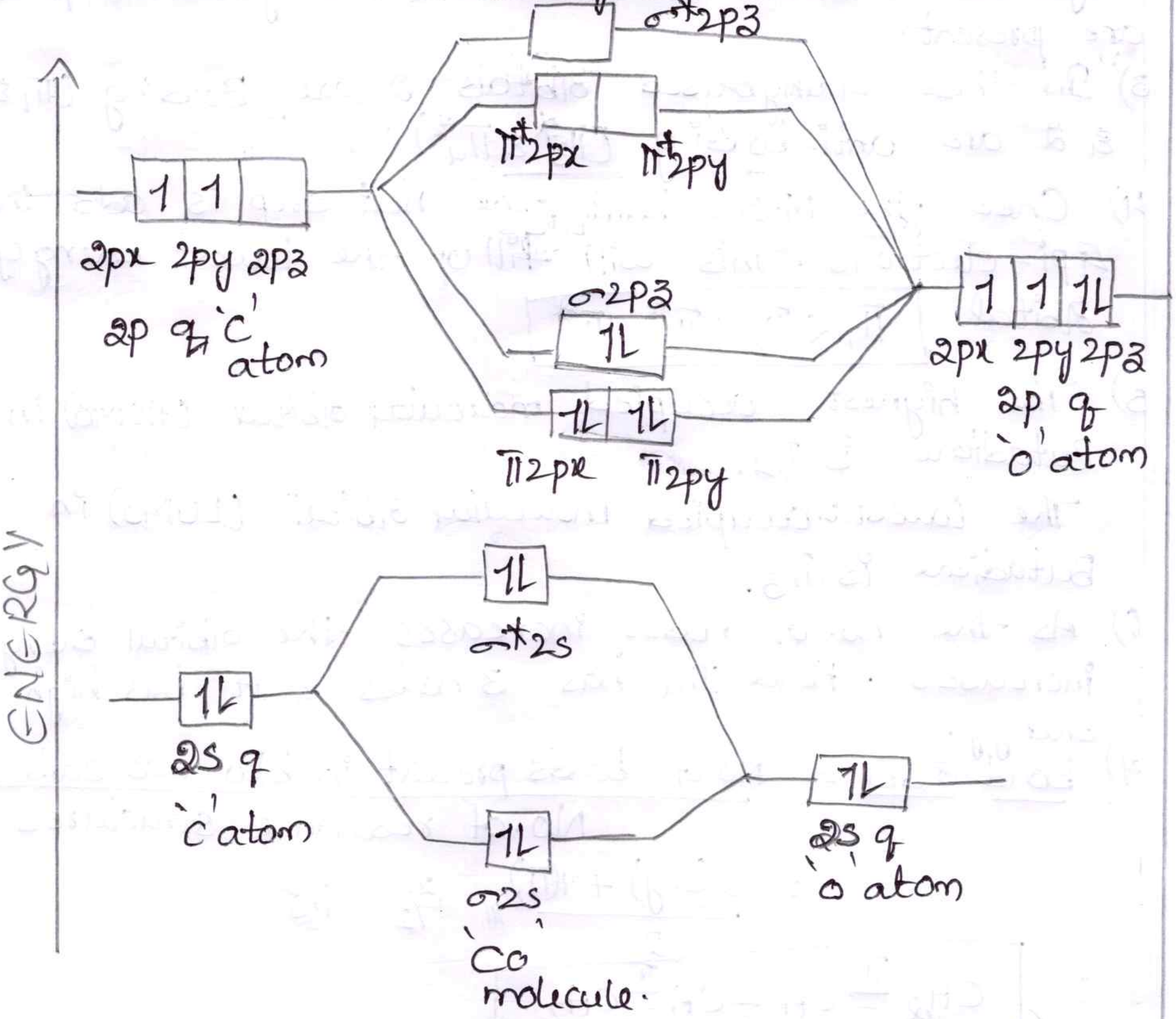
4) M.O electronic configuration of 'CO' is
$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ (\pi 2p_x^2 = \pi 2p_y^2)\ \sigma 2p_z^2\ \pi^* 2p_x^0 = \pi^* 2p_y^0$
$\sigma^* 2p_z^0$

5) Bond of 'CO': $B.O = \frac{\text{No.of Bonding orbitals} - \text{No.of Anti-bonding orbitals}}{2}$

$= \frac{10-4}{2} = 6/2 = 3$

$\boxed{C \equiv O}$

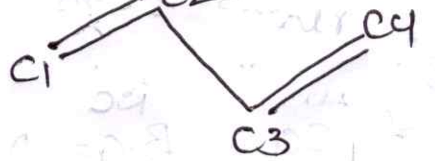
6) Since, 'CO' molecule does not have any unpaired electrons. Thus 'CO' molecule is "diamagnetic nature".



⑧ π- Molecular orbital of Butadiene:-

$CH_2 \overset{\pi}{\underset{\sigma}{=}} CH-CH \overset{\pi}{\underset{\sigma}{=}} CH_2$

1,3 butadiene



1) In Butadiene is a conjugated diene consisting of two adjacent pi-bonds & comprised of 4-pi orbitals & 4pi electrons.

2) Each carbon atom is sp^2 hybridised. Each of these carbon atom, 1 have the unhybrised p-orbital (p3) & having the single e^-. Thus in 1,3 butadiene, 4 unhybridised p-orbitals are present.

3) In these 4 unhybrised orbitals 2 are Bonding (π_1 & π_2) & 2 are anti-bonding (π_3^* & π_4^*)

4) Once the M.O.D built, the next step is add the 4pi-electrons. This will fill up the lowest energy orbital $\boxed{\pi_1 < \pi_2 < \pi_3^* < \pi_4^*}$

5) The highest occupied molecular orbital (HOMO) in Butadiene is π_2.

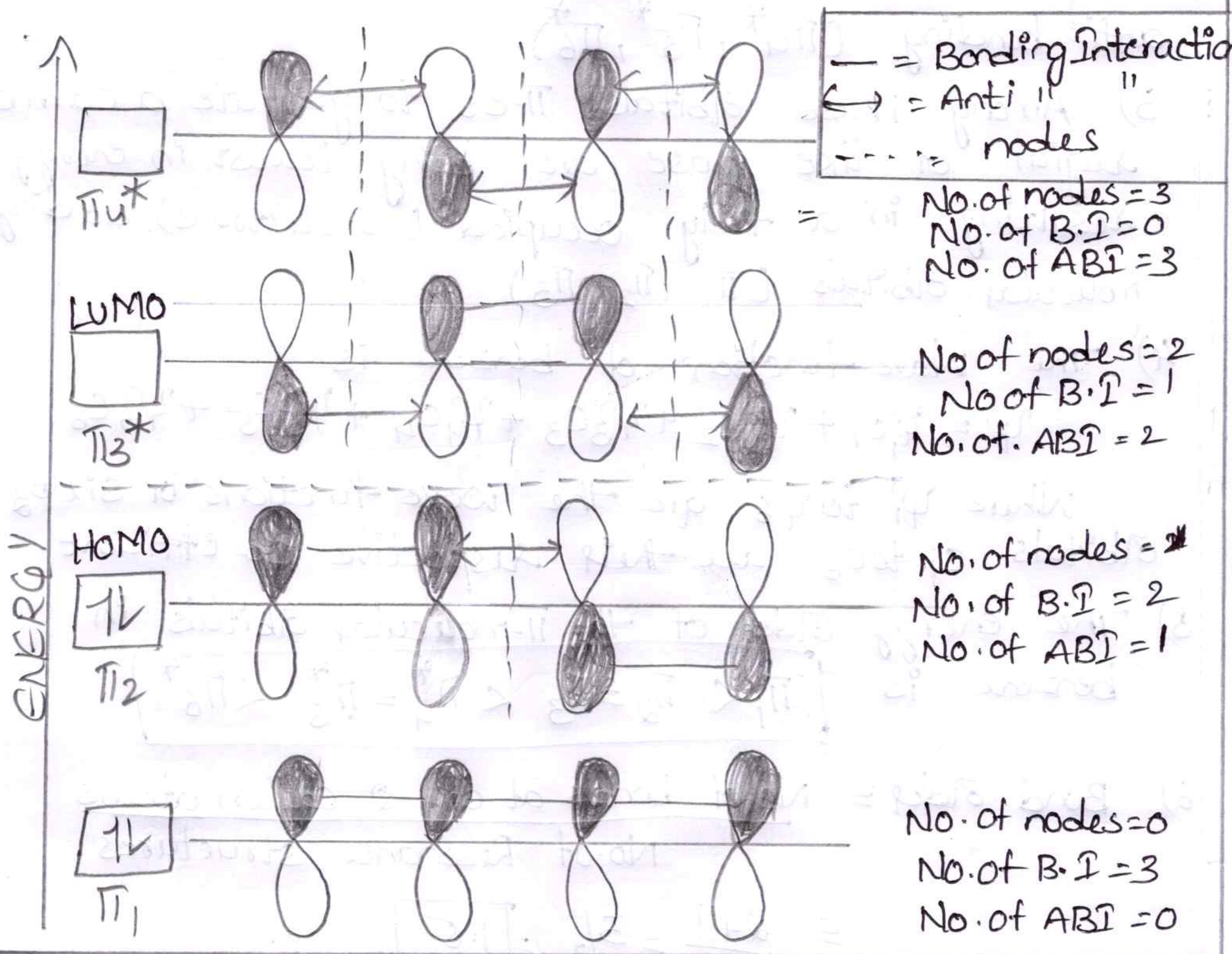
The lowest unoccupied molecular orbital (LUMO) in Butadiene is π_3.

6) As the no. of nodes increases, the orbital energy increases. Hence π_4 has 3 nodes & it has high energy.

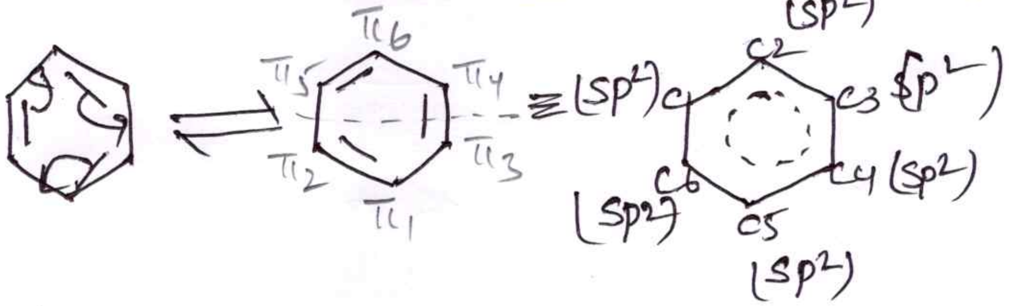
7) **Bond Order:-** $\dfrac{\text{No. of bonds present in b/w two carbon atoms}}{\text{No. of resonance structures}}$

$$= \frac{2(\text{Sig}) + 1(\pi)}{2} ,, \ 3/2 = 1.5$$

$$\boxed{CH_2 \overset{\pi}{\underset{\sigma}{=}} CH \underset{\sigma}{-} CH \overset{\pi}{\underset{\sigma}{=}} CH_2}$$



(9) π- Molecular orbitals of Benzene :- (C_6H_6)



1) Benzene has a planar hexagonal structure in which all the carbon atoms are sp^2 hybridised & all the carbon – carbon bonds are in equal Length.

2) Benzene consists of 6 pi – orbitals , This six p-orbitals overlap to generate six molecular orbitals, Three are Bonding (π_1 , π_2 , π_3) & three are

anti-bonding ($\pi_4^*, \pi_5^*, \pi_6^*$)

3) Among these orbitals π-e's to generate a common region of like phase are being Lowest in energy resulting in a fully occupied (σ electrons) bonding molecular orbitals (π_1, π_2, π_3)

4) The Wave function of benzene is

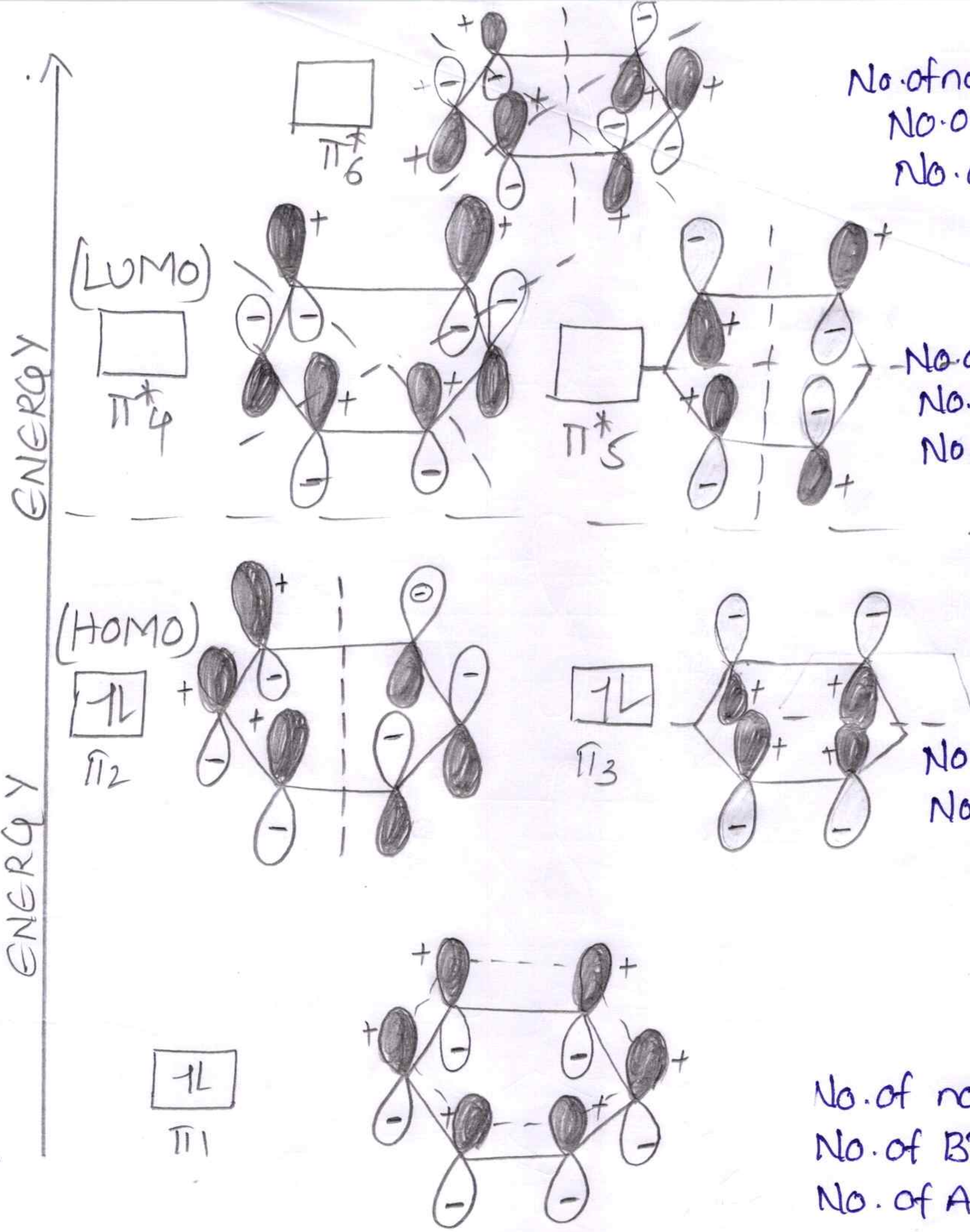
$$\psi = \psi_1 c_1 + \psi_2 c_2 + \psi_3 c_3 + \psi_4 c_4 + \psi_5 c_5 + \psi_6 c_6$$

Where ψ_1 to ψ_6 are the wave functions of six p_z orbitals. c_1 to c_6 are their respective co efficient.

5) The energy order of the π-molecular orbitals in benzene is $\boxed{\pi_1 < \pi_2 = \pi_3 < \pi_4^* = \pi_5^* < \pi_6^*}$

6) Bond order = $\dfrac{\text{No. of bonds at any 2 carbon atoms}}{\text{No. of Resonance structures}}$

$$= \frac{2+1}{2} = 3/2 = \boxed{1.5}$$



No.of nodes = 3
No.of BI = 0
No.of ABI = 6

ABMO

No.of nodes = 2
No.of BI = 2
No of ABI = 4

BMO

No.of nodes = 1
No.of BI = 4
No.of ABI = 2

No.of nodes = 0
No.of BI = 6
No.of ABI = 0

ELECTRO-CHEMISTRY UNIT-II

Electrochemistry:- deals with chemical applications of electricity i.es chemical reactions produced by passing electric current.

(or)

It is a branch of chemistry that deals with the study of transformation of chemical energy into Electrical energy and vice versa.

$$\text{chemical energy} \rightleftharpoons \text{Electrical Energy}$$

Conductors:- Material which allows free flow of energy/electric

Eg: All metals, graphite, fused salts, solution of electrolytes

Insulators:- Materials which cannot conduct electrical Current

Eg: Wood, plastics, most on non-metals.

Cell Terminology:-

1) **current:**- flow of electrons through a conductor.
2) **Electrode:** Electrode is a material (rod, bar, strip) which conducts electrons.
3) **Anode:** Electrode at which oxidation occurs.
4) **cathode.** Electrode at which reduction occurs.
5) **Electrolyte:** Water soluble substance forming ions in solut & conducts electric current.
6) **Half cell:**- part of the cell, which contains an electrolyte dipped in an electrolyte. If oxidation occurs in this half cell, then it is called the oxidation half cell. If reductio occurs at the cell, it is called the reduction half cell.
7) **Cell:** Device consisting of two half cell. The two half cell are connected by a conductor.

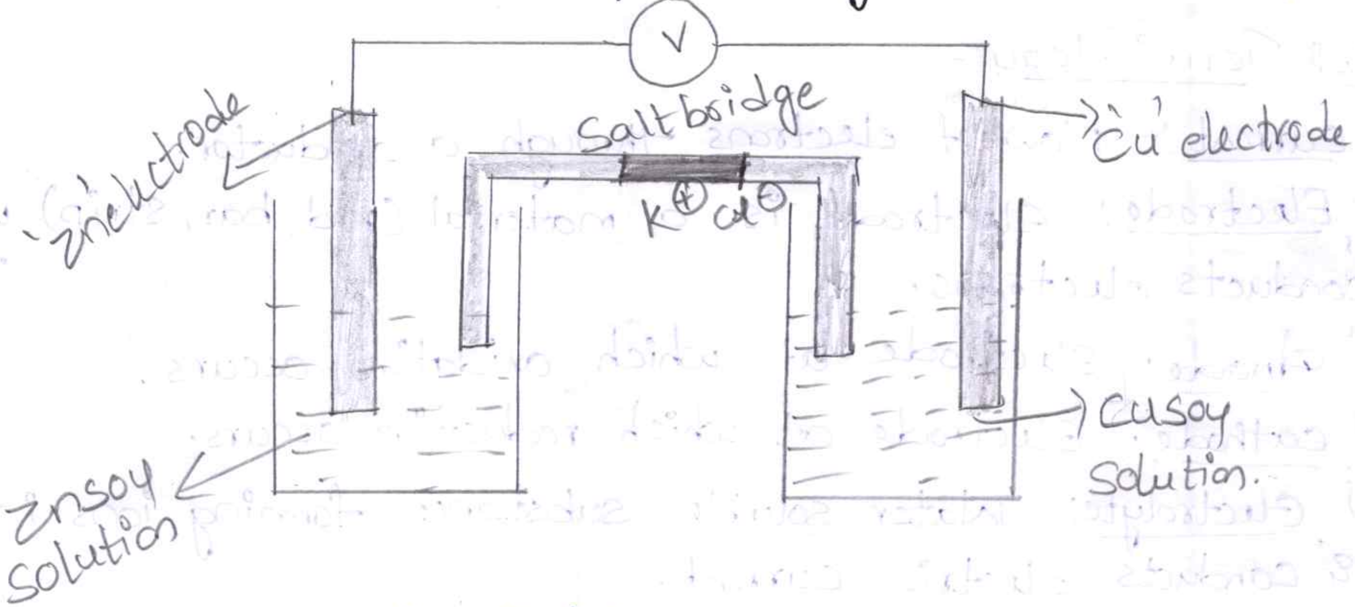
ELECTROCHEMICAL CELL / GALVANIC CELL / DANIEL CELL:-

Chemical energy is converted to electrical energy in electrochemical cells.

The cells which are used for electrolysis are called Electrolytic cells. These electrolytic cells are used in the generation of electrical energy from chemical reactions are called as Galvanic cell (or) voltaic cells.

DANIEL CELL / Galvanic cell:-

Galvanic cells are electrochemical cells in which the energy liberated during a spontaneous oxidation - Reduction reaction accompanied by electron transfer.



Cell device (construction):-

1) Zn electrode dipped in 1M $ZnSO_4$ solution & a Cu electrode dipped in $CuSO_4$.

2) Each electrode is a half cell. The solutions are inter connected by salt bridge & two electrodes are connected by wire.

Salt Bridge:- It consists of U-tube containing a saturated solution of KCl or $(NH_4)NO_3$ in agar-agar gel. It connects to two halfcells

Functions:-

1) Eliminates the liquid junction potential

2) provides a path for the flow of electrons between two half cells.

Working:-

At Anode: oxidation takes place with the Liberation of e's

At cathode: Reduction takes place by the acceptance of e's.

The electrons Liberated in oxidation reaction flow through external wire & are consumed by the copper ions at the cathode.

Reactions accuring in the cell:-

At Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ (oxidation)

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$ (Reduction)

$Cu^{2+} + Zn \longrightarrow Zn^{2+} + Cu$ (net cell Reaction)

Representation of Galvanic cell:-

1) Galvanic cell consists of two electrodes, anode & catho

2) Anode is written on the LHS & cathode on RHS

3) The anode is written with the metal first & then the electrolyte which are seperated by a vertical line

4) cathode is written first electrolyte then the metal

5) Two half cells are seperated by a salt bridge which is indicated by two vertical Lines.

The galvonic cell is represented as

$$\boxed{Zn/ZnSO_4(1M) \parallel CuSO_4(1M)/Cu}$$

ELECTRODE POTENTIAL~~A~~ (E)

It is the measure of the tendency of metallic electrode to Loose or gain of e's, when it is in contact with its own Salt Solution.

Oxidation potential:- It is the measure of the tendency of an electrode to lose e's to get oxidised is called its oxidation potential.

Reduction potential:- It is the measure of the tendency of an electrode to gain e's to get Reduced is called Reduction potential.

NERNST EQUATION FOR SINGLE ELECTRODE POTENTIAL:-

Dependence of electrode potential & EMF on conc. & Temperature of an electrode at non- standard condition.

Nernst gave the relationship between electrode potentials & the concentration & temp of an electrolyte sol under study & is known as Nernst equation.

consider the redox Reaction, forward Reaction

$$M^{n+} + ne^- \longrightarrow M$$

For such redox reversible reactions, the free energy change (ΔG) & its equilibrium constant (K) are related by

$$\Delta G = -RT \ln K + RT \ln \frac{[P]}{[R]} \longrightarrow ①$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[P]}{[R]} \longrightarrow ② \qquad (\because \Delta G^\circ = -RT \ln K)$$

ΔG° = standard free energy change

The above eq is vant's Hoff Isotherm

In the cell, if the reaction involves the transfer of 'n' electrons 'n' faraday of electricity will flow

$$\Delta G = -nEF, \quad \Delta G^\circ = -nE^\circ F \longrightarrow ③$$

Comparing ② & ③

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \quad (\because M = 1m)$$

$$-nEF = -nFE^\circ + RT \ln \frac{[1]}{[M^{n+}]} \quad (\because \ln \tfrac{1}{x} = -\ln x)$$

$$-nFE = -nFE^\circ - RT \ln [M^{n+}] \longrightarrow ④$$

Divide the eq ④ by $-nF$

$$\frac{-\cancel{n}FE}{-\cancel{n}F} = \frac{-\cancel{n}FE^\circ}{-\cancel{n}F} - \frac{RT}{-nF} \ln [M^{n+}]$$

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

$$E = E^\circ + \frac{2.303\,RT}{nF} \log [M^{n+}] \longrightarrow ⑤$$

Where, $R = 8.314\ J/K/mole$,

$F = 96500\ C$

$T = 298\ K$ the above equation becomes

$$\boxed{E_{cell} = E^\circ_{cell} + \frac{0.0591}{n} \log [M^{n+}]}$$ for reduction potential

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log M^{n+}}$$ for oxidation potential

Applications of NERNST EQUATION:-

i) To calculate unknown electrode potentials

ii) prediction of corrosion tendency of metals

iii) To ~~constant~~ construct emf series.

