

## UNIT I: POLYMER TECHNOLOGY

**[Polymerisation:-** Introduction, methods of polymerization (emulsion and suspension), mechanical properties.

**Plastics:** Compounding, fabrication (compression, injection, blown film and extrusion), preparation, properties and applications (PVC, polycarbonates and Bakelite), mention some examples of plastic materials used in electronic gadgets, recycling of e-plastic waste (waste to wealth).

**Elastomers:-** Introduction, preparation, properties and applications (Buna S, thiokol and polyurethanes).

**Composite materials:** Fiber reinforced plastics, conducting polymers, biodegradable polymers, biopolymers, biomedical polymers.

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### Introduction:

**Polymer:** Polymers are large molecules made up of many smaller molecules. 'Poly' means many and 'mer' means units.

**Monomers:** Small molecules of low molecular weight, which combine to give a polymer, are called monomers.

(mono = one, mer = unit) monomers are joined together through polymerisation to form polymers. A polymer contains hundreds of thousands of monomers.

**Homo polymer:** a polymer, in which a single type of monomer is used, is called homo polymer.

Examples : Polythene, polystyrene, Polyvinylchloride etc.

**Copolymer:** A polymer in which the monomers are more than one type is called copolymer (heteropolymer).

Examples : Buna-S is a copolymer of 1,3- butadiene and styrene.

Bakelite is a copolymer of phenol and formaldehyde.

### Degree of polymerization:

The number of repeating units (or) monomer units available in the polymer is known as degree of polymerization. Polymers with a high degree of polymersation are called High polymers.

Polymers with low degree of polymerization are called Oligo polymers

### Functionality:

The number of bonding sites (or) reactive sites (or) functional groups present in the monomer is called functionality.

When the functionality of monomer is two; it is bifunctional and Linear straight chain polymer is formed.

Examples for bifunctional monomers: a) ethylene b) styrene c) vinyl chloride d) vinyl cyanide.

When the functionality of monomer is three; it is tri-functional and three- dimensional net work polymer is formed.

Ex: phenol, glycerol.

when a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

**Classification of polymers:** Based on their sources they are classified into;

**1)Natural polymers:** The polymers, which are obtained from natural sources such as plants and animals, are called natural polymers. Eg: Wood, starch, cellulose, Jute, Cotton, Wool, Silk, Proteins, Natural rubber etc.

**2)Synthetic polymers:** These are synthesized with the help of chemicals in industries

E.g.: polythene, nylon-6, 6, synthetic rubber etc.

**3)Semi synthetic polymers:** These are the synthetic derivatives of the natural polymers.

E.g.: Cellulose acetate (Rayon) and cellulose nitrate.

### Classification based on structure:

a) Linear Polymers: These polymers consist of long and straight chains.

b) Branched chain polymers: These polymers contain linear chains having some branches.

c) Cross linked polymers (or) 3- dimensional network polymers:

**Classification Based on Composition of Polymers:** [1] Homopolymer [2] Copolymer

**Classification Based on Backbone of the polymer chain:** [1] Organic polymer [2] Inorganic Polymers.

A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer.

If chain backbone contains no carbon atom is called inorganic polymer. Glass and silicone rubber are examples.

**Polymerisation:** The process of formation of polymers from respective monomers is termed as Polymerization.

**Addition polymerization:** During the polymerization process, if the polymer is formed **without loss** of small molecules like water, ammonia etc; then this type of polymerization is called Addition polymerization. It is also known as Chain polymerization. Ex: Polyethylene (PE); Polystyrene (PS); Polyvinylchloride (PVC), Neoprene etc.

**Condensation polymerization:** During the polymerization process, if the polymer is formed **with loss** of small molecules like water, ammonia etc; then this type of polymerization is called condensation polymerization. It is also known as Step polymerization. Ex: Polycarbonates, Thiokol, Nylon-6,6, Terylene and Bakelite etc.

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❖ **Write about emulsion polymerization and suspension polymerisation method. Give its advantages.  
(or) Explain the Methods of Polymerization (or) Technology of Polymerization?**

### **1) Suspension (Bead or Pearl) polymerization:**

This polymerization occurs in heterogeneous system. The water insoluble monomer is suspended in water as tiny droplets by continuous agitation. The droplets are prevented from coalescing by using small quantities of water- soluble polymers such as polyvinyl alcohol or colloids. The polymerization is made to occur in each droplet of the monomer using a catalyst. The reaction mass is heated to initiate the polymerization. After the completion of polymerization pearl like polydispersed polymer mixture is obtained.

#### **Advantages:**

1. The viscosity build up of polymer is negligible.
2. Isolation of product is easy as it needs only filtration and washing.
3. High purity products.
4. The process is more economical since water is used.
5. Isolated products need no further purification.
6. Efficient thermal control.

#### **Disadvantages:**

1. This method is applicable only for water insoluble monomers.
2. It is difficult to control particle size.

**Application:** This technique is used for the production of polyvinyl acetate, poly styrene, styrene-divinyl benzene etc.

**2) Emulsion polymerization:** In this method emulsion of water insoluble monomer and water is prepared and is stabilized by the addition of surface acting agents (surfactants) such as soap. Polymerization is initiated by the addition of water-soluble initiator such as potassium persulphate. After adding the initiator, the system is kept agitated in the absence of oxygen at 70°C.

**Mechanism:** The surfactant has hydrophilic head and hydrophobic tail. The water- soluble initiator links to the hydrophilic end whereas the monomer is linked to the hydrophobic end. At a little higher concentration it gets dispersed. When the concentration of surfactant exceeds critical micelle concentration (cmc), the soap molecule form micelle (aggregation of 50-100 molecules) oriented with tails inwards and head outwards. Now, an initiator molecule at the polar end diffuses into the micelle to initiate the polymerization process. As the polymerization progresses, there will be depletion in the number of monomers within the micelle. They are replenished by the medium. This continues till the polymer formed is big enough to come out, the process is terminated by combination. The pure polymer is isolated from the emulsion by the addition of de-emulsifier.

#### **Advantages:**

1. The rate of polymerization is high.
2. Easy heat control.
3. A very high molecular weight polymer is obtained.

4. Molecular weight control is possible.
5. Viscosity build up is low.

**Disadvantages:** Polymer needs purification.

**Application:** This method is used for the production of PVC, Poly vinyl acetate etc.

## ❖ Explain the Mechanical properties of Polymers?

### Mechanical properties of Polymers:

#### ➤ 1. Strength:

- ✓ Strength of the polymer depends upon the intermolecular attractive forces.
- ✓ Greater is the attractive forces; higher is the strength of the polymer.
- ✓ Strength of the polymer increases with increasing molecular weight of the polymer or increasing polar groups such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{OCH}_3$ ,  $-\text{COOR}$  &  $-\text{X}$ .
- ✓ So, the lower molecular weight polymers have less strength, soft and gummy.
- ✓ In cross linked polymers, the polymer chains are strongly linked to each other by covalent bonds which cause higher strength, toughness, brittleness etc.
- ✓ Strength of the polymer depends on the shape of the molecule also.
- ✓ If the shape of the molecule is simple and uniform, polymer molecule has less strength.
- ✓ Ex: In PVC, large Cl atoms are present on alternative carbon atoms in the polymer.
- ✓ These Cl atoms and strong attractive forces restrict the movement of molecules in the polymer.
- ✓ So, PVC is tougher and stronger polymer.
- ✓ In poly ethylene attractive forces are weak due to simple structure. Thus, PE is weaker than PVC.

#### ➤ 2. Elastic character:

- ✓ Rubber is an elastomer, when applied stress is removed; the polymer gets original shape in case of elastomers.
- ✓ In an elastomer, polymer chains are randomly arranged, coiled chains with slight cross links.
- ✓ When the polymer is stretched, the cross links begin to disentangle and straight out.
- ✓ As a result, chains are regularly arranged which cause hardness, stiffness and crystallinity due to increase of the attractive forces between the chains.

#### ➤ 3. Plastic deformation:

- ✓ This is found in thermoplastics.
- ✓ In thermoplastics, polymer chains are close to each other with weak attractive forces.
- ✓ On applying heat or pressure or both, these forces become weak and the polymer chains start moving over each other.
- ✓ This results in attaining desired shape by passing the material into the mould.
- ✓ On further cooling, the attractive forces are restabilised and the shape of the material is fixed.
- ✓ Incase of thermosetting polymers, shape of the plastic material can't be changed by applying heat or pressure.
- ✓ Because the polymer chains are strongly held together by strong covalent cross linkages and there is no movement of polymer chains.

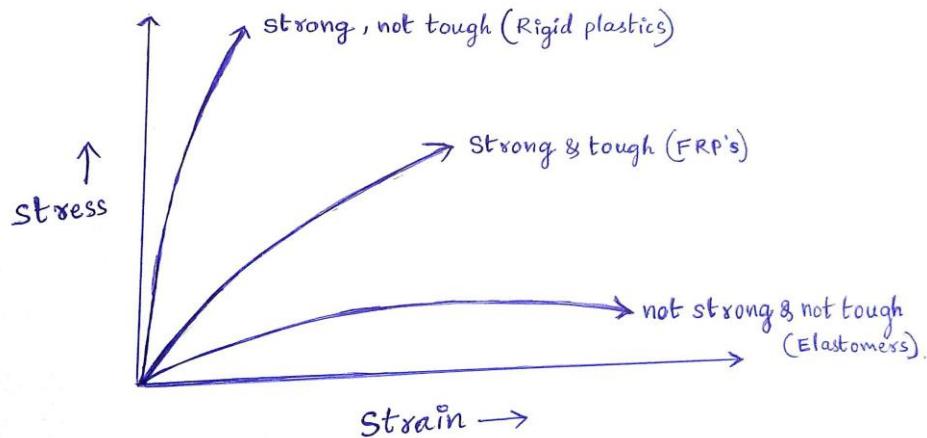
#### ➤ 4. Structure and electrical properties:

- ✓ Most of the plastic materials are good insulators.
- ✓ They are able to withstand to very small current.
- ✓ The insulating property will breakdown in a sufficiently strong field.
- ✓ In non polar polymers, only electronic polarization is responsible for dielectric constant.
- ✓ Dielectric strength is defined as the electric strength which an insulating material can withstand.
- ✓ In polar polymers, both electronic as well as dipole polarization contribute towards overall dielectric constant.

## 5. Heat effect on polymers:

- ✓ Heat greatly affects the properties of polymers.
- ✓ Amorphous polymers do not possess sharp melting points.
- ✓ At very low temperature, the amorphous material exists as glassy materials, which have lack of mobility in polymer molecules.
- ✓ If the polymer is heated, it eventually becomes soft and flexible.
- ✓ This happens only at the glass transition temperature.

## MECHANICAL PROPERTIES



## PLASTICS:

The word plastic itself comes from the Greek word *plastikos*, which means to be able to be shaped or moulded by heat.

### Advantages of plastics over other traditional materials (like wood, metals, glass etc):

- 1) Plastics are available in attractive colours.
- 2) They do not undergo corrosion.
- 3) They are not affected by insects.
- 4) They are light in weight
- 5) They are cheap.
- 6) They can be moulded into any shape easily.
- 7) They are chemically inert.
- 8) They have good abrasion resistance.
- 9) They are good insulators of heat and electricity.

### Disadvantages:

1. Recycling of plastic is a costly process.
2. Plastic undergo biodegradation after long time.
3. Incineration of plastic causes pollution.
4. Plastics are derived from petrochemicals and their production causes environmental pollution.
5. Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

## Differences between Thermo Plastics & Thermo Setting plastics :

S.no	<b>THERMOPLASTIC RESINS</b>	<b>THERMOSET RESINS</b>
1.	These resins become soft on heating and rigid on cooling.	During fabrication process these resins are moulded. Once moulded or shaped, they can not be softened.
2.	Thermoplastic resins are formed by chain polymerisation.	Thermoset resins are formed by step polymerisation.
3.	They can be reshaped.	They cannot be reshaped
4.	These plastics can be reclaimed from waste.	They cannot be reclaimed from waste.
5.	Thermoplastic resins are soft, weak and less brittle.	Thermoset resins are hard, strong and more brittle.
6.	These resins are usually soluble in organic solvents. Eg: Polyethylene, polyvinyl chloride etc.	Due to strong bonds and cross links, they are insoluble in almost all organic solvents. Eg: Bakelite, Nylon etc.

## Explain the compounding of plastics with suitable examples?

**Definition:** “The process of mechanical mixing of various additives with polymers to impart some special properties to the end product is known as compounding of plastics”. The additives get incorporated into the polymer to give a homogeneous mixture.

The principal additives used in compounding are; 1) Binders or Resins 2) Plasticizers 3) Fillers  
4) Lubricants 5) Activators or accelerators 6) Stabilizers 7) Colourants

### 1) Binders or Resins:

Resin is the binder which holds the other constituents of the plastics together and it is the major constituent.

The binders used may be natural or synthetic resins with very high molecular mass. They undergo condensation and polymerization during moulding of plastics. The resin gives the desired properties like plasticity and electrical insulating properties to the plastic.

### 2) Plasticizers:

These are materials which are added to resins to increase their plasticity and flexibility.

Commonly used plasticizers are tributyl phosphate, triphenyl phosphate, diiso-octyl phthalate, dibutyl phthalate etc.

### 3) Fillers:

Fillers are inert materials added to plastic to increase the bulk and thereby to reduce the cost of production and also to impart certain specific properties to the finished product.

Commonly used fillers are mica, silica, graphite, carbon-black (C-black), chalk, china clay, clay, wood flour etc.

### 4) Lubricants:

Lubricants such as oils, waxes, stearates, soaps etc help in easy moulding and give better glossy finish.

Prevent moulded article from sticking to the fabrication equipment.

### 5) Catalyst or Accelerators:

These are used in the case of thermosetting plastics to accelerate the condensation polymerization to form the linked products.

Examples, benzoyl peroxide,  $H_2O_2$ , metals like Ag, Cu, Pb etc

### 6) Stabilizers:

- ★ Many plastics undergo thermal (or) photo chemical degradation during their processing (or) when they are put into use.
- ★ Stabilizers protect the plastic from such degradation.
- ★ Natural rubber, PE, esters undergo such degradation.
- ★ Examples : PbO, lead silicate, lead chromate, stearates of Pb & Ba etc

These are substances added to plastic to improve the thermal stability during moulding.

## 7) Colourants :

- ★ These are inorganic (or) organic pigments used to impart pleasing colours to the plastic.
- ★ They don't cause any influence on other properties.
- ★ Ex; Carbon black, anthraquinones, azodyes, phthalocyanines,  $\text{BaSO}_4$ ,  $\text{TiO}_2$ ,  $\text{PbCrO}_4$ ,  $\text{Fe}_2\text{O}_3$ , Zinc chromate ,Organic dyestuff, opaque inorganic pigments.

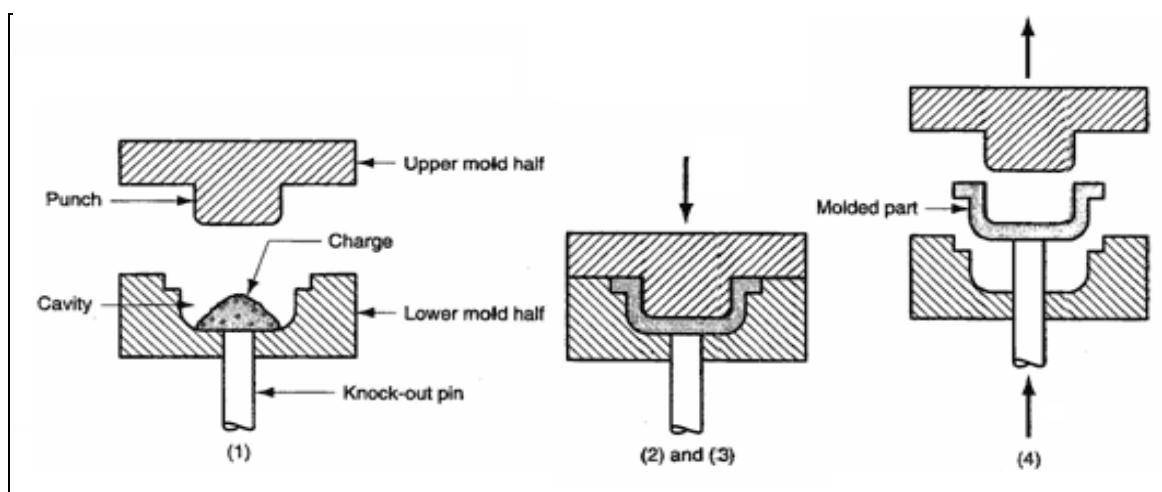
## Methods of Fabrication of plastics: [or] methods of moulding of plastics: [or] Fabrication Techniques:

The process of converting the given polymeric material into suitable designs is called moulding.

The different moulding methods used are

- a) Compression moulding
- b) Injection moulding
- c) Blow film
- d) Extrusion moulding

### Compression moulding:

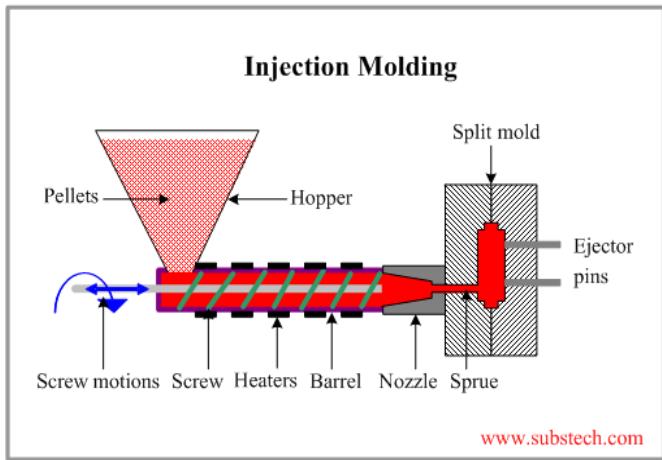


- ❖ Compression moulding method is applied to both thermoplastics and thermosettings plastics.
- ❖ Compression moulding is one of the oldest manufacturing technologies associated with plastics.
- ❖ The mould consists of two halves, the upper half and the lower half.
- ❖ The lower half contains a cavity and the upper half has a projection.
- ❖ The required amount of a compounded mixture is placed in the cavity in the lower half and the mould is closed carefully.
- ❖ The gap between the projected upper half and the cavity in the lower half gives the shape of the moulded article.
- ❖ The time given to polymer to set in the mould is called curing.
- ❖ Curing is done either by heating as in the case of thermosetting or cooling as in the case of thermoplastics.
- ❖ After curing, the moulded article is taken out by opening the mould parts. Now a days fully automatic compression moulding presses are available.

### Injection moulding:

- ❖ Injection moulding method is mainly used for thermoplastic resins.
- ❖ This process is one of the most common of all plastics manufacturing processes.
- ❖ The compounded mixture in the form of a powder (or) pellet is fed into the heated cylinder of the injection moulding machine.

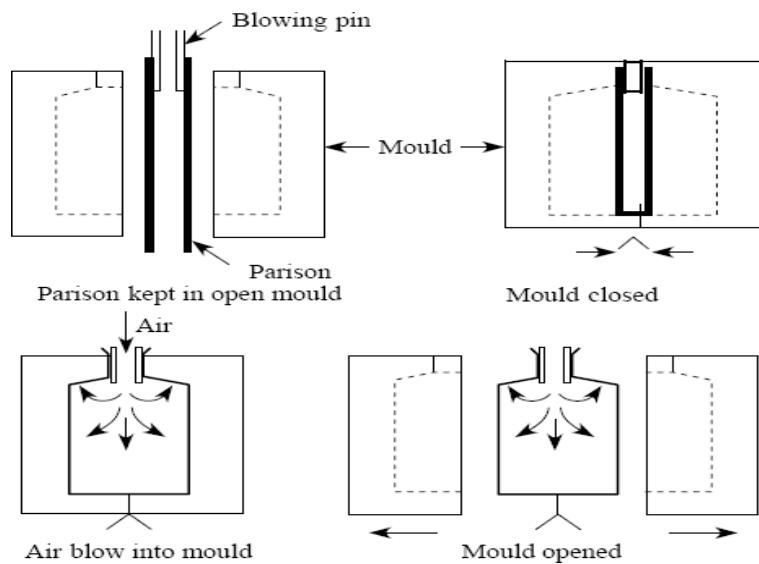
- ❖ The softened plastic mass in the cylinder is injected at a controlled rate by a screw (or) piston under high pressure into a cold mould.
- ❖ Curing of the softened plastic into rigid product occurs during cooling in the mould.
- ❖ The mould is opened after sufficient curing to remove the finished product.
- ❖ Thermosetting polymer can't be moulded by this method.



**2. Blow Moulding:** Blow moulding produces hollow plastic materials like bottles, tubes, tanks and drums.

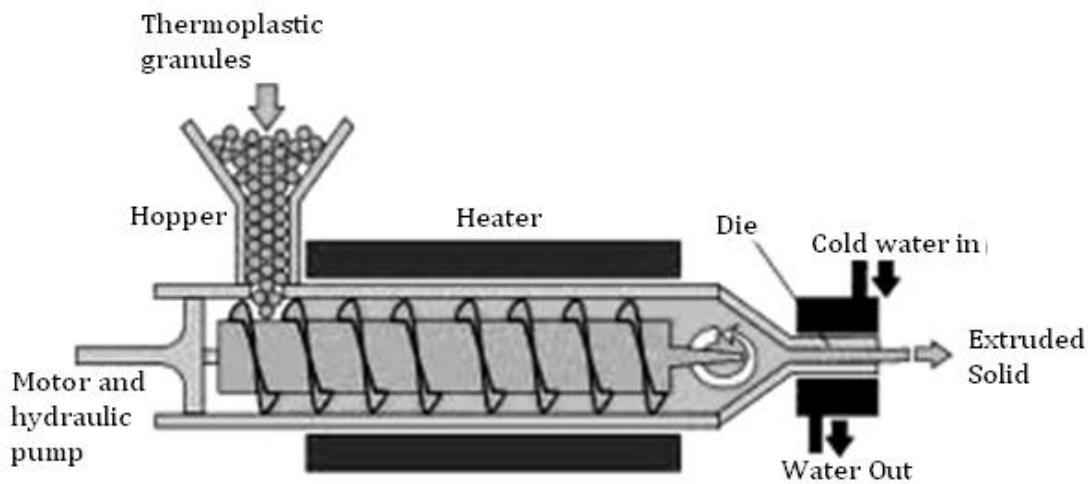
Thermoplastic materials like PVC, polystyrene, polypropylene can be blow moulded.

In this process a tube is placed inside a two piece hollow mould. One end of the tube is completely closed in heated and simultaneously air is blown to fabricate the product having the shape of mould



### Extrusion moulding:

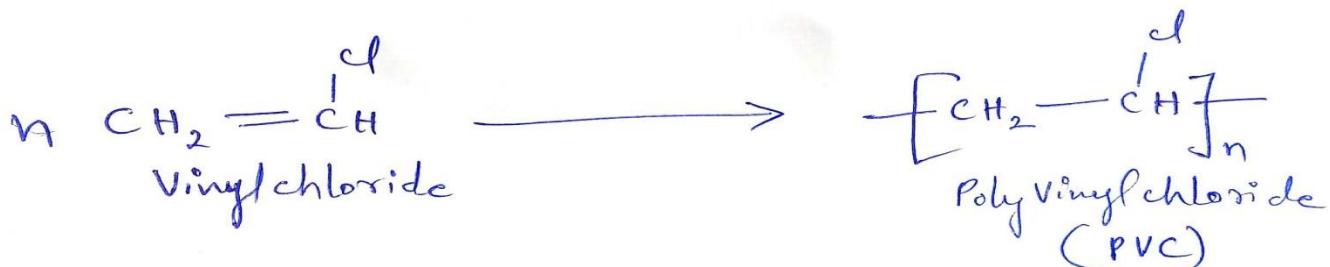
- ❖ Extrusion moulding method is used for thermoplastic resins
- ❖ This method is used to produce continuous sheets, rods, threads, tubes, cords and cables.
- ❖ It is similar to injection moulding.
- ❖ Dry plastic material is placed into heated injection chamber.
- ❖ At the end of the chamber, the material is forced out of a small ring opening (or) a die in the shape of the desired finished product.
- ❖ Extruded out plastic is placed on a moving conveyor belt for uniform cooling.



**Write preparation, properties and applications of i) PVC. ii) Polycarbonates. iii) Bakelite.**

**i) PVC (Poly vinyl chloride):**

**Preparation:** Poly vinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or  $H_2O_2$ .



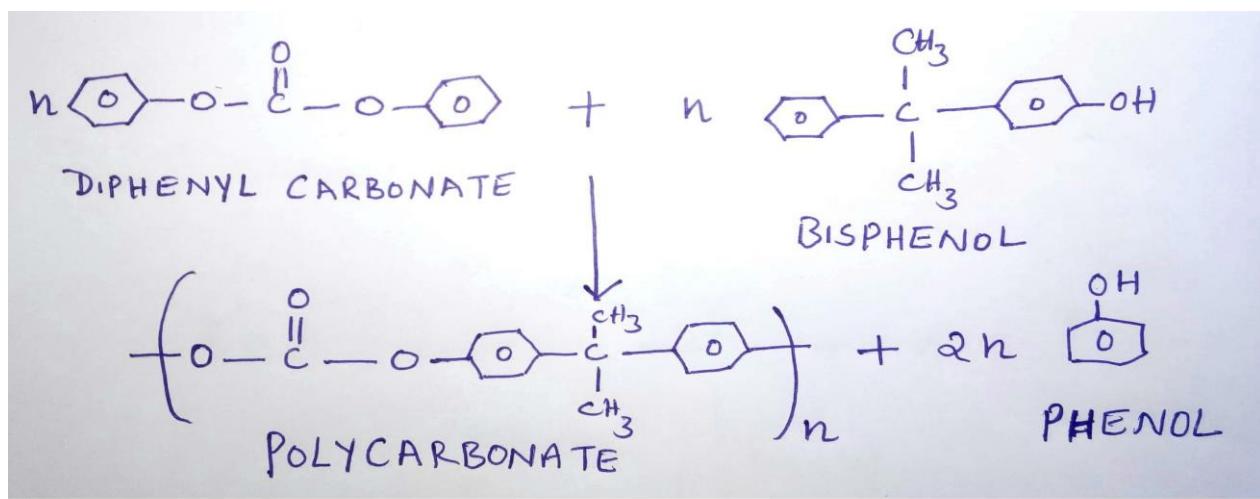
**Properties:** PVC is colourless, odourless, non-inflammable and chemically inert powder. Pure resin possesses greater stiffness and rigidity compared to poly ethylene. It is brittle in nature.

**Applications: or Uses:**

1. P.V.C is mainly used as an insulating material.
2. It is used for making table clothes, rain coats, toys, tool handles, radio components, etc.
3. It is used for making pipes, hoses, etc.
4. It is used for making helmets, refrigerator components, etc.
5. It is used in making cycle and automobile parts.

**ii) Polycarbonates:**

**Preparation:**



### Properties:

1. High melting points
2. Tensile strength and impact resistance.
3. It has excellent mechanical properties.
4. It is soluble in acids and alkali.

**Uses:** The polymer is used in the manufacture of safety goggles, telephone parts, automobile taillight lenses and unbreakable glazing appliances.