EMF: ELECTROMOTIVE FORCE:

The potential difference, causes by flow of current from one electrode which is at a higher potential than the potential to other electrode is called the electromotive force.

$$\boxed{E^\circ_{Cell} = E^\circ_{cathode} - E^\circ_{Anode}}$$

$$E_{cell} = \left[E^\circ_{cathode} + \frac{2.303RT}{nF}\log(M_2^{n+})\right] - E^\circ_{anode} - \frac{2.303RT}{nF}\log[M_1^{n+}]]$$

$$E_{cell} = E^\circ_{cath} + \frac{2.303RT}{nF}\log(M_2^{n+}) + E^\circ_{anode} + \frac{2.303RT}{nF}\log(M_1^{n+})]]$$

$$E_{cell} = E^\circ_{cath} - E^\circ_{anode} + \frac{2.303RT}{nF}\log[M_2^{n+}] + \frac{2.303RT}{nF}\log[M_1^{n+})$$

$$E_{cell} = (E^\circ_{cathode} - E^\circ_{Anode}) + \frac{2.303RT}{nF}\log\frac{[M_2^{n+}]}{[M_1^{n+}]}$$ //

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[M_{n_1}^{+}]}{[M_2^{n+}]}}$$

standard potential values to calculate the oxidation/Reduction/Emf.

$Li^+ + e^- \rightarrow Li$	−3.05V
$K^+ + e^- \rightarrow K$	−2.93V
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.90V
$Na^{2+} + e^- \rightarrow Na$	−2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23

3) Cell potential calculations:-

1) Explain briefly how the Nernest equation is useful in calculating the electrode potential. Calculate the electrode potential of copper wire (1M) dipped in 0.1M copper Sulphate solution at 25°C, The standarad electrode potential of copper is 0.34V.

$$E = E^\circ + \frac{0.0592V}{n} \log (M^{n+})$$

$$= 0.34 + \frac{0.0592V}{2} \log (0.1)$$

$$= 0.34 + \frac{0.0592}{2} \times -1$$

$$= 0.34 + 0.0295(-1)$$

$$= 0.34 - 0.0295$$

$$= 0.3105V$$

2) What is the potential of a lead electrode that is in contact with a solution of 0.015M in pb^{+2} ions. The standard electrode potential (E°) for $pb \longrightarrow pb^{+2} + 2e^-$ is equal to $-0.13V$

The standard reduction potential (E°) for $pb^{2+} + 2e^- \longrightarrow pb$ is $-0.13V$

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

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

$$= 0.13 + \frac{0.0591}{2} \log (0.015)$$

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

$$= -0.13 - 0.0539$$

$$= -0.184V$$

Hence the corresponding value of oxidation potential $= 0.184V$

3) Calculate the emf of the Zn-Ag cell at 25°C. When $(Zn^{2+}) = 0.1M$ & $[Ag^+] = 1M$. $E^\circ_{cell} = 1.56V$ at 25°C.

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[P]}{[R]}$$

$Zn \rightarrow Zn^{2+} + 2e^-$ Anode

$2Ag^+ + 2e^- \longrightarrow 2Ag$ (cathode)

$Zn + 2Ag \longrightarrow Zn^{2+} + 2Ag$ (cell Reaction.

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Ag^{2+}]}$$

$$E = 1.56 - \frac{0.0591}{2} \log \frac{0.1}{(1)^2}$$

$$= 1.56 + 0.02955$$

$$\boxed{= 1.59V}$$

(4)

$$E = E^{\circ} - \frac{0.0592}{n}\log\frac{[Zn^{2+})}{[Ag^{2+}]}$$

$$E = 1.56 - \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$= 1.56 + 0.02955$$

$$\boxed{= 1.59V}$$

Types of Electrodes / Half cells :-

① Metal - Metal ion Electrodes:-

An electrode of this type consists of a metal contact with the solution of a water soluble salt - of the same metal. Eg: $Zn(s) | Zn^{2+}(aq)$

② Metal - Insoluble metal salt - anion electrode :-

These electrodes consists of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution containing anion of the salt

Let us take an example of such a half cell, which functions as cathode as Cl^- (M) $AgCl | Ag$. The assembly for this halfcells is made by dipping a rod of silver coated with a paste of saturated AgCl at the bottom in a sol of ionic electrolyte such as KCl, NaCl or HCl.

Eg:- 1) Calomel Electrode ($Hg | Hg_2Cl_2 | Cl^-$)

2) $Ag | AgCl | Cl^-$ (CM)

3) Gas - gas ion electrode:-

In this type of electrodes a gas is bubbled into a solution of the gas ion, with a platinum rod having a sheet coated with platinum black being dipped in the gas ion sol

Eg: Hydrogen electrode, O_2 electrode etc.

The anodic half-cell reaction is represented as

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

4) <u>Redox</u> <u>Electrode</u> :- In this type of half-cell, electrode potential arises due to the presence of both oxidised & reduced species of the same metal at an inert electrode like 'pt'

The developed potential could be described due to the tendency of one form to change into another more stable form. The potential is sensed by the inert electrode 'pt'.

$$pt\ [M^{n_1+}\ (C_1M).\ M^{n_2+}\ (C_2M)$$

<u>Eg</u>: 1) Quinhydrone electrode (pt, H_2O)

2) $Pt\ (Cr^{2+} (C_1 M)\ Cr^{3+} (C_2 M)$.

<u>Reference</u> <u>Electrodes</u>:-

The best reference electrode used is a standard Hydrogen electrode. [SHE]. The SHE standard Electrode potential of standard hydrogen electrode at all temperatures is taken as Zero.

(or)

The electrode which provides a stable, reliable & reproducible potential against an indicator electrode & is used repeatedly with accuracy is called Reference electrode.

<u>Primary</u> <u>Reference</u> <u>electrode</u>:- The standard Hydrogen Electrode (SHE) is considered the primary reference electrode as it defines the zeropoint in the electrochemical series.

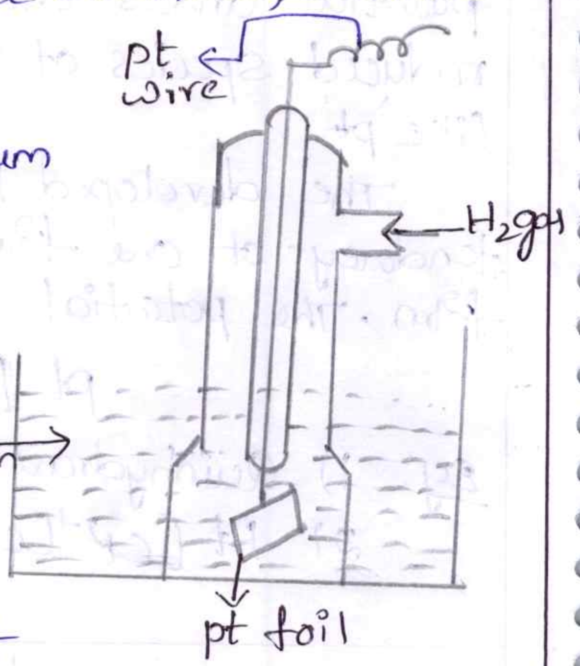
<u>Eg</u>: standard hydrogen electrode (SHE)

<u>Secondary</u> <u>Reference</u> <u>electrode</u>: Calomel electrode whose potential is obtained by connecting it to the standard hydrogen electrode acts as a secondary reference electrode.

Eg: calomel & Silver- Silver chloride electrodes.

(1) Hydrogen Electrode:-

Hydrogen Electrode is a Reference electrode, because its reduction potential "Zero".



- * It consists of a rectangular platinum foil that is connected to a platinum wire & sealed in a glass tube.
- * A jacket (which is closed at the top & open at the bottom. Surrandings this glass tube.
- * H_2 gas is ~~sub~~admitted through aside tube attached to the jacket
- * Hydrogen gas at 1 atmospheric pressure is passed into 1M HCl in which foil is platinised platinum remain immersed.

In a cell, when this electrode acts as anode, the reaction $H_2 \longrightarrow 2H^+ + 2e^-$

Thus, a part of Hydrogen gas changes into ions which go into the solution.

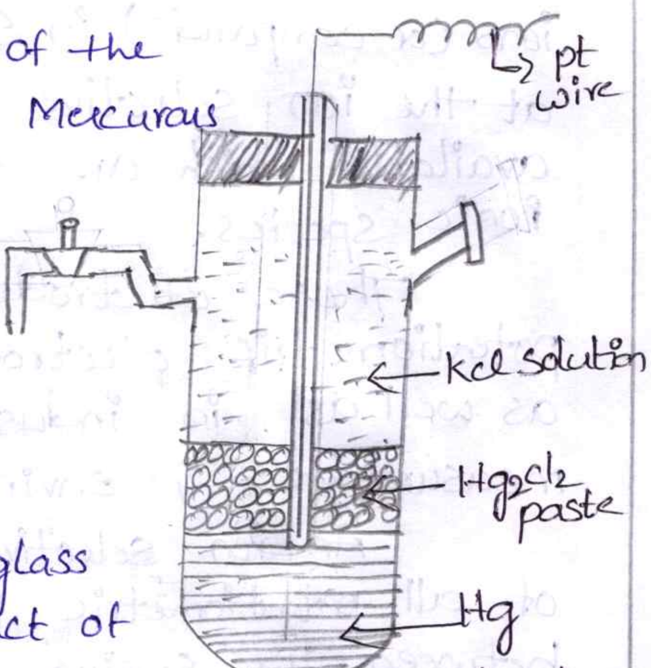
When the electrode acts as cathode.

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

Thus, some H^+ ions from solution change into H_2 gas.

(2) Calomel Electrode:-

This is the most commonly used reference electrode. It consists of mercury, solid mercurous chloride (calomel) & a solution of KCl.



Calomel electrode

* pure Mercury is put at the bottom of the tube & is covered with a paste of Mercurous chloride.

* A sol of Kcl is introduced above the paste through the side tube shown on the right. The Kcl solution also fills the side tube ending in a jet on the left.

* A platinum wire sealed into a glass tube serves to make electrical contact of the electrode with the circuit.

* The half cell whose electrode potential is to be determined is coupled with the calomel electrode through a salt bridge & the emf of the cell is measured.

If the electrode acts a anode the reaction is

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

If it acts as cathode the reaction is

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

Ion - Selective Electrodes:-

The electrodes not only can detect but also measure the conc. of a specific chemical species, directly in a given solution are refered to as a ion selective electrodes.

Ex: pH electrode, potassium, calcium & nitrate ion sensitive electrodes.

Working:- Ion selective electrodes (or chemical sensors) are miniaturized analytical devices that are used to interface b/w chemical species & electronic devices which can provide the information about the presence of specific ions (or compounds) in Samples. The potential developed at the ion selective electrodes or chemical sensors available which are sensitive selectively to a particular ionic species.

These electrodes are frequently used as potentiometric electrodes during laboratory analysis as well as in industry, process control, physiological measurements & environmental monitoring.

An ion selective membrane is the key component of all potentiometric ion sensors. The voltage developed between the sensing & the reference electrodes is a measure of the concentration of the reactive ion being measured. As the concentration of the reacting on at the sensing electrode varies so does the voltage measured between two electrodes.

1) Glass membrane Electrodes:

Glass membrane electrodes are formed by the doping of the silicon dioxide glass matrix with various chemicals. The most common glass membrane electrode is the pH electrode. Membrane electrodes are also available for the measurement of sodium ions. Glass membrane electrodes exchange H^+ ions from an acidic solution.

$$Gl^- Na^+ + H^+ \rightleftharpoons Gl^- H^+ + Na^+$$

2) polymer membrane Electrodes:-

polymer membrane electrodes consist of various ion-exchange materials (water-immiscible liquid substances) in an inert matrix such as pvc, polyethene or silicone rubber. After the membrane is formed, it is sealed to the end of a pvc tube. The potential at the membrane surface is related to the concentration of the species of interest. potassium, calcium & nitrate ion-selective electrodes are the examples.

(3) Solid-state Electrodes:-

These are selective primarily to anions. Solid state electrodes utilize relatively insoluble inorganic salts in a membrane surface. ~~due to the~~ ion solid state electrodes exist in homogenous or heterogenous forms. In both types potentials are developed at the membrane surface due to the ion-exchange process.

Eg:- 1) polycrystalline or mixed crystal membranes such as $AgCl/Ag_2S$ can be used to determined chloride.

2) Single crystal LaF_3 is widely used to determine fluoride.

4) Gas-Sensing Electrodes:-

These are available for the measurement of ammonia, carbondioxide, nitrogen oxide & Sulfur dioxide. These electrodes have a gas permeable membrane & an internal buffer solution. The pH of the buffer solution changes as the gas reacts with it. The change is detected by combination pH sensors within the housing. Due to the construction, gas sensing electrodes ~~are used in a wide variety of application~~ do not require an external reference electrode.

Applications:-

Ion selective electrodes are used in a wide variety of applications

1) pollution monitoring: CN^-, F^-, Cl^-, NO_3^- etc, in effluents & natural waters.

2) Agriculture: NO_3^-, Cl^-, NH_4^+, K^+, Ca^{+2} in soils, plant material fertilizers & feed stuffs.

3) Food processing:- Nitrates & nitrites in meat preservative
4) paper manufacture: sulphur & chloride in pulping & recovery-cycle liquors.
5) Explosives: F^-, Cl^-, NO_3^- in explosive materials & combustion products.
6) Biomedical Laboratories:- Ca^{+2}, K^+, Cl^- in body fluids (blood, plasma, serum, sweat)
7) Salt content of meat, fish, dairy products, fruit juices brewing solution.

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(5) Electrochemical Sensors:-

An electrochemical sensor is a device that detects the electrochemical information into a analytical useful Signal.

Electrochemical sensors are devices that devate information about the sample from some electrical parameter variations. They are 3 types.

1) pontentiometric sensors
2) Ampherometric sensors
3) conductometric sensors.

1) potentiometric Sensor:-

potentiometric Sensor is a type of chemical sensor which measures the potential difference between two electrodes (working & reference electrode)

Working principle:-

1) The working principle is similar & common to all ions selective electrodes. The glass electrode may be represented as $Ag, AgCl / (1M) HCl / H^+$ (test solution)
2) When glass electrode placed in a Solution, potential of a glass electrode depends upon the concentration of hydrogen ions (H^+)

3) When two solutions of different pH values are separated by a thin glass membrone there develop a potential difference b/w the two surfaces of the membrone.

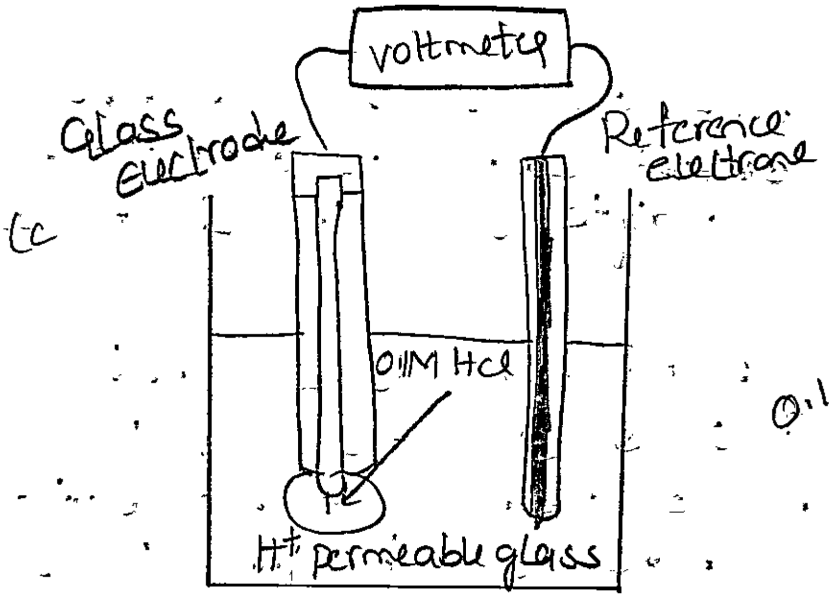
4) The potential difference developed is directly propotional to difference in the pH value. the glass membrone functions as an ion exchange region & an equilibrium is set up b/w the ions of glass electrode & H^+ ions in the test solution.

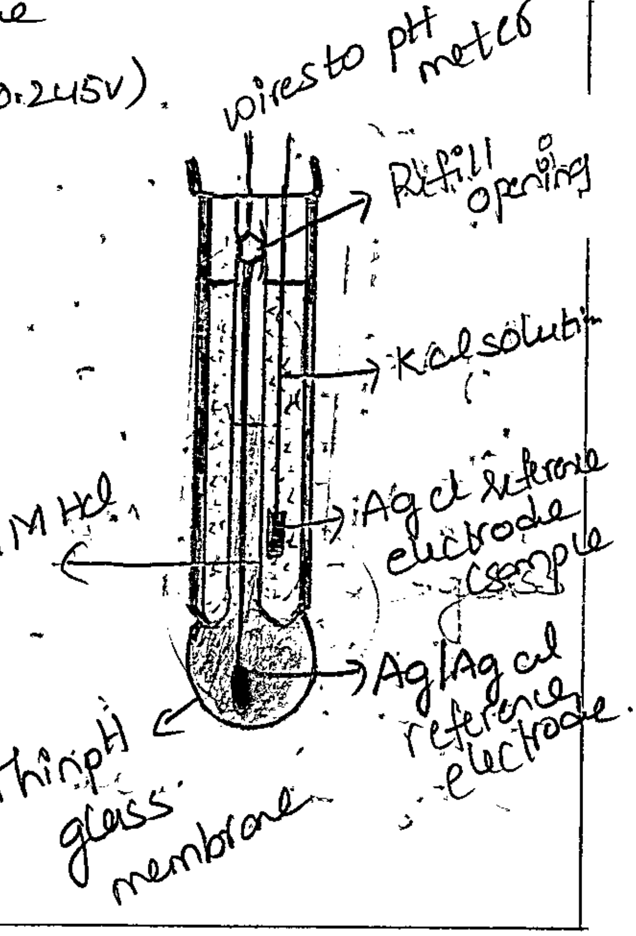
5) Usually, Calomel electrode is used as a secondary electrode. In order to determine the pH of a solution the glass electrode is placed in the solution under the test & this half cell is coupled with saturated calomel electrode. The emf of the cell is measured from the emf of the cell is measured, from the emf the pH of the test solution can be found.

$$E_{cell} = E_R - E_L$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{Ind} - E_{Ref} \ (0.245V)$$





Application of potentiometric sensor:-

Glucose potentiometric sensor:-

Glucose is an electrically neutral molecule hence, partitioning of glucose or of any other electrically neutral molecule to the membrane does not yield a signal. For design of potentiometric sensor for such molecules one more step has to be made.

Initially the neutral glucose molecule has to be converted into ions, which are them selectively detected by glass membrane electrode. Glucose is oxidised into gluconoic acid with further undergoes ionisation and liberates hydrogen ions which setups the potential difference b/w working electrode & reference electrode from the measured potential, the conc of glucose will be calculated.

$$C_6H_{12}O_6 + H_2O + O_2 \longrightarrow \underset{\text{gluconoic acid}}{C_6H_{14}O_7} + H_2O$$

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

2) Ampherometric Sensors:-

Ampherometric sensors are the device which measures the ~~current~~ current response to detect the concentration of an analyte at the fixed potential

Working principle:-

1) A thin gas permeable membrane is stretched across the end of the sensor & is separated from the working electrode & the counter electrode by a thin solution of Kcl by working electrode is a platinum disc cathode & Ag ring anode serves as the counter electrode.

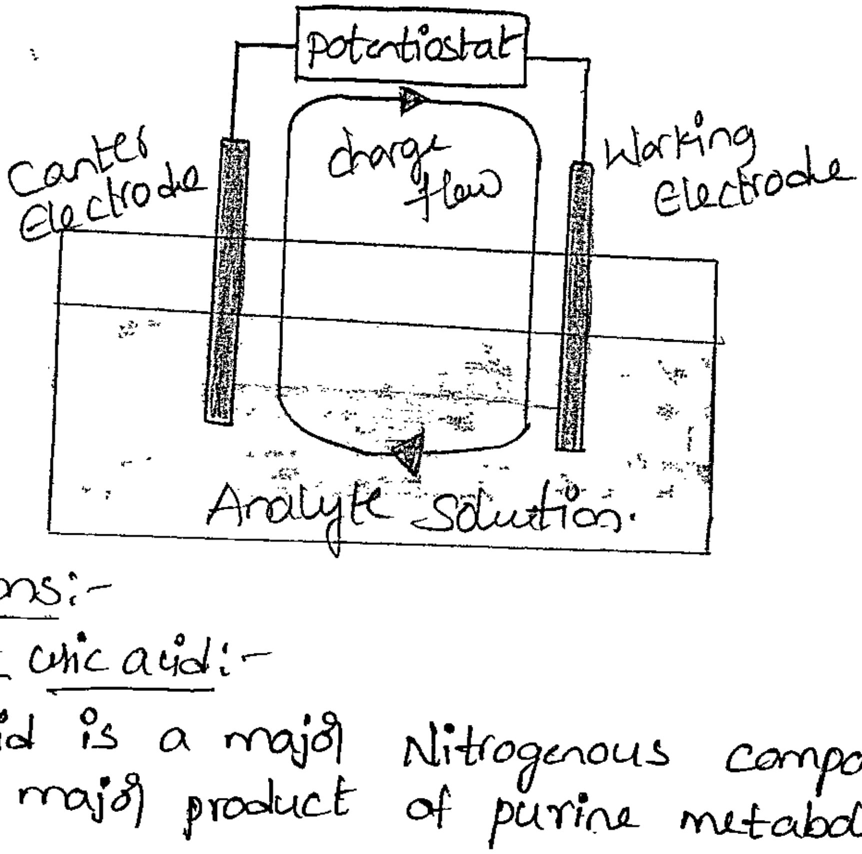
Although several gases are diffuses across a membran including O_2, N_2 & CO_2 but only oxygen undergoes reduction at the cathode with its concentration at the electrodes surface quickly reaches to '0'.

* The conc. of oxygen at the membranes in a surface is fixed by its diffusion through the membrane.

* The result is a steady state current that is propotiona to the Concentration of dissolved oxygen, because the electrode consumes oxygen the Sample is stirred to prevent the depletion of oxygen at the membranes outer Surface.

anode: $Ag + Cl^- \rightleftharpoons AgCl + 2e^-$

cathode: $O_2 + 2H_2O + 2e^- \rightleftharpoons 4OH^-$



Applications:-

Analysis of uric acid:-

* Uric acid is a major Nitrogenous compound in urine which is a major product of purine metabolism in the human body.

* The measurement of uric acid is done by enzymatic & non-enzymatic method.

* The enzymatic procedures using uricase have been

been developed based on amperometric detection of H_2O_2 produced in the reaction.

$$\text{Uric acid} + H_2O + O_2 \longrightarrow \text{Allantoin} + H_2O_2 + CO_2$$

* H_2O_2 breaks at working electrode & forms H^+ ions & release O_2

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

BATTERIES AND FUELCELLS

Introduction:-

Batteries are the storehouses of electrical energy. They provide well contained energy conversion devices which greatly contributed to needs of Mankind.

In 1799, Alessondro volta developed the first electrical battery. This battery is known as voltaic cell, consiste of two plates of different metals immersed in a Chemical Solution.

Faraday was the first use the word "electrode" as a general term for a pole of a battery "anode" = -ve electrode & 'cathode' = +ve electrode of a battery.