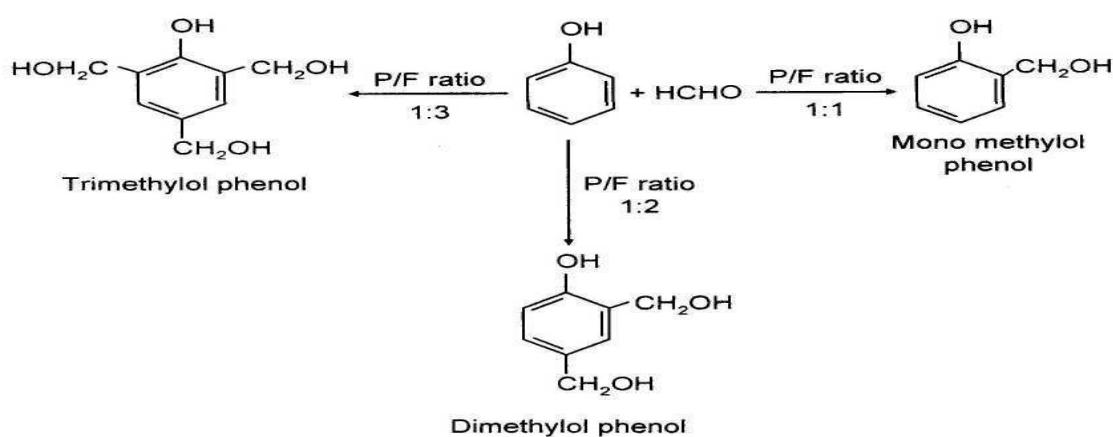
### 3. Phenol formaldehyde resins or Bakelite :

Bakelite is a condensation polymer of phenol and formaldehyde

#### Preparation :

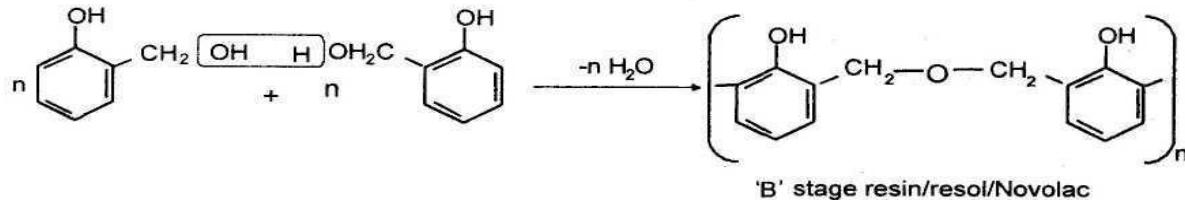
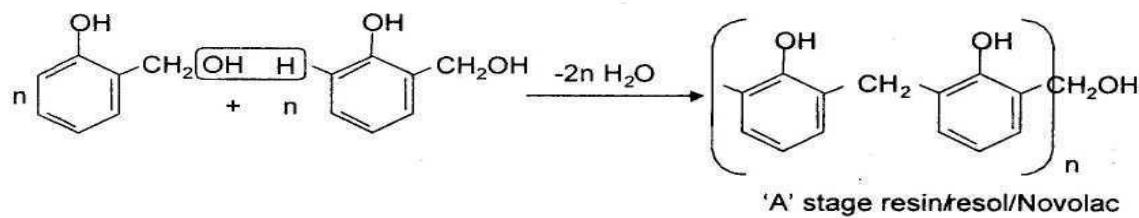
##### I stage:

Phenol is made to react with formaldehyde in presence of acid / alkali to produce non - polymeric mono, di, and tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio)

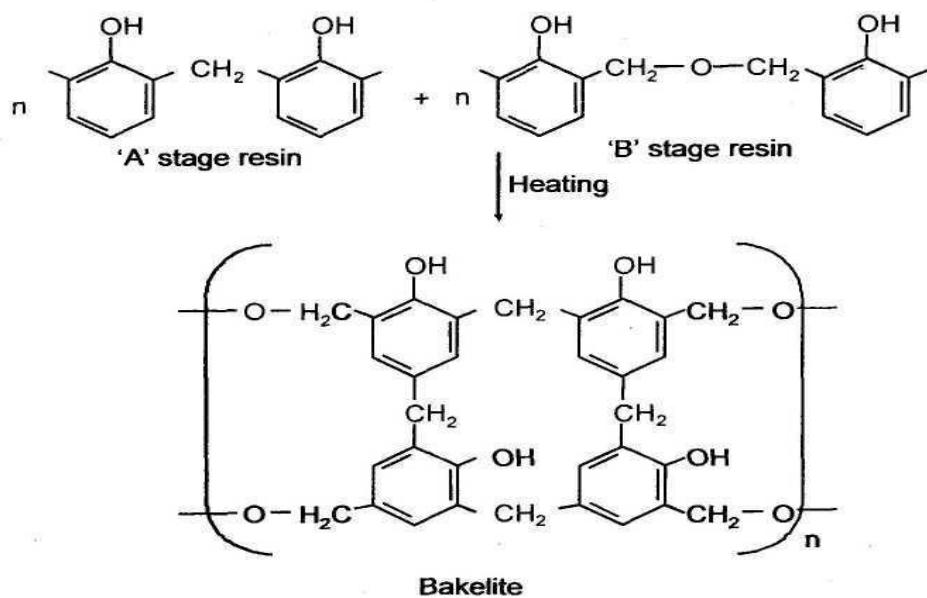


#### II) Stage:

The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.



**III Stage:** This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linking and bakelite plastic resin is produced.



#### **Properties:**

1. Bakelite plastic resin is hard, rigid, and strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents, but it is attacked by alkalies due to the presence of - OH group.
4. It is a good anion exchanging resin, exchanges - OH group with any other anion.
5. Bakelite is an excellent electrical insulator.
6. It is a very good adhesive.
7. Bakelite has very good corrosion resistance, resistant to atmospheric conditions like O<sub>2</sub>, CO<sub>2</sub>, moisture, light, U.V.radiation etc.

**Engineering applications:** Bakelite is used widely.

1. For making electrical insulator parts like switches, switch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange method in boilers.
5. As an adhesive (binder) for grinding wheels etc.

6. In paints and varnishes.
7. For making bearings used in propeller shafts, paper industry and rolling mills.

### Some examples of plastic materials used in electronic gadgets:

S.No.	Plastic materials	Uses in electronic gadgets
1	Phenol formaldehyde	Fuse boxes, knobs, switches, handles.
2	Polyamide	food processor bearings, adaptors.
3	Polycarbonate	Telephones.
4	Polyethylene	Cable & wire insulation.
5	Polypropylene	Kettles
6	Polystyrene	Refrigerator trays/linings, TV cabinets
7	Polysulphone	Microwave grills
8	Polytetrafluoroethylene	Electrical applications.
9	Polyvinyl chloride	Cable and wire insulation, cable trunking.
10	Urea formaldehyde	Fuse boxes, knobs, switches
11	Polymethyl pentane	Circuit boards, microwave grills
12	Acrylonitrile butadiene styrene	Telephone handsets, keyboards, monitors, computer housings

### Write a note on recycling of e-plastic waste.

e-plastic waste (electronic plastic waste) includes discarded electrical or electronic devices. Some examples of e plastic waste are ABS (acrylonitrile butadiene styrene), polycarbonate or PVC (polyvinyl chloride), phenol formaldehyde, polyamides etc. E-plastics are an environmental hazard, and have negative effects on human health.

Recycling e-plastics is challenging. This is because most plastics are not truly recycled. Some plastics can be melted down and used to manufacture new items, but most kinds of plastics are not recycled in this way. Instead, many plastic recycling facilities prepare the plastic to be repurposed, or “down-cycled.” For example, a plastic milk bottle cannot be used to manufacture a new plastic milk bottle. Instead, that milk bottle can be processed and “down-cycled” in the manufacturing of plastic lumber. E-plastics are so challenging to recycle because the brominated flame retardants prevent these plastics from being down-cycled. The e-plastics that contain those banned compounds cannot be reused; they must be disposed.

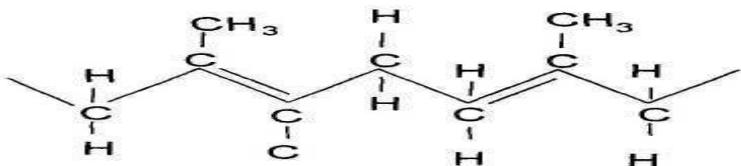
When recycling e-plastics, it is especially crucial to use a certified recycler. To maintain certification, a certified recycler must make sure that, when possible, e-plastics are processed and reintegrated back into the manufacturing process. All un-useable e-plastics, like those with banned brominated flame retardants, must be disposed in carefully controlled conditions in a properly equipped facility.

Because e-plastics are so difficult to recycle, a better environmental strategy for this material is to reuse electronics. Reuse slows the production of scrap e-plastics, and mitigates the need for more plastics to be manufactured. If reusing your corporate electronics is not possible within your own company, reselling or donating the equipment allows it to be reused by others.

### ELASTOMERS:

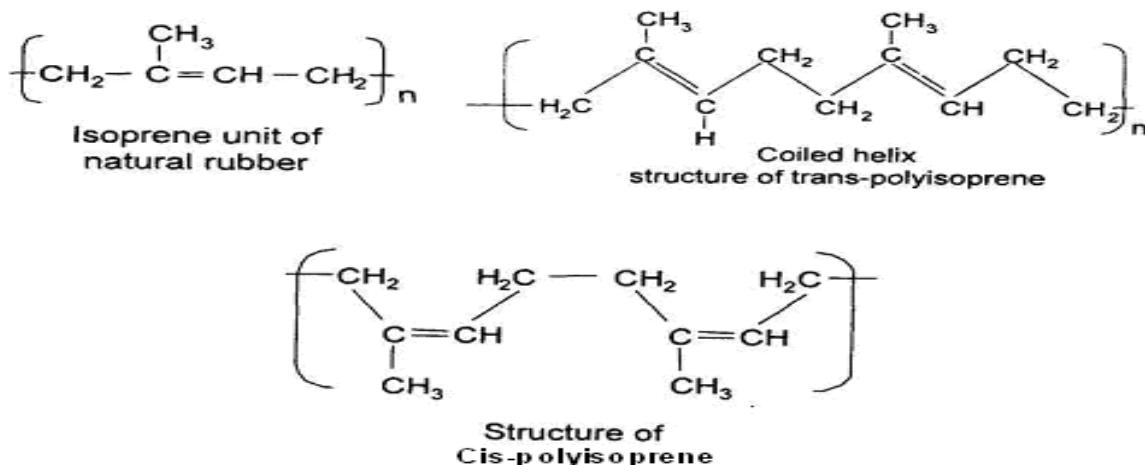
**Definition:** Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on release of stress. Those rubbers are therefore referred to as elastomers.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.



### Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries, of these *Hevea brasiliensis* is the most important source of natural rubber and the rubber obtained from this is known as "Hevea" rubber. Rubber is stored in the form of white fluid called 'latex' behind the bark of the rubber tree.



Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene).

Polyisoprene exists in two geometric isomers cis and trans forms.

Natural rubber is soft and has cis-configuration while 'Guttapercha' or, 'Ballata' has trans configuration.

**Write preparation, properties and applications of i) Buna-S ii) Thiokol iii) PolyUrethane.**

#### BUNA-S [or] SBR,[or] GRS) Styrene Butadiene Rubber) gov. regulated styrene rubber or Ameripol

BUNA - S is otherwise called styrene rubber or *GRS* (Government Rubber Styrene) or Ameripol.

BUNA - S stands for the composition of the monomers and catalyst.

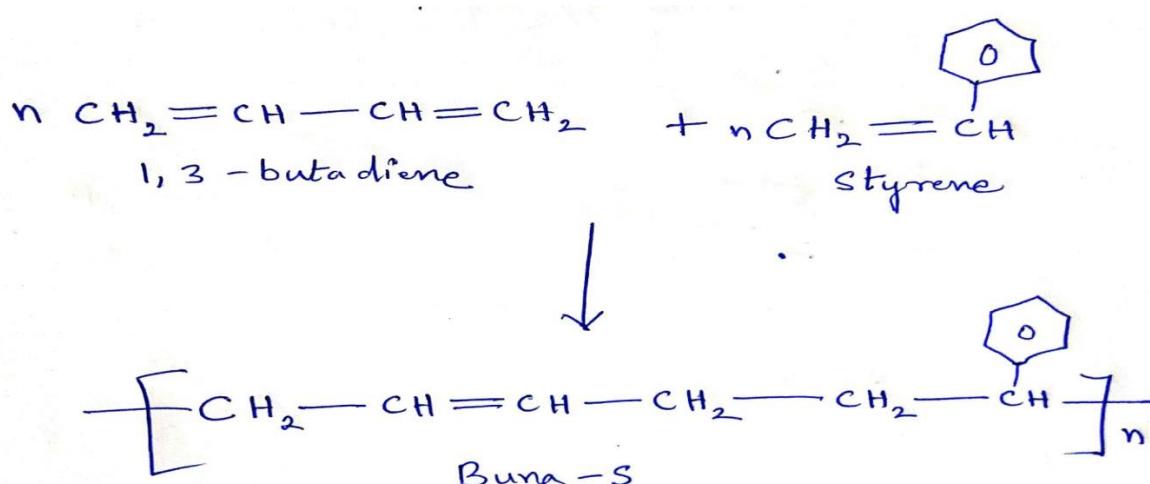
BU stands for Butadiene - monomer

NA stands for Sodium - catalyst

S stands for Styrene - monomer

Buna-S is the most important synthetic rubber it is obtained by the co-polymerization of butadiene and styrene using sodium as a catalyst.

#### Preparation :



### Properties:

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanised by sulphur monochloride ( $S_2Cl_2$ ) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA - S possess excellent abrasion resistance.
5. It is a good electrical insulator.
6. It is resistant to chemicals but swells in oils and attacked by even traces of ozone, present in the atmosphere.
7. Styrene rubber possess high load bearing capacity and resilience.

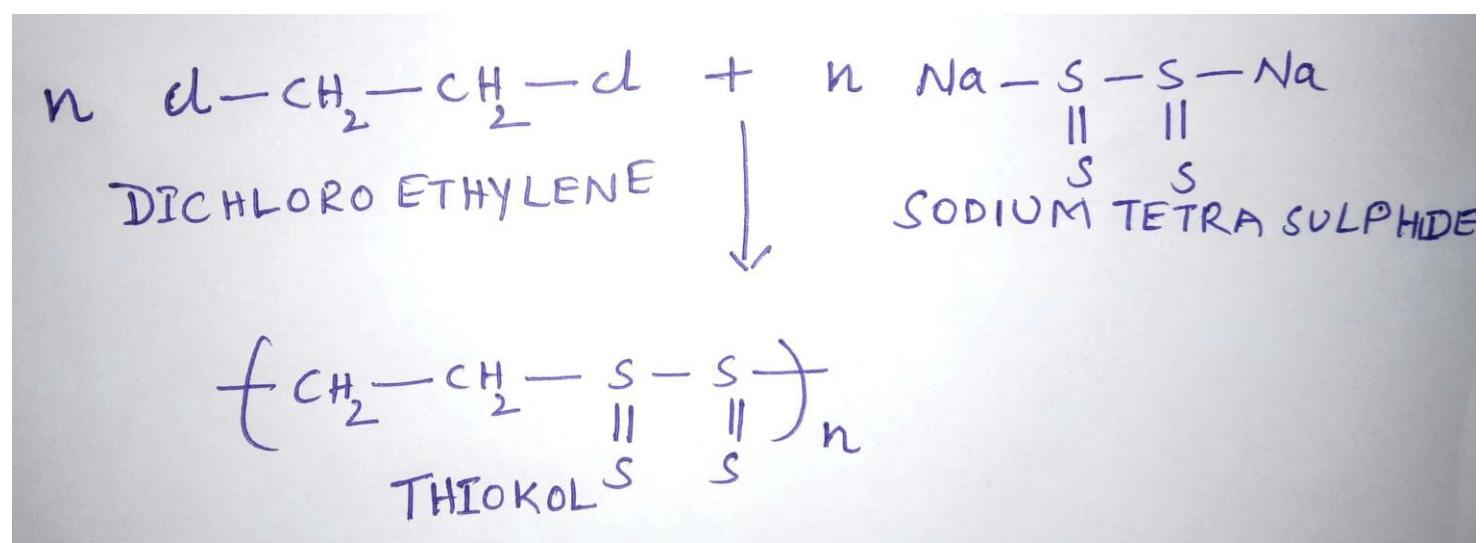
### Applications:

1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear components.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor tiles, tank linings in chemical industries and as adhesives.

### Thiokol (Polysulphide Rubber or GR-P):

Polysulphide rubbers are the condensation product of ethylene dichloride and sodium tetra sulphide.

### Preparation :



### Properties:

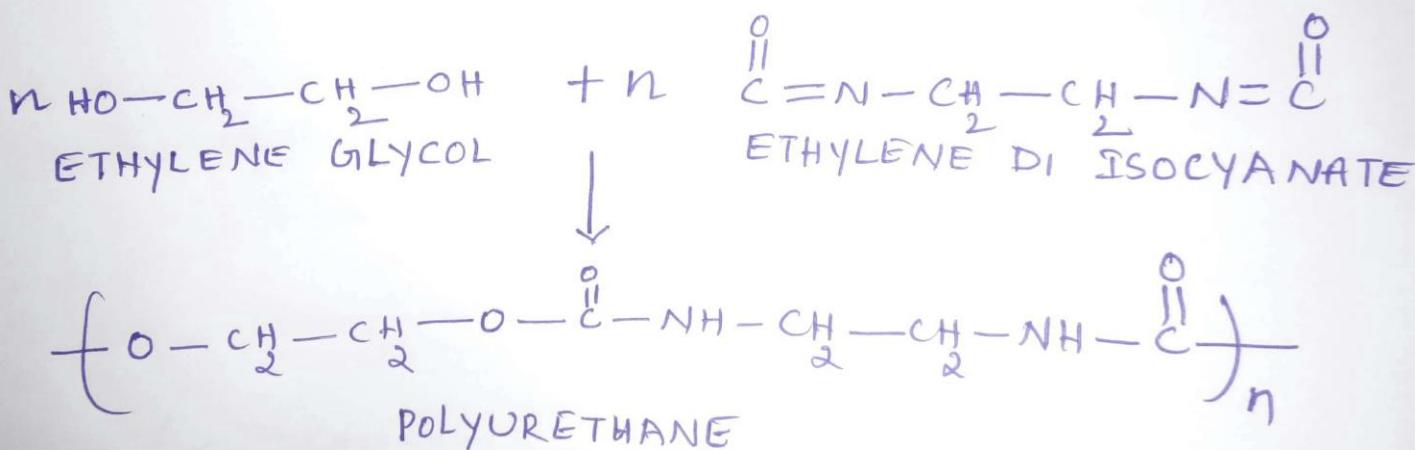
- Thiokol rubber possess strength and impermeability to gases.  
This rubber cannot be vulcanized and it cannot form hard rubber.  
Possess good resistance to mineral oils, fuels, oxygen, solvents, ozone and sunlight.  
It is also resistant to the action of petrol lubricants and organic solvents

### Applications:

- Fabrics coated with thiokol are used for barrage balloons, life rafts and jackets.  
Thiokols are used for lining for conveying gasoline and oil.  
Used for making gaskets and seals for printing rolls.  
Thiokol mixed with oxidizing agents is used as a fuel in rocket engine.

### Polyurethanes:

### Preparation :



Scanned with CamScanner

Polyurethanes are formed by the reaction between diisocyanate and diol

e.g.: Perlon-U is obtained by the reaction of 1,4-butane diol with 1,6-hexamethylene diisocyanate.

#### **Properties:**

1. polyurethanes are less stable than polyamides (nylons) at elevated temperature (because of the presence of additional oxygen in the chain which increases its flexibility, the M.P of polyurethanes is much less than that of the corresponding polyamides.)
2. They are characterized by excellent resistance to abrasion and solvents.

#### **Applications:**

1. It is used for floor coating for gymnasium and dance floors where high abrasion resistance is required.
2. Used as surface coatings, films, foams and adhesives.
3. They are used for cushions because of improved strength, lower density and easier fabrication.
4. It is used in lightweight garments and swim suits because of its stretching property.
5. They are used to cast to produce gaskets and seals.

#### **COMPOSITE MATERIALS:**

The composite materials are generally made by placing the dissimilar materials together in such a manner that they work as a single mechanical unit. The properties of new materials so produced are different in kind and scale from those of any constituents. Thus it has become possible to incorporate or alter properties, more than that, introduce a combination of properties like high strength and stiffness at elevated temperatures.

#### **Definition:**

A composite material is a material system consisting of a mixture of two (or) more micro constituents which are mutually insoluble differing in form and composition and forming distinct phases.

Thus using composites it is possible to have such combination of properties like high strength and stiffness, corrosion resistance, and ability to withstand extreme high temperature conditions.

For e.g. Wood (a composite of cellulose fibres and lignin cementing materials), rain proof cloth (cloth impregnated with water proof material) and bone (a composite of soft collagen and brittle and hard material apatite).

#### **Fibre Reinforced Plastics(FRP):**

Reinforcing a plastic matrix with a high strength fibre material results in the formation of fibre reinforced plastics.

FRP contains two components. 1) Fibre. 2) Matrix.

#### **1) Fibre:**

Fibers are used to strengthen thermoplastic compounds.

There are three main types of fibers carbon, glass & Aramid fibers.

They have different properties.

All fibers have generally high stress capacity than the ordinary steel.

## 2) Matrix:

The plastic material used in FRP is called matrix.

Matrix is a tough and relatively weak plastic that is reinforced by stronger fibers.

Generally thermosetting plastics are used as matrix.

Vinyl esters and epoxy resins are most commonly used matrixes.

### **Glass fibre - reinforced polymer(GFRP):**

Glass fibre + Polymer → GFRP

Glass fibre - reinforced polymer composites employ glass fibres for improving the characteristics of especially polymeric matrices containing nylons, polyesters etc. These composites posses lower densities higher tensile strengths and impact resistance and resistance to corrosion and chemicals.

Applications: Automobile parts, storage tanks transportation industries, plastic pipes etc.,

### **Carbon fibre - reinforced polymer(CFRP):**

Carbon fibre + Polymer → CFRP

Carbon fibre - reinforced polymer composites are employed in situations requiring excellent resistance to corrosion, lighter density retention of properties even at high temperatures.

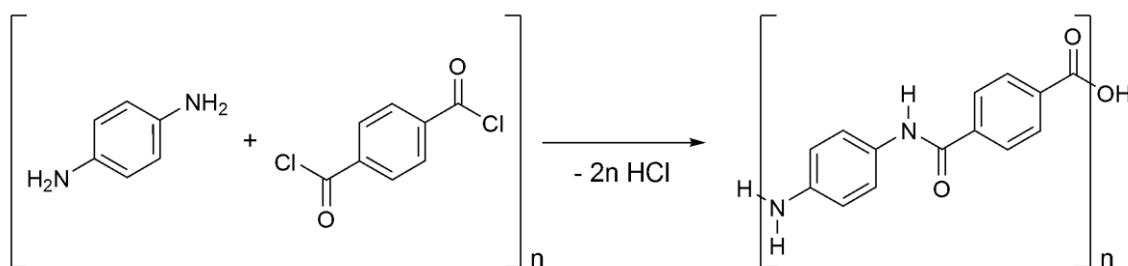
Carbon fiber reinforced composites are very strong and are often stronger than steel but lighter. They are used for making parts of aeroplanes and the space shuttle, tennis rackets and golf clubs, weaving machines, missiles, agricultural etc.

### **Aramid fiber reinforced plastics [bullet proof plastic]:**

- ↗ Aramid is a short form of aromatic polyamide.
- ↗ Ex: Nomex & Kevlar.
- ↗ These are used to make bullet proof vests & bicycle tyres.

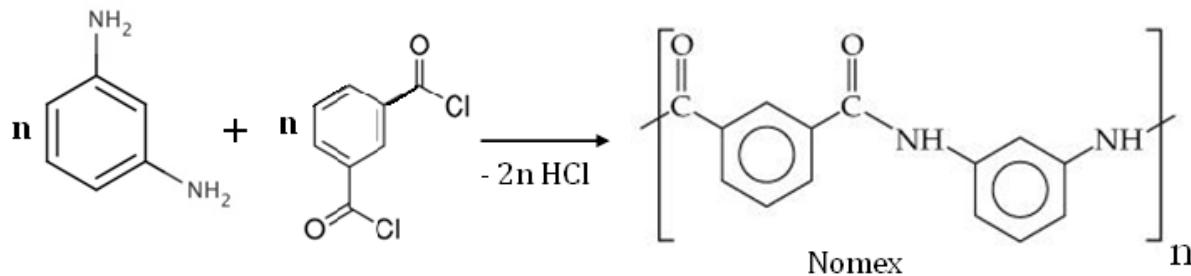
#### **Kevlar:**

- ↗ It is prepared by condensation polymerization of terephthalic acid chloride & 1,4-diamino benzene.



#### **Nomex:**

- ↗ This is produced by condensation reaction from the monomers phenylene diamine & isophthaloyl chloride.



### Properties:

- ❖ It has higher tensile strength and modulus than fibreglass.
- ❖ It has high chemical inertness.
- ❖ It has very low coefficient of thermal expansion.
- ❖ It has flame resistance and high impact resistance.
- ❖ It has low weight.

### Uses:

- ❖ Kevlar fibers are used for structures requiring good stiffness, high abrasion resistance and lightweight.
- ❖ It is used as inner lining for tires to prevent punctures (puncture resistant bicycle tyres).
- ❖ It is used in table tennis, tennis, badminton and squash racquets, cricket bats, hockey sticks.
- ❖ It is used in personal armor such as helmets, ballistic face masks, bullet proof vests etc.
- ❖ It is often used in the field of cryogenics for its low thermal conductivity and high strength.

It is used in boat hulls, helicopter blades etc.

## CONDUCTING POLYMERS:

A polymer which conducts electricity is called conducting polymer.

Eg :- Polyaniline, polyacetylene, polypyrrole, etc

They are classified into two types :   
 1) Intrinsically conducting polymers.  
 2) Extrinsically conducting polymers

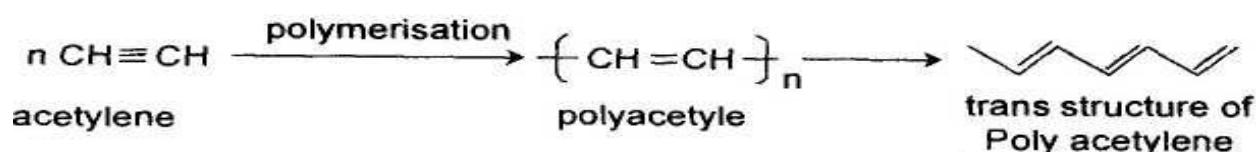
### 1. Intrinsically conducting polymers:

These have extensive conjugation in the backbone which is responsible for conductance. These polymers can be divided into two :

#### a) Conducting polymers having conjugated $\pi$ – electrons in the backbone:

eg :- polyacetylene, polyaniline etc.

These type of polymers have backbones of continuous  $sp^2$  hybridized carbon centers. One valence electron on each center resides in a  $P_z$  orbital. Overlapping of conjugated  $\pi$  – electrons over the entire backbone results in the formation of valence bonds as well as conduction bands, which extends over the entire polymer molecule. But since the valence band and the conduction band are separated by a significant band gap, conductivity of these polymers is not very high.