Components of Battery:-

1) Anode: Anode is the electrode where oxidation takes place. Here electrons are released to the external circuit

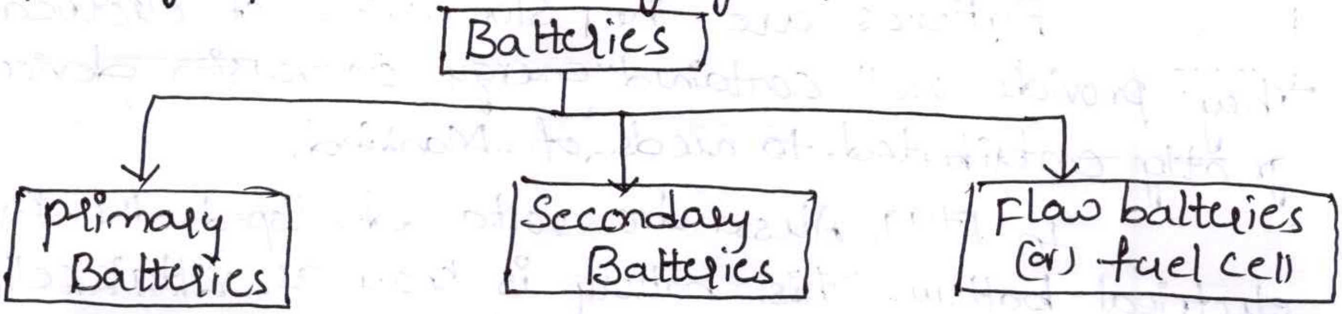
2) Cathode: Cathode accepts the e^-s produced at anode & the active pieces gets reduced. It is +ve terminal of the cell.

3) Electrolyte: Electrolyte is an ionic conductor that provides connectivity between anode & cathode of the battery. The electrolyte used are acids, bases, or salts having high ionic conductivity. It allows electronic movement between the electrodes during charging & discharging.

4) Separator:- Direct contact of anode & cathode produces internal short circuit. These are insulating membrane that prevents or isolates anode & cathode electrically to prevent short circuit. Rubber, cellulose, vinyl polymers etc are widely used as separators.

Types of Batteries :-

Batteries are classified into three categories depending upon the recharging capacities.



1) Primary Battery (or) Primary cell :-

These are cells in which the electrode reactions cannot be reversed by passing an external current. The reactions are possible only once & the battery will be dead after use. Hence it is non-rechargable battery.

Eg: Daniel cell, Leclanche cell, Mercury cell.

2) Secondary battery (or) Secondary cell :-

These are cells in which the electrode reactions can be reversed by passing an external current. Thus a secondary battery may be used through a large number of cycles of charging and discharging. Hence it is a rechargeble battery.

Eg: Li-ion battery, Ni-cd battery, pb-acid battery.

3) Fuel cell (or) flow battery :-

It is a device which converts chemical energy of the fuel directly into electrical energy. The chemicals used are usually very simple ones such as H_2 & O_2.

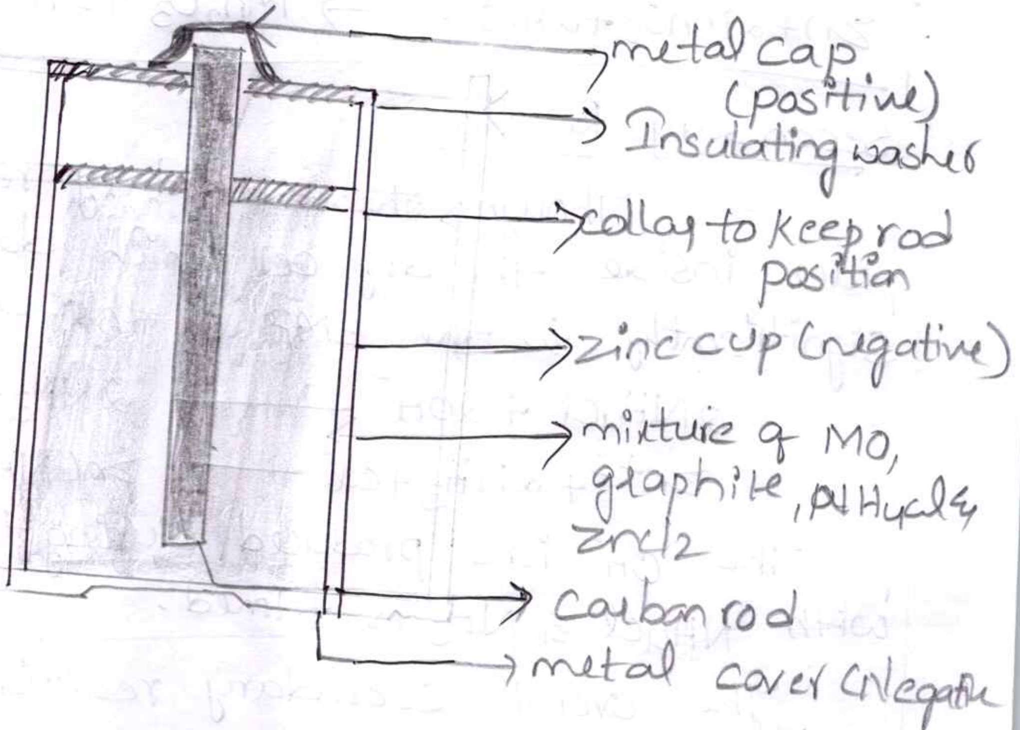
Eg: H_2-O_2, fuel cell, Methonol fuel cell etc.

Primary Batteries	Secondary Batteries
1) primary batteries are used only once	1) Secondary batteries can be used for several cycles
2) Irreversible battery	2) Reversible battery
3) They are cheap	3) They are expensive
4) Initial cost is low	4) Initial cost is very high
5) Disposable.	5) periodic recharging & regular maintenance is required.

PRIMARY BATTERIES:-

DRY CELL / LECLANCHE CELL ($Zn- MnO_2$) cell:-

A dry cell is a device that generates electricity based on chemical reactions. When the two electrodes of the cell are connected via a closed path, then the cell forces the electrons to flow from one end to the other. The flow of e^-s causes the current to flow in the closed circuit.



1) This is a primary battery, popularly known as the dry cell.
2) It consists of a graphite rod at the centre, which acts as the cathode of the cell.
3) The cathode is surranded by a thick moist paste of graphite & MnO_2.
4) The outer layer consists of a paste of $ZnCl_2 + NH_4Cl$.
5) The entire assembly is placed inside a thin zinc wrapper, which acts as an anode.
6) The whole assembly is kept inside polypropylene or cardboard materials which prevents leakage, if any.

The electrochemical representation of a $Zn-MnO_2$ dry cell is

$$Zn/Zn^{+2} \| NH^{4}/MnO_2/C$$

electrode reaction of the primary cell is

$$Zn \longrightarrow Zn^{+2} + 2e^- \text{ (Anodic oxidation)}$$

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^- \text{ (cathodic Reduction)}$$

$$Zn + 2MnO_2 + 2H_2O \longrightarrow Mn_2O_3 + Zn^{2+} + 2OH^-$$

Secondary Reaction:

Though the secondary reactions also take place inside the dry cell which do not contribute significantly to the EMF of the dry cell.

$$2NH_4Cl + 2OH^- \longrightarrow 2NH_3 + 2H_2O + 2Cl^-$$

$$Zn^{+2} + 2NH_3 + Cl^- \longrightarrow Zn(NH_3)_2Cl_2$$

The OH^- ions produced during the electrode reacts with NH_4Cl & NH_3 is formed.

The overall secondary reactions taking place inside the cell is the formation of a $Zn(NH_3)_2Cl_2$ complex.

Limitations:-

1) The capacity of the battery is low, they are not suitable for high drain applications.
2) The batteries are not chargeable
3) The self life of the battery is not long.
4) The optimum temp range of observation is 20-40°c outside temp range performance deteriorates markedly.

Applications:-

1) The battery is convenient source of poses for portable electronic & electric devices.
2) It has low cost, reasonable power density, reliable performance & readily availability.

Secondary cells/Battery:

Li-Ion-Battery:-/ Li/CoO_2 cell:-

These cells donot contain metallic Lithium hence they are called Lithium ion cells & use Lithium ions instead Infact, the cell's operation does not actually involve true oxidation & reduction. But it uses the transport of Li^+ ions through the electrolyte from one electrode to the other accompanied by the transport of electrons through the external circuit to maintain charge balance.

Li^+ ions are able to slip between two layers of atoms in certain crystals such as graphite & $LiCoO_2$ When the cell is constructed, it is in its uncharged state with no Li^+ ions between the layers of carbon in the graphite. When the cell is discharged, Li^+ ions leave $LiCoO_2$ & travel through the electrolyte to the glaphite (C_6)

Initial charging:-

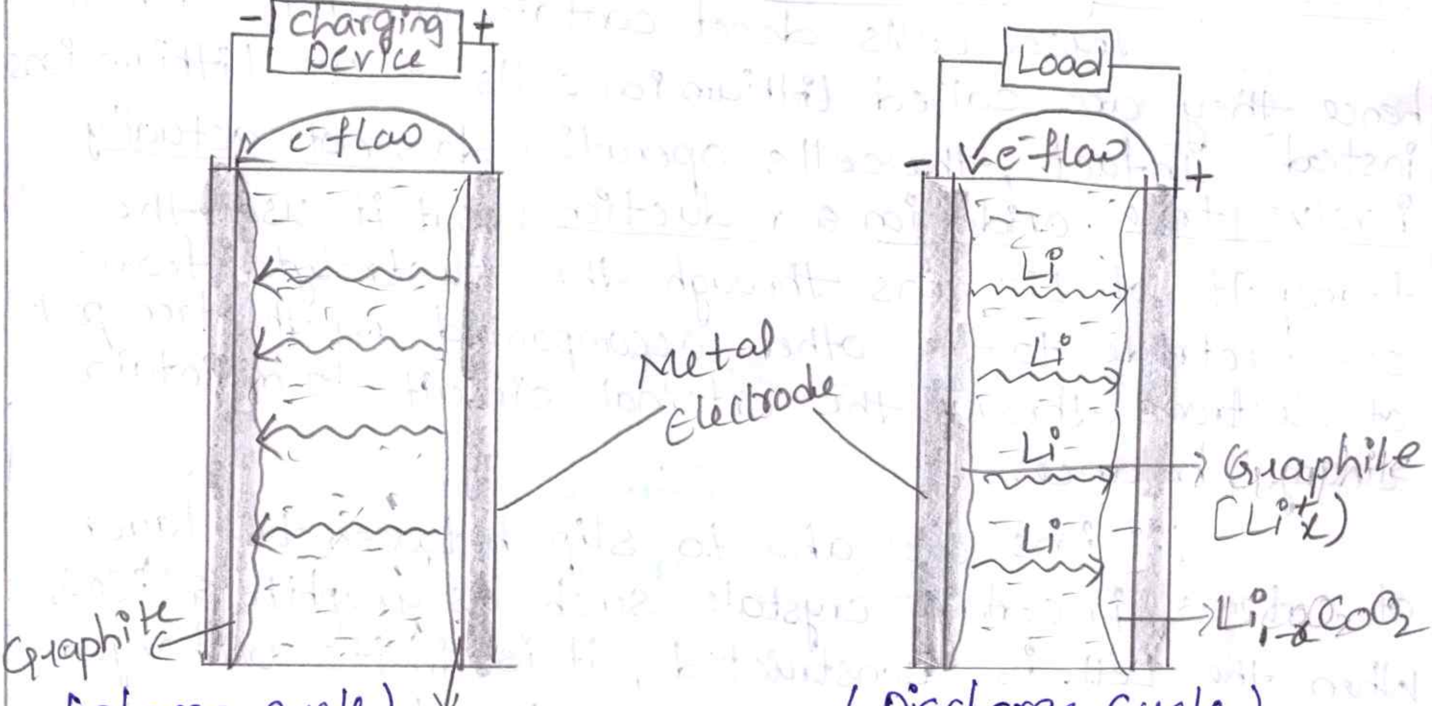
$$LiCoO_2 + \text{graphite } (C_6) \rightarrow Li_{1-x}CoO_2 + Li_xC_6$$

When the cell spontaneously discharges to provide electrical power, Li+ ions move back through the electrolyte to the cobalt oxide while the e^-s move through external circuit from the graphite electrode to the cobalt oxide electrode. If we represent amount of Li^+ transferring by 'y' the discharge reaction is

Dicharge:-

$$Li_{1-x}CoO_2 + Li_xC_6 \longrightarrow Li_{1-x+y}CoO_2 + Li_{x-y}C_6$$

Thus, the charging & discharging cycle simply sweep Li+ ions back & forth between the electrodes with electrons flow through external circuit to keep the charge balance.



(Charge cycle)

(Discharge Cycle)

Applications:-

1) High energy density, wide operating temperature range high discharge rates, & low cost.
2) It is used widely such as, long term memory back up, safety & security devices
3) cameras, lightening equipment etc.

FUEL CELLS:-

1) It is an electrochemical device that converts the chemical energy of fuel (hydrogen - methanol & gasoline etc) & oxidant (air or oxygen) into electricity.

2) A fuel cell also has two electrodes & an electrolyte

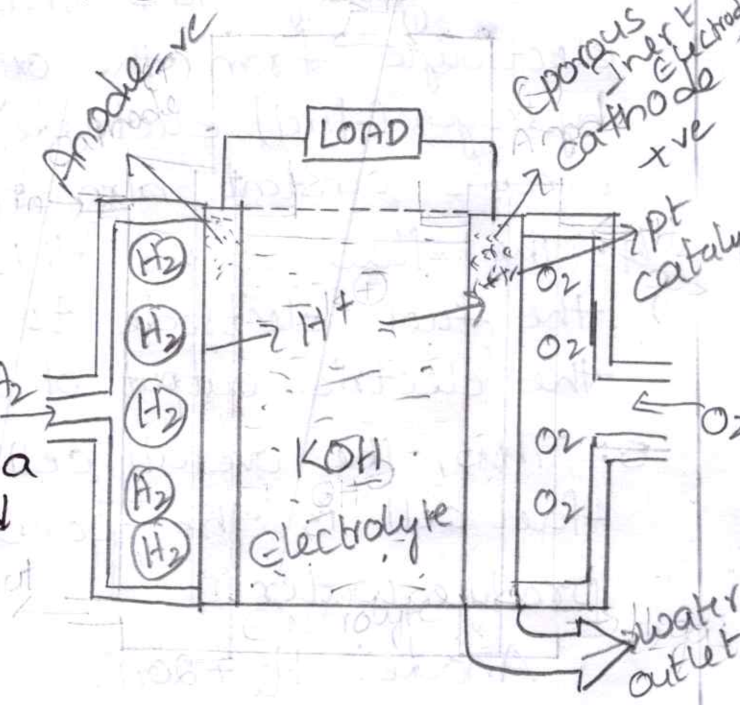
3) At the anode, fuel undergoes oxidation, liberating electron & the oxidation products of the fuel.

4) The electron so liberated from the oxidation process reduce the oxidant at the cathode

5) Thus, movement of e^-s constitute electric current.
varieties of fuel cells are in use.

Hydrogen - Oxygen fuel cell:-

Construction:-



1) At the anode, hydrogen gas is diffused through a porous carbon electrode.

2) The surface of the carbon electrode is embedded with a catalyst such as finely divided platinum or palladium.

3) At the cathode, oxygen is diffused through a porous carbon electrode, impregnated with cobalt oxide, platinum or silver as catalyst.

4) The two electrodes are separated by electrolyte such as KOH solution.

Working :-

1. As hydrogen gas diffuses through the anode, it is absorbed on the electrode surface in the form of H_2 atoms & reacts with hydroxyl ions (of the electrolyte) to form water.

2. The electrons released in the above process flow through the external circuit to the cathode. The O_2 gas diffusing through the cathode, is absorbed on the electrode surface, where is reduced to hydroxyl ions.

3. The hydroxyl ions thus produced migrate through the electrolyte from the oxygen (oxidant) electrode to the hydrogen (fuel) electrode. The electrolyte concentration remains constant almost.

4. The flow of e^-s through the external circuit from the fuel electrode to the oxidant electrode constitutes the electric output of the fuel cell (voltaic)

5. Thus, the overall cell reaction of a hydrogen-oxygen fuel cell is the combination of hydrogen & oxygen to produce water.

At Anode: $H_2 \rightarrow 2H^+ + 2e^-$

cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

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

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

Applications :-

1) Fuel cell can be used in portable devices like smart phones, Laptops & tablets.
2) Fuel cell can be used in submarine vehicles.
3) Fuel cell is used as constructive equipment
4) Fuel cell are used in hybrid vehicles like cars & buses.

UNIT-III

POLYMER CHEMISTRY

Introduction to polymers, functionality of monomers, Thermoplastics & Thermosetting plastics, properties & applications of PVC & Bakelite.
Fibers – polyester, mechanical requirements for fibres – Crystalinity, stress strain curve. Biodegradable polymers – properties & applications of polyglycolic acid (PGA), polylactic Acid (PLA).
Elastomeres – properties & applications of Buna-N & Buna-S & Thiokol.
Conducting polymers – polyacetylene – mechanism of conduction & applications.

Introduction to polymers:-

polymer:

A polymer is a high molecular weight compound formed by combining large no. of small molecules called monomers.
Eg:- polyvinyl chloride, polyethylene, polystyrene etc.

Monomer:-

Monomer is defined as a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecules to form the macro-molecule (polymer)

All simple molecules cannot behave as monomers but only those with two or more bonding sites can act as monomers. Alkenes, vinyl chloride, adipic acid, glycol with two binding sites act as monomers.

Polymerization:-

polymerization is defined as the chemical reactions in which a monomer is converted to the polymer under specific conditions. Monomer alone cannot undergo polymerization, but requires the presence of a chemical called initiator.

Degree of polymerization:-(n)

The no. of repeating units present in a polymer chain is known as degree of polymerization. DP is represented as 'n' DP gives an idea about the size of the polymer.

Mol.wt of the polymer = DP X molecular wt of each

Classification of polymer:

S.No	Basis of classification	Types of polymers	Examples
1.	Source	1. Natural polymers 2. Synthetic polymers	cotton, silk, wool, starch pvc, polythene, plastics.
2.	Backbone	1. Organic polymers 2. Inorganic polymers	pvc, polyethene, polystyrene silicones, Magnesium oxides
3.	Heat treatment	1. Thermoplastics 2. Thermosetting plastic	pvc, polythene, Teflon Bakelite, polyester.
4.	Utility	1. plastics 2. Elastomers 3. Fibers 4. Resins	pvc, polystyrene synthetic rubber, silicone rubber Nylon, Terylene Epoxy adhesives, polysulphide Sealants.
5.	Structure	1. Linear polymers 2. Branched polymers 3. Cross-linked polymers	pvc, polystyrene LDPE Low density polythene Bakelite.

S.NO	Basis of classification	Types of polymers	Examples.
6.	Composition	1. Homopolymers 2. Heteropolymers (co-polymers)	pvc, polythene Buna-s, Nylon 6-6.
7.	Tacticity (configuration)	1. Isotatic polymers 2. Syndyatic polymers 3. Atactic polymers	polyvinyl alcohols, Natural rubb pvc, Guttapercha polypropylene
8.	Synthesis method	1. Addition polymers 2. condensation polymers	pvc, polythene Bakelite, polyester.

Tacticity :-

The difference in configuration because of orientation of functional groups in polymer in an orderly or disorderly manner with respect to the main chain is called Tacticity.

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

Eg: polyvinyl alcohol, Natural rubber

b) Syndiotactic polymer :- If the functional groups are arranged in alternative fashion with respect to the main chain, it is called syndiotactic polymer.

Eg: polyvinyl chloride, Guttapercha.

c) Atactic polymer : If the functional groups are arranged at random around the chain, it is called Atatic polymer

Eg:- polypropylene.

(2) Functionality of Monomers:-

The number of bonding sites (or) fnctional groups present in a monomer is known as its functionality. Every monomer to give rise to a polymer must have at least two bonding sites.

(i) Bifunctional monomer:- A bifenctional monomer is one that can react with two molecules under the conditions of the polymerization reactions, linear or straight chain polymers are formed.

Eg:- Ethylene, styrene, vinyl chloride

2) Trifunctional monomer:- A trifunctional monomer is one that can react with three moleculs under the conditions of the polymerization reactions.

Eg:- Glycerol, Titonium isopropoxide, phenol

3) polyfunctional monomer:- polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions.

Eg: polyethylene, polypropylene.

classification of polymers:-

polymers are with different chemical structure physical properties, mechanical behaviour, thermal behaviour etc. so they can be classified into different types.

① Natural & Synthetic
② Organic & Inorganic
③ Thermo setting & Thermoplastic
④ plastics, Elastomers, Fibers & Liquid resins.

① Natural & Synthetic polymers:-

Depending on origin, polymers are classified into two types as Natural & Synthetic polymers

Natural polymers:- These polymers are isolated from natural materials.

Ex: cotton silk, wool, Rubber etc.

Synthetic polymers:- These polymers are prepared from laboratoly techniques.

Ex: polyethene, PVC, Teflon etc.

② Organic & Inorganic polymers:-

Based on chemical structure polymers are classified into two types as Organic & Inorganic

Organic polymers:- polymers whose back bone is made up of carbon atoms are called organic polymers. The side valencies are filled by usually hydrogen, oxygen, nitrogen etc.

Ex: polyethene, PVC etc.

Inorganic polymers:- Inorganic polymers generally contain no carbon atoms in their backbone chain.

Ex: Glass & Silicone rubber.

③ Thermo & Thermosetting plastics:-

Based on thermal behavior, these are classified into two types.

Thermoplastics:- polymers which soften on heating & harden on cooling are termed as thermoplastics.

Ex: polythene, polystyrene etc.

Thermosetting plastics:- polymers on heating sets into ~~[illegible]~~ infusible mass. once it set cannot be reshaped.

Ex: Bakelite, polyesters etc.

④ plastics, Elastomers, Fibers & Liquid resins:-

Depending on its ultimate form & use, polymers can be classified as plastics, elastomers, fibers, resins.

a) polymers is shaped into hard & tough utility articles by the application of heat & pressure it is used as plastic.

Ex: polystyrene, pvc, polythene etc.

b) When vulcanised into rubbery products exhibiting good strength & elongation, polymers are used as elastomers.

Ex: Natural rubber, synthetic rubber etc.

c) If drawn into long filaments like materials whose length is atleast 100times greater to its diameter polymers are said to have been converted into fibres.

Ex: Nylon & Terylene.

d) polymers used as adhesives in liquid form are described as liquid resins. Ex: Epoxy resins.

Classification of polymer :-

Based on the Monomer structures

polymers may consists of identical monomers (or) monomers of different chemical structures. According to this, polymers are classified into ~~two~~ three types,

a) **Homopolymer:-** polymers in which monomers are identical (or) belongs to only one chemical compand

$-M-M-M-M-M-M-$

b) **Heteropolymers:-** The polymers chain is made up of different series of atoms is called heteropolymers

$-C-C-O-C-C-O-C-C-O-$

c) **Co-polymers:-** polymers in which monomers are not identical, they belongs to two (or) more chemical compand are called co-polymers.

$-M-M_1-M_2-M_3-M-M_1-M_2-M_3-$

Functionality of Monomers:-

for a substance to act as a monomer, it must have atleast two reactive sites (or) bonding sites.

"The no. of bonding sites in a monomer is referred to functionality."

Based on functionality monomers are classified into three types.

1) Bifunctional
2) Trifunctional
3) poly functional

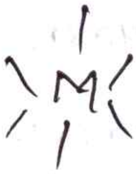
1) **Bifunctional Monomers:-** Monomers with two bonding sites. $-M-$ (or) XMX

2) Trifunctional :- Monomers with three bonding sites

$-\overset{|}{M}-$ (or) $X\overset{X}{M}X$

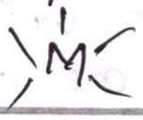
3) poly functional :- Monomers with more than three bonding sites.

a) Tetra-functional , b) penta ⓒ



Hexafunctional

$-\overset{|}{\underset{|}{M}}-$



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plastics :-

These are the high polymers which can be moulded into any desired form by applying heat & pressure in presence of catalyst.

* plastics attained ~~agains~~ great importance in everyday life because of their unique properties like

1) Light weight
2) Good thermal & electrical insulation
3) High corrosion resistance
4) High chemical Inertness
5) Low maintainance cost
6) Toughness & Water resistance
7) Easy fabrication & remarkable colour change
8) Easy work ability like moulding , casting etc

Thermoplastic polymers :-

polymers which soften on heating & harden on cooling are termed as thermoplastics.

Ex: pvc , polyethene , polystyrene etc.

Thermo setting plastics :-

polymers on heating sets into infusible mass once it set cannot be reshaped

Ex: Bakelite , polyesters etc.

Differences between the Thermoplastics & Thermo-setting polymers.

Thermoplastics	Thermosetting plastics
1. The polymers which soften on heating & harden on cooling are called Thermoplastics.	1. The polymers which are fusible on initial heating, but become hard, rigid & infusible on further heating are called thermosetting plast
2. These are soft, weak & less brittle.	2. These are hard, strong & more brittle.
3. These can be reshaped many times	3. These cannot be reshaped many times.
4. These are formed by addition polymerization.	4. These are formed by condensation polymerization.
5. These consist of linear long chain polymers	5. These consist of three-dimensional network joined by strong covalent bonds.
6. These are soluble in some of the organic solvents	6. These are insoluble in almost all organic solvents.
7. These can be reclaimed from wastes.	7. These cannot be reclaimed from wastes.
8. There is no change is chemical composition & structure during moulding process	8. These undergo chemical changes & cross links during moulding process.
9. polymer chains are connected by weak vanderwaals forces Eg:- polyethene, pvc, Teflon etc.	9. polymer chains are connected by strong covalent bonds. Eg: Bakelite, polyester etc.

preparation, properties & Application of PVC :-

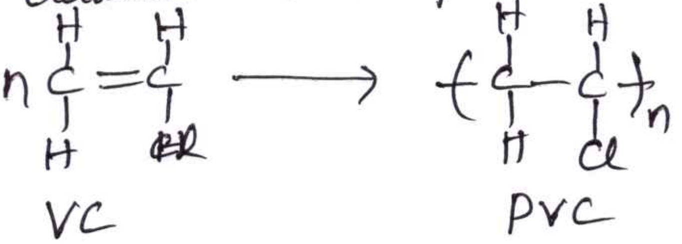
Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at 100-150°c in the presence of metal salt catalyst.

$$HC \equiv HC + HCl \longrightarrow H_2C = CH(Cl)$$

Acetylene

vinyl chloride

PVC is prepared by heating a water-emulsion of vinyl chloride in presence of benzoyl peroxide or H_2O_2 in an autoclave under pressure.



$$n\,CH_2{=}CHCl \longrightarrow (CH_2{-}CHCl)_n$$

VC PVC

properties:-

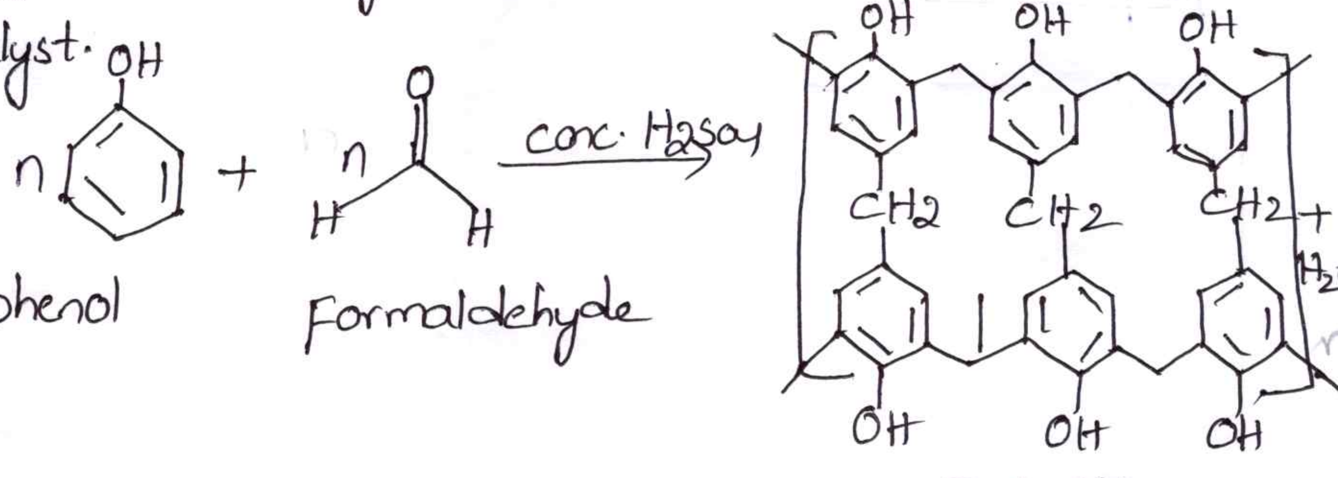
1) PVC is a colourless & odourless powder.
2) It is non-inflammable & chemically inert.
3) It is soluble in chlorinated hydrocarbons like ethyl chloride, etc, & ketones
4) It has high resistance to light, inorganic acids, alkalis & atomspheric oxygen.

Applications:-

1) plasticised PVC is used for making table cloths, raincoats, for electric wire & cables, toilet articles, radio, T.V. components, pipes, coupling, valves etc.
2) unplasticized PVC or rigid PVC is used for making refrigerators components, cycle & motor cycle mudguards tubes, pipes, etc.

Preparation, Properties & Application of Bakelite:-

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



Bakelite

Properties:-

1) Bakelite is a rigid, hard, scratch resistant, infusible Solid substance
2) It is resistant to acids, salts & most organic solvent but attacked by alkali.
3) It possesses excellent electrical insulating character.

Applications:-

1) It is used for making electrical equipment like switches plugs, holders, switch boards, heater ~~[illegible]~~ handles etc.
2) It is used in making telephone parts, radio & TV. cabinets
3) It is used in paints & varnishes
4) It is used for making bearings, propeller shafts for paper industry & rolling mills.
5) It is used in the production of ion-exchange resins.

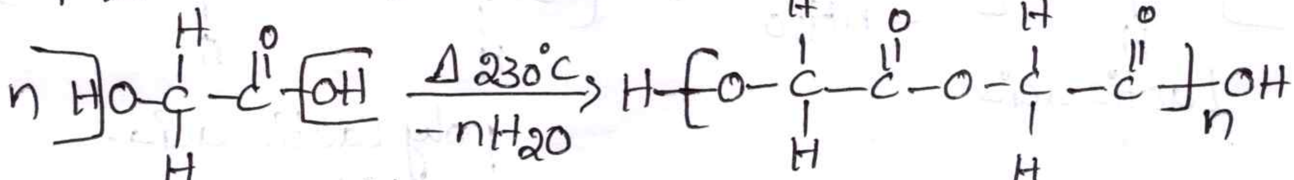
BIO-Degradable polymers:-

Those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of micro-organisms/enzymes. These materials develops like Starch, cellulose & polyesters.

PolyGlycolic Acid:-

Preparation:- PGA is prepared by condensation polymer-sation of Glycolic acid Monomers.

PGA is obtained from



$$n\,\boxed{H}O-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{||}{C}}-\boxed{OH}\xrightarrow[-nH_{2}O]{\Delta\,230^{\circ}C}H-\left[O-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{||}{C}}-O-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{||}{C}}\right]_{n}OH$$

Glycolicacid poly glycolic acid

properties:-

1) polyglycolic acid is a crystalline polymer with a crystallinity of 46~52%, a density of 1.5~1:64g/cm³. (a glass transition temperature of about 36°c, a melting point of about 224°c, and good mechanical properties of light molecular weight polyglycolic acid)
2) PGA is biodegradable simple aliphatic polyester.
3) The fibres of PGA exhibit in high strength & very stiff
4) It has good mechanical properties
5) Due to Low molecular weight of PGA is insoluble in organic Solvent.
6) It is a thermoplastic material.

Applications:-

1) In Medicine PGA is used as sutures (sitches) in Surgery. Sutures made of PGA Loose their mechanical strength over a period o 2-4 weeks implantations
2) In controlled drug delivery
3) As food packaging material.

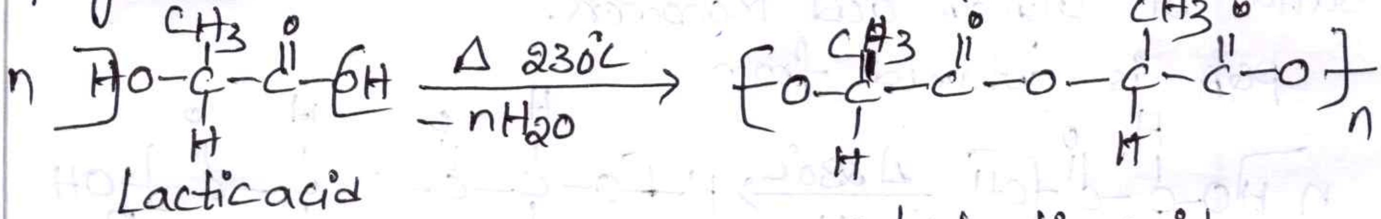
4) As medical implants like rods, pins, rings, plates.

5) In tissue engineering.

6) PGA is much less reactive & is expeimentally better able to resist infection from contaminating bacteria.

poly Lactic acid (PLA) :-

Preparation:- It is a biodegrable polymer by condensation polymerization of lactic acid Monomer.



$$n\left[H-O-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH\right] \xrightarrow[-nH_2O]{\Delta\ 230^\circ C} \left[O-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O\right]_n$$

Lacticacid

poly Lactic acid.
PLA

properties:-

1) PLA is a biodegradable polyester.

2) Its Melting point range is 170-180°c

3) PLA is a linear thermoplastic

4) These fibers are strong.

5) The degree of crystalinity of PLA is around 37%

6) The glass transition temp between 60-65.

7) PLA has good optical properties, providing transparency & gloss similar to traditional plastics.

Applications:-

1) poly Lactic acid based polymers are available for controlled drug releases, implantable composites & bone fixation.

2) It is suitable for sustainable resource release of pesticides & fertilizers & composite bags.

3) PLA - based disposable cutlery, plates & cups are popular alternatives to traditional plastic equivalents for single-use items at events, parties & food service establishments.

4) PLA fibers can be used to produce textiles, PLA based fabrics are used in clothing bedding & other textile applications.

5) PLA's properties make it a popular choice for 3D printing filaments. It is widely used in desktop 3D printers for creating prototypes.

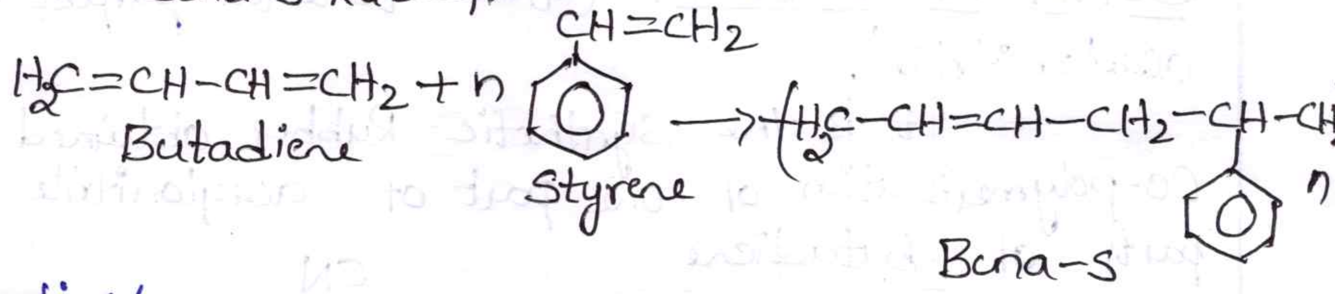
Elastomers :-

Elastomers is defined as a long chain polymer which under stress undergoes elongation by several times & regains its original shape when the stress is fully released.

BUNA-S - preparation, properties & Applications :-

preparation :-

Butadiene (about 75% weight) & styrene (25% by weight) co-polymerize to give styrene butadiene Rubber (SBR) or Buna-S Rubber.



properties :-

1) High abrasion resistance, high bearing capacity & resilience.
2) Gets oxidised in the presence of traces of ozone.
3) Swells in oils & solvents

4) It needs more accelerators for more vulcanization

5) It can be vallcanised by sulphur but quantity requird is less.

Vulcanization:- It is a chemical process in which the rubber is heated with sulphur accelerator & activator at 140-160°C.

Applications:

1) It is widely in pneumatic tires in shoe heels & soles gaskets & even chewing gum.

2) It is a commodity material which competes with natural rubber.

3) It is extensively used in coated papers, being one of the most cost-effective resins to bind pigmented coatings.

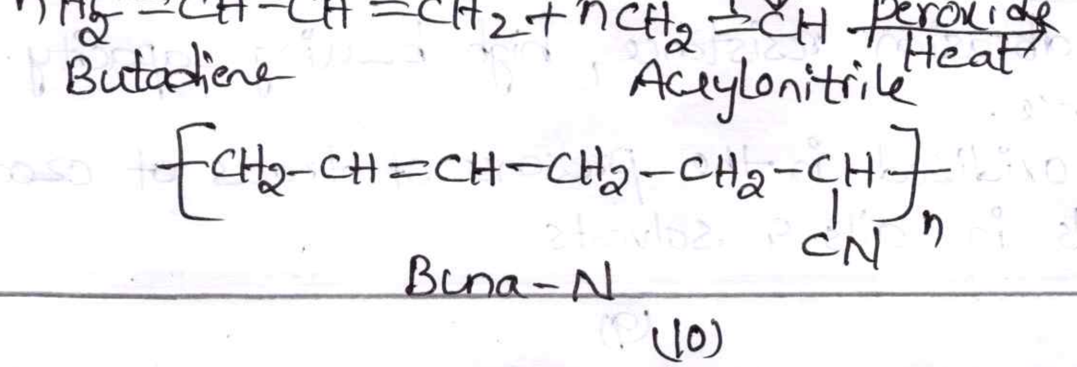
4) It is also used in building applications, as a sealing & binding agent behind renders ~~are~~ as alternative to PVA.

5) Additionally, it is used ~~to~~ in some rubber cutting boards.

6) It is used in making autotypes, floor tiles, footwear components, cable insulation etc.

BUNA-N- RUBBER:- (GRA - General purpose rubber acrylonitrile).

It is the synthetic Rubber obtained by co-polymerization of one part of acrylonitrile & two parts of butadiene



$$n\,H_2C=CH-CH=CH_2 + n\,CH_2=\overset{CN}{\overset{|}{C}}H \xrightarrow[Heat]{peroxide}$$

Butadiene Acrylonitrile

$$\left[CH_2-CH=CH-CH_2-CH_2-\underset{CN}{\underset{|}{C}}H\right]_n$$

Buna-N

Properties:-

1) Buna-N is resistant to oil, fuel & other chemicals aliphatic hydrocarbons.
2) It has tensile strength of $>= 10 N/mm^2$ as well as excellent abrasion & compression set resistance.
3) It is not resistant to solvents. It can be attacked by ozone, ketones, esters & aldehydes.
4) Buna-N should not be stored near ozone generating electric motors, welding equipment or in UV light.
5) Buna-N performs good in petroleum oils & fuels, silicone oils & greases, ethylene glycol, dilute acid & water below 212F.

Applications:-

1) Buna-N is used in the automotive & aeronautical industry to make ~~food~~ fuel & oil handling hoses, seals & grommets.
2) It is used to make protective gloves in the nuclear industry.
3) Buna-N latex is used in the preparation of adhesive & as a pigment binder.
4) XNBR is an improved version of Buna-N, is used for hoses, rubber belts, sealing parts, special purpose article in oil well, reciprocating oil seal, rubber seal, gaskets roll covers, shoe varieties moulded parts for shoe heels & O-rings.

THIOKOL: polysulphide, synthetic rubber:-

Preparation:- Thiokol is prepared by condensation polymerisation of 1,2-dichloroethane with sodium poly sulphide.

$$\underset{\text{dichloroethane}}{n\,Cl-CH_2-CH_2-Cl} + \underset{\text{Sodium polysulphide}}{n\,Na-S-S-Na} \rightarrow \underset{\text{Thiokol}}{(CH_2-CH_2-S-S)_n} + n\,NaCl$$

propeties:-

It cannot be vulconized because of absence of unsaturation in the polymer back bone. Hence it does not form hard rubber.

1) It is resistant to mineral ~~oo~~ oils, fuels, Oxygen, Ozone, sunlight, solvents, gasoline & Kerosene.
2) It is impermeable to gases.
3) It has a bad odour.
4) It has low tensile strength.
5) It has less heat resistance.
6) It has poor abrassion resistance
7) It may lose its shape under continuous

Uses:- Applications:

1) These are used to make sealants, gaskets, balloons, fabric coating.
2) These are used in gasoline pipes.
3) These are used in solid fuel rocket propellants.
4) These are used in Adhesives, Binders, paint spray hoses.

CONDUCTING POLYMERS:-

An organic polymer with highly delocalized pie electrons (conjugated) system having electrical conductance is called a Conducting polymer.

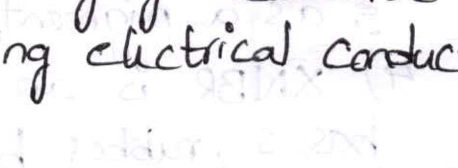
Eg: polyacetylene, polyaniline, polythiophene etc.

polyacetylene:-

In this acetylene molecule undergoes co-ordination polymerization reaction in the presence of Ziegler-Natta catalyst.

$$n\ H-C\equiv C-H \xrightarrow[\text{catalyst}]{\text{Ziegler Natta}} -\!\!\left(CH=CH\right)\!\!-_n$$

polyacetylene



Conducting Mechanism of polyacetylene:-

The mechanism of conduction in the polyacetylene can be explained by p-doping & n-doping

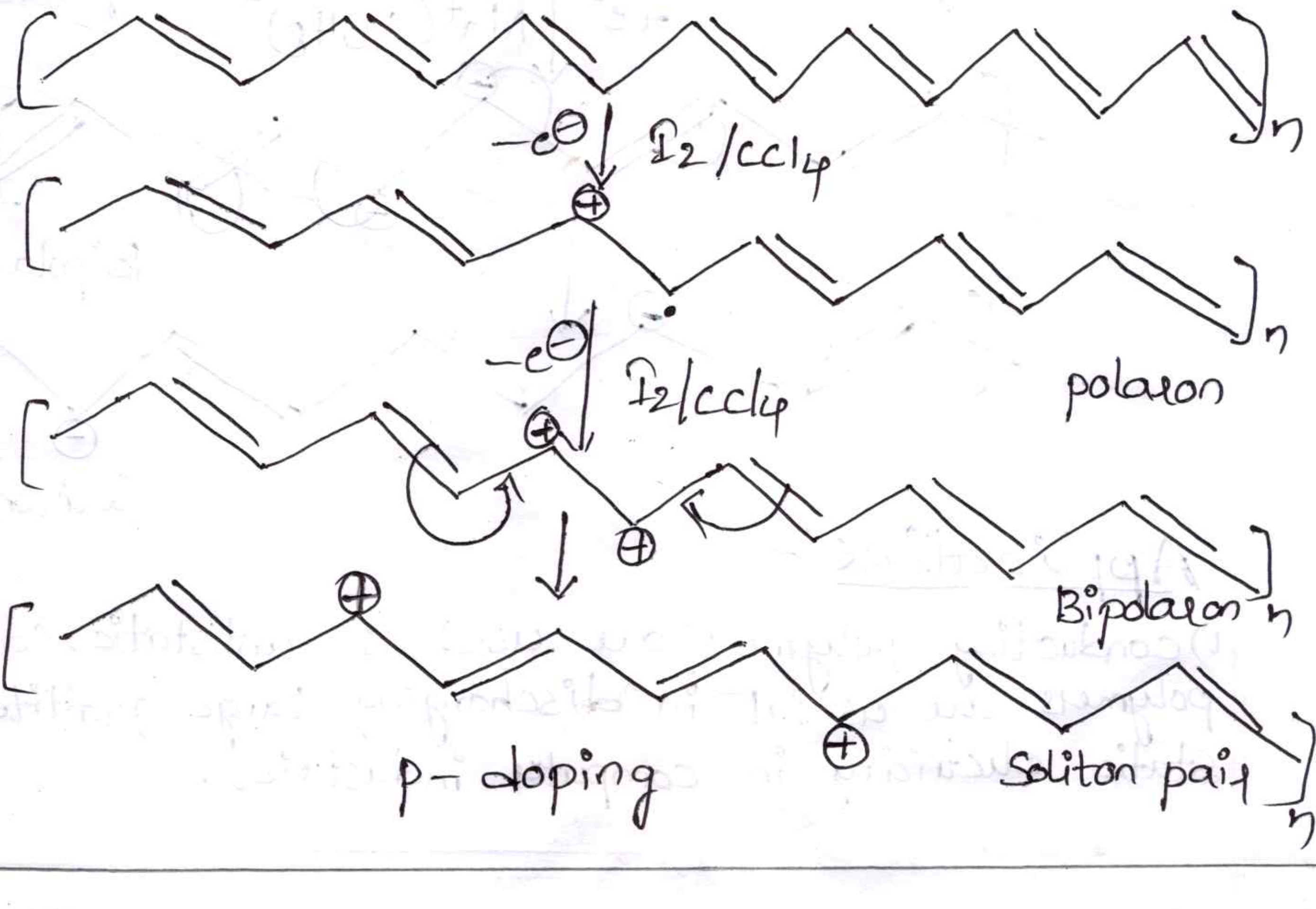
p-doping:-

In this process the polymers are treated with p-doping agents like AsF_3, Br_2, I_2, $HClO_4$ etc which are primarily electron acceptors.

1) The first step is the reaction between polyacetylen & Iodine (in CCl_4). In this process a positive (+ve) charge is formed due to removal of an electron (acceptance of an electron by the dopant) from the polymer. i.e, the formation of polaron ~~ion~~ takes place.

2) Subsequently attack of another molecule of Iodine (in CCl_4) results in the formation of bipolaron

3) Due to separation of charges in bipolaron conduction process takes place.