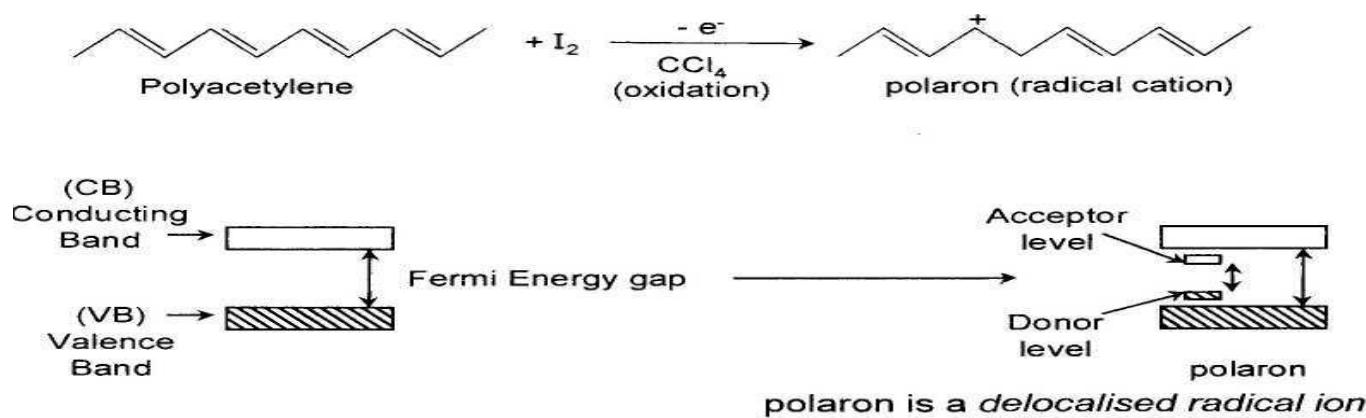


#### b) Doped conducting polymers:

Conductivities of polymers having conjugated  $\pi$  – electrons in the backbone can be increased by creating either +ve or –ve charges on the polymer backbone by oxidation or reduction. This process is called doping. It can be done in two ways :

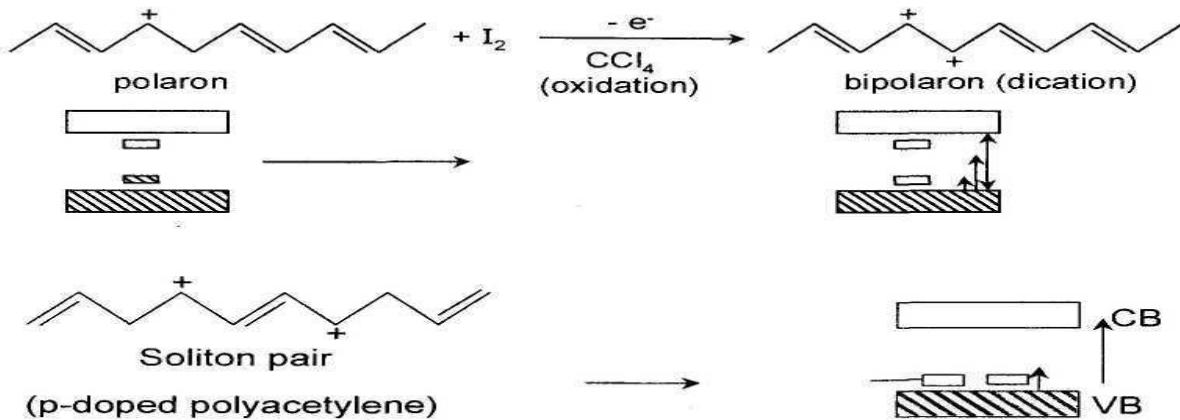
### i) Oxidative doping (P – doping):

It involves treating the conjugated polymer with a Lewis acid like  $\text{FeCl}_3$  thereby oxidation takes place and +ve charges are created on the back bone.



### ii) Reductive doping (n – doping):

It involves treating the polymer with a Lewis base like  $\text{RNH}_2$  thereby reduction takes place and -ve charges are created on the polymer back bone.



## 2. Extrinsically conducting polymers:

Some of the polymers conduct electricity due to externally added ingredients to them. They are of two types.

a) Polymers with conductive elements filled Polymers. b) Blended conducting polymers.

### a). Polymers with conductive elements filled:

In these polymers, the polymer acts as a 'binder' and holds the conducting element added so that the polymer becomes a conductor. Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.

Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold. The conductive elements added to create a conducting path in the polymer.

### b). Blended conducting polymers:

These polymers are obtained by blending a conventional polymer with a conducting polymer.

The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength.

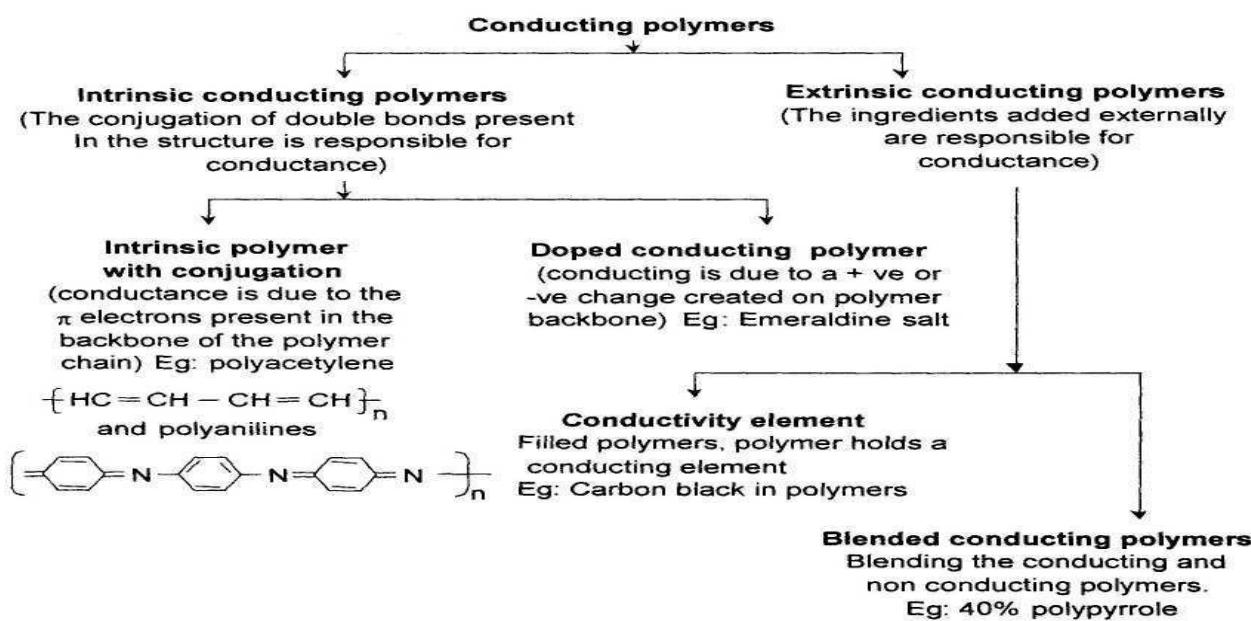
Ex: 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

### Applications of conducting polymers in biomedical devices:

- ★ Conducting polymers are used in preparation of artificial devices like Heart valves, kidneys, and lungs.
- ★ Poly methyl methacrylate is used as bone cement used for some fracture repairs.
- ★ Poly methyl methacrylate is also used for artificial teeth.
- ★ Used in preparation other medical devices include sutures, pins, screws used during surgery on bones, ankles, hands etc.
- ★ They are used to prepare contact lenses which permit O<sub>2</sub> to the eyes. These lenses are called rigid gas permeable lenses (RGP).

### Applications of conducting polymers in electronics:

- ✉ They are used in rechargeable batteries.
- ✉ They are used in analytical sensors of pH, O<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> etc.
- ✉ Used in photo voltaic cells. Ex; Al/polymer/Au.
- ✉ Used in telecommunication systems.
- ✉ Used in transistors and diodes.
- ✉ Used in solar cells.
- ✉ Used as wiring in air crafts and aerospace parts.



### **Write a note on Biodegradable polymers.**

- ◆ Biodegradation is the chemical breakdown of materials by physiological environment.
- ◆ Some polymers undergo degradation when exposed to moisture, heat, oxygen, ozone and micro organism.
- ◆ These agents change the chemical structure of the polymer and lead to change in properties of polymer.
- ◆ Generally materials obtained from plants, animals and other living organism and synthetic materials similar to plant and animal material undergo degradation by microorganism.
- ◆ These organic materials can be degraded either aerobically or anaerobically.
- ◆ During biodegradation, microorganism secrets biosurfactant which facilitates degradation easily.
- ◆ These microorganisms can perform various activities like degradation, transformation or accumulation of compounds like hydrocarbons, poly aromatic hydrocarbons, pharmaceutical substances, radio nucleids and metals.
- ◆ The activity of aerobic bacteria is measured by the amount of O<sub>2</sub> consumed or the amount of CO<sub>2</sub> produced.
- ◆ The activity of anaerobic bacteria is measured by the amount of CH<sub>4</sub> gas produced.

<b>Biodegradable Plastics</b>	
<b>Hydro Biodegradable Plastics (HBP)</b>	<b>Oxo Biodegradable Plastics (OBP)</b>
Hydro biodegradable plastics	Oxo biodegradable plastics
<ul style="list-style-type: none"> <li>➤ They undergo degradation by hydrolysis.</li> <li>➤ It is rapid process.</li> <li>➤ End products are <math>H_2O</math> &amp; <math>CO_2</math>.</li> <li>➤ It is expensive process.</li> <li>➤ HBP emits <math>CH_4</math> in anaerobic condition.</li> <li>➤ HBP can be prepared from corn, wheat, sugar cane etc.</li> </ul>	<ul style="list-style-type: none"> <li>➤ They undergo degradation by oxidation.</li> <li>➤ It is rather slow process.</li> <li>➤ End products are <math>H_2O</math> &amp; <math>CO_2</math>.</li> <li>➤ It is less expensive process.</li> <li>➤ It does not emit <math>CH_4</math>. It emits only <math>H_2O</math> &amp; <math>CO_2</math>.</li> <li>➤ OBP can be prepared from byproducts of oil or natural gas.</li> </ul>

**Properties:**

- ♣ These are non – toxic.
- ♣ They are able to maintain good mechanical integrity until degraded.
- ♣ Capable of controlled rates of degradation.

**Applications:**

- ♠ It is used in drug delivery systems.
- ♠ It is used to coat a stent and release drugs in a controlled way.
- ♠ It is used in dental devices and orthopedic fixation devices.
- ♠ Ex: Poly lactic acid, Poly glycolic acid, Poly hydroxyl butyrovalerate (PHBV).

**Write a short notes on Biopolymers.**

Biopolymers are naturally occurring long chain molecules which are involved in biological changes important for our lives. These polymers are present in living matter.

Biopolymers are classified into four types. They are

- a. Carbohydrates
- b. Proteins
- c. Lipids
- d. Nucleic acids.

**Carbohydrates:**

Carbohydrates are a group of compounds represented by the general formula,  $C_x(H_2O)_y$

Carbohydrates are classified into following classes depending upon whether these undergo hydrolysis and if so on the number of products form: Monosaccharides, Disaccharides, Trisaccharides, Oligosaccharides, Polysaccharides.

- 1) **Monosaccharides** (also known as simple sugars) are the simplest carbohydrates containing 3-7 carbon atoms. A sugar containing: – an aldehyde is known as an aldose – a ketone is known as a ketose.
- 2) **Disaccharides** :When two monosaccharides are combined together with elimination of a water molecule it is called disaccharide. Monosaccharides are combined by glycosidic bond.
- 3) **Oligosaccharides** contain 2-10 monosaccharides bonded together (building block = residue) Example: Sucrose
- 4) **Polysaccharides**: Polysaccharides are polymerized products of many monosaccharide units.

**Proteins:**

Proteins are complex nitrogenous organic compounds of high molecular masses, synthesized by plants and animals, which on hydrolysis yield amino acids. Proteins are essential for the growth and maintenance of life.

**Role of proteins:**

- 1) They serve as fuel to yield energy.

- 2) They help in maintenance of fluid-balance.
- 3) They are responsible for functional characteristics.
- 4) They help in the formation of haemoglobin, chromosomes, etc.

### **Lipids:**

Lipids are a heterogeneous group of organic compounds, which are essential constituents of all plants and animal cells. They may be defined as the group of naturally occurring substances of the higher fatty acids.

**Types of lipids:** Fats and oils, waxes, phospholipids, Glycolipids, Steroids.

### **Role of lipids:**

- 1) They act as structural components of cell membranes.
- 2) They act as transport forms of various metabolic fuels.
- 3) They facilitate the absorption of the fat soluble vitamins. (such as vitamin A, D, E and K).
- 4) Their presence in tissues of animals serve as good heat insulators and shock-absorbers.

### **Nucleic acids:**

A nucleic acid is a polymer in which the monomer units are nucleotides. There are two Types of Nucleic Acids:

- 1) **DNA: Deoxyribonucleic Acid:** Found within cell nucleus for storing and transferring of genetic information that are passed from one cell to other during cell division
- 2) **RNA: Ribonucleic Acid:** Occurs in all parts of cell serving the primary function is to synthesize the proteins needed for cell functions.

Nucleic acids are the carriers of genetic information. In all living organisms, the hereditary information is stored in deoxyribonucleic acid (DNA), which is a molecule formed by the repetition of nucleotides (making DNA a polymer). There are four different nucleotides in DNA, which form a universal code for hereditary information. Ribonucleic acid (RNA), the other kind of nucleic acid, is a related molecule to DNA. It is also a polymer of four nucleotides, three of which are the same as in DNA while the fourth one is slightly different. It has many functions in cells, notably acting as the intermediate between DNA and proteins. Some viruses even store their genome in the form of an RNA molecule rather than DNA

### **Write a note on Biomedical polymers.**

Biomedical polymers are the materials that can be implanted in the body to provide special functions or in diagnostic, surgical and various therapeutic applications without causing adverse effect on blood and other tissues. They are tailor-made or modified at will suit specific body functions.

Polymers used for medical application should be biocompatible. It should possess the following characteristics.

- 1) It should have purity and reproducibility.
- 2) It should have optimum physical and chemical properties.
- 3) It should be fabricated into any desired shape without being degraded.
- 4) It should be sterilized easily.
- 5) Biopolymers that come in contact with blood and tissues should not damage cellular elements of blood, enzymes and protein.
- 6) They should not produce toxic and allergic reactions.
- 7) They should not deplete electrolytes present in the body.

### **Biomedical uses of polymers:**

Applications of biomedical polymers in medicine are given below.

S.No	Polymer	Applications
1	Polyurethane	Heart valves, blood filters, artificial hearts, vascular tubes, etc.
2	Polyvinyl chloride (PVC)	Disposable syringes, etc.
3	Polypropylene	Heart valves, blood filters, etc.
4	Polyethylene	Disposable syringes, etc.
5	Polymethyl methacrylate	Contact lenses, dental restoratives etc
6	Silicone rubber	Heart valves, drain tubes etc.

**Long answer type questions:**

- 1) What is Polymerization? Explain types of polymerisation with examples.(Addition & condensation polymerisation)
- 2) Explain Emulsion and Suspension polymerization techniques. (or) Explain the methods of polymerisation.(or) Write a brief account on techniques of polymerisation.
- 3) Write a brief account on mechanical properties of polymers?
- 4) Explain Compounding of plastics with suitable examples. (or) What is compounding of plastics? What are the additives added to the resins before moulding them?
- 5) Differentiate between thermo plastics & thermosetting plastics. Give two examples for each type ?
- 6) Describe with neat sketches, the following moulding techniques of plastics (or) fabrication of plastics.  
a) Compression moulding.      b) Injection moulding    c) Extrusion moulding.      d) Blown film.
- 7) Write preparation, properties and applications of i) PVC.    ii) Polycarbonates.    iii) Bakelite.
- 8) Mention some examples of plastic materials used in electronic gadgets.
- 9) Explain about recycling of e-plastic waste.
- 10) Write preparation, properties and applications of i) Buna-S    ii) Thiokol    iii) Poly Urethane.
- 11) What are composite materials. Explain about bullet proof plastics.
- 12) Write a note on Fibre reinforced plastics (FRP).
- 13) Write a note on conducting polymers with examples.
- 14) Explain about Biodegradable plastic materials.
- 15) Write a note on Biopolymers.
- 16) Write a note on Bio-medical polymers.

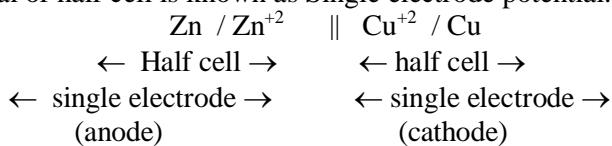
## UNIT II: ELECTROCHEMICAL CELLS AND CORROSION

[Single electrode potential, electrochemical series and uses of series, standard hydrogen electrode, calomel electrode, construction of glass electrode, batteries.(Dry cell, Li ion battery and zinc air cells), fuel cells (H<sub>2</sub>-O<sub>2</sub>, CH<sub>3</sub>OH-O<sub>2</sub>, phosphoric acid and molten carbonate).

**Corrosion:-** Definition, theories of corrosion (chemical and electrochemical), galvanic corrosion, differential aeration corrosion, stress corrosion, galvanic series, factors influencing rate of corrosion, corrosion control (proper designing and cathodic protection), Protective coatings (surface preparation, cathodic coatings, anodic coatings, electroplating and electroless plating [nickel]), Paints (constituents, functions and special paints).]

### Q1) Write a note on Single Electrode Potential.

The Potential of half cell is known as Single electrode potential.



The total cell emf is equal to the sum of the single electrode potentials.

$$\begin{aligned} E(\text{cell}) &= E(\text{anode}) + E(\text{cathode}) \\ \text{or } E(\text{cell}) &= E(\text{oxidation}) + E(\text{reduction}) \quad \text{or } E(\text{cell}) = E(\text{right}) - E(\text{left}) \end{aligned}$$

Where; E(cell) = e.m.f of cell

E(right) = reduction potential of right hand side electrode.

E(left) = reduction potential of left hand side electrode.

### Q 2) What is Electrochemical Series. Give its significance.

**Definition:** The arrangement of various metals in the order of increasing values of standard reduction potential is called emf series.

**Applications of Emf Series: [or] Importance of Electrochemical Series:**

- 1) Relative ease of Oxidation or Reduction.
- 2) Replacement tendency.
- 3) Predicting spontaneity of the reactions.
- 4) Calculations of equilibrium constant.

#### 1) Relative ease of oxidation or reduction:

An electrode with high reduction potential easily undergoes reduction and it does not undergo easy oxidation.

Ex: Fluorine  $F + e^- \rightarrow F^-$

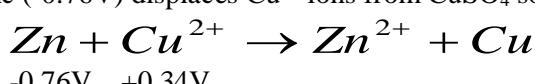
An electrode with the low reduction potential easily undergoes oxidation and it does not undergo easy reduction.

Ex: Lithium  $Li \rightarrow Li^+ + e^-$

#### 2) Replacement tendency:

The electrode with lower standard electrode potential displaces the metal ions of higher standard electrode potential from its solution.

Ex: Zinc (-0.76V) displaces Cu<sup>2+</sup> ions from CuSO<sub>4</sub> solution.



#### 3) Predicting spontaneity of the reactions:

Spontaneity of the reaction can be predicted from EMF values.

A reaction with +ve EMF is spontaneous.

A reaction with -ve EMF is non spontaneous.

#### 4) Calculations of equilibrium constant:

The standard electrode potential is

$$E^o = \frac{RT}{nF} \ln K_{eq}$$

$$E^o = \frac{2.303RT}{nF} \log K_{eq}$$

$$\log K_{eq} = \frac{nFE^o}{2.303RT}$$

$$\log K_{eq} = \frac{nE^o}{0.059}$$

By measuring standard electrode potential for a cell reaction, its equilibrium can be calculated.

S.No:	Element name	Element	Electrode Reaction	Standard electrode potential ( $E^o$ ) volts
1	Lithium	Li	$Li^+ + e^- \rightarrow Li$	- 3.05
2	Potassium	K	$K^+ + e^- \rightarrow K$	- 2.925
3	Sodium	Na	$Na^+ + e^- \rightarrow Na$	- 2.714
4	Magnesium	Mg	$Mg^{+2} + 2e^- \rightarrow Mg$	- 2.370
5	Aluminium	Al	$Al^{+3} + 3e^- \rightarrow Al$	- 1.66
6	Zinc	Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	- 0.76
7	Iron	Fe	$Fe^{+2} + 2e^- \rightarrow Fe$	- 0.44
8	Tin	Sn	$Sn^{+2} + 2e^- \rightarrow Sn$	- 0.14
9	Lead	Pb	$Pb^{+2} + 2e^- \rightarrow Pb$	- 0.12
10	Hydrogen	H	$2H^+ + 2e^- \rightarrow H_2$	0.00
11	Copper	Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+ 0.34
12	Mercury	Hg	$Hg^{+2} + 2e^- \rightarrow Hg$	+ 0.88
13	Silver	Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.79
14	Platinum	Pt	$Pt^{+2} + 2e^- \rightarrow Pt$	+ 1.2
15	Gold	Au	$Au^{+3} + 3e^- \rightarrow Au$	+ 1.5

#### Reference Electrodes:

A Reference electrode is an electrode which has a stable and well-known electrode potential. Electrode potential is determined with respect to a reference electrode. Reference electrodes are two types:

**Primary reference electrode.** Eg: Standard Hydrogen electrode.

**Secondary reference electrode.** Eg: Calomel electrode.

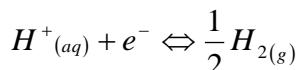
SHE or NHE is taken as the best reference electrode whose potential taken as zero.

### Q 3) Explain the construction and working of Hydrogen electrode:

#### Construction:

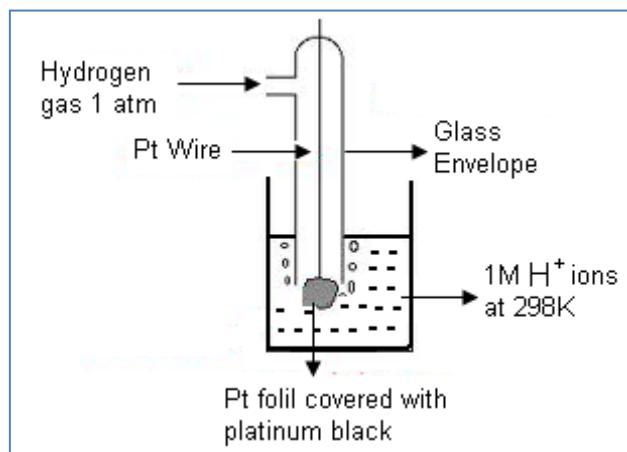
- A small platinum foil coated with platinum black is connected to a platinum wire is enclosed in a glass tube.
- Platinum electrode is placed in a solution of  $H^+$  ions of 1M concentration.
- $H_2$  gas with 1 atm pressure is passed over platinum electrode through the solution at 25°C.
- This whole assembly is considered as hydrogen reference electrode.

Using hydrogen electrode  $P^H$  of the solution can be determined.



Applying Nernst equation to the above equilibrium

$$\begin{aligned}
 E &= E^0 - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]} \\
 E &= 0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[H^+]} \quad (\because [H_2] = 1) \\
 E &= -\frac{0.059}{n} \log \frac{1}{[H^+]} \\
 E &= 0.059 \times \log [H^+] \quad (\because n = 1 \text{ for } H^+ \text{ ions}) \\
 \therefore P^H &= -\log [H^+] \\
 E &= -0.059 P^H
 \end{aligned}$$

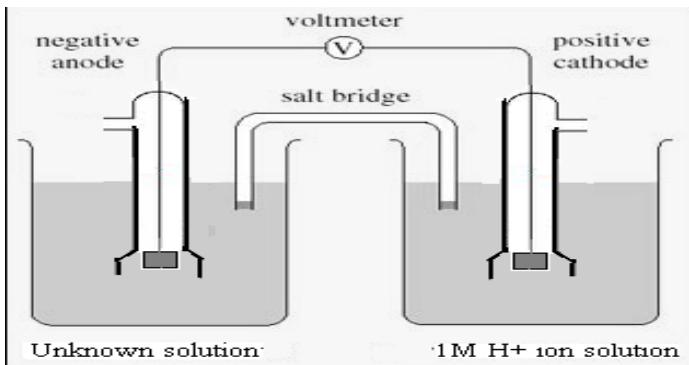


#### Measurement of $P^H$ using hydrogen electrode:

The above half cell (left side) placed in the solution of unknown  $P^H$  is connected to NHE through salt bridge.

The EMF of the cell is measured by using potentiometer.

$$\begin{aligned}
 E_{cell} &= E_{right} - E_{left} \\
 E_{cell} &= 0 - (-0.059 P^H) \\
 E_{cell} &= 0.059 P^H \\
 P^H &= \frac{E_{cell}}{0.059}
 \end{aligned}$$



#### Limitations:

- Hydrogen electrode can't be used in the solutions containing compounds of Hg, As, S and oxidizing agents like  $Fe^{3+}$ ,  $Cr_2O_7^{2-}$ , and  $MnO_4^-$ .
- It can't be used in the presence of ions of many metals.
- It is difficult to set up a hydrogen electrode. It cannot be used in solutions containing redox systems.

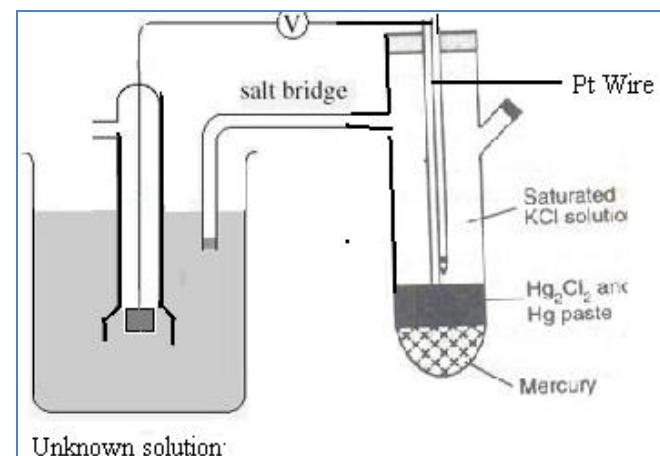
**Q 4) Explain the construction and working of Calomel electrode (Secondary reference electrode):**

- Sometimes calomel electrode is used as reference electrode instead of NHE or SHE.
- The potential of saturated calomel electrode is 0.2422V.

**Construction:**

- A glass tube is filled with a layer of mercury at the bottom.
- It is covered with a paste of  $Hg + Hg_2Cl_2$  and saturated KCl solution.
- A platinum wire is placed in the mercury layer for making electrical contact.

By combining calomel electrode with  $H_2$  electrode,  $P^H$  of unknown solution can be determined.



$$E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = 0.2422 - (-0.059P^H)$$

$$E_{cell} = 0.2422 + 0.059P^H$$

**Ion Selective Electrode: (ISE):**

Ion Selective Electrodes (ISE) use a membrane which is sensitive to a particular chemical species. ISE respond to certain specific ions present in a mixture while ignoring others and develop potential. The potential developed is a measure of the concentration of the species of interest.

Examples: Glass electrode and Fluoride electrode.

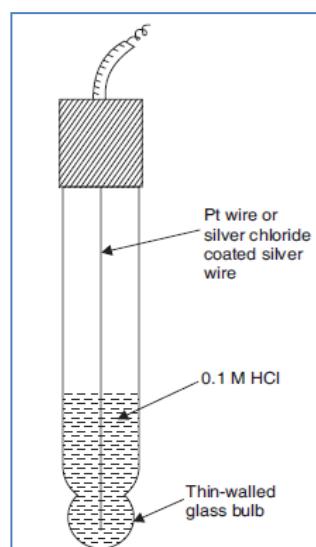
**Q 5) Explain the construction and working of Glass electrode:Principle:**

- When two solutions of different  $P^H$  values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane.
- The potential difference developed is proportional to the difference in  $P^H$  value.
- The glass membrane functions as ion exchange resin and set up an equilibrium between  $Na^+$  ions of glass and  $H^+$  ions of solution.
- Potential of glass electrode is given by the expression

$$E_G = E_G^o + 0.059VP^H \text{ at } 25^\circ C$$

**➤ Construction:**

- It consists of a thin walled glass bulb containing  $AgCl$  coated  $Ag$  electrode in 0.1M HCl.
- It is shown as  $Ag / AgCl_{(s)}; HCl(0.1M) / Glass$
- HCl in the bulb furnishes a constant  $H^+$  ion concentration.
- Thus, it is a silver-silver chloride electrode, reversible w.r.t to chloride ions.



- In order to determine the  $P^H$  of a solution, the glass electrode is placed in the solution and this half cell is coupled with saturated calomel electrode, the EMF of the cell is measured.