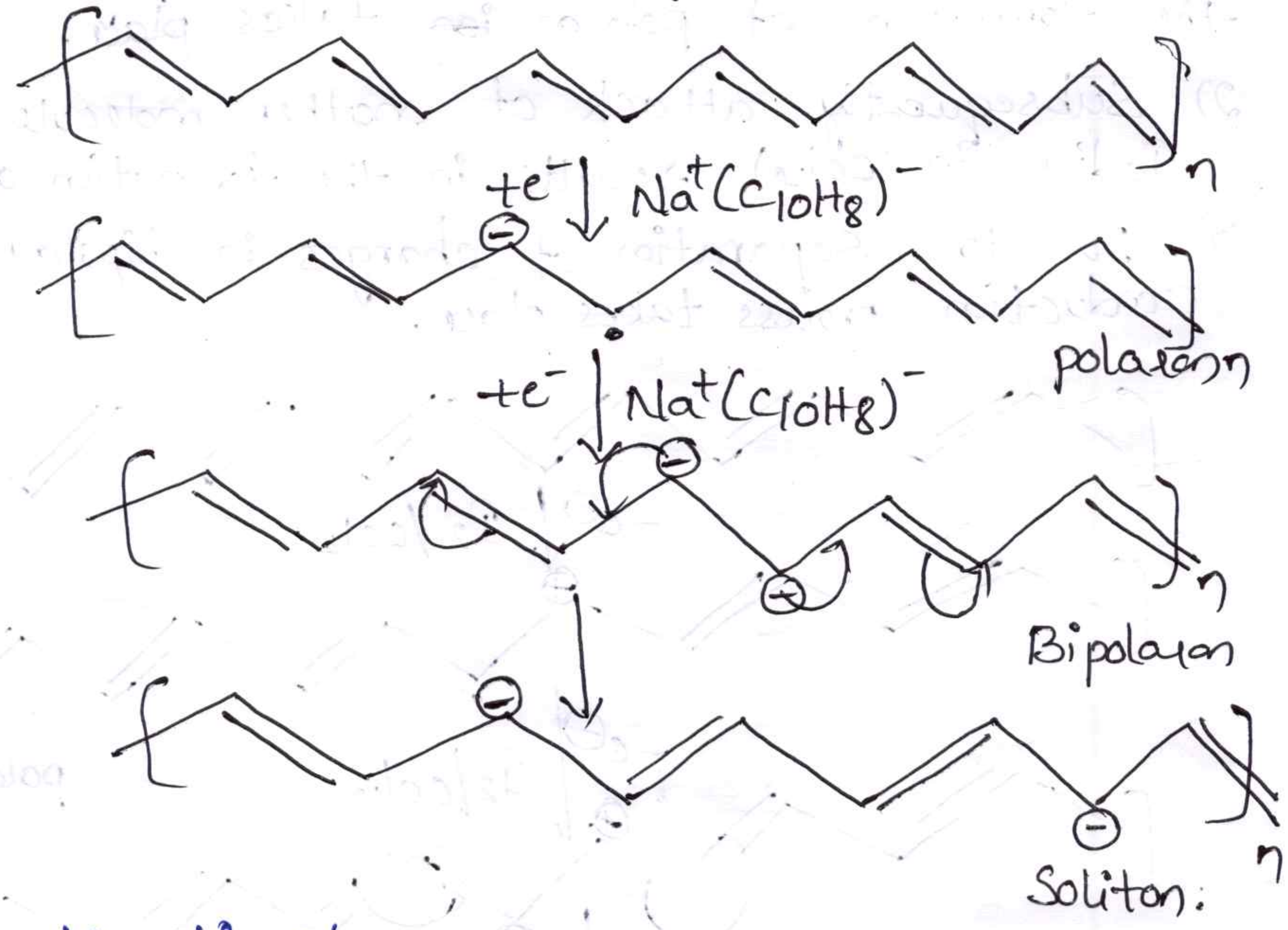
n-doping:-

In the case of n-doping, n-doping agents adds electron to the polymer leading to the formation of negative charge.

Mechanism:

In this mechanism the first step is the formation of polaron followed by ~~a~~ bipolaron & finally Soliton.

This can be done by dopping the film in solution of an alkali metal napthalide dissolved in tetrahydrofuran. Here charged solitons are responsible for conduction in polyacetylene.



Applications:-

1) conducting polymers are used as antistatic. Conducting polymers are useful in discharging large quantites of static electricity in computer industries.

2) These are useful as corrosion inhibitors

3) These are used in solar cells.

4) These are used in photo voltaic devices.

5) These have wide applications in telecommunication systems.

6) These can be used to shield electronic circuits from electromagnetic radiation.

7) conducting polymers can be used in supercapacitors, which are power storage devices.

8) These are used to develop chemical or biosensors. These sensors rely on changes in the optical & electrical properties of the conducting polymers.

FIBRES:-

Fibres are a class of materials that are continous filaments or discrete elongated pieces. They are crystalline present in both plants & animals.

They are used for making textiles, ropes, utilities, strings etc.

These are of two types (1) Natural fibres
(2) synthetic fibres

1) Natural fibres:- produced by plants, animals & geological materials.

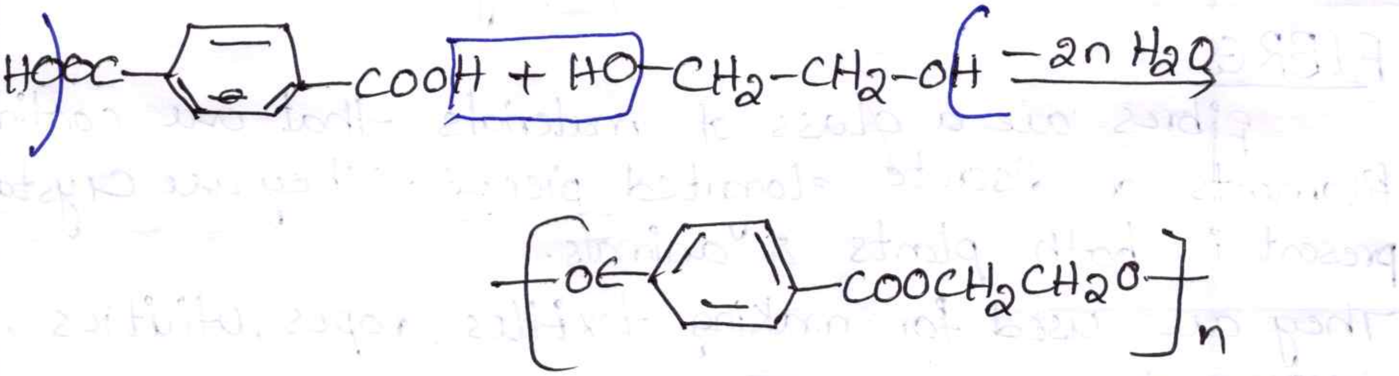
2) Synthetic fibres:- This type fibers can be produced in large quantities & are cheaper than some of the natural fibers like pure silk. polyamide nylons, polyesters, pvc, phenol-formaldehyde resin, polyethylene are often used for making textiles.

polyester: (or) Terylene (or) polyethylene terephthalate:-

This category of polymers ~~are~~, hase ester linkages in the mainchain. It takes 18% of market share of synthetic polymers.

preparation:-

Terylene is a polyester fibes made from ethylene glycol & terephthalic acid. Terephthalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.



(poly ethylene terephthalate)
(polyester)

propeties:-

1) This occurs as a colourless rigid structure
2) This is highly resistance to mineral & organic acids but is less resistant to alkalis.
3) This is hydrophobic in nature.
4) This has high metting point due to presence of aromatic ring.

Applications:-

1) It is mostly used for making synthetic fiber.
2) It can be blended with wool, cotton for better use & wrinkle resistance.

3) other applications of polyester is electrical insulation.

Mechanical Requirements of fibres:-

Crystallinity:-

The crystallinity of a fiber is a "measure of the degree to which its constituent particles are arranged in a regular, ordered lattice structure". The crystalinity of a fibre affects its mechanical & chemical properties.

1) chemical Reactions: Hydrolysis, deuteration or saponification can be measure by crystallinity.

2) physical methods: X-ray diffraction, density, IR spectroscopy are all physical methods that can be used to measure crystallinity.

Crystalinity affects the strength & chemical reactivity of a fibre.

a) strength: The crystalline regions of a fiber give its strength

b) chemical reactivity: The amount of amorphous material in a fiber determines how accesible its reactive.

Degree of crystallinity:-

The degree of crystallinity of a fiber is the three-dimensional order of the polymer chains with in the fiber.

$$\%C = \frac{\rho c}{\rho s}\left(\frac{\rho s-\rho a}{\rho c-\rho a}\right)\times 100$$

Where ρc = crystalline density

ρa = Amorphous density

ρs = polymer density.

STRESS - STRAIN CURVE :-

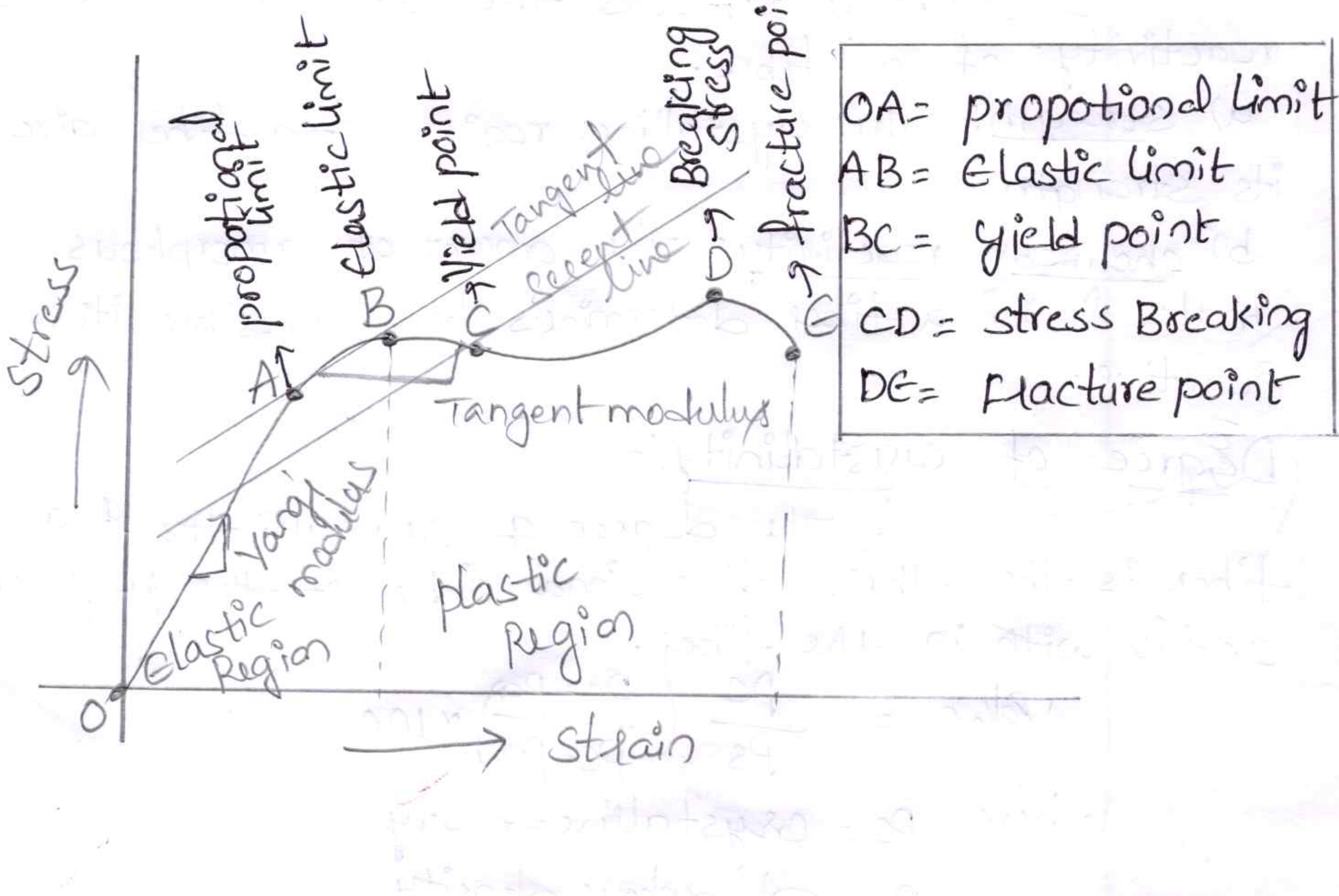
STRESS: stress is defined as force per unit area within material arises from externally applied forces, uneven heating or permanent deformation & that permits an accurate description & prediction of elastic, plastic & fluid behavior

formula $\boxed{\sigma = \frac{F}{A}}$ Where σ = is the stress applied
F = force
A = Area of the force applied

STRAIN:- Strain is the amount of deformation experienced by the body in the direction of force applied.

$\boxed{\varepsilon = \frac{\delta l}{L}}$, ε = Strain due to stress applied
δl = change in the length
L = Original length.

Stress & Strain Curves:-



OA = propotional Limit
AB = Elastic limit
BC = yield point
CD = stress Breaking
DE = Fracture point

The mechanical properties, regarding their elastic properties is most important. The elastic properties of materials by studying the stress-strain relationships.

Stress - Strain Graph:-

The differential regions in the stress-strain diagram are:

(i) <u>proportional</u> Limit:- The point 'OA' in the graph represents the proportional Limit, this limit of stress-strain ratio gives us a <u>proportionality</u> constant known as Yang's modulu

$\boxed{\text{Hooke's Lao} = \text{Strain} \propto \text{stress}}$

(ii) <u>Elastic</u> <u>Limit</u>:- It is the point in the graph up to which the material returns to its original position when the stress is completely removed. A plastic deformation starts to appear in it.

(iii) <u>Yield</u> point:- Yield point defined as the point at which the material starts to deform plastically. After Yield point is passed permonent plastic deformation occurs.

(iv) ultimate <u>stress</u> <u>point</u>:- It is a point that represents the maximum stress that a material can endure before failure.

(v) <u>fracture</u> (or) <u>Breaking</u> <u>point</u>:- It is the point in the Stress - strain curve at which the failure of the material takes place.

Applications:-

1) Textile,
2) packaging
3) films
4) Composites

UNIT - IV

Nanomaterials:-

The term Nanoscale refers to the dimension of 10^{-9} meters. It is the one billionth part of a meter. "The particles which their has external dimensions (or) internal structure dimension lies in the range of 1nm to 100nm are considered as Nanomaterials. They exhibits unique properties like melting point, reactivity, reaction rates, electrical conductivity, colour, transparency etc.

properties of Nanomaterials:-

* The magnetic properties increases with decrease in size of materials.

* Melting point of the Nanomaterials increases when compared with other material depending on size of particles.

* Solubility of nanomaterials is more than other materials due to decreased size.

* Colour: The physical property colour is again size dependent.

* Transparency:- Transparency of nanomaterials is more than other materials.

* Catalytic Behaviour:- Due to increased surface area, the catalytic activity of nanomaterials is more than other materials.

* Chemical Reactivity:- Nanoparticles possess high chemical Reactivity.

* The Nanomaterials exhibit good dispersibility.

* The nanomaterials can be used as good conducting, semi conducting & insulating materials.

Classification of Nanomaterials:-

Nanomaterials can be classified in various way. On the basis of electrical properties, they classified as

* Conducting (Metallic)

* Superconductivity (semi conductor)

* Non-conducting (Insulators)

On the basis of Magnetic properties, they can be classified as:

- * Magnetic Nanomaterials.
- * Non- Magnetic Nanomaterials.

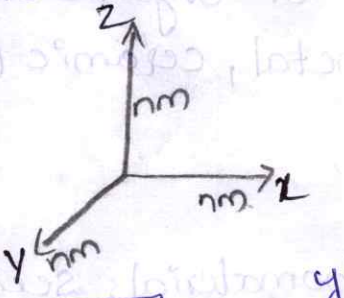
The most commonly adopted method of classification is based on their dimension. On the basis of dimension, they are classified as:

(1) Zero - dimensional Nanomaterials :- Here all dimensions (x, y, z) are at nanoscale, ie, no dimensions are greater than 100nm. It includes nanospheres and Nanoclusters, Fullerenes

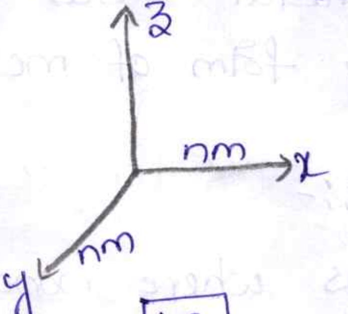
(2) One - dimensional Nanomaterials :- Here two dimensions (x, y) are at nanoscale & the other is outside the nanoscale. It includes Nanofibres, nanotubes, Nanorods & Nanowires.

(3) Two - dimensional Nanomaterials :- Here, one dimensions (x) is at nanoscale & the other two are outside the nanoscale. It includes Nanofilms, nanolayers & Nanocoatings with Nanometre thickness., Graphene.

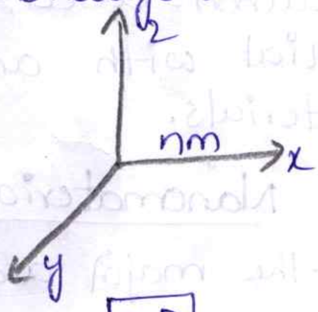
(4) Three dimensional Nanomaterials :- These are the nanomaterials that are not confined to the nanoscale in any ~~direction~~ dimension These materials have three arbitrary dimensions above 100nm. It includes dispersion of nanoparticles, bundles of nanowires & Nanotubes as well as multi nanolayers.



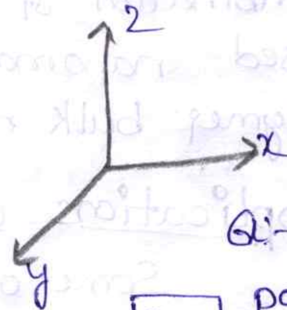
0D



1D



2D



3D

Q:- liposome
polycrystal
Dendrimer

On the basis of the Composition, Nanomaterials are again classified as given below.

(1) Carbon based Nanomaterials :-

These Nanomaterials are mainly composed of Carbon. These carbon based Nanomaterials ~~exists~~ exists into diff forms & Morphologies such as carbon nanotubes (CNT) fullerenes, Graphene, carbon nanofibres, & carbon black.

(2) **Metal based Nanomaterials:-** These nanomaterials are composed of different metals. These nanomaterials include Silver nanoparticles (nps), Gold nps, copper nps, Iron nps, platinum nps, Aluminium nanoparticles (nps - nanoparticles)

(3) **Metal oxide Nanomaterials:-** These nanomaterials are constituted of metal oxide. These nanomaterials includes Titanium dioxide (TiO_2) nps, Zinc oxide (ZnO) nps, Nanosilica, nanoalumina, Iron oxide, & Cerium oxide nps.

(4) **Dendrimers:-** These Nanomaterials are nanosized polymers which are made from branched units. There are numerous chain ends on the surface of the dendrimer. These chain ends can be tailored to perform specific chemical functions This characteristic makes it useful for catalysis.

(5) **Composite Based Nanomaterials:-** These Nanomaterials are made by combining nanoparticles with another nanoparticle. (or) With larger bulk materials. In composites nanoparticles can also be confined with more complex structures such as metal-organic frameworks. Composite can be the combination of carbon-based, metal-based or organic based nanomaterial with any form of metal, ceramic (or) polymer bulk materials.

Applications of Nanomaterials:-

Some of the major areas where nanomaterials seem highly applicable are listed below

- * Electronics & Nanoelectronics
- * Nanosensors & Nanoprobes, Nano catalysts
- * Food & Agriculture Industry,
- * personal care products & consumer goods.
- * Automobile Industry.
- * Water treatment & the environment
- * Medical diagnostics and related applications
- * Textiles, paints.

~~(b) BORON BUCKY BALLS :- A type of Buckyballs which uses Boron atoms instead of a carbon atom is Boron fullerene.~~

~~(c) Metallo fullerenes :- These are a class of novel Nanoparticles, comprises 20 carbon atom (C_{20}) forming a sphere which encloses a complex of three metal atoms & one Nitrogen atom.~~

CARBON NANOTUBES :- (CNT)

* Carbon Nanotubes is one of the allotrophy of carbon.

* In 1991, a Japanese physict, Sumio Lizima inverted the CNT.

* CNT is a hollow tube made up of carbon of nanoscale diameter. CNT are also called as Buckytubes.

* CNT are formed by folding or rolling two-dimensional graphite into a cylindrical shape structure. The diameter of nanotube is 1-3nm. The length of the CNT is much higher than ~~the~~ its diameter.

Types of CNT :-

(1) Single - Wall Nanotubes (SWNT) :- These may be zigzag, arm chair & chiral depending on the manner in which the graphene sheets are rolled

* The diameter of single-walled carbon nanotubes is 2nm. The length of single-walled CNT is around 2 micro meters. They exist in a one-dimensional structure.

* Their band gap varies from 0-2 electron volts (ev). They show conductivity like a semiconductor. Therefore, they exhibit both metallic & semiconductive behaviour.

(2) Multi - wall Nanotubes (MWNT) :-

It consists of several single walled nanotubes with different diameters. A multi-wall

The outer diameter of multi walled carbon nanotubes is arand 2-20nm. The inner diameter of MWCNT is 1-3nm The length is about 5-6-micrometers.

Properties of CNT:-

(1) Carbon Nanotubes (CNTs) are electrically & thermally conductive & have a high mechanical strength

(2) In terms of tensile strength & elastic modulus, CNT are the strongest & stiffest materials yet found.

(3) Thermal conductivity & Expansion:- The carbon bond's rigidity aids in the transmission of vibrations throughout the nanotube, resulting in excellent heat conductivity.

(4) CNT are chemically neutral. So, they are chemically stable. Therefore, CNT resist corrosion.

(5) The crystalline structure of CNT exists in the form of regular hexagons.

(6) In CNT, each carbon atom is surranded by three other carbon atoms through covalent bonds. These carbon carbon covalent bonds form lattices in the shape hexagons.

(7) The density of the CNT is one-fourth of that of steel

(8) CNT are elastics.

Applications of CNT:-

1) CNT are used in pharmacy & medicine to absorb or conjugate a wide range of medicinal

(1) CNT can used as drug delivery vehicles, carrying medications directly to targeted cells or tissues.

2) CNTS, can be used to create sensitive ~~bacteria~~ biosensors for detecting various substances in the body like glucose, choline or hydrogen peroxide.

3) CNTS are used as electrode materials in batteries & supercapacitors, enhancing their performance & lifespan.

4) CNTS can ~~be~~ improve the efficiency & performance of fuel cells.

5) CNTs can be used to storage H_2 gas.

6) CNTs can be used to create high-performance transisters replicating silicon-based transistors in some applications.

7) CNTs can act as antennas for various electromagnetic devices.

8) CNTs can be used to create thin-film electronics, including touchscreens & flexible displays.

9) CNTs can be used in composite materials to enhance their strength & flexibility such as sporting goods, aerospace components & bulletproof jackets.

10) CNTs can be used in Water & air filters due to their high surface area & pore size.

11) CNTs can ~~b~~ serve as supporting material for catalysts in various Chemical Rn's.

12) CNTs can be used ~~as~~ in photocatalytic reactions to break down pollutants in Water & air.

Applications:-

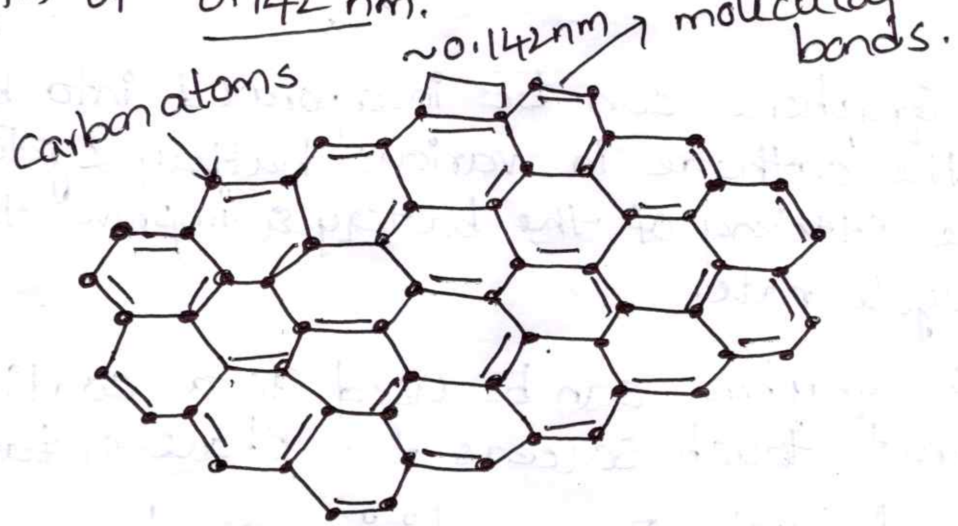
1) ~~protective coating~~
2) ~~Thin-films & fiber~~
3) ~~Opto-mechanical~~
4) ~~Nanoscale powder~~
5) ~~Medicine.~~

GRAPHENE :-

Graphene is a single layer of carbon atoms that are tightly bound together by strong covalent bonds.

GRAPHENE:

Graphene is a two-dimensional material (2D) made up of a single layer of carbon atoms arranged in a hexagonal honey comb lattice. The carbon atoms of graphene are tightly band together by strong covalent bonds. It is an allotrope of carbon in the form of a plane of sp^2-bonded atom with a molecular bond length of 0.142 nm.



Graphene

Properties:-

Graphene has many excellent properties.

1) Graphene is 200times stronger than steel.
2) Graphene has good electrical conductivity.
3) Graphene is very trasparent.
4) Graphene has high melting & Boiling ~~[illegible]~~ points.
~~5) Graphite occurs~~
5) High hardness & high Resistance
6) Able to generate electricity by exposure to sunlight
7) Antibacterial effect, Bacteria are not able to grow in it.
8) High elasticity & flexibility
9) Low electricity consumption compared to other compounds.

Applications:-

1. Sensors: Graphene could be used in sensors in various fields including bio-sensors, diagnostics, field effect
2. transistors, DNA sensors, & gas sensors, to name a few.
2. Batteries: Graphene can be incorporated into both the anode & the cathode in various battery system to increase the efficieny of the battery & improve the charge/discharge cycle rate.
3. Electronics: Graphene can be used as a coating to improve current touch screens for phone & tablets.
4. Rust free future:- By combining graphene with paint a unique

[illegible]) ~~[illegible]~~

Applications of Graphene:-

5) Telecommunications:-
Graphene can enhance the efficiency & quality of data transmission in 5G & 6G networks.

6) Solar cells:- Graphene improves the efficiency of solar cells, enabling them to convert sunlight into electricity more effectively.

7) Water purification:- Graphene's unique structure allows it to be used in water filteration & purification technologies.

Nanomaterial Synthesis:-

preparation of Nanomaterial by sol-gel method: (or) Wet chemical Method:

Introduction:

Sol-gel is a wet chemical process that involves the formation of an organic colloidal suspension (sol) & gelation of the sol in a continous liquid phase (gel) to form a three-dimensional network structure. from: Corrosion protection & control using Nanomaterials.

Bottom up Approach:

- Bottom up approach means small to big.
- In this method, Nano materials are from atoms or molecules by self assembly.
- Atom - clusters - Nanoparticles.

Top - Down - Approach:

- Top Down approach means big to small.
- In this method, bulk solid is disassembled into fiber particle of nano size.
- Bulk material - powder - Nanomaterial.

SYNTHESIS / PREPARATION:-

The stages of the sol-gel process:-

1) Hydrolysis (sol formation):

In this process, is an aqueous sol of the metal alkoxide M-OR, where R is the alkyl group.

The Metal alkoxide reacts with the surranding water & forms the colloidal suspension (sol) of the metal hydroxide, M-OH according to the hydrolysis reaction

Reaction:

$$MO\boxed{R + OH}-H \xrightarrow[TEOS]{Si\cdot(OC_2H_5)_4} M-OH + R-OH$$

2) Poly condensation: (Gelation):

It results in a formation of the Gel - a rigid 3-D network of polymeric molecules surranded with the solvent.

Reaction:

$$M-\boxed{OH} + MO\boxed{R} \longrightarrow MOM + R-OH$$

$$M-\boxed{OH} + M-O\boxed{H} \longrightarrow MOM + H_2O$$

3) Aging:

During the aging stage the poly condensation reaction contineou, completing the formation of the gel.

The gel structure is reinforced with additional cross-links, which cause contraction of the gel matrix & explusion of the solution from the shrinking pores.

4) Drying:-

The water & other liquid entrapped within the ~~papers~~ poles of gel structure are removed during the stage. Drying is performed at a temperature of about 400°F (-200°C) after drying, the gel convert into high density micro-porous structure called Xerogel.

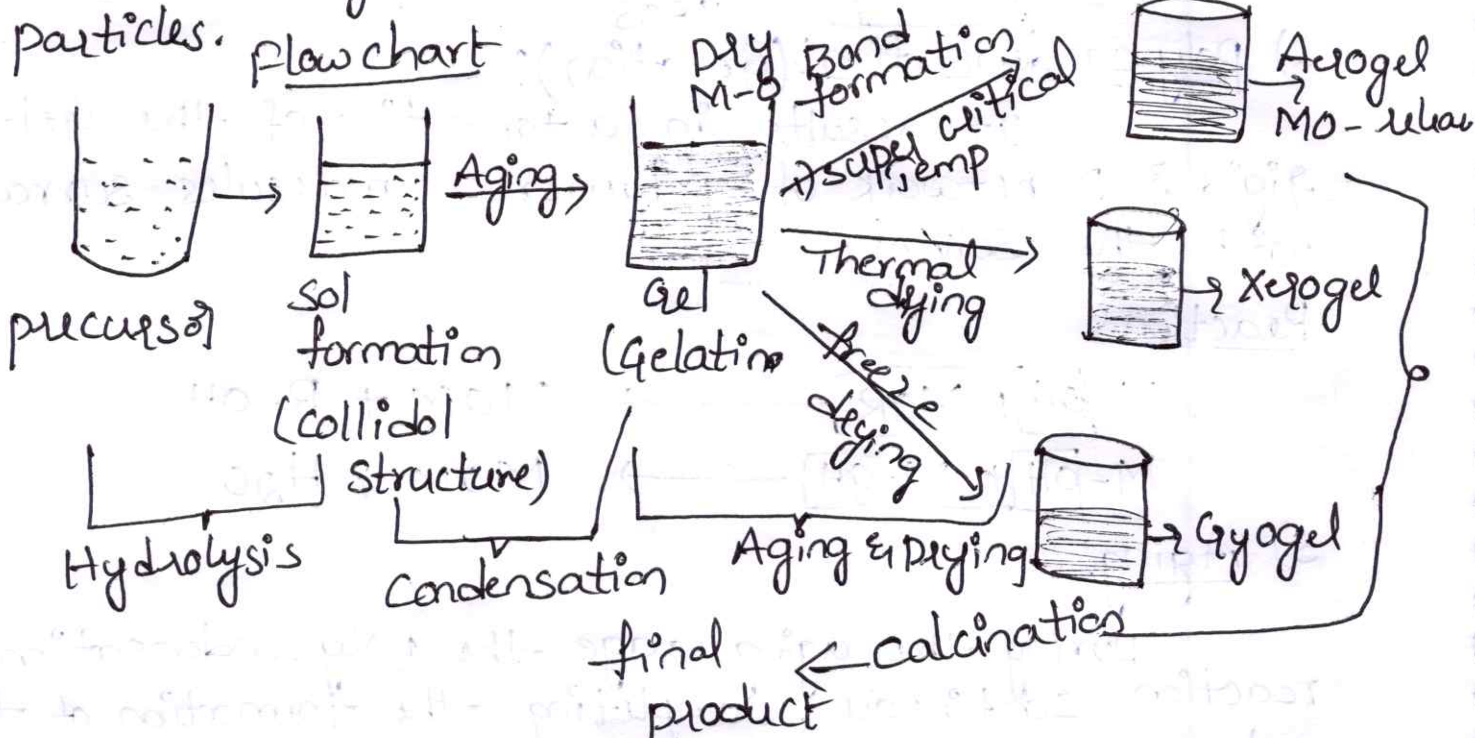
Drying a super-critical conditions preventing collapsin of the gel network results in a formation of a macro-porous low density structure called Aerogel.

5) Calcination:-

Calcination is performed at increases temp-erature. varying within the range 780-1470°F (400-800°C).

It prevents rehydration of the gel.

Calcinid gels contains nanosized metal oxide particles.



Advantages:

1) Simple, low cost & highly yield.
2) synthesis at low temperature
3) control on the chemical composition.
4) producing high quility materials
5) High scale homogeneity & purity.

Disadvantages:

1) This technique is quite substrate dependent.
2) Metal alkoxides are the most prefered precursor. But they are expensive
3) Formation of gel is a slow process, which makes sol gel a time consuming fabrication technique as compared to other methods.

Applications:-

(1) protective coating, (2) Thin-films & fiber
(3) opto-mechanical (4) Nanoscale powder
5) Medicine

Example: Synthesis of SiO_2 Nanoparticles.

A typical sol-gel reaction is hydrolysis & condensation of Tetra ethyl ortho silicate (TEOS) as a precursol of Silica Nanoparticles. TEOS & Water were mixed in the following molar ratios of H_2O 4:1. During the sol-gel process, TEOS was first hydrolysed to silicic acid. Then condensation Reaction has led to formatio of si-o-si bonds. The overall sol-gel reaction employed in the production of the SiO_2 by sol-gel method as follows.

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH$$

Tetra Ethyl Orthosilicate

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$$

POTENTIOMETRY:-

It deals with a estimation of chemical substances in the solution by measuring the potential value.

potentiometric Titration:- (PRINCIPLE :-

potentiometric titration is a volumetric method in which the changes in the emf between two electrodes (Ref & Indicator electrode) on the addition of titrant of known concentration (titrant) to the unknown solution (analyte).

Ref Electrode: potential remains constant & independent of analyte to solution (E_{Ref})

Indicator electrode: potential varies with conc. of analyte solution (E_{Ind})

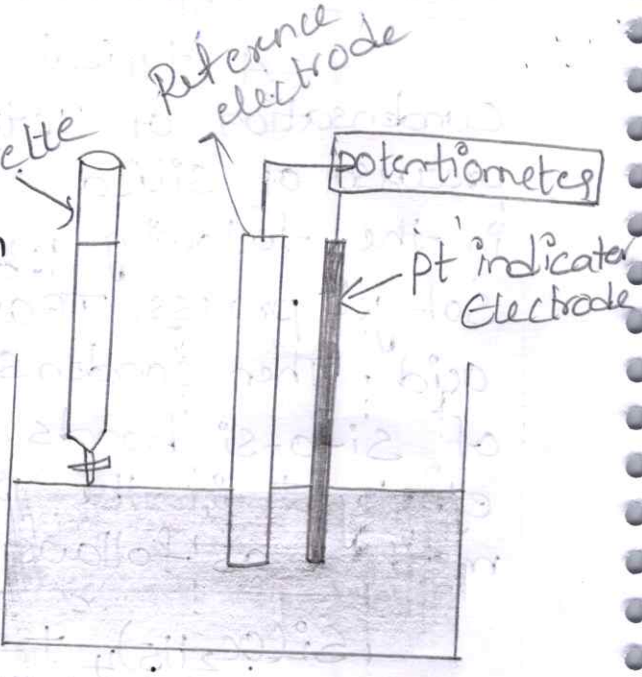
$$\boxed{E_{cell} = E^0_{Ind} - E^0_{Cal}}$$

The relation between electrode potential & metal ion concentration is given by Nernst eq:

$$\boxed{E = E^0 + \frac{0.0591}{n} \log M^{n+}}$$

INSTRUMENTATION:-

1) potentiometer consists of 2 electrodes ie a Ref electrode & an Indicator electrode which are connected to a device (potentiometer) for measuring the potential.



2). The indicator electrode (cal) responds rapidly to the changes in the potential is mea due to the concentration changes of on analyte

3) Burette is filled with the titrant sol. stirrer is used to stir the sol for uniform concentration.

Detection of end point:

1) The EMF of the cell changes by the addition of small amants of titrant, so the concentration of reversible ion in contact with indicator electrode changes.

2) The change of potential will be slow at first, but at equivalence the point change will be sharp or quite sudden.

3) The values are then plotted against corresponding volume changes.

4) A curve is obtained like shown in fig (a).

5) The end point corresponds to the point of inflexion, i.e, point where the slope of the curve is maximum.

6) Alternatively, change in emf(ΔE) with every small addition of titrant is plotted again volume (ΔV). The maximum of curve gives the end point. (fig (b).

$K_2Cr_2O_7 + 2FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 7H_2O$

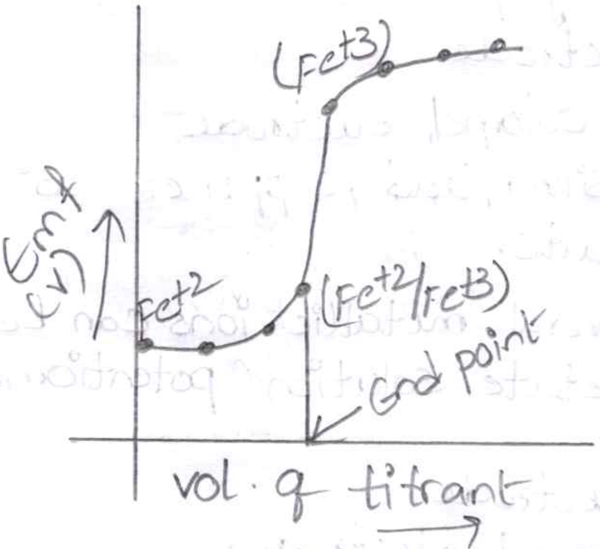


fig (a)

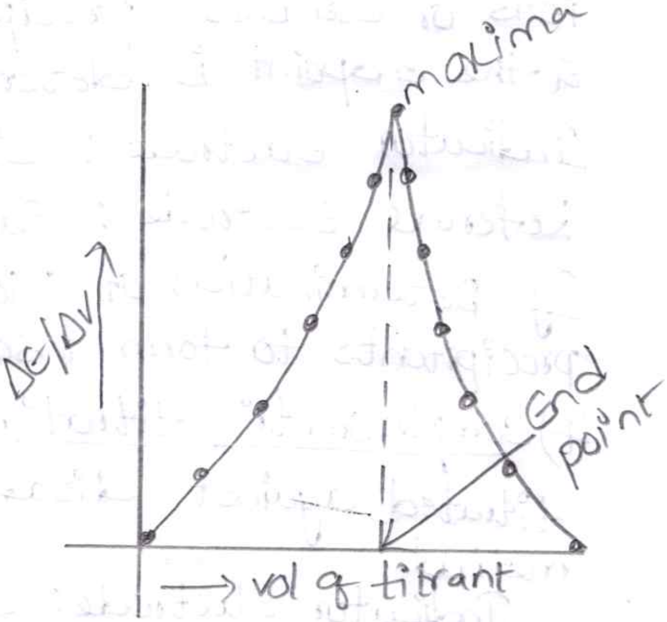


fig (b)

Applications:- of potentiometric Titration:-

1) Acid-Base titrations:- Acid-base titrations can be done in ageous medium or non-aqueous medium.

Indicator electrode : Glass electrode
Reference electrode : Saturated calomel electrode.

Eg: 1) strong acid vs strong Base : HCl vs NaOH
2) Weak acid vs strong Base : CH_3COOH vs NaOH
3) Mix. of acids vs strong Base : HCl + CH_3COOH vs NaOH

2) Redox titrations:- Oxidation reduction titration to estimate the concentration of analyte of the sample solut

In redox titration the Indicator electrode such as platinum electrode & the reference electrode - generally a calomel electrode is used. The potential of the electrode depends on the conc. of substance being oxidise or reduced.

$$E_{cell} = E^{\circ}_{cell} + \frac{0.059}{n}\log\frac{[\text{Oxidised}]}{[\text{Reduced}]}$$

Eg: 1. Ferrous Ammonium sulphate in dil. H_2SO_4 vs $KMnO_4$
2. Ferrous Ammonium sulphate in dil. H_2SO_4 vs $K_2Cr_2O_7$

3) precipitation Titrations:-

For the quantitative determination of several ions or elements, precipitating agents are used as titrants & the endpoint is determined by potentiometric method.

Indicator Electrode : Silver Electrode

Reference Electrode : Saturated calomel electrode

Eg: Determination of Mercury, silver, lead, copper etc using precipitants to form insoluble salts.

4) complexometric titrations:- Several metallic ions can be titrated against disodium edetate solution potentiometric method.

Indicator electrode: Silver electrode

Reference electrode: sat. calomel electrode.

Eg: Divalent ions, trivalent ions CN^-, etc vs EDTA.

5) Diazotization: Titrations:-

Drugs or substances containing aromatic primary amino group can be titrated against sodium Nitrite in acidic medium. This results in diazonium salt formation. This is called Diazotization.

Indicator electrode: silver electrode/Glass electrode

Reference electrode: Sat. calomel electrode/ H_2 electrogen

ELECTROMAGNETIC SPECTRUM (EMR) :-

- Light is a form of electromagnetic radiation, which are the fields that are associated with light energy.
- Some properties of Light include Wavelength & frequen

frequency: (Hz) The number of waves ~~of~~ in a specific time

Wavelength (nm) The distance b/w the two points in a wave.

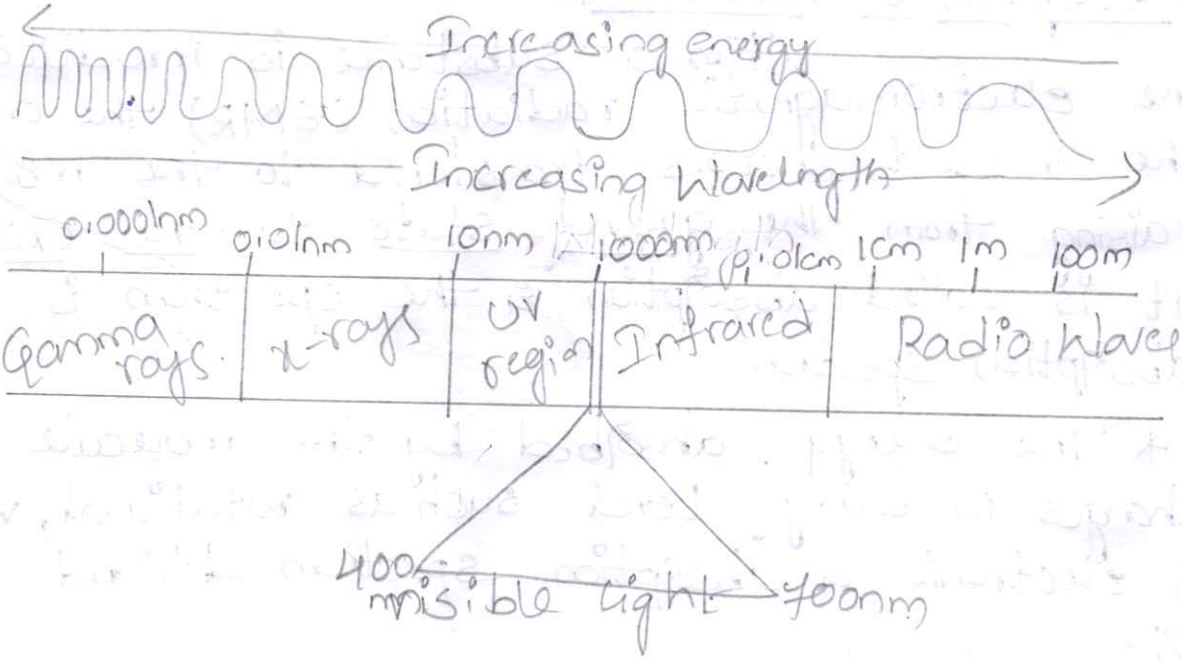
- Just as Wavelength & frequency are related to Light, they are also related to energy. The shorter the Wavelen & higher the frequency corresponds with greater energy.
- so Longer the Wavelength & Lower the frequency resul in Lower energy.

Energy $\boxed{E = h\nu}$

E = Energy

h = planc's constant $(6.626 \times 10^{-34}$ J

ν = frequency.



Electro Magnetic Radiation:-

It is defined as range of frequncies of electromagnetic Radiation & their respective Wavelengths & photon energies of given analyte. (unknown solution).

Electromagnetic Radiation	Wavelength Range
Gamma rays	$<10^{-12}$ nm
X-rays	1nm - 1pm
ultraviolet rays	400nm - 10nm
visible	750nm - 400nm
Near IR	2.5μm - 750nm
IR	25μm - 2.5μm
Far IR	300nm - 1nm
Micro Waves	1mm - 25μm
Radio Waves	> 1mm

Absorption of Radiation:-

When a substance is irradiated with the electromagnetic radiation (EMR) the energy of the incident photons transfered to the molecules raising from the grand state to the excited state. It is called absorption & the spectrum is known as absorption spectrum.

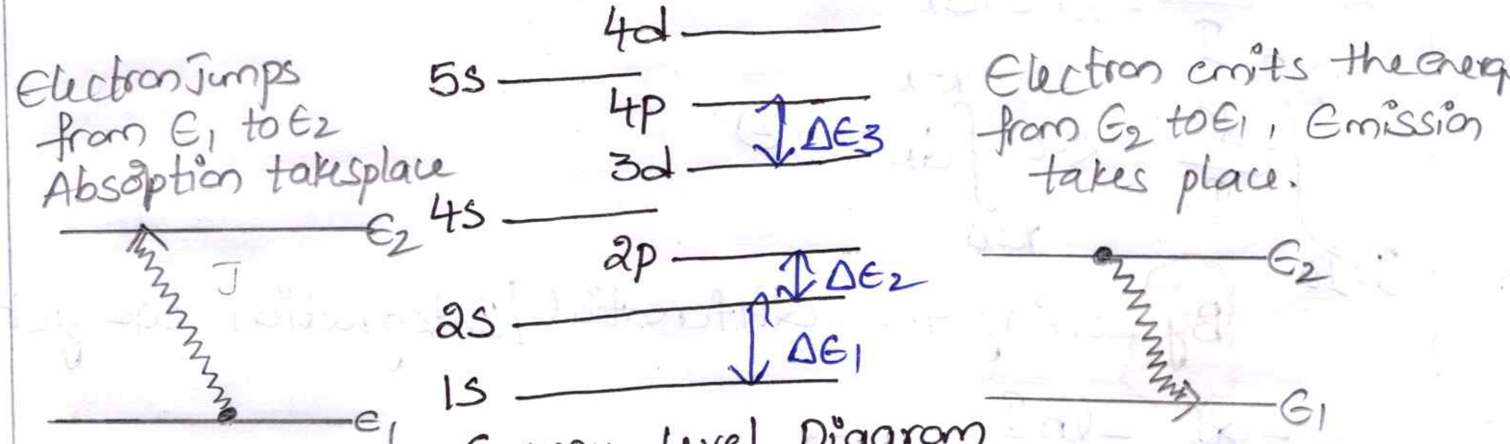
* The energy absorbed by the molecule will bring changes in energy Level such as rotational, vibrational & electronic & absorption spectrum divided into two types.

1) Atomic absorption spectrum.
2) molecular absorption spectrum.

Atomic Absoption spectra:-

This spectrum is produced by atoms, excited by the absoption of electromagnetic radiation (EMR) excited atom come to grand state, electronic transitions occurs

$1s \longrightarrow 2s$ (ΔE_1) (x-ray)
$2s \longrightarrow 2p$ (ΔE_2) (UV)
$3d \longrightarrow 4p$ (ΔE_3) (visible)



Energy level Diagram

Molecular Absoption spectra:-

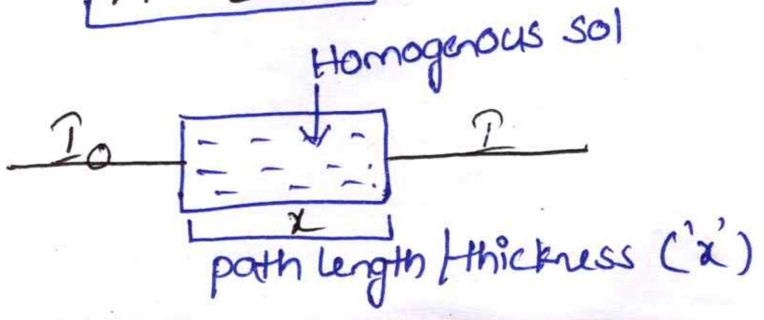
A molecule absorbs electromagnetic radiation enter into excited & return to grand state, it will gives bonds & this spectrum is called molecular Spectra.

Electronic changes are vibrational & rotational.

BEER'S LAMBERT'S LAW:-

When a beam of monochromatic light is passe through a homogenous absorbing medium, then rate decrease in intensity of light with thickness of the medium is directly propotional to the intensity of incid-ent light & conc. of solution as well as path length.

$$\boxed{A = \varepsilon c l}$$



DERIVATION :-

$$-\frac{dI}{dx} \propto Ic \longrightarrow ①$$

$$-\frac{dI}{dx} = KIc$$

$$-\frac{dI}{I} = Kc.dx \longrightarrow ②$$

I = Intensity of incident light
c = Conc. of solution
k = constant
x = thinckness or path length of sol

By integrating the above eq ② we get

$$\int_{I=I_0}^{I=I} -\frac{dI}{I} = Kc\int_{x=0}^{x=x} dx \longrightarrow ③$$

Solving the intergration we get

$$-\ln\frac{I}{I_0} = K.cx$$

$\ln\frac{I_0}{I} = Kcx$ (ln converts log we get)

$$2.303 \log\frac{I_0}{I} = Kc.x$$

$$\log\frac{I_0}{I} = \frac{K}{2.303}c.x \longrightarrow ④$$

Since, we have some constant values like

$$T = \frac{I}{I_0}, \quad A = \frac{1}{T},$$

$$A = \log\frac{1}{\frac{I}{I_0}} = \log\frac{I_0}{I}$$

And in the place of $\frac{K}{2.303}$, we are keeping on another constant i.e, 'ε'.