The EMF of cell is given by

$$E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = 0.2422V - [E_G^o + 0.059VP^H]$$

Then,  $P^H = \frac{0.2422V - E_{cell} - E_G^o}{0.059V}$

Here  $E_G^o$  value of glass electrode is determined by using a solution of known  $P^H$ .

#### **Limitations:**

- $P^H$  beyond 12 cannot be measured because cations of solution affect the glass membrane.
- Since the resistance of glass membrane is 10 to 100 million ohms, a special potentiometer is used to measure  $P^H$ .

#### ➤ **Advantages:**

- It can be used easily.
- Results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.

### **Storage batteries:**

A device that stores chemical energy and releases it as electrical energy is called as battery or storage battery.

Cell is a device in which chemical energy is converted into electrical energy. Many cells connected in series are called battery.

Batteries are classified as follows;

- i) Primary battery.
- ii) Secondary battery.
- iii) Fuel battery or Flow battery

#### **1) Primary battery:**

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. They are use and throw type.

Example: Dry cell, Laclanche cell etc.

#### **2) Secondary battery:**

Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged.

Example: Nickel-Cadmium cell, Lead-acid cell (storage cell), etc.

#### **3) Fuel battery or Flow battery:**

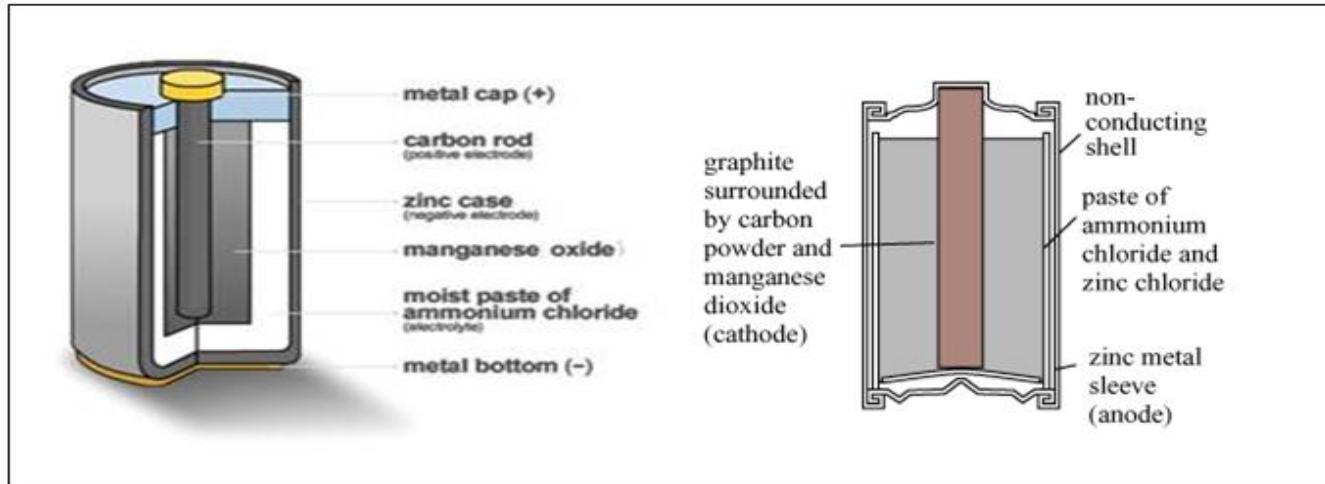
Flow battery is an electrochemical cell that converts the chemical reaction into electrical energy. When the reactants are exhausted, new chemicals replace them.

Example: Hydrogen-oxygen cell, Aluminium-air cell, etc. In Aluminium-air cell, when the cell is exhausted, a new aluminium rod is used and the solution is diluted with more water as the electrochemical reaction involves aluminium and water.

#### Q 6) Explain the construction and working of Dry cell with a neat diagram.

Dry or Leclanche cell: The dry cell is a primary cell.

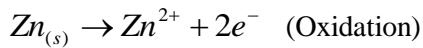
Dry cell (or) Leclanche cell	
Anode :	Zinc
Cathode :	Graphite rod (or) Carbon rod
Electrolyte :	( $MnO_2$ + $NH_4Cl$ + $ZnCl_2$ + Starch ) Paste



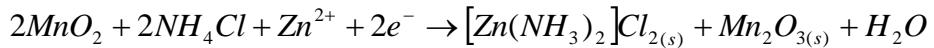
**Construction:** The anode of the cell is Zinc can contain an electrolyte consisting of  $NH_4Cl$ ,  $ZnCl_2$  and  $MnO_2$  to which starch is added to make it thick paste. A carbon rod acts as the cathode which is immersed in the electrolyte in the centre of the cell.

Cell reactions:

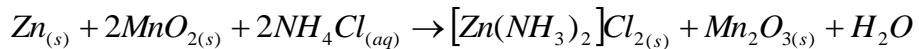
The anode half cell reaction is



At cathode, reduction of  $MnO_2$  takes place



Net reaction is



The dry cell is a primary cell, since various reactions involved cannot be reversed by passing electricity into the cell. The voltage of the cell is 1.5V.

**Disadvantages:** When current is drawn immediately from it, products formed at electrodes thereby causing drop in voltage. Since the electrolytic medium is acidic, Zinc dissolves slowly thereby the cell rundown slowly even it is not in use.

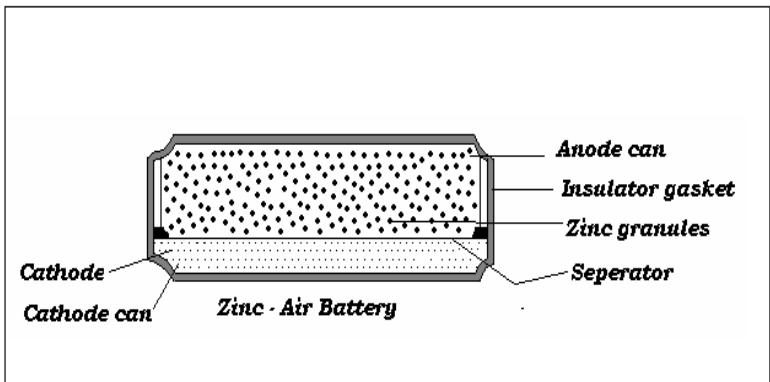
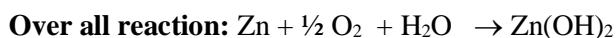
**Uses:** Dry cell finds applications in flash lights, transistor radios and calculators.

#### Q 7) Explain the construction and working of Zinc air battery (or) Modern battery?

Zinc air cell : ( Modern battery )	
Anode :	Zinc (Zn)
Cathode :	Oxygen
Electrolyte :	Potassium hydroxide (KOH)

Zinc air battery consisting of anode containing granules of zinc mixed with 20%NaOH electrolyte. Cathode can contains a porous carbon plate which provides site for the reduction reaction and do not involves in the reaction. Carbon is catalytically activated to absorb oxygen gas. The anode and cathode compartments are separated by a separator and both are encased in plastic or ebonite insulator. The reactions are as follows.

**Cell reactions:**



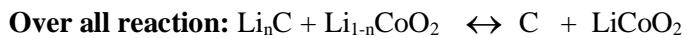
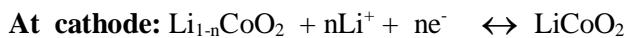
**Advantages:** 1) High energy density. 2) Low cost and compact 3) Does not produce harmful products.

**Applications:** Used in Military radio receivers, transmitters, hearing aids.

**Q 8) Write about Lithium ion battery:**

Lithium ion battery	
Anode :	Lithium doped graphite
Cathode :	Lithium Cobalt (III) Oxide
Electrolyte :	Complex Lithium compounds dissolved in organic solvents.

**Cell reactions:**



**Advantages:**

- They have high energy density than other rechargeable batteries.
- They are light weight.
- They produce high voltage out of 4 V.
- They have improved safety, i.e., more resistance to overcharge.
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate.

**Disadvantages:**

- They are expensive.
- They are not available in standard cell types.

**Applications:**

- The Li-ion batteries are used in portable devices: these include mobile phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers.
- Because of their light weight, Li-ion batteries are used for energy storage for many electric vehicles from electric cars to pedelec (pedelec is a bicycle where the rider's pedalling is assisted by a small electric motor), from hybrid vehicles to advanced electric wheelchairs, from radio-controlled models and model aircraft to the Mars Curiosity rover.
- They are used in cardiac pacemakers and other implantable devices.
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.

### Q 9) Define fuel cell. How fuel cells are represented. Mention its advantages and disadvantages?

**Definition:** Fuel cells are the galvanic cells which converts chemical energy of fuels into electrical energy by the combustion of fuels.

$$\text{Fuel} + \text{Oxygen} \rightarrow \text{Oxidation products} + \text{Electricity}$$

**Fuel cell Representation:** A fuel cell essentially consists of the following arrangement:

Fuel / electrode / electrolyte / electrode / oxidant.

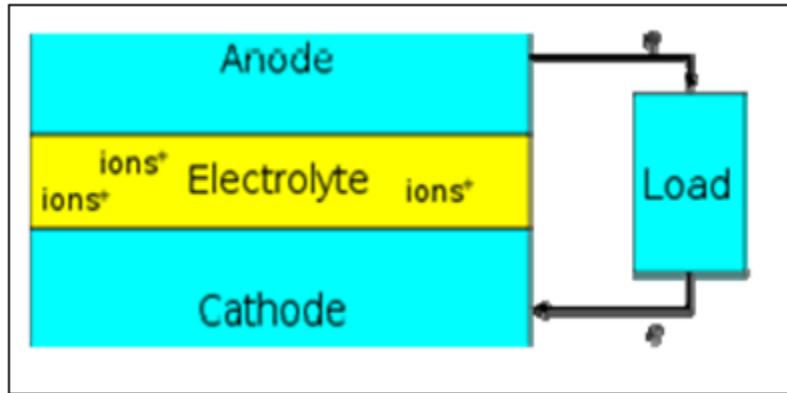
At the anode, fuel undergoes oxidation: Fuel  $\rightarrow$  Oxidation product +  $ne^-$

At the cathode, the oxidant gets reduced: Oxidant +  $ne^- \rightarrow$  Reduction products.

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

#### Advantages of the Fuel cells:-

- 1) Their power efficiency is high.
- 2) The cells have high energy density.
- 3) They are ecofriendly.
- 4) Space required for fuel cell is less.
- 5) Produce harmless biproducts.
- 6) Produces direct current for a long time.
- 7) No moving parts and so elimination of wear and tear.
- 8) They operate very silently.
- 9) Absence of harmful waste products.
- 10) No need of charging.



#### Limitations of Fuel cells:-

- 1) Fuel cells produce energy only as long as fuels and oxidants are supplied.
- 2) Electrodes are very costly.
- 3) Power output is very costly.
- 4) Fuels in the form of gases and oxygen need to be stored in tanks under high pressure.
- 5) Reactions are constantly supplied and the products are constantly removed from the cell.

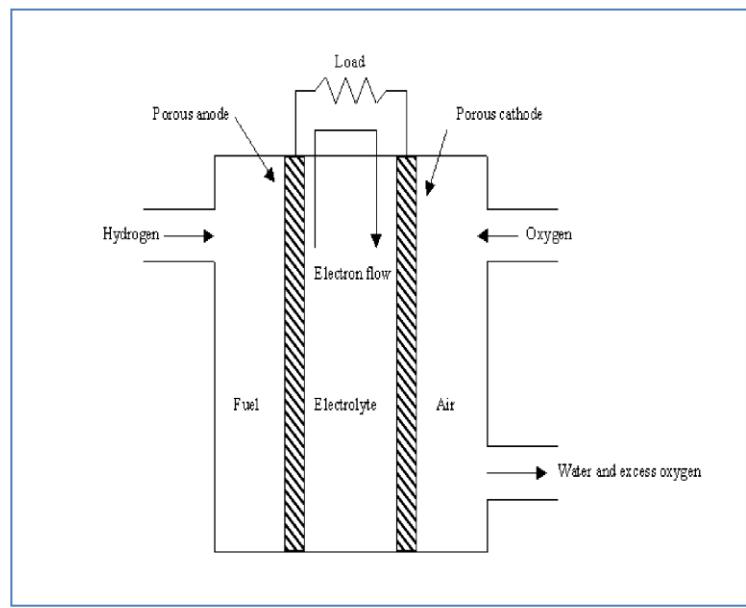
### Q 10) Describe the construction and working of hydrogen – Oxygen fuel cell?

#### Hydrogen – oxygen fuel cell:

In these cells, the reactants and electrolytes are continuously supplied to the cell. It is the simplest and most successful fuel cell. The fuel-hydrogen and the oxidiser-oxygen and the liquid electrolyte are continuously supplied to the cell.

**Description:** The cell has two porous electrodes, anode and cathode. The electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag). Between the two electrodes an electrolytic solution, 25% KOH is filled. Between the two electrodes an electrolytic solution, 25% KOH is filled.

**Working:** Hydrogen passes through the anode compartment, where it is oxidised. Oxygen passes through the cathode compartment, where it is reduced.



### Cell reactions:

- ★ At anode  $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
- ★ At cathode  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- ★ Net reaction  $2H_2 + O_2 \rightarrow 2H_2O$

- ★ The product discharged in water and the standard EMF of the cell is  $E^\circ = 1.23V$ .
- ★ A number such fuel cells are stacked together in series to make a battery.

### Applications:

- ★ They are used as auxiliary energy source in space vehicles, submarines etc.
- ★ Because of light weight and pure drinking water formation, they are highly useful in space crafts.

### Advantages:

- ★ The efficiency is high.
- ★ Drinking water is produced for astronauts.
- ★ No noise and thermal pollution.
- ★ Maintenance cost is low.

### Limitations:

- ★ Life time of fuel cells is not known accurately.
- ★ Initial cost is high.
- ★ The distribution of  $H_2$  is not proper.

## Q 11) Describe the construction and working of Methanol-Oxygen Fuel cell ?

### Methanol-Oxygen Fuel cell:- (DMFC)

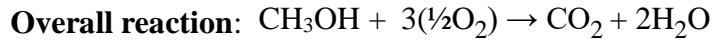
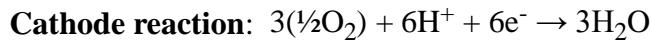
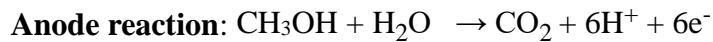
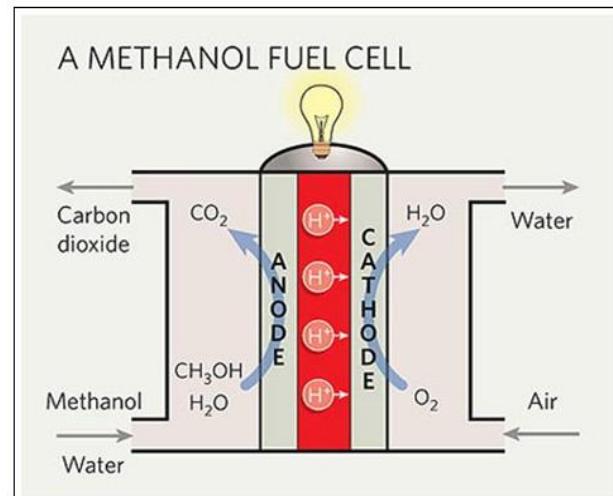
- ★ Methanol is preferred as a fuel in fuel cells because of the following reasons.
- ★ It has low carbon content.
- ★ It possesses a readily oxidisable alcoholic group.
- ★ It has high solubility in aqueous electrolytes.

### Construction:-

It consists of anodic and cathodic compartments and both the compartments contain platinum electrode.

Methanol containing  $H_2SO_4$  is passed through anodic compartments. Oxygen is passed through cathodic compartments. Electrolyte consists of sulphuric acid. A membrane is provided which prevents the diffusion of methanol into the cathode.

**Working:** - At anode,  $CH_3OH$  undergoes oxidation to  $CO_2$  liberates electrons, the liberated electrons taken by oxygen gets reduced into water with liberation of energy at cathode..



Fuel (methanol) and air or oxygen are fed to the electrodes. The cell potential is 1.21 V at 25 °C. The acid electrolyte offers the advantage of easy removal of  $CO_2$ , a product of the cell reaction.

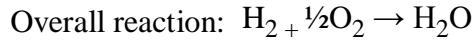
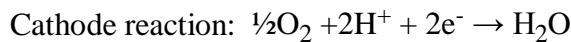
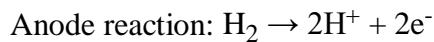
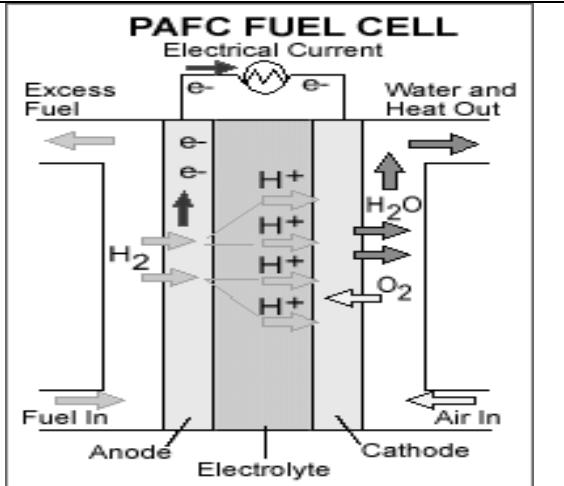
### Uses:

- ★ In all kinds of portable, automotive and mobile applications like, Powering laptop, computers, cellular phones, digital cameras.
- ★ In Fuel cell vehicles (FCVs).
- ★ It is used in Spacecraft applications.
- ★ It is used in any consumables which require long lasting power compared to Li-ion batteries.
- ★ It is also used in Military applications.

### Q 12) Write a note on phosphoric acid fuel cells?

#### Phosphoric Acid Fuel cell:- (PAFC)

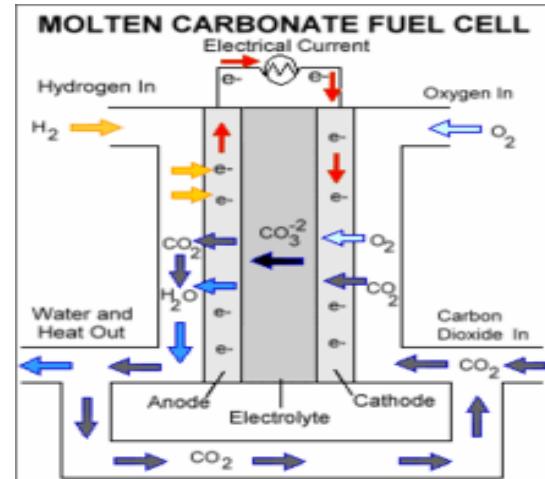
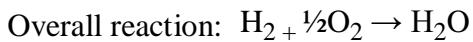
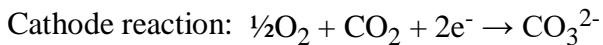
- ★ In phosphoric acid fuel cell the electrolyte is concentrated phosphoric acid.
- ★ Porous C + SiC + Teflon impregnated with Pt-catalyst acts as anode.
- ★ Porous C + SiC + Teflon impregnated with Ag-catalyst acts as cathode.
- ★ Pure H<sub>2</sub> gas is anodic fuel and pure O<sub>2</sub> gas is cathodic fuel.
- ★ These operate at a temp 190 to 200 °C. Platinum alloys such as platinum- cobalt- chromium, are used as electro catalyst.
- ★ It can produce electricity 1KW to 5KW.
- ★ **Uses:** These cells are used to provide light and heat in large buildings.



### Q 13) Write a note on molten carbonate fuel cells?

#### Molten Carbonate fuel cell:- (MCFC)

- ★ In Molten carbonate fuel cell the electrolyte is a mixture of alkaline carbonates of sodium and potassium.
- ★ Anode is porous Ni/Ni-Cr alloy.
- ★ Cathode is porous NiO.
- ★ H<sub>2</sub> gas (or) CO gas is fuel at anode and O<sub>2</sub> gas is Fuel at cathode and operates b/w 600 °C -650 °C.
- ★ It is efficient than phosphoric acid fuel cell.
- ★ **Uses:** These are used in chemical industries such as aluminum Cloroalkali industries.



## Corrosion:

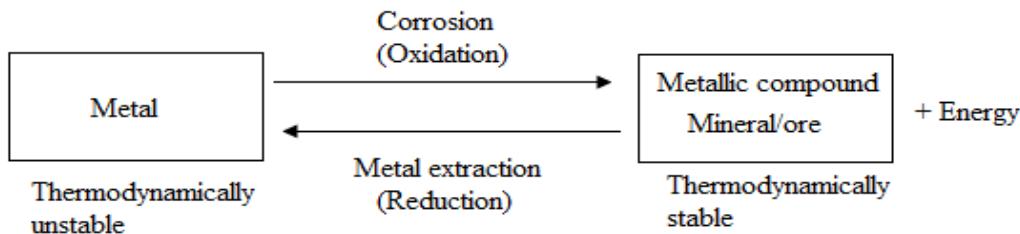
**Definition:** Corrosion is defined as the deterioration of a metal by chemical or electro chemical reactions with its environment. Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost. The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

### Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ( $Fe_2O_3 \cdot xH_2O$ ) is formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [ $CuCO_3 + Cu(OH)_2$ ] on the surface of copper.
- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.

### Cause of corrosion:

- ▲ The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
- ▲ During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
- ▲ Hence the isolated pure metals are regarded as excited states than their corresponding ores.
- ▲ So metals have natural tendency to go back to their combined state (minerals/ores).
- ▲ When metal is exposed to atmospheric gases, moisture, liquids etc., the metal surface reacts and forms more thermodynamically stable compounds.



### Consequences of corrosion:

- ▲ Enormous waste of machineries and different types of metallic materials
- ▲ It leads to sudden failure of machines.
- ▲ It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is an expensive.
- ▲ It may leakage of inflammable gas from the corroded pipe lines resulting into fire accidents etc.
- ▲ It causes contamination of potable water.
- ▲ It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

### Theories of corrosion :

#### Q 1) Dry corrosion (or) Chemical corrosion (or) Direct chemical attack theory (or) Mechanism of dry corrosion:

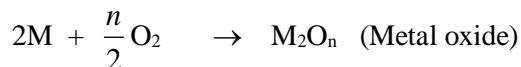
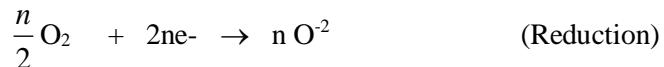
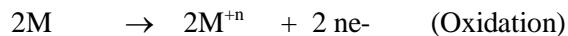
This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like  $O_2$ , halogens,  $H_2S$ ,  $SO_2$ ,  $N_2$  or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

- (1.) Oxidation corrosion
- (2.) Corrosion due to other gases
- (3.) Liquid metal corrosion.

#### (1.) Oxidation corrosion:

- ★ This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture.
- ★ This theory explains dry corrosion.
- ★ Corrosion is initiated in a metal, when it is contacted directly with oxygen.
- ★ Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- ★ The metal ion and oxide ion combine to form metal oxide on the metal surface.

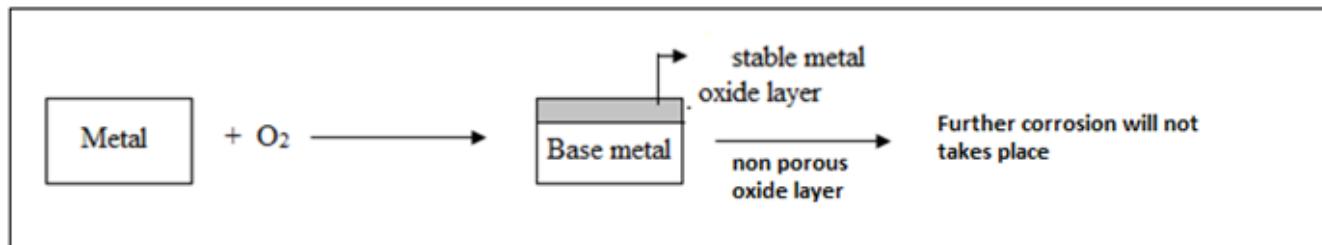


- ★ The extent of corrosion depends upon the nature of metal oxide.
- ★ The nature of metal oxide layer formed plays an important role in determining further corrosion.

#### a) Stable oxide layer (or) Protective and non porous oxide film :

If the metal oxide is stable, it behaves has a protective layer which prevents further corrosion.

E.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

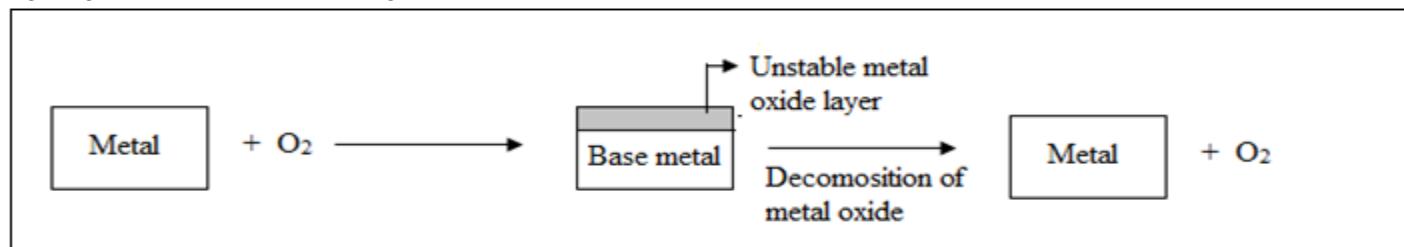


#### (b) Unstable oxide layer:

If the metal oxide layer is unstable, the oxide layer formed decomposes back into metal and oxygen.

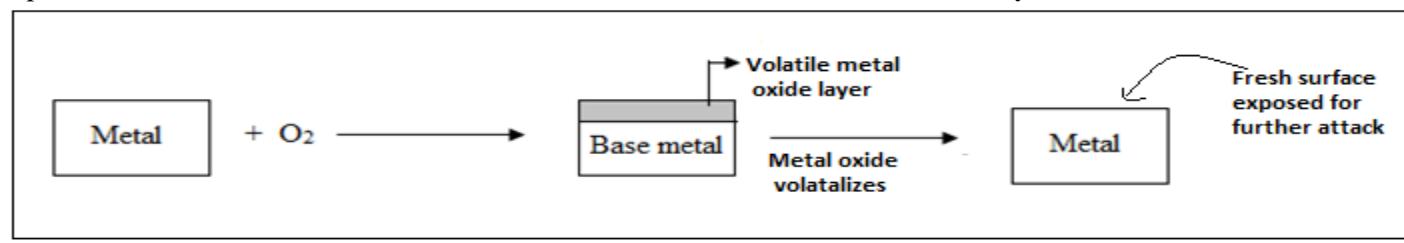
So, oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.



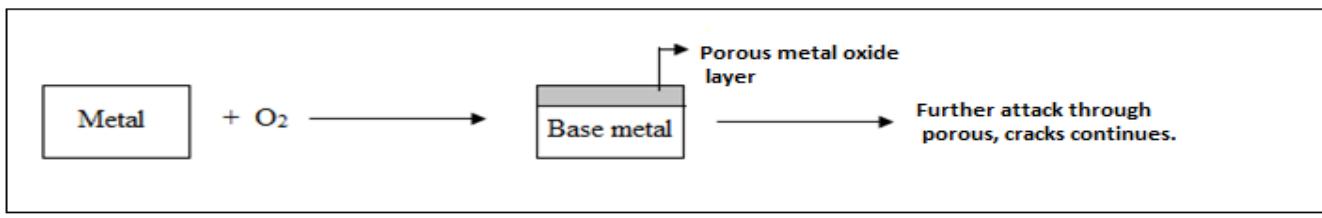
#### (c) Volatile oxide layer:

If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO<sub>3</sub>)



#### (d) Porous and non protective oxide layer:

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed. Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



### Pilling-Bedworth Rule:

This rule states the extent of protection given by the corrosion layer. An oxide is protective or non – porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

It is the ratio of the volume of metal oxide to volume of metal.

$$\text{specific ratio} = \frac{\text{volume of metal Oxide}}{\text{Volume of Metal}}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which the oxygen can diffuse and increases the corrosion further.