By Substituting the 'A' & ε in the above eq ④ we get (or) the equation get changes to

$$\boxed{A = \varepsilon C \cdot l}$$

Where = A = Absorbance
ε = Molar Absorbity
C = conc. of solution
l = path of solution.

Applications:

1) It is used for analysis of a mixture by spectrometry
2) It is used to determine concentration of substance
3) It is used to analyse qualitative & quantitative analysis of biological & domenstic materials.

Limitations:-

1) In this law, we can use only monochromatic light (not polychromatic light)
2) It is applicable for dilute solutions, not applicable for concentrated solutions.

UV-VISIBLE SPECTROSCOPY:

PRINCIPLE:

The absorption of EMR by substances in the visible & ultravoilet regions of the spectrum changes in electronics structure & ions & molecules. UV & visible light are energetic enough to promote outer electrons to higher energy levels.

* UV-visible spectroscopy is applied for qualitative & quantitative analysis of molecules & inorganic ions or complexes in solution.

* The conc. of an analyte in the solution can be determined by measuring the absorbance at some wave-length & applying Beer-Lambert Law.

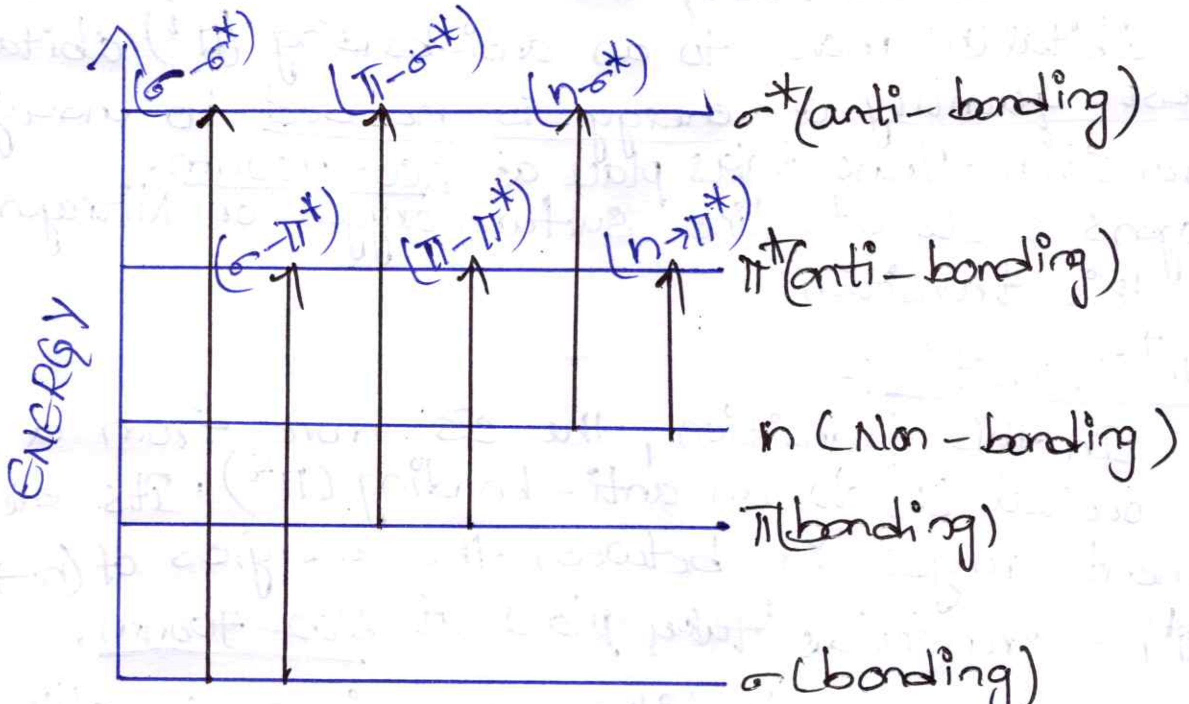
ELECTRONIC TRANSITIONS :-

The absorption of UV or visible radiation corresponds to the excitation of outer electrons of atoms of analyte specimen.

The three kinds of electrons responsible for electronic transitions are:

- Sigma (σ) electrons in saturated molecules
- pi (π) electrons in unsaturated molecules.
- Non-bonding (n) electrons in non-bonded elements.

These electrons absorb ultraviolet radiation, which causes excitation. The movement from grand state to exited state to a higher energy state is categorized into four types of electronic transitions. They are as follows.



1) $\sigma \rightarrow \sigma^*$ Transitions :-

In this transition, the electrons in a molecule move from a bonding(σ) orbital to its antibonding orbital (σ^*). This transition takes place due to the EMR that gets absorbed. Transitions takes place at 125nm

- The highest quantity of energy is needed to transition
- It can be observed in methane molecule due to presence of C-H bond.

2) $n \rightarrow \sigma^*$ Transitions :-

- In this transitions, the electrons from a non-bonding orbital (n) move to an anti-bonding(σ^*) orbital. The lowest quantity of energy is needed to undergo this transition. Transitions takes place at 150-250nm
- Halogens & elements like Sulfur, Oxygen, & Nitrogen display this transition.

3) $n \rightarrow \pi^*$ Transitions:-

In this transition, the electrons from a non-bonding orbital (n) move to an anti-bonding (π^*) orbital. The lowest quantity of energy is needed to undergo this transition. Trans takes place at 200-700nm.

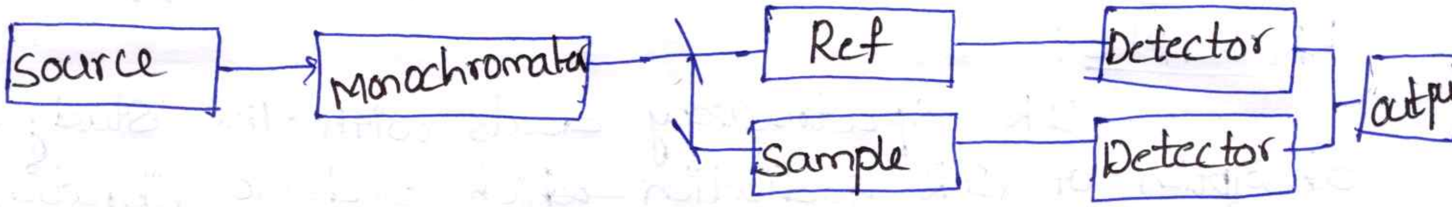
- Halogens & elements like Sulfur, oxygen or Nitrogen display this transition.

4) $\pi \rightarrow \pi^*$ Transition:-

In this transition, the e's move from a bonding orbital (π) to an anti-bonding (π^*). Its energy requirement ranges in between the energies of ($n \rightarrow \sigma^*$) & ($n \rightarrow \pi^*$) - Transitions takes place at 200-700nm.

Organic compounds like aromatic ones, alkenes, alkynes, nitriles, & carbonyl compounds display this transition.

INSTRUMENTATION :-



SOURCES:- Tungsten/Halogen lamps very efficient & their output extends well into the UV.

MONOchromator:-

polychromatic radiation enters the monochro-mator through the entrance slit. The beam is splits into its component wavelengths by the prism.

By moving the dispersing element or the slit radiation of only particular wavelength leaves the monochromator through the exit slit.

Cuvette:

The containers for the sample & reference solutio must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required.

Detectors:- The photomultiplier tube is commonly used detector. It consists of a photo emissive cathode several dynodes & an anode.

Applications:-

1) UV/visible spectroscopy is applied to qualitative & quantitative analysis of molecules & inorganic ions or complexes in solution Quantitative estimation of ionic solutions Transition metals.

2) versatility of UV-vis spectroscopy has been adapte to detection in HPLC Technique.

3) It is used to determine concentration of substance by absorption spectra.

IR- SPECTROSCOPY :- / Vibrational Spectroscopy :

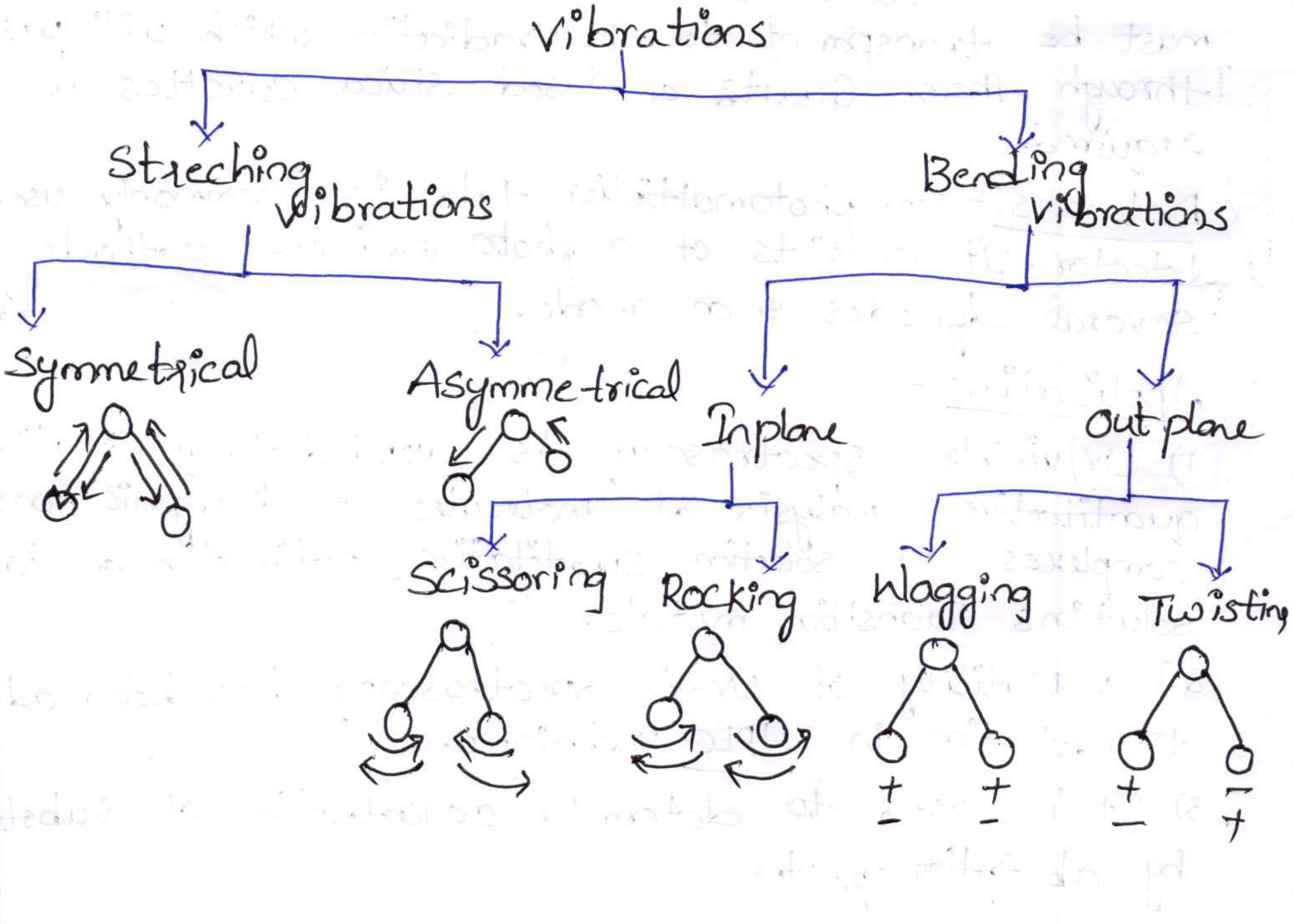
PRINCIPLE :-

IR spectroscopy deals with the study of absorption of IR radiation which undergo vibrational transitions.

In a Molecule, number of atoms are connected with bonds, due to continuous movement of molecule, vibrations will occur with some frequeny, it is called Natural frequeny.

When energy in the form of IR Radiation is applied is equal to the natural frequeny. Absorption of molecule takesplace & a peak apperance is observed.

Types of vibrations :- / Fundamental modes of vibrations :-



① **Streching vibrations:-** In this the bond length changes increases or decreases.

a) **Symmetlical:-** In this vibrations two length of two bonds increase or decrease symmetrically.

b) **Asymmetrically:-** In this vibrations one bond length decreases & other increases.

② **Bending vibrations:-** In this bond angles changes

a) **Inplane:-** Bending of bonds takes place within the same plane. (i) **Scissoling**: Bond angle decreases

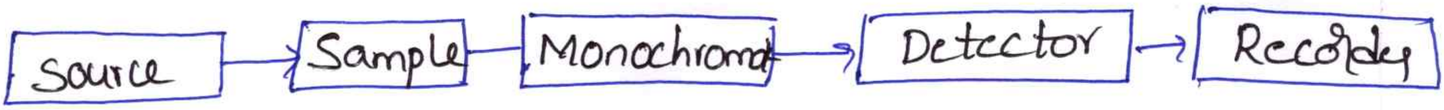
(ii) **Rocking**: Bond angle is same but bonds move to same direction in plane.

b) **Out of plane:-** Changes in plane above (or) below.

(i) **Wagging:-** Both atoms are in above plane (or) Both atoms are below the plane.

(ii) **Twisting:-** One atom above & one atom below the plane.

INSTRUMENTATION:-



Source:- Nernst glower, Nichrome Wire global source, is using as a IR-light source.

Sample:- Solid samples mixed with KBr liquid & make pellet for analysis.

Monochromator:- Filters made by Lithium fluoride prism made by KBr Diffracting gratings made by alkyl halides are used.

Detector:- It is a device used to detect signals, unabsorbed radiation was detected by thermocouple bolometeres, thermistors.

Recorder:- It is used to record IR spectra.

Applications:-

1) Identification of functional groups at frequency region 4000 - 1500cm^{-1}, & finger print region 1500 - 400cm^{-1}.
2) structure elucidation / determination of organic componds
3) Identification drugs & impurities of organic compounds
4) study of Hydrogen - bonding.
5) provides valuable information of molecular symmetry dipole moments, bond lengths etc.
6) Distinguishing positional isomers of a compound.

CONDUCTOMETRIC TITRATIONS :-

Conductometric titration is a titration used to measure the amount of an analyte present in the given solution by measuring the change in the conductance as a function of volume of titrant.

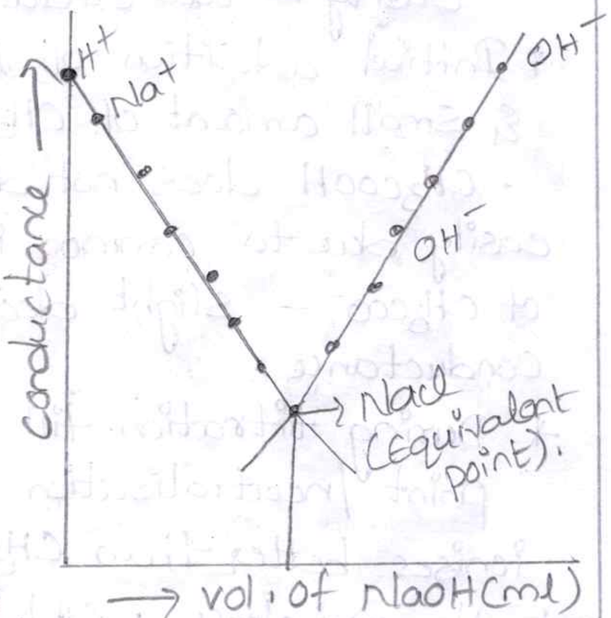
- > Conductance is due to the movement of ions in the solution.
- > One ion replaces with another ion of different ionic conductivity during the titration.
- > Equivalent point is determined graphically.

(1) Strong Acid vs Strong Base :- (HCl vs NaOH)

$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$

analyte titrant

High Ionic conductivity - $\{H^+, OH^-\}$
Low Ionic conductivity - $\{Na^+, Cl^-\}$



* Before titration :- only HCl present

*presence of H^+ with high Ionic conductivity - high conductance

* During titration till equivalence point / neutralisation point.

H^+ with high Ionic conductivity is replaced by Na^+ with low Ionic conductivity - conductance decreases.

* At equivalence point/neutralisation point - NaCl & H_2O are present - least conductance

* After equivalence point - excess NaOH is added

* Accumulation of OH^- with high ionic conductivity - Conductance increases.

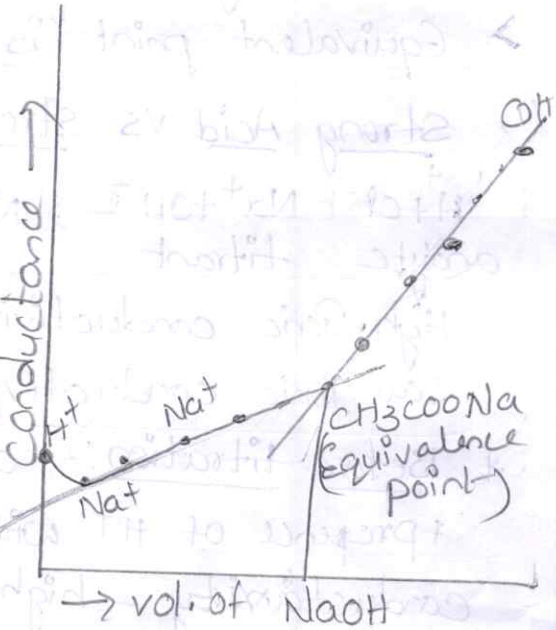
(2) Weak acid vs strong Base :- (CH_3COOH vs NaoH)

$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$
analyte titrant

CH_3COOH - does not dissociate easily
NaoH - dissociates immediately
CH_3COONa - dissociates better than CH_3COOH
Na^+ - has low Ionic conductivity

*Before titration:-
only CH_3COOH present
- CH_3COOH doesnot dissociate easily ← Low conductance

* Initial addition of NaoH - CH_3COOH & small amount of CH_3COONa
- CH_3COOH does not dissociate easily due to common ion effect ([illegible]) of CH_3COO^- - slight decrease in conductance.



* During titration till equivalence point/neutralisation point - CH_3COONa ionises better than CH_3COOH - conductance increases slowly.

* At equivalence point/neutralization point - CH_3COO^- & Na^+ are present - conductance increases.

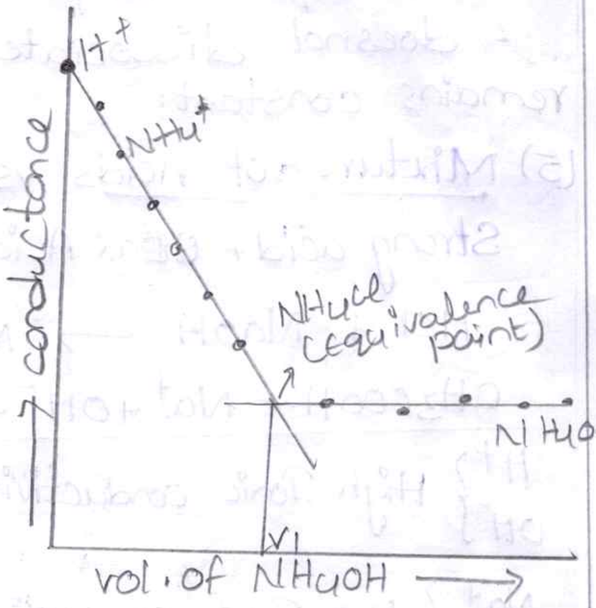
* After equivalence point - excess NaoH is added - accumulation of OH^- with high Ionic conductivity - conductance increases drastically.

(3) strond acid vs weak Base :- (Hcl vs NH_4OH)

$H^+ + Cl^- + NH_4OH \longrightarrow NH_4^+ + Cl^- + H_2O$
analyte titrant

High Ionic conductivity - H^+
Low Ionic conductivity - NH_4^+
Cl^-

* Before titration:- Only HCl present.
  - prensence of H^+ with high ionic conductivity - high conductance
* During titration till equivalence point / neutralisation point.
* H^+ with high Ionic conductivity is replaced by NH_4^+ with low Ionic conductivity - conductance decreases
* At equivalence point / neutralisation point - NH_4Cl & H_2O are present - least conductance



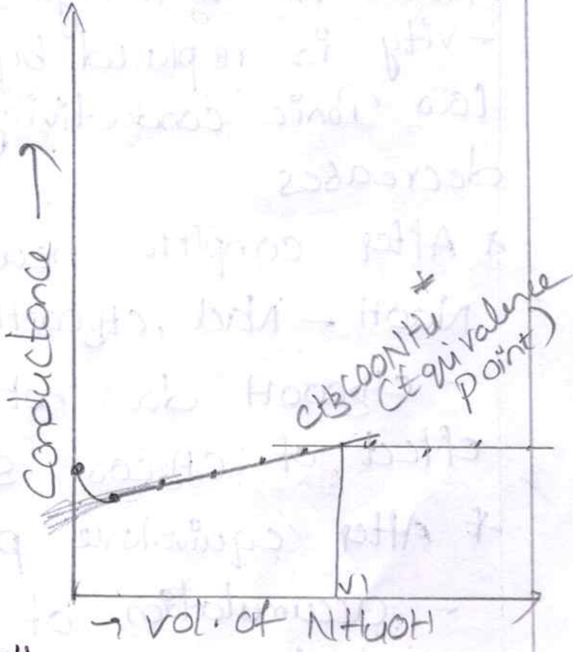
* After equivalence point - excess NH_4OH is added, does not dissociate due to common ion effect - conductance remains constant

(4) Weak Acid vs Weak Base:- (CH_3COOH ~~vs~~ NH_4OH)

$CH_3COOH + NH_4OH \longrightarrow CH_3COO^- + NH_4 + H_2O$
analyte titrant

CH_3COOH & NH_4OH - does not dissociate easily
CH_3COONH_4 - dissociate better than CH_3COOH
NH_4^+ - has low Ionic conductivity.

* Before titration:-
  - Only CH_3COOH present
  - CH_3COOH does not dissociate easily - Low conductance
* Initial addition of NH_4OH - CH_3COOH & small amount of CH_3COONH_4.
  - CH_3COOH does not dissociate easily due to common ion effect of CH_3COO^- - slight decrease in conductance



* During titration till equivalence point / neutralisation point.
  - $CH_3COONH_4^+$ Ionises better than CH_3COOH - conductance increases slowly.

* After equivalence point - excess NH_4OH is added - doesnot dissociate due to common ion effect - Conductance remains constant.

(5) Mixture of Acids vs strong Base: ($HCl + CH_3COOH$ Vs $NaOH$)

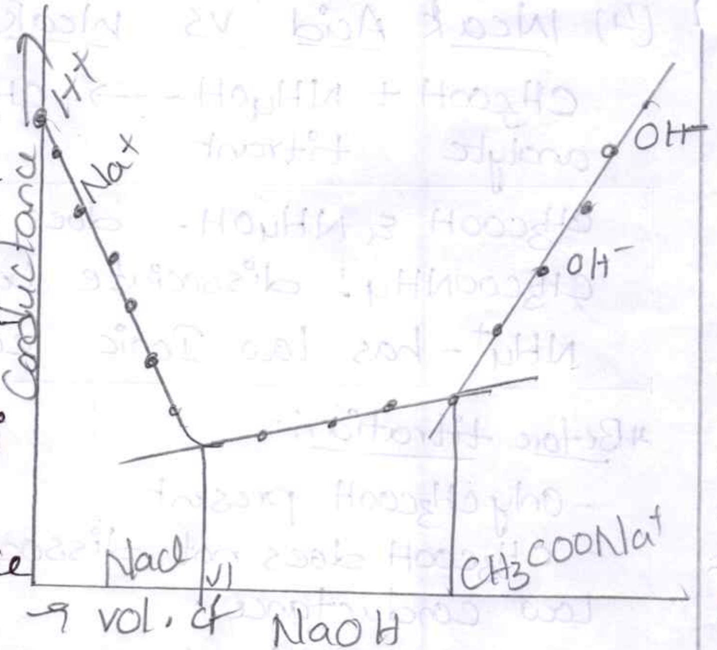
Strong acid + Weak Acid vs strong Base

$HCl + NaOH \rightarrow Na^+Cl^- + H_2O$

$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COONa + H_2O$

H^+, OH^- } High Ionic conductivity Na^+, Cl^- } low Ionic conductivity	CH_3COOH - does not dissociate easily CH_3COONa - dissociates better than CH_3COOH $NaOH$ - dissociates Immediately Na^+ - has low Ionic conductivity

* Before titration:
  HCl & CH_3COOH present
  - CH_3COOH does not dissociate
  - HCl dissociates & presence of H^+ with high Ionic conductivity - high conductance
* During the titration till equivalence point / neutralisation point of HCl - H^+ with high Ionic conductivity is replaced by Na^+ with low Ionic conductivity - conductance decreases



* After complete neutralisation of HCl - Initial addition of $NaOH$ - $NaCl$, CH_3COOH & Small amount of CH_3COONa
  - CH_3COOH does not dissociate easily due to common ion effect of CH_3COO^- Slight decrease in conductance
* After equivalence point of CH_3COOH - excess $NaOH$ is added - accumulation of OH^- with high Ionic conductivity - Conductance increases drastically.

Applications:-

1) For Analysing acid-base reactions, precipitation reactions & mixture of acids or bases.
2) Water quality monitoring
3) pollution Detection
4) Assesing the Ionic content of drugs & other Substances.
5) Ensuring the correct acidity & alkainity of pharmaceutical products & food items.

UNIT-5

GREEN FUELS / Alternate energy Resources

Solar Energy:-

Solar power is the conversion of sunlight into electricity, either directly (example: pv cells, Solar heaters), or indirectly (example: fossil fuel, ocean-thermal energy)

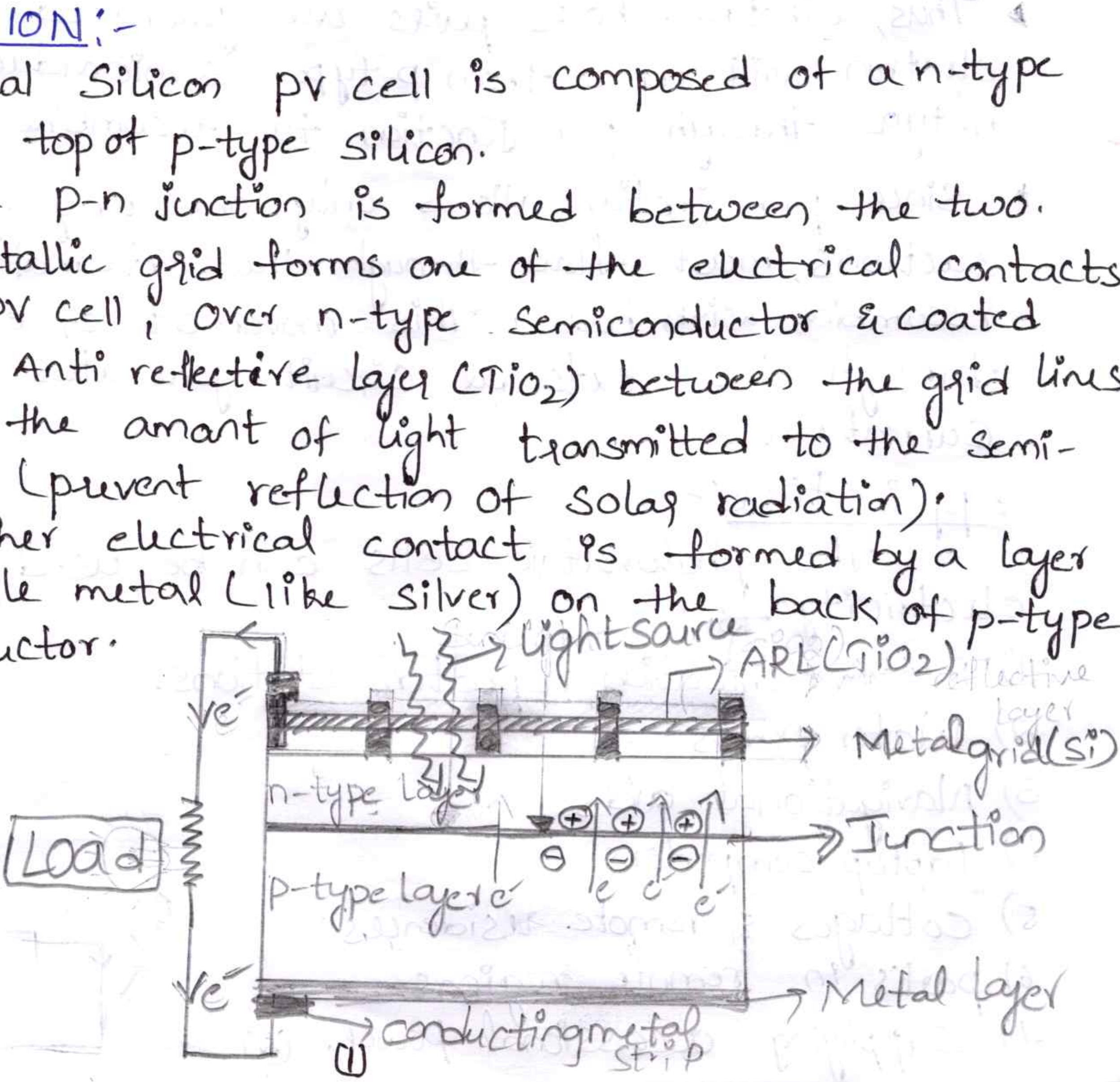
"photovoltaic cells:" - PHOTO VOLTAIC CELLS:-

photovoltaic cells are semiconductor device which convert solar energy into electrical energy.

photovoltaic cell is based on the principle of photoelectric effect.

CONSTRUCTION:-

- A typical Silicon pv cell is composed of a n-type silicon on top of p-type silicon.
- Hence a p-n junction is formed between the two.
- A Metallic grid forms one of the electrical contacts of the PV cell, over n-type Semiconductor & coated with an Anti reflective layer (TiO_2) between the grid lines increase the amount of light transmitted to the semiconductor (prevent reflection of solar radiation).
- The other electrical contact is formed by a layer of mobile metal (like silver) on the back of p-type semiconductor.



WORKING of PHOTOVOLTAIC CELL:-

Electromagnetic radiation consists of particles called photons. The photons carry energy given by the planck's Quantum theoly.

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

E = Energy
h = planck's constant
ν = frequency
c = velocity of light/speed of light
λ = Wave Length

- When electromagnetic radiation (sunlight) is incident to the plane of solar cell, the photons are absorbed (Which possess energy sufficient to overcome the barrier potentially). That results in drifting of electrons.
- Thus, electron - hole pairs are generated. The drifted electron will move from p-type semiconductor towards n-type through p-n junction to recombine with holes)
- Since p-n junction allows only one way movement of electrons, must flow through the external circuit to recombine with holes. This movement of electrons through the external circuit generates & electric current.

Applications:-

The photovoltaic cells can be used to supply electricity for:

1) Telecommunication repeater stations.
2) Water pumps
3) Navigational aids
4) Laptop computers
5) cottages & remote residences
6) parks in remote regions
7) Supplying occassional power. ②

Alternative Energy Sources

Alternative energy sources also known as renewable energy sources, are natural resources that are self replenishing & have a low or zero-carbon footprint.

Green fuels:-

Green fuels are energy sources that are produced from renewable energy sources or have a low carbon footprint. They can be used as a substitute for fossil fuels in transportation & industrial sectors.

Types of Green fuels:-

1) Bio-fuels:

Biofuels are ~~no~~ can be produced from plants or from agricultural, domestic or industrial biowaste.

Bio-fuels is a fuel that is produced over a short time span from biomass, rather than by the very slow natural process, involved in the formation of fossil fuel such as oil.

Biofuels are mostly used for transportation, but can also be used for heating & electricity.

2) Solar Energy:-

Solar energy is the radiant energy from the Sun's heat & light that can be captured & used to generate electricity & heat. Solar panels use the photovoltaic effect to convert light into an electric current.

3) Wind Energy:-

Wind turbines use the force of the wind to spin a rotor, which is connected to a generator that creates electricity. Wind power is a clean renewable energy source that uses wind to generate electricity.

4) Green Hydrogen Energy:-

Green hydrogen is a clean sustainable & emission free fuel that can help reduce Carbon emission & replace fossil fuels. Its produced by splitting water into hydrogen & oxygen using renewable energy sources like Solar, wind or hydropower.

5) Geo-thermal Energy:-

Geothermal energy is heat energy that comes from the Earth's core & is extracted to be used by humans.

Wells are drilled into underground reserviors to tap the hot water & steam. The heated water is then pumped to the surface for use.

Advantages of Green-fuels:-

a) **Environmental benefits:-** Green fuels reduce emissions that contribute to climate change & air pollution, for example: Biodiesel & biomethane reduce particulates in the air, which can improve air quality & reduce the risk of lung disease & cancer

b) **Economic benefits:** Green fuels can create jobs & stimulate economic growth.

c) **Energy security:-** Green-fuels can be produced domestically, which can increase energy security & reduce dependence on foreign oil.

d) **compatability:** Green fuels can be used in existing vehicles & infrastructure.

e) Green fuels can be produced from a variety of feedstocks & production technologies.

f) Green fuels can help transition from fossil fuels to sustainable energy sources.

HYDROGEN ENERGY:-

Hydrogen power, also known as hydrogen fuel, is an alternative energy source that has the potential to change the way we power our homes, vehicles to businesses.

Electrolysis Of Water:-

- Water electrolysis is the process of splitting the water into Hydrogen & Oxygen through the application of electrical energy.
- Electrolysis of water is one of the most capable method for the production of hydrogen because it uses renewable H_2O & produced only pure oxygen as by-product.
- Additionally, electrolysis of water process is utilizes the DC power from Sustainable energy sources such as solar, wind & Biomass.

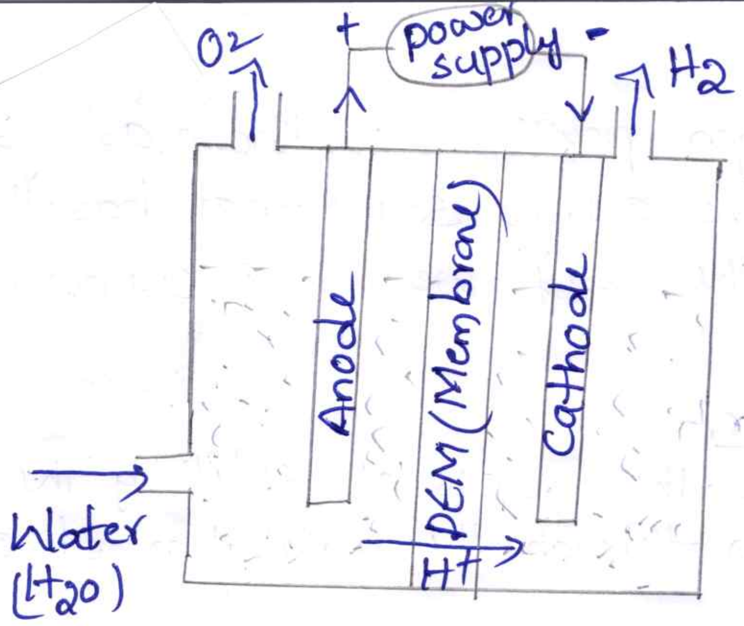
Different electrolyzers function in Different ways, mainly due to the different type of electrolyte material involved & the ionic species it conducts.

a) Polymer Electrolyte Membrane Electrolytes:-

1) In a polymer Electrolyte membrane (PEM) electrolyzer, the electrolyte is a solid specialty plastic material.
2) Water reacts at the anode to form oxygen & positively charged hydrogen ions (protons).
3) The electrons flow through an external circuit & the hydrogen ions selectively move across the PEM to the cathode.
4) At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas

At Anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

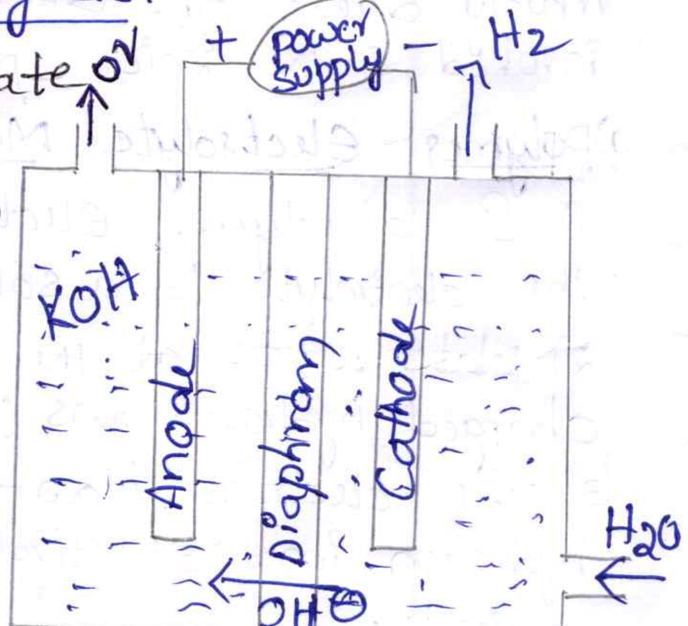
At cathode: $4H^+ + 4e^- \longrightarrow 2H_2$



2) ~~Alka~~ Advantages:-

1) High current density
2) Greater energy efficiency
3) Low gas permeability
4) Wider operating Temp (20-80°c)
5) Easy handling & maintainance.

2) Alkaline Electrolysis / Electrolyzers:-



1) Alkaline electrolyzers operate via transport of hydroxide ions (OH^-) through the electrolyte from the cathode to the anode with H_2 being generated on the cathode side.

2) Electrolyzers using a liquid alkaline solution of sodium or potassium hydroxide as the electrolyte have been commercially available for many years.

At Anode : $2OH^{-} \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

At cathode : $\underline{2H_2O + 2e^- \longrightarrow H_2 + 2OH^-}$

overall : $\underline{H_2O \longrightarrow H_2 + \frac{1}{2}O_2}$

Advantages:-

1) Cheaper catalysts with respect to the platinum-base catalysts.
2) Higher durability due to an exchangeable electrolyte
3) Lower dissolution of anodic catalyst
4) Higher gas purity due to lower gas diffusivity in alkaline electrolyte.

Advantages of Hydrogen Energy:-

1) **Clean fuel**: Hydrogen is a clean fuel that produces only water, when consumed in a fuel. It doesn't emit harmful substances like NO, hydrocarbons etc.

2) **Renewable energy**:- Hydrogen can be produced from renewable power like solar & wind, or from other domestic resources like natural gas, nuclear power & biomass.

3) **storable**: H_2 gas can be compressed & stored in tanks for a long time.

4) **Transportable**: H_2 is a very light element, so compresse hydrogen tanks ~~Con~~ are easier to handle than Lithium batteries.

5) **Zero emission power source**:- Hydrogen fuels ~~operate~~ cells emits only water vapour & heat significantly reduce emissions.

6) **Cost effective**:- H_2 fuel cells offer low operational costs due to their minimal maintainance requirements & long service life.

E-waste Management

Definition of E-waste management:-

E-waste management refers to the processes & systems used to collect, transport, treat, & dispose of e-waste (electronic & electrical waste) in an environmentally responsible & safe manner.

1) Sources of Electronic waste:-

The main sources of electronic waste include:

1) consumer electronics such as smart phones, laptops, televisions & household appliances.
2) office equipment such as computers, printers, copiers & fax machines.
3) Medical equipment such as x-ray machines monitors & diagnostic equipment.
4) Electronic toys & games.
5) Military & government surplus equipment.
6) Obsolute technology such as outdated computer equipment & VCRS.
7) Discarded or broken electronic devices
8) colleges often use electronic equipment such as projectors computer equipment, & audio-visual equipment in classrooms & laboratolies.

2) Composition of E waste:-

The composition of e-waste can vary depending on the types of device & its components. It general e-waste contains a mixture of materials including:

1. Metals:- e-waste often contains valuable metals such as copper, gold, silver & aluminium

2) plastics:- Many electronic devices contain plastic components, including casings, insulation & cables.

3) Glass:- Electronic devices often contain glass components such as screens & lenses.

4) circuit boards:- Many electronic devices contain circuit boards, which contain a mixture of metals & other materials

5) Batteries: Some electronic devices contain batteries, which can contain hazardous materials such as lead, mercury & cadmium.

6) Other hazardous materials: E-waste may also contain other hazardous materials such as flame retardants, heavy metals, & polychlorinated biphenyls (PCBS)

3) Toxic materials used in manufacturing Electronic & Electrical products:

Electronic & Electrical products can contain a variety of toxic materials including:

1) Lead:- Lead is a toxic heavy metal commonly used in the manufacture of batteries, computer monitors & other electronic components.

2) Mercury:- Mercury is used in some fluorescent lights, batteries & other electronic devices.

3) Cadmium:- Cadmium is a toxic heavy metal used in rechargeable batteries, pigments & plastic stabilizers.

4) polyvinyl chloride:- (pvc) is a common plastic used in electronic cables & other components. It can release toxic chemicals, such as dioxins, when burned or during disposal.

5) Brominated flame retardants (BFRS) :- BFRs are used in the manufacture of electronic products to prevent fires. However, they are toxic & can harm the environment & human health.

6) Barium :- Barium is used in some electronic components including cathode ray tubes.

7) Rechargeable Batteries :- RB contains Lithium is used in batteries, but it can be toxic if not handled properly. Cadmium, lead, Sodium, Lithium, Nickel etc.

8) Chlorofluorocarbons (CFCS) :- are toxic chemicals that were widely used as coolants & Solvents in electronic products such as refrigerators, air conditioners. They cause ozone depletion.

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④ Health - Hazardous due to exposure of e-waste :-

Exposure to electronic waste (e-waste) can have serious health consequences including:

a) poisoning :- E-waste can contain toxic substances, such as lead, cadmium & mercury that can cause poisioning if they enter the body.

b) Respiratoly problems :- Exposure to dust & fumes generated during the dismantling & disposal of e-waste can cause respporatoly problems, such as asthma & bronchitis.

c) Neurological effects :- Exposure to toxic substances in e-waste, such as lead & mercury, can cause neurological effects, including memoray loss, tremors & co-ordination problems.

4) Reproductive problems:- Exposure to toxic Substances in e-waste, such as cadmium, can cause reproductive problems, including infertility & birth defects.

5) Cancer:- Exposure to carcinogenic substances, such as dioxins & polychlolinated biphenyls (PCBs), found in e-waste, can increase the risk of cancer.

It is important to efffectively manage e-waste to minimize the exposure of workers & the public to hazardous materials & to prevent serious health problems.

5) Need of E-waste Management:-

E-waste management is necessary because it helps to address several environmental, health, & resource-related concerns, including:

a) Protecting the environment:- E-waste contains toxic Substances, such as lead, mercury & cadmium that can have harmful effects on the environment & human health if not properly managed.

b) Conserving Resources:- E-waste contains valuable resources, such as metals, that can be recovered & reused through proper recycling.

c) Reducing greenhouse gas emissions:-

The production of new electronic products releases greenhouse gases, such as CO_2 into the atomsphere. proper recycling & disposal of e-waste can reduce the environmental impact of electronic products.

d) Reducing land filling:- Land filling of electronic waste can result in the release of toxic materials into the environment & contribute to soil & water pollution.

e) Protecting public health:-

Improper handling & disposal of e-waste can expose workers & the public to hazardous materials & cause serious health problems.

f) E-waste can be toxic, is not biodegradable & accumulates in the environment, in the soil, air, water & Living things.

g) Causes air pollution, soil pollution & water pollution.

h) Electronic Recycling promotes soil fertility & maintain Nutrient.

i) E-waste management programs aim to promote responsible recycling & disposal of electronic waste & minimize the release of hazardous materials into the environment This helps to protect the environment. This helps to protect the environment, Conserve resources & promote public health & safe.

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⑥ E- waste Recycling & Recovery Different approches: (Recycling, Separation & thermal treatment)

E-waste recycling & recovery can be achieved through different approches including separation & thermal treatments.

a) Separation :-

This involves physically separating different components of e-waste, such as metals, plastics & circuit boards. This can be done manually or through automated processes, & the separated materials can then be processed further for recycling or disposal. Such as using specialized equipment to sort materials by density, size or magnetic properties. Some common examples of e-waste components that are separated during the recycling process include:

(i) Thermal treatments:-

E-waste thermal treatment refers to the use of high temperatures to recover valuable metals & other materials from electronic waste. This process can include incineration or other pyrometallurgical techniques, & typically involves melting down the waste to separate the metal components. The separated metals can then be recovered & reused. Thermal treatment can be an effective method for e-waste recycling.

(ii) Hydrometallurgical extraction of Ewaste:-

E-waste hydrometallurgical extraction is a process used to extract valuable metals & other materials from electronic waste through chemical reactions in aqueous solutions. The process typically involves the following steps:

pre-treatment: This involves the fragmentation & size reduction of e-waste to prepare it for further processing.

1) Leaching:- The e-waste is treated with chemical reagents in a solution to dissolve the metals & other materials, creating a leachate.

2) Separation:- The leachate is then processed to separate & purify the metals & other materials, through methods such as precipitation or ion exchange.

3) Recovery:- The extracted metals & other materials are then recovered & processed for reuse. Hydrometallurgical extraction is a more environmentally friendly alternatives to thermal treatments, as it generates less hazardous

waste & can be more easily regulated to minimize environmental impact.

(iii) Pyrometallurigical methods E-waste Recycling:-

E-waste pyrometallurgical methods refer to the process of extracting valuable metals & other materials from electronic waste using high temperatures. These methods include;

1) Smelting: The e-waste is melted in a furnace & then separated into individual metals & other materials.

2) Refining:- The metals from the smelted e-waste are further processed to remove impurities & improve their quality.

3) Incineration:- Electronic waste is burned at high temperatures to reduce its volume. & recover metals.

pyrometallurgical methods are effective at recovering valuable metals from e-waste, but they also generate hazardous byproducts & require significant energy inputs. Additionally, these methods can pose a risk to the environment & human health if not properly regulated & monitored.

(iv) Direct recycling of E-waste:-

Direct recycling of e-waste refers to the process of recovering valuable materials from e-waste without the need fol intermediate processing steps. This can include processes such as shredding, granulating, & sorting which are used to separate the different components of e-waste, such as metals, plastics & glass. The separated materials are then processed to extract the valuable components & prepare them for reuse.

(7) Extraction of gold from E-waste:-
(Explain the principle & Experimental procedure)

Principle:-
The principle behind the extraction of gold from e-waste is based on the fact that gold is a relatively non-reactive metal, which allows it to be recovered from complex e-waste matrices through a series of chemical & physical processes.

Experimental procedure:-

(1) **collection & segregation of e-waste:-** The first step involves collecting & segregating the e-waste into different categories, such as computer motherboards, cell phones, & other electronic devices.

2) **physical separation:-** The e-waste is physically separated into different components, such as plastics, metals & glass

3) **Leaching:-**
The metals, including gold are leached from the e-waste using a suitable reagent, such as aqua regia (a mixture of Hcl & HNO_3) to dissolve the gold.

$$Au + HNO_3 + 4HCl \longrightarrow HAuCl_4 + NO + 2H_2O$$

4) **precipitation:-**
The dissolved gold is then precipitated out of the solution through the addition of a suitable reducing agent, such as sodium metabisulfate.

$$2H[AuCl_4] + 3Na_2S_2O_5 + 3H_2O \longrightarrow 2Au + 3SO_2 + 3Na_2SO_4 + 8HCl.$$

5) purification:-

The precipitated gold is then purified through processes such as ion-exchange, electro-winning or distillati to remove impurities & improve its quality.

6) Recovery:-

The purified gold is then recovered for reuse.

Advantages:-

1) High yield expected
2) Faster extraction of gold is possible.

Disadvantages:-

1) chemicals are used.
2) Acid residues are not disposed of properly, which harms the environment.