- 1) If the volume of the metal oxide layer is at least as great as the volume of the metal, no corrosion occurs as the oxidation of metal reaches to zero. i.e; specific ratio  $\geq 1$

For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten (W).

- 2) If the volume of metal oxide is less than the volume of the metal, the oxide film will develop cracks and pores. The atmospheric oxygen reaches the metal and increases the corrosion. In this case corrosion is continuous and rapidly increases. i.e; specific ratio  $< 1$

For example, Li, Na and K.

### (2) Corrosion due to other gases:

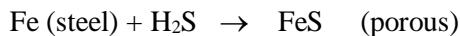
- ★ This type of corrosion is due to gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  etc.
- ★ In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
- ★ The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases. For example when Cl reacts with Ag forms  $\text{AgCl}$  film which prevents further reaction of Cl with Ag.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry,  $\text{H}_2\text{S}$  gas at high temperature reacts with steel forming a  $\text{FeS}$  scale.



### (3.) Liquid metal corrosion:

- ★ This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy.
- ★ The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

### Q 2) Wet Corrosion (or) Electrochemical corrosion:

- ★ This type of Corrosion occurs where a conducting liquid is in contact with the metal.
- ★ This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- ★ At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

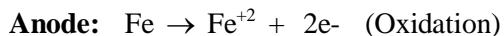


The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

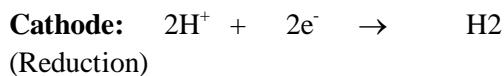
### Evolution of hydrogen : [ Formation of Rust with evolution of H<sub>2</sub> in Wet corrosion ]:

- ★ This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



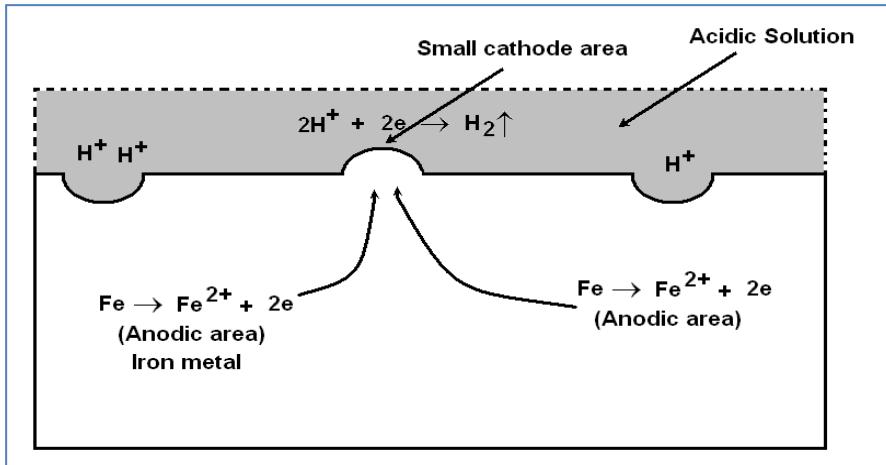
- ★ The electrons released flow through the metal from anode to cathode, whereas H<sup>+</sup> ions of acidic solution are eliminated as hydrogen gas.



- ★ **The overall reaction** is:  $Fe + 2H^+ \rightarrow Fe^{+2} + H_2$

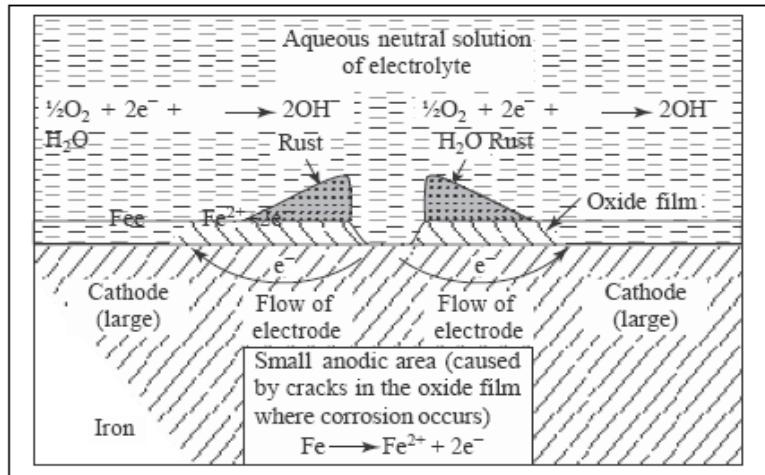
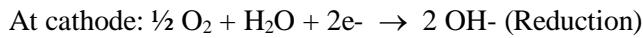
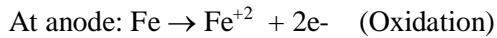
- ★ This type of corrosion causes displacement of hydrogen ions from the solution by metal ions.

- ★ All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H<sub>2</sub> gas. The anodes are large areas, whereas cathodes are small areas.



### Absorption of oxygen: [ Formation of Rust with evolution of O<sub>2</sub> in wet reaction ] :

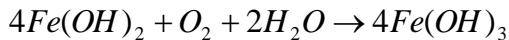
For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes. The released electrons flow from anode to cathode through iron metal.



(b)

- ★ Fe<sup>2+</sup> ions and OH<sup>-</sup> ions combine to form Fe(OH)<sub>2</sub> precipitate.

- ★ If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

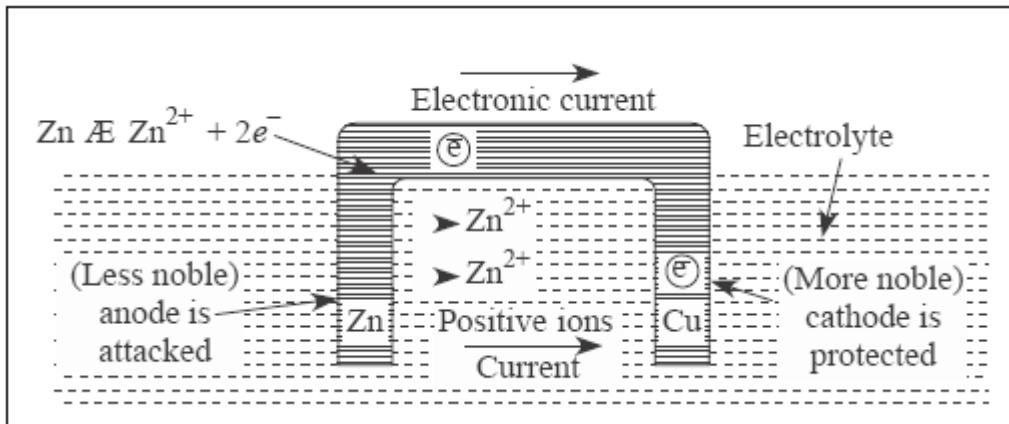


- ★ This product called yellow rust actually corresponds to Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O.

- ★ If the supply of oxygen is limited, the corrosion product may be black magnetite Fe<sub>3</sub>O<sub>4</sub>.

### Q 3) What is galvanic corrosion? How is it prevented? Give examples?

Galvanic corrosion: This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected.



**Eg:** When Zn an Cu are connected and exposed to corroding environment, Zinc (higher in electrochemical series) forms the anode; undergoes oxidation and gets corroded. Cu (lower in electrochemical series) acts as cathode; undergoes reduction and protected as the electrons released by Zn flow towards Cu.

#### Prevention:

- 1) Galvanic corrosion can be avoided by coupling metals close to the elec- trochemical series.
- 2) Fixing insulating material between two metals.
- 3) By using larger anodic metal and smaller cathodic metal.

#### Example of galvanic corrosion:

- 1) Steel screws in brass marine hardware,
- 2) steel pipe connected to copper plumbing,
- 3) steel propeller shaft in bronze bearing,
- 4) zinc coating on mild steel,
- 5) lead-tin solder around copper wires.

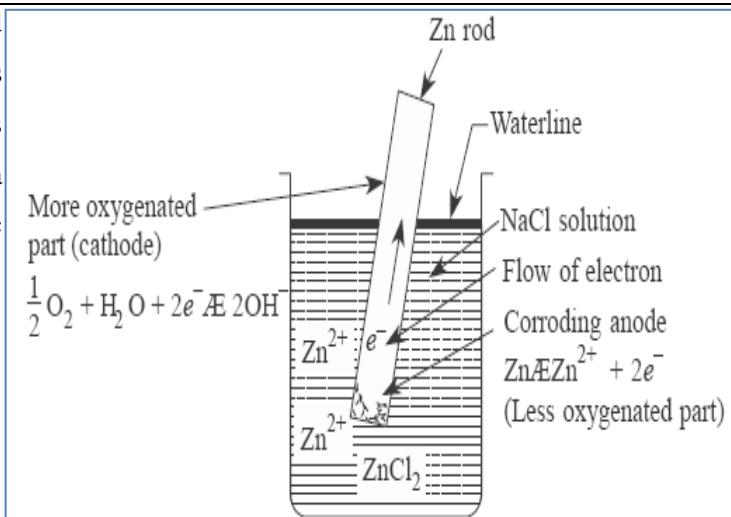
### Q 4) Differential aeration corrosion: or Concentration cell corrosion:

If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cathode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$Zn(OH)_2$  appears as corrosion products .

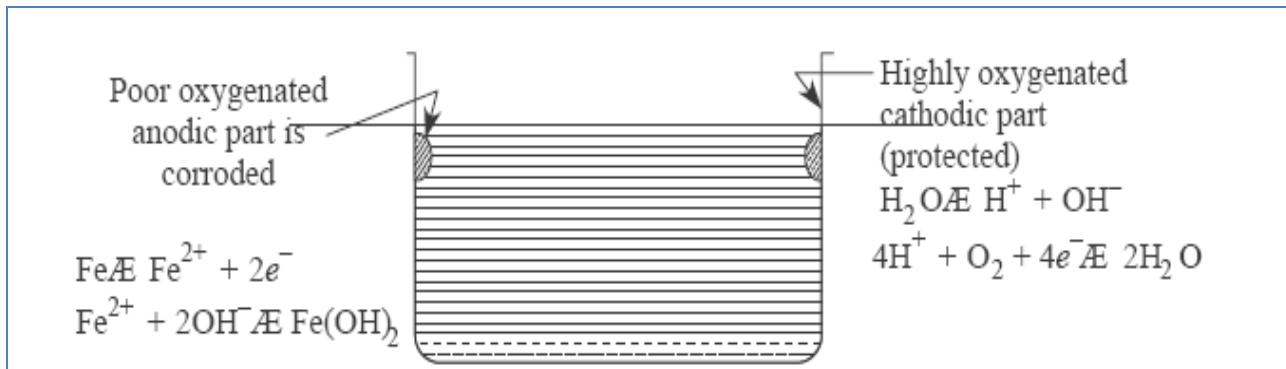
Examples: 1) Water line corrosion,

2) Drop corrosion.



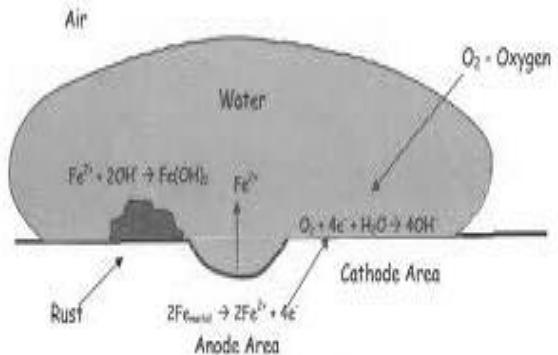
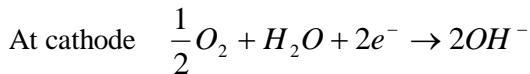
### 1) Waterline corrosion:

It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode.



### 2) Water Drop corrosion:-

- ★ For instance iron metal surface is covered with a drop of water.
- ★ The area covered by a drop has low oxygen concentration and thus acts as an anode and suffers corrosion, the uncovered area of the metal acts as large cathode due to high O<sub>2</sub> concentration.



### Q 5) Write notes on Stress corrosion.

- ★ When a metal is subjected to uneven stress and exposed to corrosion environment, it undergoes stress corrosion.
- ★ The stressed portion is in thermodynamically unstable state that's why areas under stress act as the anode and other areas act as the cathode.
- ★ It is due to the combined effect of static tensile stresses and corrosive environment.
- ★ Stressed areas of alloys are chemically active and they are attacked by even mild corrosive environment, as a result cracks are developed and they propagate in a direction perpendicular to operating stress.
- ★ Examples;

Season cracking (stress corrosion of brass):

- ▲ Season cracking is observed in brass (Copper + Zinc alloy) articles.
- ▲ Pure copper is immune to stress corrosion but presence of alloying agents such as Zn, Al etc makes it prone to corrosion.
- ▲ In the presence of NH<sub>3</sub> or RNH<sub>2</sub>, it undergoes corrosion due to formation of complexes like [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>.

This leads to dissolution of brass which ultimately results in the formation of cracks in the presence of stress.

**What is passivity? Explain.**

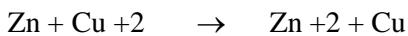
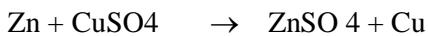
The process in which a metal exhibits higher corrosion resistance is called passivity. When a very thin, invisible and highly protective film is formed on the surface of a metal or an alloy, it is called passivity. This film is insoluble and non-passive. A metal is passive in a certain environment if its corrosion rate is very low. By the change of the environment, the passivity of a metal may change and may become active towards corrosion.

The formation of a passive film on the metal surface is determined by the Pourbaix diagram, which depends on the electrode potential and pH of the medium. Low carbon steel does not corrode in conc. HNO<sub>3</sub> due to protection effect of passive film. However, in dil. HNO<sub>3</sub> does not form a stable passive film and therefore dissolves steel. Passive film is formed on the surface of aluminium, Cr, Si, Ti in air, water and dilute acids. There is a good corrosion and oxidation resistance of stainless oxide passive layer.

A damage of passive film may cause intensive localised corrosion (pitting corrosion). Passive oxide layers are dissolved in electrolytes containing SO<sub>4</sub><sup>2-</sup> and chloride. Phosphate and chromate ions stabilise passive films, promoting the regain of its defects.

**Q 6) What is Galvanic series? Explain.**

Electrochemical reactions are predicted by electrochemical series. A metal having higher position can replace (reduce) other metals that have lower position in the series. For example, that is,



Or in other words, zinc will corrode faster than copper.

Some exceptions have been observed in this generalisation. For example, Ti is less reactive than Ag.

Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e. sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble nature.

More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni-Mo-Fe alloys, Brasses, Cu, Ni, Cr-steel alloy, Ag, Ti, Au, Pt towards noble nature.

**Differences between electrochemical series and galvanic series:**

S.No:	Galvanic series	Electrochemical series
1	This series was developed by the study of corrosion of metals and alloys in sea	This was developed by dipping pure metals in their 1M salt solution in water without their oxide film.
2	The position of the given metal may shift.	The position of the metal is fixed.
3	The corrosion of alloys can be studied.	No information regarding alloys.
4	The position of a metal is different from that of the position of the alloy which contains the same metal in it.	The position of the metal is fixed.

## **Q 7) Explain about the Factors Influencing rate of Corrosion.**

The rate and extent of corrosion depends upon various factors.

1. Nature of metal
2. Nature of corroding atmosphere

### **Nature of the metal:**

#### **1. Position in the galvanic series:**

Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

#### **2. Purity of metal:**

Heterogeneity is produced if impurities are present in a metal, which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded. As the extent of exposure and impurities increase, the extent of corrosion increases. For example in case of zinc metal;

% Purity	99.999	99.99	99.95	99
Corrosion rate	1	2650	5000	7200

#### **3. Relative areas of the anodic and cathodic parts:**

When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. i.e, the corrosion is more rapid, severe and highly localised if the anodic area is small. For example, a small pipe made of steel fitted in a large copper tank.

$$\text{In general Rate of corrosion of anodic region} \propto \frac{\text{CathodicArea}}{\text{AnodicArea}}$$

#### **4. Nature of surface film:**

In aerated atmosphere, practically all metals produce a thin surface film of metal oxide.

The ratio of the volumes of the metal oxide formed to the metal is called "specific volume ratio".

$$\text{specific ratio} = \frac{\text{volumeofmetalOxide}}{\text{VolumeofMetal}}$$

If the specific volume ratio is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.

For example, the specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. The rate of corrosion for tungsten (W) is least even at elevated temperatures.

#### **5. Physical state of metal:**

The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion. The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility. The areas under stress become anodic and corrosion takes place in these areas.

#### **6. Volatility of corrosion products:**

If the corrosion produced volatilizes as soon as it is formed, the metal surface is exposed for further attack. This creates rapid and excessive corrosion.

For example the corrosion product of molybdenum as molybdenum oxide ( $\text{MoO}_3$ ) is volatile.

7. **Solubility of corrosion product:** If the oxide film formed as corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate. The corrosion product acts as a physical barrier between the metal and environment. For example PbSO<sub>4</sub> film formed by Pb on sulphuric acid medium.

8. **Passive character of metal:**

Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series. This is because the metal forms very thin, highly protective corrosion film, by reacting with atmospheric oxygen. If the film is broken, it compensates the film by re exposure to oxidising conditions. Thus they produce "self healing film". This property is called passive character of metal.

For example the corrosion resistance of "stainless steel" is due to passivating character of chromium present in it.

**Nature of corroding environment:**

1. **Temperature:**

The rate of corrosion increases with increase of temperature.

2. **Humidity of air:**

Increase of moisture in the environment increases the rate of reaction.

3. **Presence of impurities in atmosphere:** Atmosphere is contaminated with gases like CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S; fumes of H<sub>2</sub>SO<sub>4</sub>, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion

4. **Nature of ions present in the medium :**

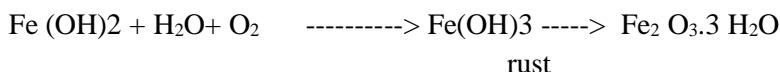
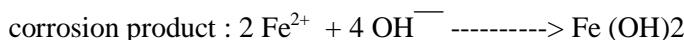
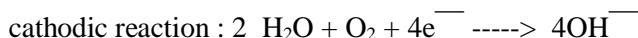
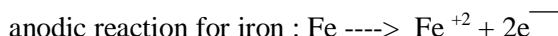
The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which "inhibit" further corrosion. On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal, thereby exposing the metal surface for fresh corrosion attack. Presence of traces of copper in marine waters enhances the corrosion of the iron pipes or steel body of the ships.

5. **Conductance of the corroding medium:**

For the corrosion of underground or submerged structures the conductance of the corroding medium plays an important role. The conductance of dry sandy soils is lower than the conductance of clayey and mineralised soils. Hence the rate of corrosion is more in clayey and mineralized soils, causing severe damage to metallic structures buried.

6. **Amount of oxygen in atmosphere:**

As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.



7. **Velocity of ions which flow in the medium:**

As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

8. **pH value of the medium:**

pH value of the medium has greater effect on corrosion. When pH value is lowered, the corrosion is increases.

## Corrosion Control Methods:

As we have discussed the disadvantages and different mechanisms of corrosion so far, it is essential to know the different corrosion control methods. The following are the important control methods of corrosion.

- 1) Proper designing
- 2) Cathodic protection.
- 3) Application of protective coatings.
- 4)

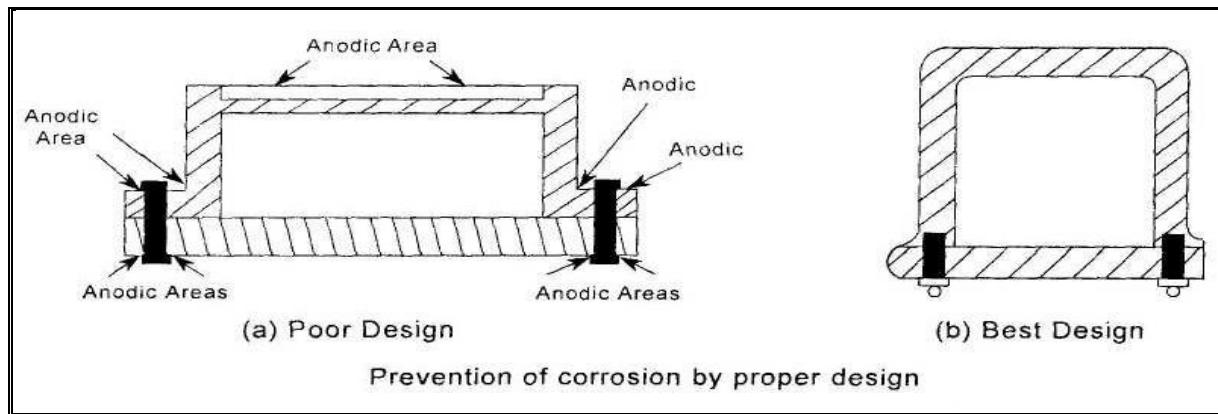
### **Q 8) Explain how proper selection and design of materials minimize corrosion.**

The design of the metal under corroding atmosphere must be such that it is uniform and does not produce intense and localised corrosion, important principles of proper designing are:

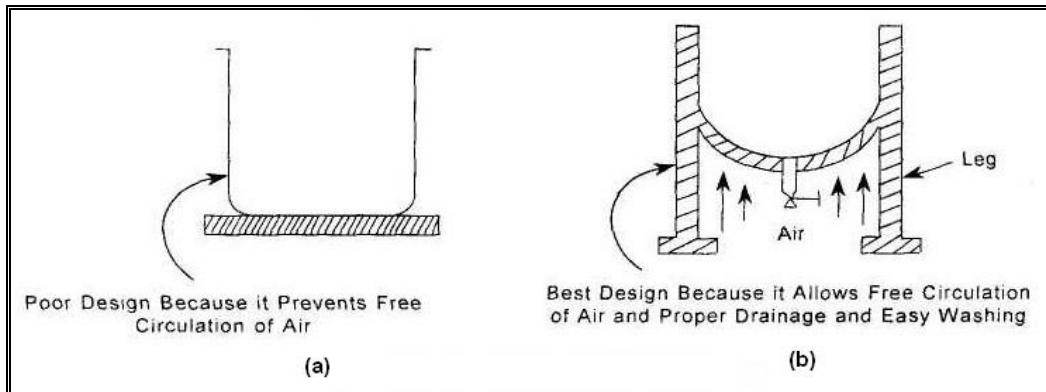
1. Avoid the contact of two dissimilar metals in the presence of corroding solution.
2. When two dissimilar metals are in contact, the anodic metal must possess large surface area, whereas cathodic metal must possess smallest surface area so that the corrosion takes place is minimum.
3. If two dissimilar metals are in contact, their position in the electrochemical series must be very close, so that minimum corrosion occurs.
4. A direct metal to metal contact between two dissimilar metals must be avoided by fixing an insulating fitting in between them, so that the corrosion velocity can be minimised.
5. The anodic metal should not be painted or coated. When the anodic metal is in contact with the cathodic metal, the anodic metal should not be painted or coated, because any break in the paint would lead to rapid localisation corrosion. A proper design should avoid the presence of crevices, between the adjacent parts of the structure, even in the case of the same metal.

For example, electrical box is shown as below. The design (a) is such that rain water collects at the top and also seeps between the bolt and two housing and remains there because of capillary action producing anodic parts.

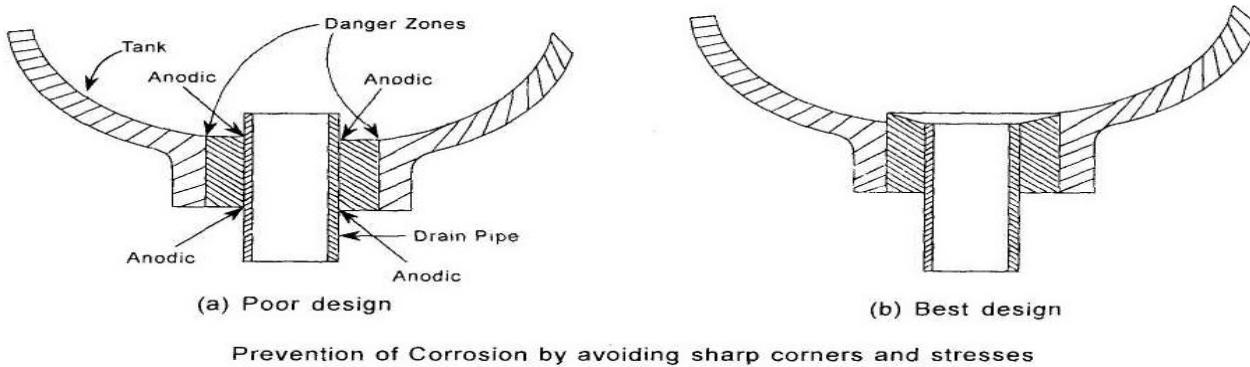
The defects can be corrected by slight modification in the designs shown in (b).



The design of the equipment should allow free circulation of air proper drainage and easy washing as shown below.



The design should eliminate sharp corners and stresses as shown in (b), along with a modification of the poor design.



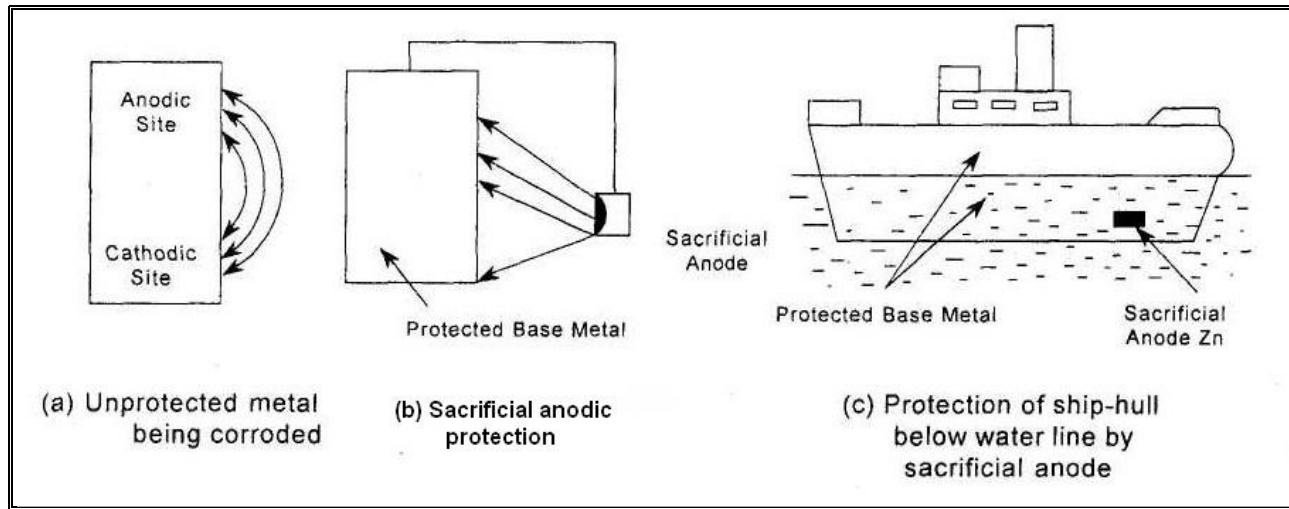
**Q 9) Explain the cathodic protection method with neat diagrams and examples.**

- ★ The basic principle of cathodic protection is to force the metal to behave like a cathode.
- ★ The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.
- ★ There are two types of cathodic protection;
  - (a) Sacrificial anodic protection method.
  - (b) Impressed current cathodic protection method.

**a) Sacrificial anodic protection method :**

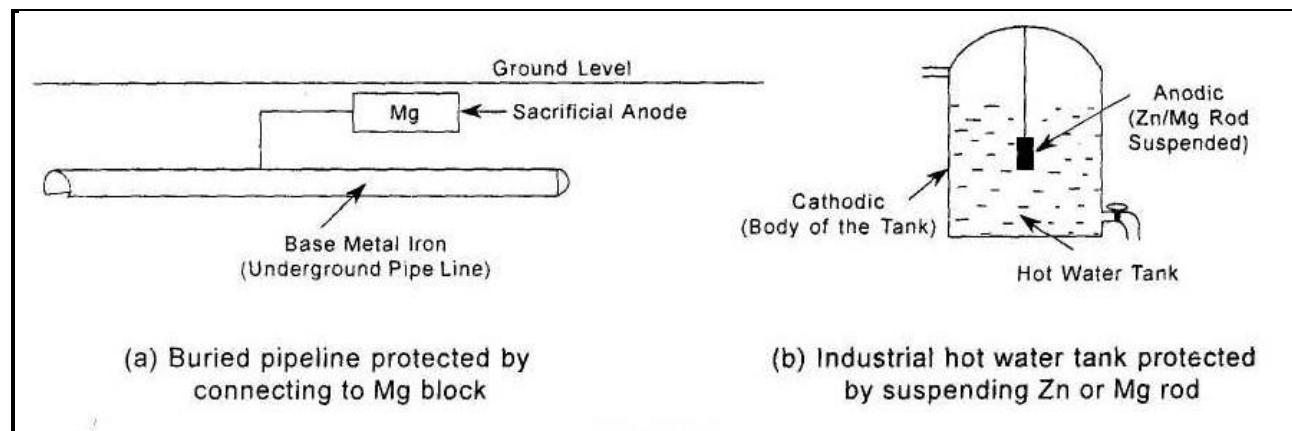
- ★ In this protection method, the metallic structure to be protected is called a base metal.
- ★ The base metal is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- ★ The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected.
- ★ The more active metal so employed is called sacrificial anode.
- ★ The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- ★ Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.



Example 2:

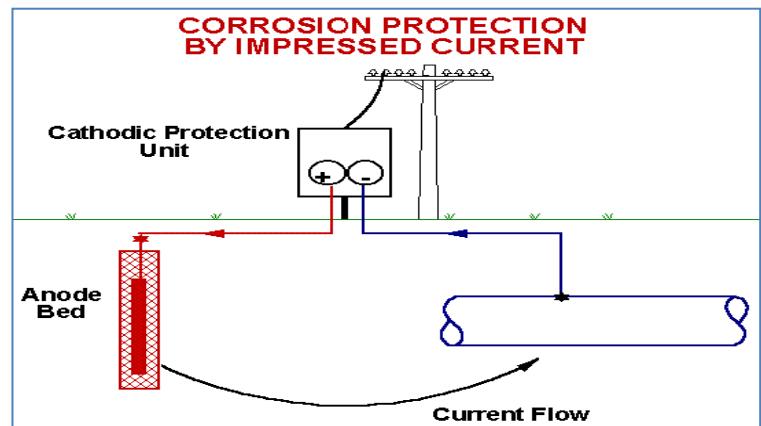
The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



#### **(b) Impressed current cathodic protection:**

- ★ In this method an impressed current little more than corrosion current is applied in the opposite direction to nullify the corrosion current producing a reverse cell reaction.
- ★ Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- ★ The impressed current is taken from a battery or rectified on A.C. line.
- ★ The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- ★ Usually a sufficient D.C. current is passed on to the insoluble anode kept in a 'back fill' composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.
- ★ This type of impressed current cathodic protection is given to
 

(1) open water box coolers	(2) water tanks	(3) buried water pipe lines or oil pipelines
(4) condensers	(5) transmission line towers	(6) marine pipes



★ This type of protection is more useful for large structures for long term operations.

### **Disadvantages of cathodic protection:**

1. The cathodic protection may be efficient in protecting a pipeline, yet may increase the corrosion of the adjacent pipelines or metal structure because of stray currents.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e., the use of much higher potential than the open circuit voltage for the metal/metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H<sub>2</sub> or formation and accumulation of OH<sup>-</sup> will take place.

In spite of these disadvantages, cathodic protection has been widely used with success, when suitable precautions are taken.

### **Protective coatings or Surface Coatings - Methods Of Application On Metals:**

The oldest and common method of protection of a metal from its surroundings is applying a protective coating on the surface of the metal. The coated surface isolates the metal from its corroding environment.

The coating should have the following property.

The coating applied must be chemically inert to the environment under particular conditions of temperature and pressure.

### **Q 10 ) What are the methods of cleaning the metal surface before applying the surface coatings.**

Before applying any protective coating the metal surface must be thoroughly cleaned to remove dirt, old protective coatings like paints, greases, corrosion products etc.

The following are some of the methods adopted for metal cleaning .

#### **Solvent cleaning:**

In this method the metal surface is cleaned with organic solvents like naphtha , carbon tetrachloride toluene, zylene or acetone. Then the metal surface is cleaned with steam and hot water containing wetting reagents this treatment is adopted for electroplating . This used method is to remove oils, greases, fatty substances.

#### **Alkali cleaning :**

In this method the metal surface is cleaned with alkali cleanin agents like trisodium phosphate along with wetting agents like coustic soda. It is followed by thorough rinsing with water and then immersion In 0.1% chromic acid,to remove last traces of alkalies This method is to remove old paint coatings from metal surfaces.

#### **Mechanical cleaning:**

In this method the metal surface is cleaned by using brushes and sand papers. Bristle brushes and metal brushes are used to remove loosely adhering impurities. Sand papers are used to remove strongly adhering scales and rust . This mehod is followed by steam or hot water treatment.

#### **Flame cleaning:**

This method involves heating the metal surface with a hot flame to remove loosely adhering scales,followed by wire brushing.

#### **Sand blasting:**

For sand blasting samples of sand of different grain size were blasted on the metal surface with a pressure of 25-100 atmospheres. It removes the scales on the metal surface . This method is used for cleaning large surface areas like large steel structures etc.

#### **Pickling and etching :**

In this process metals except aluminium are immersed in acid pickling solution. Aluminium is pickled in alkaline solution. Acid pickling of steel is carried out in warm dil.H<sub>2</sub>SO<sub>4</sub> solution . for cleaning copper,brass and nickl articals mixture of dilute HNO<sub>3</sub> and dil.H<sub>2</sub>SO<sub>4</sub> is used. It is followed by water and steam treatment.

**Q 11) What is meant by metallic coating? Explain anodic coating and cathodic coating with examples.**

## Metallic coatings :

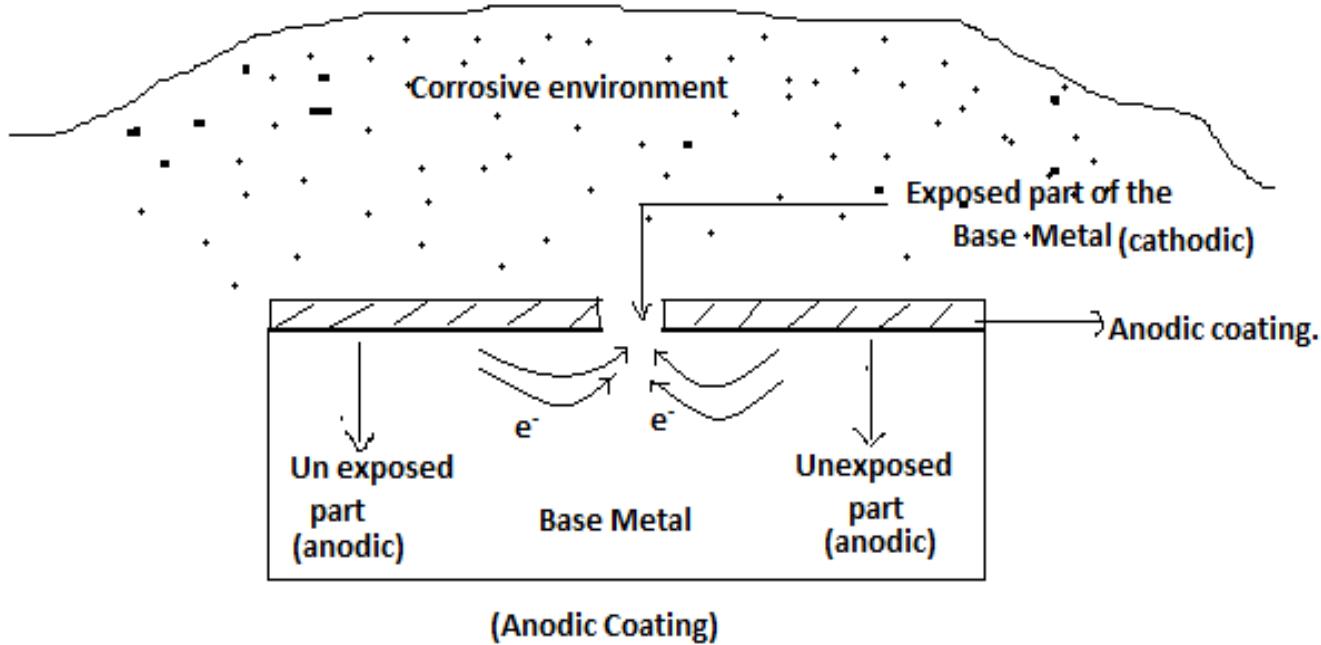
Metallic coatings are produced by coating one metal on the surface of another metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Metallic coating are of two types: **1. Anodic coating:** **2. Cathodic coating:**

## ANODIC COATINGS:

The metal used for the surface coating is more anodic than the base metal which is to be protected.

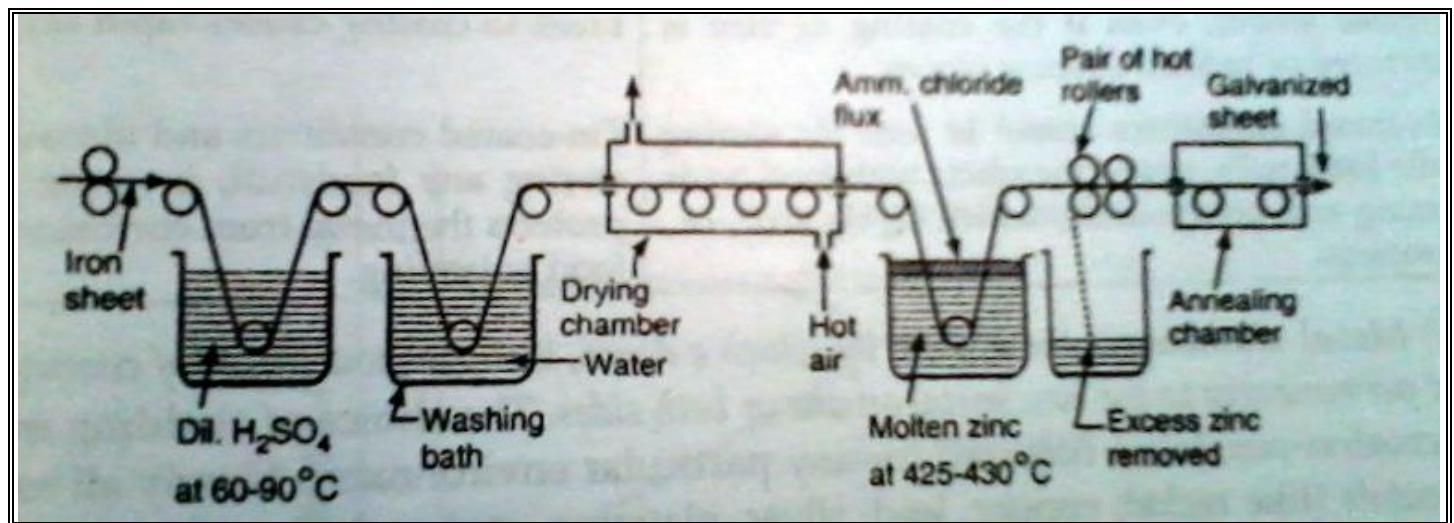
For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially. The formation of pores and cracks over the metallic coating exposes the basemetal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.



## Example: Galvanization:

**Def:** The process of coating zinc metal on the surface of iron is called Galvanization. It is the anodic protection offered by the zinc.

**Process:** In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried. Then after dipped in the bath containing molten zinc which is at 425-450 °C. To prevent it from oxide formation, the surface of bath is covered with a ammonium chloride flux. When the iron sheet is taken out it is coated with a thin layer of zinc. To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450 °C followed by cooling.



#### Applications:

- 1) It is mostly used to protect iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, and tubes.
- 2) Galvanised utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because zinc dissolves to form highly toxic or poisonous compounds.

**Q 12 ) What is meant by metallic coating? Explain cathodic coating with examples.**

#### Metallic coatings :

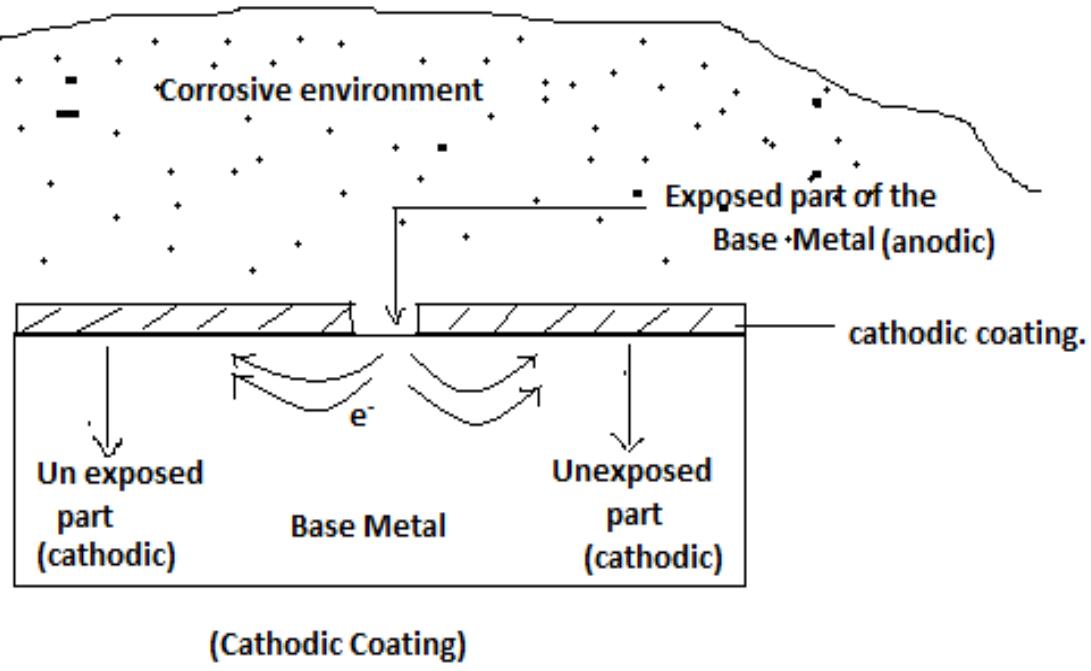
Metallic coatings are produced by coating one metal on the surface of another metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Metallic coating are of two types: **1. Anodic coating:**

**2. Cathodic coating:**

#### CATHODIC COATINGS:

Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature. Cathodic coating protect the base metal only when the coating is uniform and free from pores. The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.



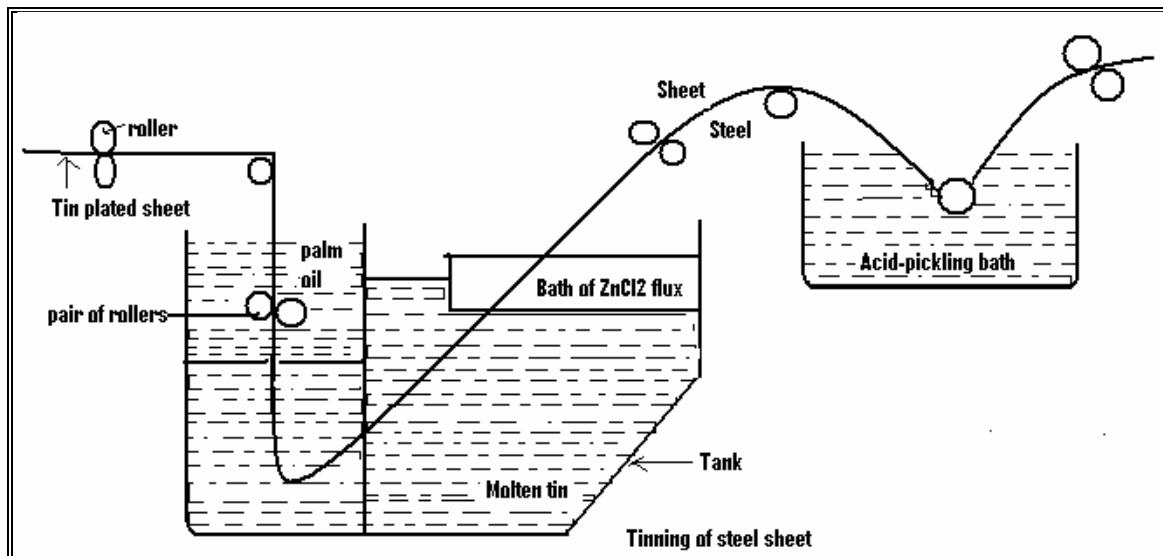
### Example: Tinning.

**Def:** The process of coating tin metal on the surface of iron is called Tinning.

- ★ Tin is a noble metal and therefore it possess more resistance to chemical attack.
- ★ It is the cathodic protection offered by the tin.

**Process:** In this process the surface of the base metal i.e iron sheet is cleaned by acid pickling with dil  $H_2SO_4$  and passed through a bath of zinc chloride flux. The flux helps the molten metal to adhere to the metal surface.

Then the sheet is passed through molten tin bath and passed between rollers from a layer of palm oil. Palm oil helps to protect the tin coated surface against oxidation. The rollers remove excess of tin and produce a thin film of uniform concentration. An alloy of the base metal and coating metal at their junction is produced.



**Applications of tinning:**

1. Tin metal possess good resistance against atmosphere corrosion. Tin is non toxic and widely used for coating steel, copper, and brass sheet.
2. The containers coated with tin are used for storing food stuffs, ghee, oils etc., and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

**Q 13 ) Write the differences between anodic coatings and cathodic coatings.**

Anodic coatings	Cathodic coatings
<ol style="list-style-type: none"> <li>1) These coatings involve coating of an anodic metal on the surface of base metal.</li> <li>2) Protects the underlying base metals “Sacrificially”</li> <li>3) The redction potential of the coating metal is lower than the base metal</li> <li>4) If pores, breaks or discontinues are produced in the metallic coating, the base metal is not corroded beacuse it is cathodic to coating metal. The coating metal undergo severe corrosion</li> <li>5) The coating metal posses lower reduction potential than base metal</li> <li>6) Ex: Galvanisation</li> </ol>	<ol style="list-style-type: none"> <li>1) These coatings involve coating of anoble metal on the surface of base metal</li> <li>2) Protects the base metal by their noble character and higher corrosion resistance.</li> <li>3) The redction potential of the coating metal is higher than that of base metal</li> <li>4) If pores, breaks or discontinues are produced in the metallic coating, the base metalbecomes anodic and faces severe corrosion due to smaller anodic area and the protecting metal becomes cathodic and does not undergo corrosion</li> <li>5) The coating metal possess higher reduction potential than base metal</li> <li>6) Ex: Tinnings</li> </ol>

**Q 14 ) Write the differences between galvanizing and tinning****Comparison of Galvanization with Tinning :**

Galvanization	Tinning
The process of coating Zn on the surface of iron or steel is called galvanization.	The process of coating tin on the surface of iron or steel is called tinning.
Zinc is anodic to the base metal iron or steel.	Tin is cathodic to the base metal iron or steel.
Zinc protects iron “ sacrificially”	Tin protects iron due to its noble coating.

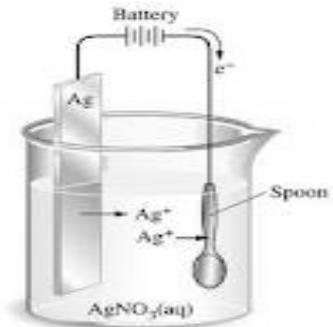
Zinc is more electropositive than iron , it does not permit iron to pass into the outside solution in other words corrosion does not occur to iron.	Tin is less electropositive than iron, it protects the iron till the coating is perfect.
Any break in the protective Zinc layer does not cause corrosion to the base metal.	Any break in the protective tin layer severe corrosion to the base metal.
Galvanised containers cannot be used for food storing.	Tin coated containers are used for food storing materials.
After galvanization , the galvanized sheet is subjected to annealing process.	No annealing process.

### **Q 15 ) Describe Electroplating with suitable examples.**

- ★ Electroplating is the method of electro-deposition of metal by means of electrolysis over surface of metals and alloys.
- ★ The base metal is first subjected to acid pickling to remove any scales, oxides etc.
- ★ The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- ★ The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- ★ When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- ★ Low temperature, medium current density, low metal ion concentration conditions are maintained for better electroplating.
- ★ It is widely used to coat the base metals with protective metallic coatings of copper, nickel, zinc, lead etc.

#### **Eg: Electroplating with gold:**

- Cathode: Article to be electroplated (Spoon)
- Anode: Block of gold metal
- Electrolyte: Aqueous solution of  $\text{AuCl}_3$  or Potassium auro-cyanide  $\text{K}[\text{Au}(\text{CN})_2]$



For example for electroplating of nickel on iron article, the following are maintained;

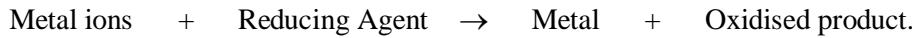
1. electrolytic bath solution : Nickel sulphate, nickel chloride and boric acid.
2. pH maintained . : 4 (by boric acid buffer)
3. Temperature maintained : 40 - 70° C
4. Current density : 20 - 30 mA/cm<sup>2</sup>
5. Additives added : Saccharin or coumarin or acetylene derivatives
6. Anode : Nickel pellets (99% pure) taken in a titanium mesh basket
7. Cathode : Base metal article

#### **Factors affecting electroplating:**

- Cleaning of the article is essential for strong adherent electroplating.
- Concentration of the electrolyte.
- The electrolyte selected should be highly soluble and should not undergo any chemical reactions.
- $\text{P}^{\text{H}}$  of the electrolytic bath.

#### **Q 16 ) Explain Electroless plating with suitable examples.**

Electroless plating is a technique of depositing a noble metal on a catalytically active surface of the metal to be protected by using a suitable reducing agent without using electrical energy.



##### **Step 1: Pretreatment and activation of the surface:**

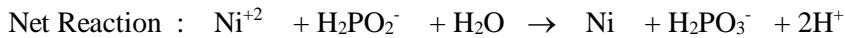
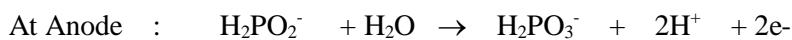
The surface to be plated is first degreased by using organic solvents or alkali, followed by acid treatment. Example: The surface of stainless steel is activated by dipping in hot solution of 50% dil.  $\text{H}_2\text{SO}_4$ .

##### **Step 2: Plating bath :**

Nature of the compound	Name of the compound	Quantity(g/l)	Function
Coating solution	$\text{NiCl}_2$	20	Coating metal
Reducing agent	Sodium hypophosphite	20	Metal ions reduced
Complexing agent	Sodium succinate	15	Improves the quality
Buffer	Sodium acetate	10	Control the pH
Optimum pH	4.5	-----	-----
Optimum temperature	93°C	-----	-----

##### **Step 3: Procedure:**

The pretreated object is immersed in the plating bath for the required time.



##### **Applications:**

1. Electroless Ni plating is extensively used in electronic appliances.
2. Electroless Ni plating is used in domestic as well as automotive fields.

##### **Advantages of electroless plating over electro plating:**

- i) Electricity is not necessary
- ii) Complicated parts are uniformly coated
- iii) Plastics, glass etc, are easily coated
- iv) Good mechanical, chemical and magnetic properties are obtained.

#### **Q17 ) Define paints. What are the Constituents of Paints. Write their functions.**

##### **PAINT:**

Paint is a mechanical dispersion of one or more fine pigments in a medium (thinner + vehicle). When a paint is applied to metal surface, the thinner evaporates. The vehicle undergoes slow oxidation to form a pigmented film.

##### **Requirements or requisites of a good paint**

A good paint should,

- 1) have good covering power
- 2) spread easily on the surface
- 3) not crack on drying
- 4) adhere well to the surface
- 5) give a glossy film

- 6) be corrosion and water resistant
- 7) have stable colour

### **Constituents of Paints and their functions.**

- 1) Pigment
- 2) Vehicle
- 3) Thinner
- 4) Drier
- 5) Filler
- 6) Plasticizer
- 7) Anti skinning agent

**1. Pigment :** It is a solid that gives colour to the paint.

#### **Functions:**

- a) To give colour and opacity to the film.
- b) To provide strength to the film.
- c) To protect film by reflecting U.V. rays.
- d) To provide resistance to abrasion and weather.

#### **Example:**

White pigment - White lead,  $TiO_2$

Blue pigment - Prussian blue

Green pigment - Chromium oxide

Red pigment - Red lead,  $Fe_3O_4$

### **2. Vehicle (or) Drying Oil**

It is the film-forming liquid. It holds the ingredients of the paint. It is a nonvolatile high molecular weight fatty acid of vegetable or animal.

#### **Functions:**

- a) To hold the pigment on the surface.
- b) To form a protective layer by oxidation and polymerization.
- c) To impart water repellency, toughness and durability of film .
- d) To improve adhesion of film.

**Example:** Lin seed oil, Castor oil.

**3. Thinner:** It is the volatile portion of paint. It is added to reduce the viscosity of the paint for easy application on the surface. It easily evaporates after paint is applied.

#### **Functions:**

- a) To reduce viscosity of paint.
- b) To dissolve vehicle and other additives.
- c) To suspend the pigments.
- d) To increase elasticity of film.
- e) To increase penetration of vehicle.
- f) To improve drying of film.

**Example:** Turpentine, Dipentine, Xylol.

**4. Drier.** It is a substance used to speed up drying of the paint.

#### **Functions:**

- a) To act as oxygen carrier or catalyst.
- b) To provide oxygen essential for oxidation and polymerization of drying oil.

**Example:** Metallic soap, linoleate and resinate of Co, Mn etc.

**5. Extender or Filler:** These are white pigments that form bulk of the paint.

**Functions:**

- a) To reduce cost of paint
- b) To prevent shrinkage and cracking of film
- c) To modify shades of pigment
- d) To retard settling of pigments in paint.

**Example:** Talc gypsum, china-clay.

**6. Plasticizer:** It is added to the paint to provide elasticity to the film and prevent its cracking.

**Example:** Triphenyl phosphate, Tricresyl phosphate etc.

**7. Antiskinning agents:** It is a chemical added to the paint to prevent gelling and peeling of the paint.

**Example:** Polyhydroxy phenols.

### **Q 18) Write notes on special paints.**

In addition to the normal ingredients some special chemicals are incorporated to paints for some specific purposes. They are commonly known as special paints.

#### **1. Luminescent paints:**

Luminescent paints contain luminophor pigments used for visibility in the dark. They find application in inks, advertising signboards, road marks, number plates of vehicles, watch dials, etc. The active components in luminous paint are specially prepared phosphorescent materials like  $\text{CaS}$ ,  $\text{ZnS}$ , etc. They absorb light radiations and emit them in the dark. For colour effect in luminous paints, certain chemicals like copper salts (green), silver salts (blue), cerium and uranium salts (yellow), etc. are used.

#### **2. Heat Resistance paints:**

When the surfaces are exposed to high temperatures such as in chimneys, exhaust pipes, furnaces, oil stills, etc. Oil paints tend to decompose or get charred, they being organic in nature. Then the surfaces become liable for corrosion. To overcome this problem, a suspension of graphite or lamp black in small amounts of drying oils and more thinners can be used. But more recently, silicone paints are used for heat resistance.

#### **3. Fire-retardant paints:**

These are paints containing chemicals which are fire-resistant in nature. In other words, they produce gases like  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$  on heating which are themselves non-combustible and do not support combustion, thereby minimizing the rate of burning or extinguishing the fire.

#### **4. Antifouling paints:**

Oil paints are liable for attack by living organisms because of the organic content in them. So, in places where living organisms are handled or are present, such paints cannot be used. For use in breweries and biochemical laboratories, the paint is mixed with compounds having fungicidal properties. The active ingredients employed are  $\text{HgO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Hg}_2\text{Cl}_2$ , DDT, pentachlorophenol, etc. Such paints are called Antifouling paints.

#### **5. Cement Paint**

Cement paint is the coating, which is applied on plastered brickwork, concrete work, etc. The ingredients are

1. White cement (about 70%)
2. Hydrated lime  $[\text{Ca}(\text{OH})_2]$
3. Pigment (a colouring agent)
4. Very fine sand (an inert filler) and
5. Water-repellent compound

Such paints of different colors are marked in powder form (eg Snowcem, Smocem). The powder is mixed with a suitable quantity of water to get a thin slurry, and applied on surfaces. For good results, a 1.5% to 2% aqueous solution of sodium silicate and Zinc sulphate is applied as primer coat.

## UNIT-3, MATERIAL CHEMISTRY "PART-1"

### Non-elemental semi conducting materials :-

Besides 'Si' and 'Ge', many intermediate and ceramic compounds exhibit semi conductivity. These compounds are grouped into

- ① stoichiometric semi conducting compounds
- ② Defect semiconductors
- ③ Controlled valency semiconductors
- ④ chalcogen photo conductors.

Q: Explain stoichiometric semi conducting Compounds?  
A: ① stoichiometric semi conducting compounds :-

These are intermediate compounds having an average of four valency electrons per atom. These intermediate semi-conducting compounds prepared by combining,

- (i) elements of Group-III (Ga, In) and Group-II (P, As, Sb)
- (ii) elements of Group-IV (Cd, Pb) and Group-VI (S, Se, Te)

For example,

GaAs is a III-V group combination,



when 'Ga' & 'As' overlap, and yield a hybrid band containing  $4N$  electrons per 'N' atoms of 'Ga' and 'As'.

'GaAs' has wide energy gap ( $E_g$ ) = 1.35 ev.

The energy gap in the stoichiometric semiconductors can be reduced by substituting one of its element by an element of higher atomic number belong to the same group.

Ex:- Gap = 2.24 ev

GaAs = 1.35 ev

GaSb = 0.67 ev.

Energy gap of Gap = 2.24 ev is reduced to 1.35 ev in GaAs (since at.no. of 'As' is higher than that of 'P' and both belongs to VI group). The energy gap can further reduced to 0.67 ev on replacing 'As' with 'Sb'.

Q. Explain Defect Semiconductors with examples?

A: ② Defect Semiconductors :-

Many non-stoichiometric compounds act as semiconductors. For example, some metallic oxides and sulphides having non-stoichiometric defects in their crystal structures.

FeO, which is made of  $\text{Fe}^{+2}$  and  $\text{O}^{-2}$  ions. On heating, some  $\text{Fe}^{+2}$  ions are oxidised to  $\text{Fe}^{+3}$ . For example, a crystal of compound  $\text{Fe}_{0.90}\text{O}$  actually contains  $\text{Fe}_{0.70}^{+2} \text{Fe}_{0.20}^{+3} \text{O}$ . and  $\text{Fe}^{+3}$  ion is short by one electron and can be considered as a positive hole. Under the influence of electric field, the positive holes can move from  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$ , thereby producing electrical conductivity. These non-stoichiometric compounds, can be represented as  $\text{M}_{(1-x)}\text{Y}$  and these metal-ion deficient compounds act as p-type semiconductors. EX:-  $\text{FeO}$ ,  $\text{NiO}$ ,

when  $\text{ZnO}$ , is exposed to reducing atmosphere, non-stoichiometric compounds such as  $\text{Zn}_{1.1}\text{O}$  ( $\text{Zn}_{0.9}^{+2} \text{Zn}_{0.2}^{+1} \text{O}$ ) are produced. In such compound,  $\text{Zn}^{+1}$  ion is rich by one electron and  $\text{Zn}^{+1}$  ion is capable of donating one electron. Hence, under the influence of electric field,  $\text{ZnO}$  act as an n-type semiconductor. These metal-ion excess non-stoichiometric semiconductors can be represented as  $\text{M}_{(1+x)}\text{Y}$ .

Q. Explain Controlled Valency Semiconductors?

A: ③ Controlled Valency Semiconductors :-

There is one problem with defect semiconductors i.e. the difficulty in controlling their conductivity. This limitation of defect-semiconductor is overcome by preparing controlled valency semiconductor.

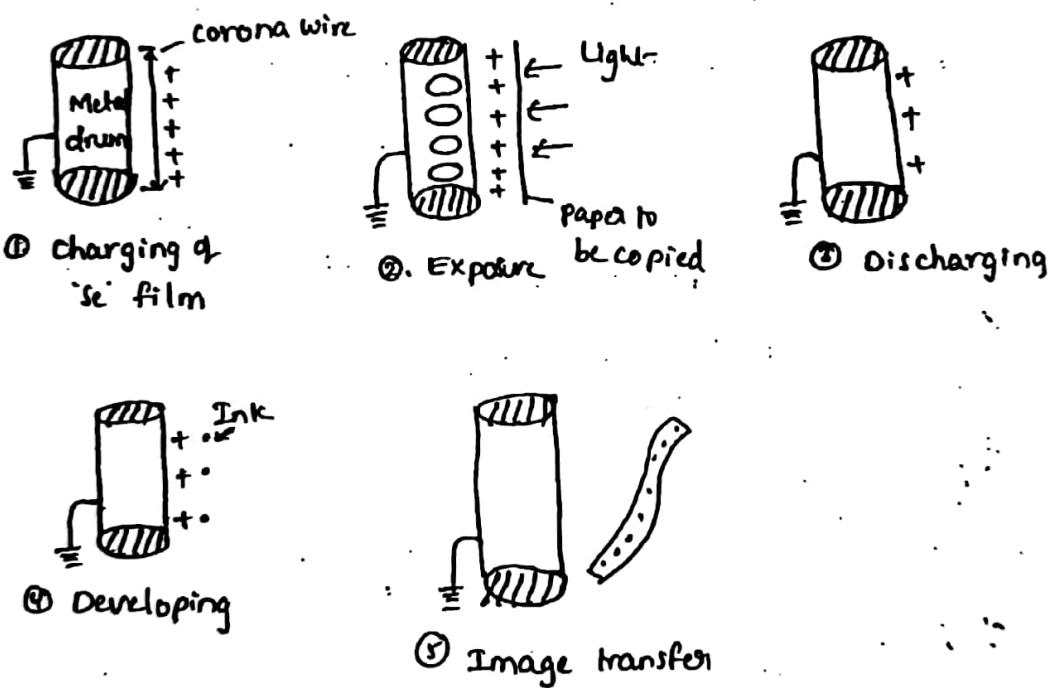
In order to control the concentration of  $\text{Ni}^{+3}$  ions in  $\text{NiO}$  and hence its conductivity, a calculated amount of lithium oxide ( $\text{Li}_2\text{O}$ ) is reacted with  $\text{NiO}$  and cause to form compound  $\text{Li}_x \text{Ni}_{1-2x}^{+2} \text{Ni}_x^{+3} \text{O}$ , which exhibit temperature dependent conductivity. Such semiconductors are used in thermistors (thermally stable resistors).

Q. Discuss the working of xerox machine in chalcogen Semiconductor? (6/7M)

A: ④ chalcogen photo conductors :-

chalcogens (sulphur, Se, Te) on melting give viscous liquids, which quickly form glasses on cooling. chalcogen-based glasses behave as photo conductors. 'Se' is an excellent photo conductor and its electronic conductivity enhances on exposure to light. the principle of photo conduction is used in xerography (photo copying) process.

The xerox machine essentially consists of a cylindrical rotating metallic drum with a very thin film of amorphous selenium on it. The photocopying process involves the following steps:



\* Preparation of semiconductors :- For preparing semi-conducting devices, the basic materials 'Si & Ge' must be pure. For preparation of highly pure Si & Ge, the following methods are used,

- 1) preparation of pure Si/Ge
- 2) Doping techniques.
- 3) cutting into chips.

2) Preparation of pure Si/Ge :- This is carried by following methods,

- a) Distillation
- b) Zone refining

a) Distillation:- It is based on separation of materials due to difference in boiling points (b.p's). The raw materials  $\text{GeCl}_4$  and  $\text{SiHCl}_3$  are used for preparation of pure Ge & Si respectively.

pure  $\text{GeCl}_4$  is obtained, by passing vapours through the fractionating column. pure  $\text{GeCl}_4$  so, obtained is treated with extra pure water to get  $\text{GeO}_2$ , which is then reduced (in an atmosphere of hydrogen) to get elemental germanium, which is then subjected to purification.

Q Explain zone-refining method of Semiconductor ?

A: b) Zone refining:- It is a technique of purification, which involves 're-crystallization', principle of this technique is "impurities are more soluble in the molten than in the solid material".

The following fig. shows a vertical zone refiner, used for the purification of Ge.

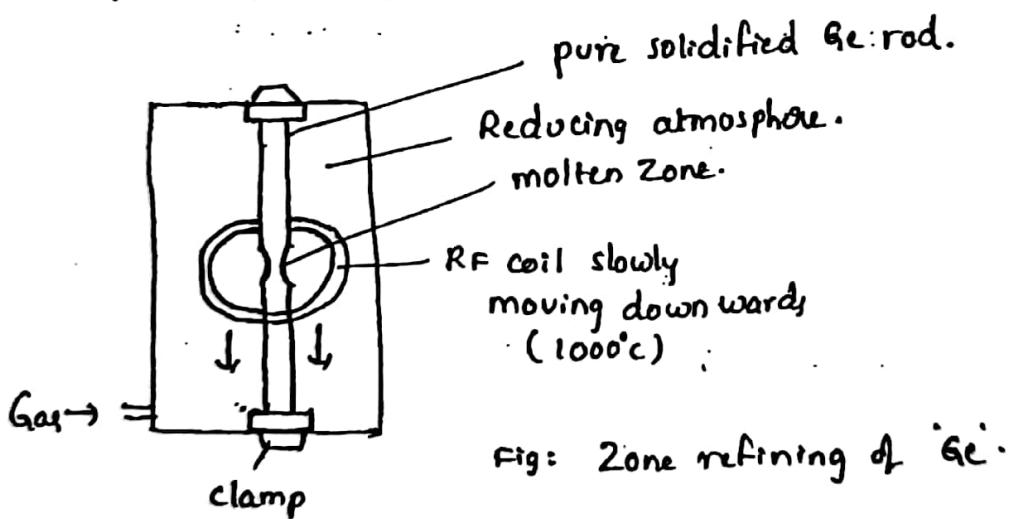


Fig: Zone refining of Ge.

In this method, a rod of Ge is placed vertically and heated by a RF coil to about  $1000^\circ\text{C}$  in a reducing atmosphere. When the heating coil moves slowly from top to bottom, the impurities are swept down with molten material, while the pure Ge rod solidifies at the upper portion. When the purification of upper portion of the rod is complete, the bottom portion of the rod (where impurities are more) is separated.

② Doping techniques :- For getting doped material, calculated amount of dopant ('B' or 'P') is added to the molten Si or Ge. and the dopants are added in order of 1 atom of 'B' (or) 'P' per  $10^8$  atoms of Ge (or) Si. Methods used for doping are,

- a) Epitaxy
- b) Diffusion
- c) Ion implantation technique.

a) Epitaxy :- It involves deposition of thin layer of dopants on Si (or) Ge. In this method, Si (or) Ge wafer is placed in a long cylindrical quartz tube reactor, which is then heated by RF coil. Then, gases containing Ge (or) Si mixed with calculated amount of dopant are introduced into the reactor. The heating process is continued, till deposition of dopant over Si (or) Ge wafer.

b) Diffusion :- It involves diffusion of gaseous dopants into semi-conducting material without any melting. The process consists of heating dopants, and this causes dopants to condense on the surface of Si (or) Ge wafer and diffuse.

c) Ion implantation technique :- It involves in bombarding the semi conductor material with an electrically controlled beam of high energy ions of 'B' (or) 'P'. This causes implantation of dopant atoms into the crystal lattice of semi conductor.

③ Cutting into chips :- The wafers obtained by above methods, are then cut into 'chips' by using laser beams etc.

\* Semi conductor devices :- semiconductors have unique electrical properties, hence they are used in devices to perform specific electrical functions.

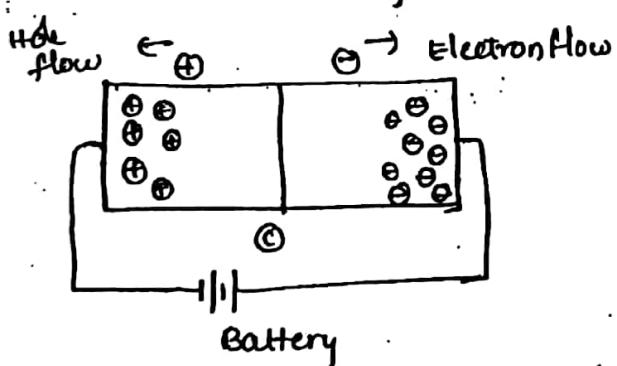
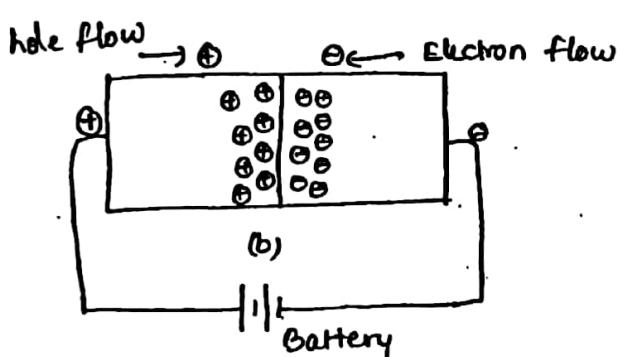
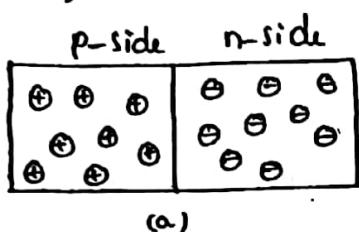
Ex :- Diodes and transistors, which are replaced by old vacuum tubes.

1) p-n junction diode as rectifier

2) Junction transistor.

Q: Write notes on P-n junction diode as rectifier?  
A: P-n junction diode as rectifier :- A rectifier is an electronic device that allows the current to flow in one direction only.

A rectifier transforms an alternating current (A.c) into direct current (D.c).



For p-n rectifying junction, representation of electron and hole distribution.

- (a) NO electrical potential
- (b) forward bias
- (c) Reverse bias.

(positive).

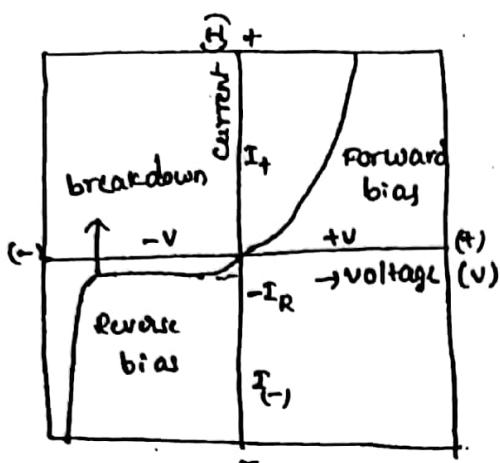
Forward-bias :- when p-terminal <sup>positive</sup> of battery is connected to the p-side and the negative-terminal to the n-side, is referred to as forward bias.

The holes on the p-side and the electrons on the n-side are attracted to the junction.

Electron + hole  $\rightarrow$  Energy.

For this bias, large number of charge carriers flow across the semiconductor and towards the junction, as junction by an appreciable current and a low resistivity.

The current - voltage characteristics of p-n junction for forward and reverse biased,



Reverse bias :- when positive terminal of battery is connected to n-side and negative terminal to p-side, is referred as reverse bias.

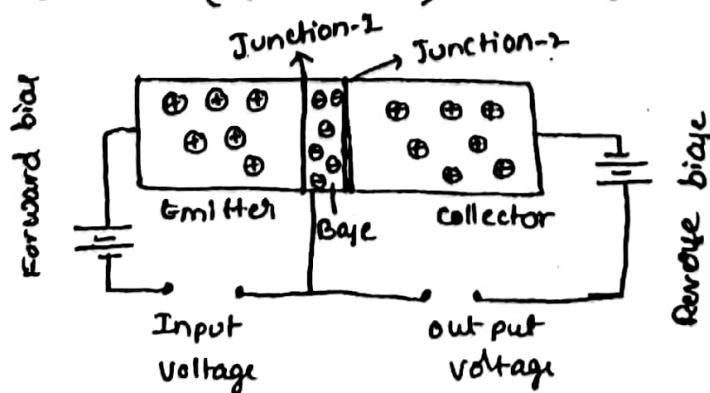
For this bias, both holes and electrons are drawn rapidly away from the junction and the junction is highly insulative.

At high reverse bias voltage, large number of electrons and holes are generated and gives rise to increase in current, this phenomenon is known as 'break down'.

Q. Write notes on p-n junction transistor? 7M

A. 2) Junction transistor :- Transistors can amplify an electrical signal.

p-n-p junction transistor is formed when a thin n-type (base) is sandwiched in between p-type (emitter) and (collector) regions. The emitter-base junction (junction 1) is forward biased, whereas base-collector junction (junction 2) is reverse biased.



The emitter is p-type and junction-I is forward biased, so a large number of holes enter the base region. If the base is extremely narrow, most of the injected holes move through the base without recombination, then across the junction-2 and enter into p-type collector.

A small increase in input voltage within the emitter-base circuit produces a large increase in voltage across junction-2.

#### \* Magnetic materials :-

Every substance has some magnetic property. The origin of property lies in the electrons. Each electron in an atom behaves like a tiny magnet.

Q. What are ferro and ferri magnetism? Give examples.  
A: Ferromagnetism:- Substances like Iron, cobalt, Ni, are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. and these substances are permanently magnetised.

In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called 'domains' and each domain acts as a tiny magnet. In an un-magnetised piece of a ferromagnetic substance, the domains are randomly oriented and net magnetic moments are non-zero.

When the substance is placed in a magnetic field, all the domains orient in the direction of magnetic field and a strong magnetic effect is produced. This ordering of domain persist even when magnetic field is removed and ferromagnetic substance becomes a permanent magnet.

Ferrimagnetism:- Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to

ferro magnetic substances.  $Fe_3O_4$  (magnetite) and ferrites like  $MgFe_2O_4$  and  $NiFe_2O_4$  are examples of such substances. These substances lose ferromagnetism on heating and in the absence of magnetic field.

(a)  - Ferro magnetic

(b)  - Ferri magnetic.

### ~~Hall effect~~

A. \* what are Insulators? Explain Thermal insulators?

Insulators :-

Insulating materials are the substances which resist the flow of heat, sound and electricity through them.

There are two types of insulators,

① Thermal insulators

② Electrical insulators. (or) Di electrics.

Thermal insulators :- They resist the flow of heat.

Ex:- asbestos, glass wool, fibre board, foamed polystyrene etc.

"A substance that reduces the rate of transfer of heat between objects in thermal contact, is a thermal insulator".

A thermal insulating material is placed between a warm region and a cooler region to reduce the rate of heat flow to the cooler region.

Properties :- A thermal insulator should have,

- Thermal stability
- Dimensional stability
- Chemical stability
- Light in weight
- Non inflammable and water proof.

Applications :- Thermal insulators are used in

- (a) Buildings
- (b) Industries
- (c) Space crafts.

Q. Explain Electrical insulators?

A. ② Electrical insulators (or) Di electrics :-

These are also called as di electrics and these materials resist the flow of electric current.

Some materials such as glass, paper and teflon have high resistivity are regarded as good electrical insulators.

Characteristics :-

- (a) They possess low conductivity.
- (b) They have high di-electric strength.
- (c) They should have low thermal contraction and expansion.
- (d) They should be resistant to chemicals, solvents, acids and alkalis etc.
- (e) Should have low porosity.
- (f) They should have high mechanical strength and tensile strength.

Ex :- ① Gaseous electrical insulators -  $SF_6$ .

② liquid electrical insulators - oils, chlorinated hydrocarbons.

③ solid electrical insulators - Glass, synthetic rubber, paper, poly ester etc.

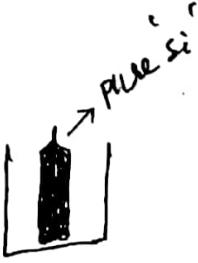
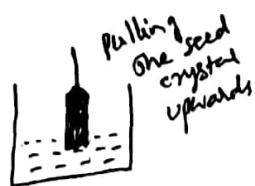
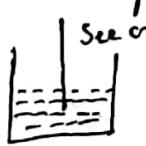
Q. Explain CZECHRALSKI process of Si wafers?

A :- It is a step wise process, to preparation of Si

Step: 1 - preparation of high purity of molten silicon.

Step: 2 - Dipping Seed crystal

Step: 3 - pulling the Seed upwards



- THE END -

**UNIT – 3**

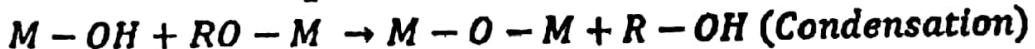
**PART - II**

**Nanomaterials:** A nanomaterial is defined as a material having at least one dimension in the nanometer range. Nanoparticles have great scientific interest because they are effective intermediates between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties irrespective of its size, but at the nano-scale this is always not the same.

Size-dependent properties such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and super Para magnetism in magnetic materials.

**Q1) Explain the Sol-gel process for the preparation of Nanomaterials?**

**Sol-Gel process:** The sol-gel process is an example of bottom-up process and is very long known since the late 1800s. Sol-gel is a chemical solution process used to make ceramic and glass materials in the form of thin films, fibers, or powders. A sol is a colloidal (the dispersed phase is so small that only Van der Waals forces and surface charges are present) or molecular suspension of metal or metalloid dispersed in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network.



- The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel).
- Metal alkoxides and metal chlorides are common starting materials. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent which is generally an alcohol. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).
- Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.
- After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order enhance mechanical properties.

**Advantages:** (i) Able to get uniform and controlled size of nanoparticles. (ii) Can be carried out at low temperatures and can have better control over the reactions.

**Q2) How nano-materials are characterized using BET, TEM and SEM methods?**

- The characterization of nanoparticles can be done by using BET, SEM and TEM methods.

**1. Brunauer Emmett Teller (BET) method:** This method is used to determine Specific surface area ( $m^2/g$ ) of nanoparticles by the absorption of an inert gas (typically  $N_2$ ) on the surface.

**Working:** The sample is weighed and placed into a vacuum chamber to remove moisture and absorbed gases. The sample is then cooled down to a constant temperature by means of liquid nitrogen.  $N_2$  gas is adsorbed on the sample surface. From the amount of gas adsorbed at a given pressure an adsorption isotherm is derived. The BET theory is then used to determine the amount of gas necessary to form a monolayer on the surface, also called the monolayer capacity. From the monolayer capacity, the specific surface area in  $m^2/g$  can be calculated. Other inert gases, such as Ar or Kr, can also be used.

**Note:** Dry samples required. Fast and relatively cheaper method.

**2. Transmission Electron Microscopy (TEM):** This method is used to determine primary particle size, aggregate (particle size) and agglomerate size of nanoparticles.

**Working:** Transmission electron microscopy (TEM) is a technique involves a beam of electrons is transmitted through a thin sample. An image is formed from the interaction of the electrons transmitted through the sample, the image is magnified and focused onto an imaging device such as a fluorescent screen, for viewing the sample, or onto photographic film, for a record of the sample. Areas of dense material (such as solid nanoparticles) absorb the electrons and appear as dark areas on the viewing screen. Less dense material (such as coating around the nanoparticles) allows the electrons to pass through more freely and appear as lighter areas. Typically a final image will be 200,000 times normal magnification and the TEM is capable of achieving a magnification as high as 1 million, but the quality of the image decreases as magnification increases.

**3. Scanning Electron Microscopy (SEM):** is a test process that scans a sample with an electron beam to produce a magnified image for analysis. The method is also known as SEM analysis and SEM microscopy, and is used very effectively in microanalysis.

SEM is a method for high resolution surface imaging. The SEM uses electrons for imaging, much as light microscopy uses visible light. The advantages of SEM over light microscopy include greater magnification (up to 100,000X) and much greater depth of field. A random straight line is drawn through the micrograph. The number of grain boundaries intersecting the line are counted. The average grain size is found by dividing the number of intersections by the actual line length. Average grain size =  $1/(\text{number of intersections/actual length of the line})$ . TEM give information about the internal structure of a sample, but can only produce a 2D image of a small area, where as SEM is better of 3D surface morphology. TEM would be useful for imaging protein molecules, for example, and SEM would more likely be used to look at the surface features on a cell membrane.

**Q3) Give the preparation, properties and applications of Carbon nano tubes?**

**Carbon nanotubes (CNTs):** Carbon nanotubes are composed of carbon atoms linked in hexagonal shapes, with each carbon atom covalently bonded to three other carbon atoms. Carbon nanotubes have diameters as small as 1 nm and lengths up to several centimeters. Carbon nanotubes are strong, they are not brittle. They can be bent, and when released, they will spring back to their original shape.

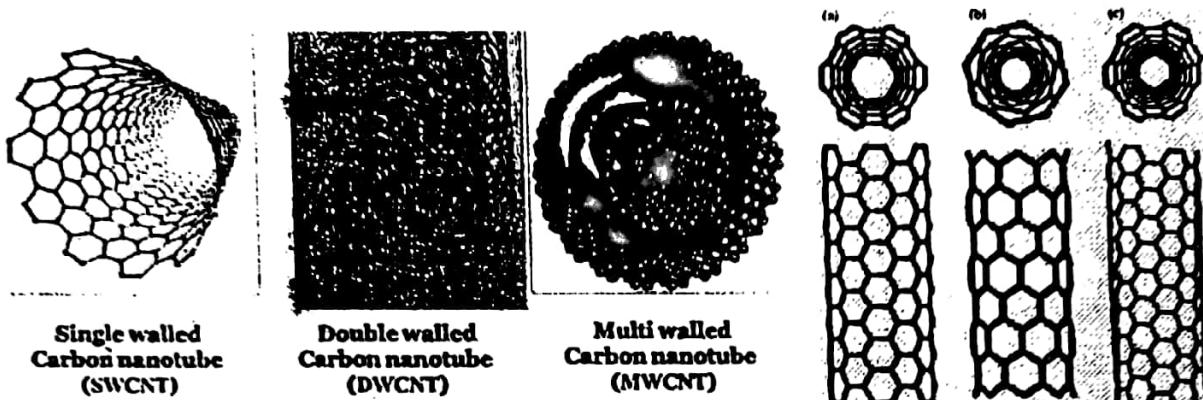
**The cylindrical allotropes of carbon having length to diameter ratio 1 lakh times are called Carbon Nano Tubes.**

These sheets can be tightened (rolled) into different form, which have different (mechanical) properties. The names for these twisted forms are: (a) Armchair, (b) Zigzag, and (c) Chiral.

Depending on the number of layers present, carbon nanotubes are classified into three types.

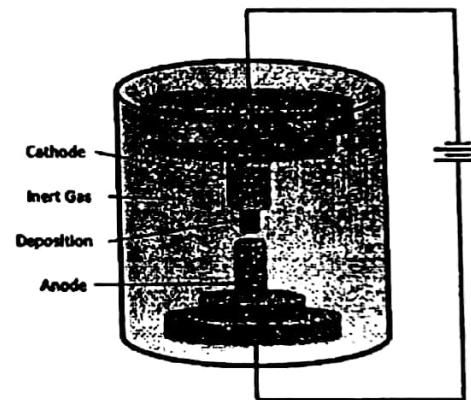
1. single-walled nanotubes (SWNTs),
2. Double-walled nanotubes (DWNTs), and
3. Multi-walled nanotubes (MWNTs).

Single-wall carbon nanotubes (SWNTs) are a special class of carbon materials known as one-dimensional materials. They consist of sheets of graphene, rolled up to form hollow tubes with walls one atom thick. Much like graphene, SWNTs have properties that differ considerably to those of bulk carbon (e.g. graphite). Due to its chemical structure and dimensional constraints, this material exhibits exceptional mechanical, electrical, thermal, and optical properties.

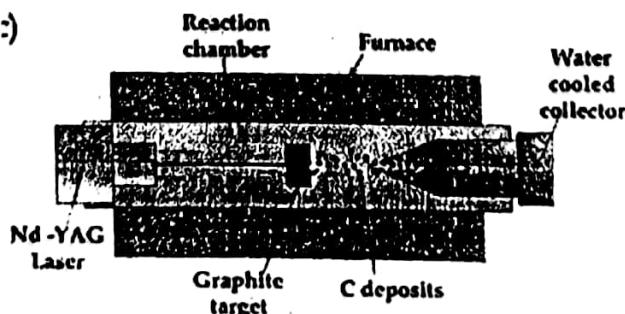


**Synthesis of Carbon nanotubes:** Carbon nanotubes can be synthesized by using the following methods.

**1. Arc-discharge method:** This method was first used by Sumio Iijima in 1991, this technique is also used for the synthesis of fullerenes. The experiment is carried out in a reaction vessel containing an inert gas such as helium, argon, etc. at a constant pressure. A potential of around 18 V (50-100 A) is applied across two graphite electrodes separated by a short distance of usually 1-4 mm within this chamber. As a result, carbon atoms are ejected from the anode and are deposited onto the cathode. The black carbonaceous deposit containing CNTs is seen growing on the cathode. The produced CNTs will have fewer structural defects, better electrical, mechanical and thermal properties. The synthesis product yield is 60%.

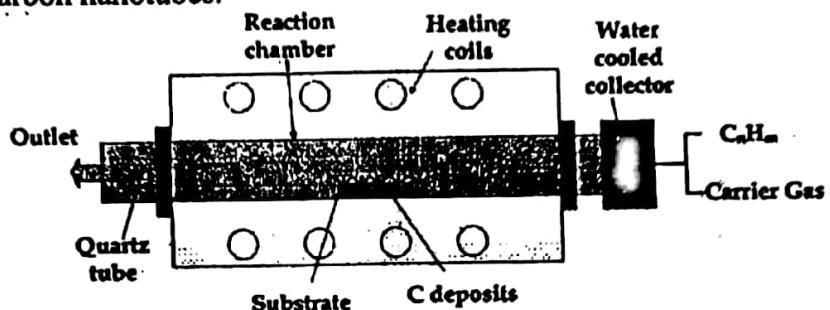


**2. Laser ablation method:** This process was developed by Dr. Richard Smalley and co-workers at Rice University in 1995. In laser ablation, a pulsed laser vaporizes a graphite target at 1200 °C in a high-temperature reactor while an inert gas like helium or argon is sent into the chamber. A water-cooled Cu surface may be used to collect the vaporized carbon as nanotubes by condensation.



The laser ablation method yields around 70% and produces mainly contains single-walled carbon nanotubes with a controllable diameter. However, it is more expensive than either arc discharge or chemical vapor deposition.

**3. Chemical Vapour Deposition method:** The chemical vapour deposition method (CVD) is an alternative method in which CNTs are developed on metal catalyst surface like Ni, Co, Fe, etc. and their alloys. The gaseous hydrocarbon like methane ( $\text{CH}_4$ ) or ethane ( $\text{C}_2\text{H}_6$ ) along with a carrier gas like nitrogen, helium or argon are sent into the reaction chamber at  $700^\circ\text{C}$ . The CNTs grow at the surface of the metal catalyst surface by dissociation of hydrocarbon molecules. Use of catalysis reduces the need for high temperatures. Very high yields (90%) are reported by using this method. CVD is the most widely used method for the commercial production of carbon nanotubes.



#### Properties of Carbon Nanotubes:

- 1) Carbon nanotubes are one dimensional conductor along the tubular axis with conductivity either metallic or semiconducting nature.
- 2) Carbon nanotubes are the strongest and stiffest materials due to presence of covalent  $\text{sp}^2$  bonds between the individual C atoms.
- 3) CNTs are highly flexible- can be bent considerably without damage
- 4) CNTs are very elastic  $\sim 18\%$  elongation to failure
- 5) CNTs have high thermal conductivity along the axis but these are good insulators lateral to the tubular axis.
- 6) CNTs have a low thermal expansion coefficient.
- 7) CNTs are good electron field emitters.
- 8) MWCNTs possess kinetic properties with inner nanotube core may slide without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing.
- 9) CNTs have good optical properties due to absorption, fluorescence, Raman spectroscopy.

#### Applications of Carbon Nanotubes:

- 1) Because of superior mechanical properties, CNTs are used to make space elevators, bullet-proof clothing.
- 2) CNTs are used for producing field effect transistors provided with digital switching.
- 3) These are also used for making polymer nano composites used for making wires and cables.
- 4) CNTs are used to make paper batteries which can provide stable output comparable to conventional batteries.
- 5) CNTs are used to prepare solar panels due to their strong UV-Vis, near IR radiation.
- 6) There are used in fuel cells to store fuel like hydrogen.
- 7) CNTs are used in treatment of cancerous cells by exciting with radio waves.
- 8) Because of the high surface energy, CNTs are used in catalysis.

#### **Q4) Explain the properties and applications of Fullerenes.**

$C_{60}$  is most studied fullerene due to its availability, high symmetry and low price. In 1985, James R. Heath, Robert Curl and Richard Smalley, from Rice University discovered  $C_{60}$ , and shortly thereafter came to discover the fullerenes. Buckminster fullerene ( $C_{60}$ ) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome.

**Definition:** The spherical allotropes of carbon containing 60 carbon atoms are called fullerenes.

Fullerenes are closed hollow cages consisting of carbon atoms interconnected in pentagonal and hexagonal rings. Each carbon atom on the cage surface is bonded to three carbon neighbors therefore is  $sp^2$  hybridized.

- In fullerenes, 12 pentagonal rings are necessary and sufficient to affect the cage closure.
- Fullerenes contain carbon atoms arranged as a combination of 12 pentagonal rings and  $n$  hexagonal rings.
- Fullerene cages are about 7-15 Å in diameter, and are one carbon atom thick.
- The chemical formula is  $C_{20+2n}$ .



#### **Types of Fullerenes:**

- i. **Buckyball clusters:** smallest member is  $C_{20}$  (unsaturated version of dodecahedrane) and the most common is  $C_{60}$ .
- ii. **Nanotubes:** Hollow tubes of very small dimensions, having single or multiple walls.
- iii. **Megatubes:** Larger in diameter than nanotubes and prepared with walls of different thickness.

**Preparation of fullerenes:** The fullerenes were prepared by evaporation of carbon electrodes in an electric arc discharge process in helium atmosphere. In a chamber, an electrical discharge is applied between graphite electrodes in Helium atmosphere at 100 torr. As a result, soot is ejected from the graphite and is deposited inside the chamber. The resulting soot is scraped from the evaporation chamber and dissolved in benzene. Further separation and purification leads to  $C_{60}$  in gram scale.

#### **Properties of $C_{60}$ and its derivatives:**

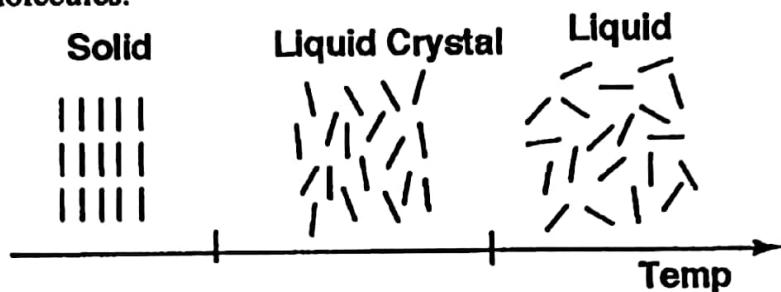
1. Fullerenes are sparingly soluble in many solvents. Common solvents for fullerenes are toluene,  $CS_2$ , benzene,  $CH_2Cl_2$ , etc.
2. Fullerene is a black crystalline solid and is thermally stable up to 400 °C.
3. When doped with alkali metals, they act as conductors and superconductors.
4. Fullerenes are very difficult to oxidize but can easily reduce.
5. Because of presence of unsaturation, fullerenes show broad UV-vis absorption.
6. Fullerenes behave like an electron deficient alkenes and reacts readily with electron rich species and acts as acceptors of electrons and electronic energy.

#### **Applications of fullerenes:**

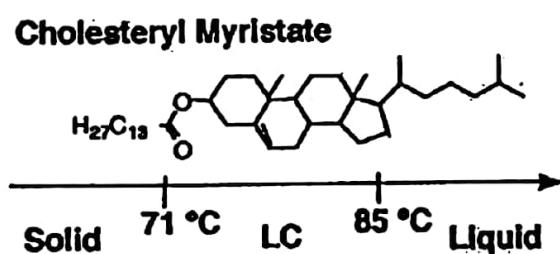
1. Fullerenes have been extensively used for several biomedical applications including MRI, X-Ray imaging, drug and gene delivery.
2. Bucky balls may be used to store hydrogen, possibly as a fuel tank for fuel cell.
3. They inhibit the spread of the HIV virus and are used in treatment of HIV.
4. Fullerenes are chemically reactive and can be added to polymer composites with specific physical and mechanical properties.
5. Fullerenes are also used to produce inexpensive solar cells.
6. These are used in several applications like coatings, lubricants, catalyst, electronic and optical devices.

**Q5) Give the types and applications of Liquid crystals?**

Liquid crystal is a state that occurs between a solid & a liquid. They possess properties characteristics of both liquids & crystalline solids. It also possesses properties not found in either liquids or solids. A fluid phase in which a liquid crystal flows and will take the shape of its container. It differs from liquid that there are still some orientational order possessed by the molecules.

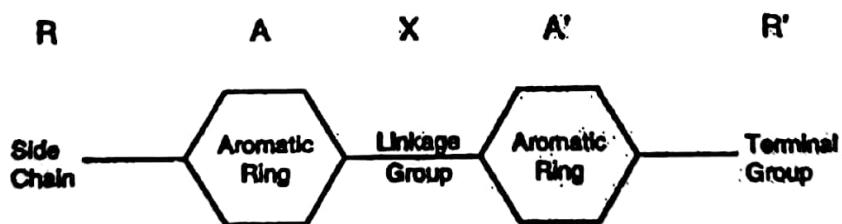


Liquid crystals are discovered in 19<sup>th</sup> century when studying a cholesterol derivative.



**Orientational Order:** Assuming that the direction of preferred orientation in a liquid crystal is  $\uparrow$ , this direction can be represented by an arrow, called the director of the liquid crystal.

**Criteria for a molecule being liquid crystalline:** The molecule must be elongated in shape-length should be significantly greater than its width. Molecule must have some rigidity in its central region. The ends of the molecule are somewhat flexible.



**Types of Liquid Crystals:** The liquid crystal state can be attained either by the action of heat or by action of solvent on amphiphilic systems. These are classified into two types.

1. **Lyotropic Liquid Crystals:** LC phases formed by dissolving the compound in an appropriate solvent (under given concentration and temperature conditions) are known as lyotropic LCs.

2. **Thermotropic Liquid Crystals:** The liquid crystal phases obtained by changing the temperature are called thermotropic LCs.

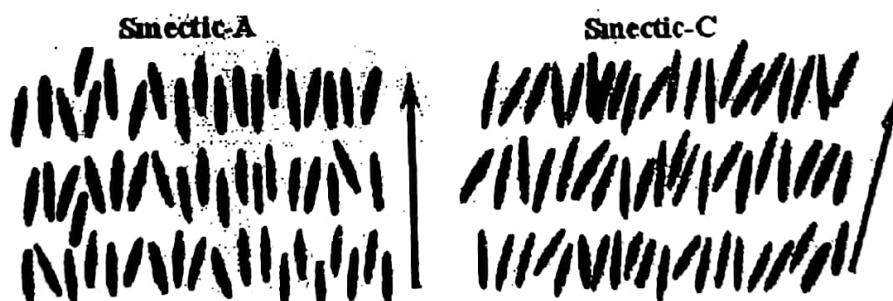
Thermotropic LCs are further classified into three types

A **Nematic Phase:** One of the most familiar liquid phase phases is the nematic. The word *nematic* derived from the Greek word, „*nema*“ which means "thread". In nematic phase molecules have same direction in space but change the order.

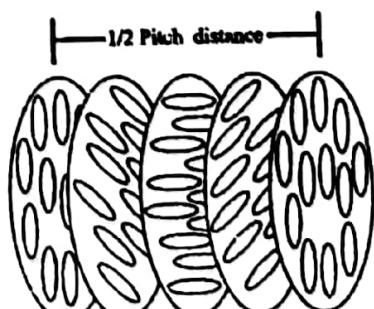
B **Smectic Phase:** "Smectic" is a Greek word which means soap. This is just like a slippery soap which is present in the lower side of soap dish. In the smectic state, the molecules are arranged in layers or planes they show general structural order in nematics. Some compound are develop many types of smectic phase.



- **Smectic-A:** In smectic-A, there is parallel position of director and smectic plane. The orientation of molecules is disturbed in the plane.
- **Smectic-B:** In mesophase, orientation of molecules are just like a smectic A, the molecules are arranged in layer which form hexagonal structure.
- **Smectic-C:** In mesophase, molecules are oriented as same order A, B but in smectic-c smetic having a tilted angle between molecular alignment and the surface of the layer, the phase is measure by rotation of angle.



C **Cholesteric Phase:** These types of liquid are also known as chiral nematic liquid crystal. Like the nematic phase, the molecules in this phase are also parallel to each other within layers. The director axis changes regularly in nature to form a helical structure. This regular change is called pitch. The pitch changes with temperature and by the boundary conditions.  
*Eg:* Hydroxypropyl cellulose and cholesteryl benzoate.



#### Applications of liquid crystals:

1. These are used in Liquid Crystal Displays (LCDs).
2. These are used in Liquid Crystal Thermometers.
3. These are used in Helmets and Bullet-proof vests.
4. These are used in Battery testing strips (used by DuraCell).
5. These are used in Radiation and Sensors.
6. These are used in Switchable Light Panels for windows.

7. These are used in Optical Memories.
8. These are used in solvents for GC, NMR, reactions, etc.
9. These are used in Biological systems and medicine.

## Superconductors

### Q1) Explain the Meissner effect.

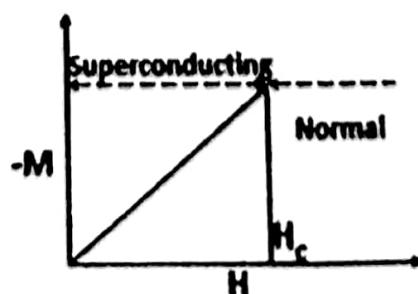
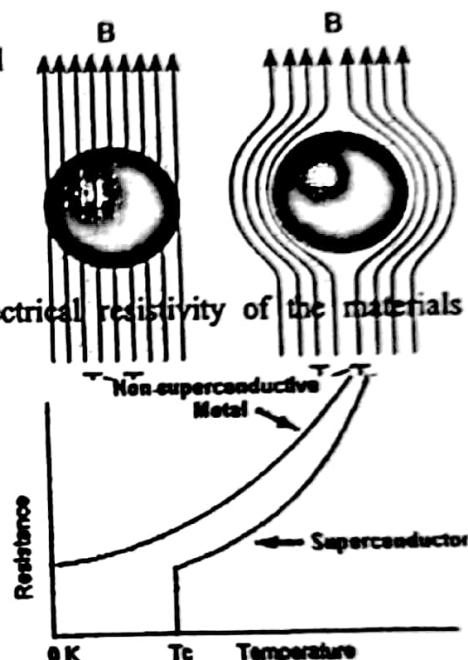
1. When Superconducting material cooled below its critical temperature ( $T_c$ ), it becomes resistance less and perfect diamagnetic.
2. When superconductor placed inside a magnetic field in ( $T_c$ ), all magnetic flux is expelled out of it the effect is called Meissner effect.
3. Perfect diamagnetism arises from some special magnetic property of Superconductor.
4. If there is no magnetic field inside the superconductor relative permeability or diamagnetic constant  $\mu_r = 0$ .

### Q2) What are SuperConductors and their types.

**Superconductors:** The phenomenon in which the electrical resistivity of the materials suddenly falls to nearly zero when it is cooled to a very low temperature is known as *superconductivity*, and the materials under this condition are called *superconductors*.

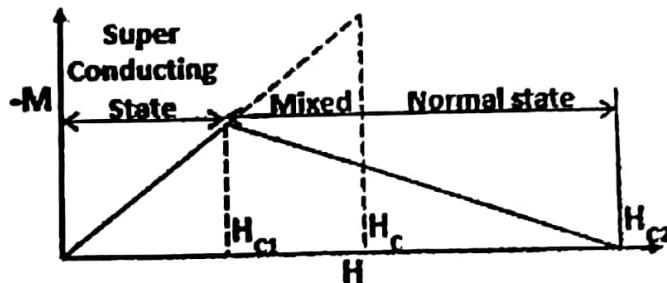
Superconductors are classified into two types:

1. Type-I superconductors or Soft superconductors, and
  2. Type-II superconductors or Hard superconductors.
- 1. Type-I Superconductors or Soft superconductors:** These were discovered first and usually consist of pure metals, elemental metals and not alloys, they show some conductivity at room temperature. These were discovered first and usually consist of pure metals. Type-I superconductors are also called as the "soft" superconductors. When the magnetic field is applied on a superconductor and increased gradually, the inverse magnetization increases linearly up to a certain value called critical field ( $H_c$ ) and then sharply falls to zero.
- i. Type-I superconductors have only one critical field.
  - ii. These exhibit complete Meissner effect.
  - iii. The values of  $H_c$  are too low to have any useful magnetic applications.



- 2. Type-II superconductors or Hard superconductors:** Type-II superconductors are also known as the "hard" superconductors. In Type-II superconductors, the transition from a superconducting state to a normal state does not occur sharply but occurs through a mixed

region. When magnetic field is applied on a super conductor and increased gradually, the inverse magnetization increases linearly up to a certain value called first critical field ( $H_{c1}$ ). From this point, the penetration of magnetic field into type-2 super conductor begins. After another value of magnetic field called second critical field ( $H_{c2}$ ) or vortex region, the superconductivity disappears and material returns to the normal state.



- i. Most of these are developed from alloys, ceramics, transition metals, etc.
- ii. These do not exhibit complete Meissner Effect.
- iii. The transition between super conducting and normal state is not sharp.
- iv. They have higher  $T_c$ s than Type 1 superconductors.

#### Properties of superconductors:

1. Superconductors offer more resistance than other elements at room temperature.
2. Critical temperature of super conductor is low when a small amount of impurity is added.
3. The superconducting state will be lost in the presence of a magnetic field greater than a critical value, even at absolute zero.
4. In superconducting state, the material becomes diamagnetic.
5. The thermal expansion and elastic properties of material remain unchanged during phase change from normal to superconducting state.

#### Applications of superconductors:

1. Superconductors were used to build experimental digital computers.
2. They are used in diagnostic tools like MRI in the field of medicine, NMR machines, and mass spectrometers.
3. They are used in transformers, power storage devices, electric power transmission to transmit power over long distances without resistive losses.
4. They are used in electric motors (e.g. for vehicle propulsion, as in bullet trains), magnetic levitation devices, etc.
5. These can be used as memory and storage devices in computers.
6. These can be used in wind turbines, the lower weight and volume of superconducting generators could lead to minimize construction and tower costs.
7. Some super conductors are acts as excellent catalyst for industrial process.
8. For computers, super chips made up of superconductors can function 1000 times faster than silicon chips.

## UNIT IV: SPECTROSCOPIC TECHNIQUES & NON CONVENTIONAL ENERGY SOURCES

### Part A: SPECTROSCOPIC TECHNIQUES

**Electromagnetic spectrum-UV** (laws of absorption, instrumentation, theory of electronic spectroscopy, Frank-condon principle, chromophores and auxochromes, intensity shifts, applications), **FT-IR** (instrumentation and IR of some organic compounds, applications)-magnetic resonance imaging and CT scan (procedure & applications).

### Part B: NON CONVENTIONAL ENERGY SOURCES

Design, working, schematic diagram, advantages and disadvantages of photovoltaic cell, hydropower, geothermal power, tidal and wave power, ocean thermal energy conversion.

#### Part A: SPECTROSCOPIC TECHNIQUES:-

##### ➤ Electromagnetic radition:-

- Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter.
- The electric and magnetic fields come at right angles to each other and combined wave moves perpendicular to both magnetic and electric oscillating fields thus the disturbance.

#### General Properties of all electromagnetic radiation:

1. Electromagnetic radiation can travel through empty space. Most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard.
2. The speed of light is always a constant. (Speed of light :  $2.99792458 \times 10^8 \text{ m s}^{-1}$ )
3. Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol  $\lambda$ .

#### Amplitude:-

- Amplitude is the distance from the maximum vertical displacement of the wave to the middle of the wave. This measures the magnitude of oscillation of a particular wave.

#### Wavelength

- Wavelength ( $\lambda$ ) is the distance of one full cycle of the oscillation. Longer wavelength waves such as radio waves carry low energy; this is why we can listen to the radio without any harmful consequences.

This wavelength frequently relationship is characterized by:

$$c = \lambda v$$

where

- $c$  is the speed of light,

- $\lambda\lambda$  is wavelength, and
- $\nu\nu$  is frequency.

## Frequency

- Frequency is defined as the number of cycles per second, and is expressed as  $\text{sec}^{-1}$  or Hertz (Hz). Frequency is directly proportional to energy and can be express as:  $E=h\nu$

where

$E$  is energy,  
 $h$  is Planck's constant, ( $h= 6.62607 \times 10^{-34} \text{ J}$ ), and  
 $\nu$  is frequency.

## ➤ Electromagnetic spectrum:-

- Electromagnetic waves have an extremely wide range of wavelengths, frequencies, and energies.
- The highest energy form of electromagnetic waves are gamma ( $\gamma$ ) rays and the lowest energy form are radio waves.

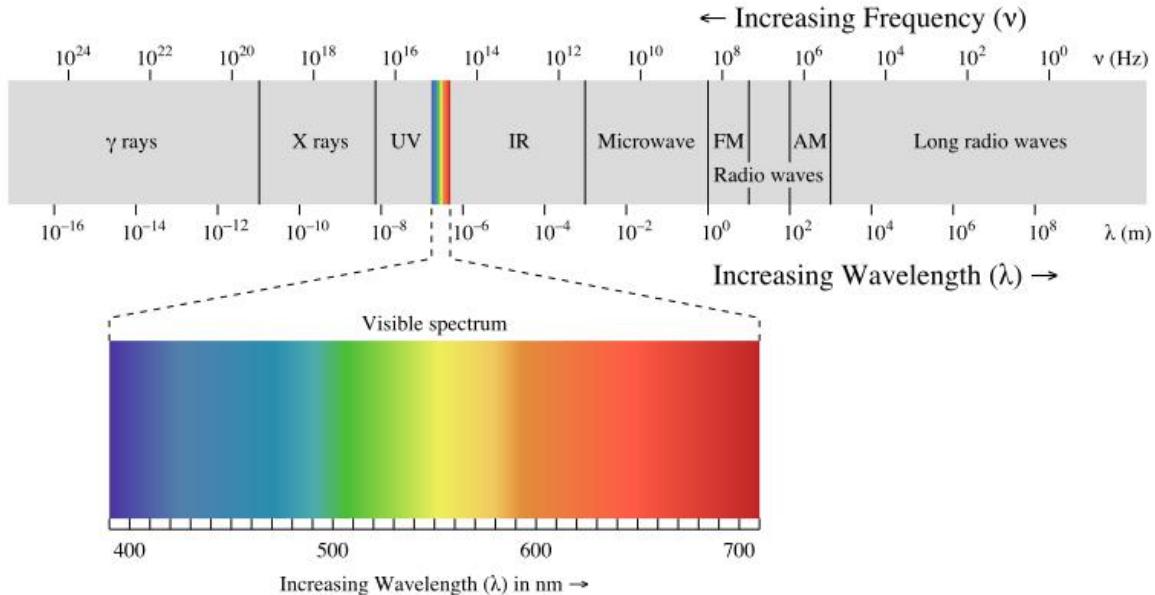


Fig:-Electromagnetic spectrum with light highlighted

- As a wave's wavelength increases, the frequency decreases, and as wave's wavelength decreases, the frequency increases.
- When electromagnetic energy is released as the energy level increases, the wavelength decreases and frequency decreases.
- Thus, electromagnetic radiation is then grouped into categories based on its wavelength or frequency into the electromagnetic spectrum.

- The different types of electromagnetic radiation shown in the electromagnetic spectrum consists of radio waves, microwaves, infrared waves, visible light, ultraviolet radiation, X-rays, and gamma rays. The part of the electromagnetic spectrum that we are able to see is the visible light spectrum.

➤ **laws of absorption:-**

- Absorption of light takes place when matter captures electromagnetic radiation, converting the energy of photons to internal energy.
- Energy is transferred from the radiation to the absorbing species.

### **The Effect of Light Absorption on Matter:-**

- Since the energy levels of matter are quantized, only light of energy that can cause transitions from one existing energy level to another will be absorbed.
- We describe the energy change in the absorber as a transition or an excitation from a lower energy level to a higher energy level.

➤ **Instrumentation and working of the UV spectrometers:-**

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-

❖ **Light Source**- Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region.

❖ **Amplifier**- The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer.

❖ **Recording devices**- Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

❖ **Photometer:-**

An instrument for measuring the intensity of light or the relative intensity of a pair of lights. Also called an illuminometer. It utilizes filter to isolate a narrow wavelength region.

❖ **Spectrophotometer:-**

An instrument measures the ratio, or a function of the two, of the radiant power of two EM beams over a large wavelength region.

❖ **Colorimeter:-**

An instrument which is used for measuring absorption in the visible region is generally called colorimeter.

➤ **Theory of electronic spectroscopy:-**

- **Electron spectroscopy** is an analytical technique to study the electronic structure and its dynamics in atoms and molecules.
- In general an excitation source such as x-rays, electrons or synchrotron radiation will eject an electron from an inner-shell orbital of an atom.
- Detecting photoelectrons that are ejected by x-rays is called x-ray photoelectron spectroscopy(XPS) or electron spectroscopy for chemical analysis (ESCA).
- Detecting electrons that are ejected from higher orbitals to conserve energy during electron transitions is called Auger electron spectroscopy (AES).
- Experimental applications include high-resolution measurements on the intensity and angular distributions of emitted electrons as well as on the total and partial ion yields.

**Various methods emanate from the electron spectroscopy are:**

- Electron spectroscopy for chemical Analysis
- Auger electron spectroscopy

**Electron spectroscopy for chemical Analysis:-**

In typical laboratory use, a sample is placed in the specimen chamber of a scanning electron microscope (SEM). Because the SEM uses a beam of electrons to illuminate the sample and produce the three dimensional images often seen in lay news reports and publications as well as professional journals, the sample must be able to conduct electricity

**Auger electron spectroscopy (AES)** is a common analytical technique used specifically in the study of surfaces and, more generally, in the area of materials science.

➤ **Frank-condon principle:-**

- The Franck–Condon principle is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions.
- Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.
- It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change.
- This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond.
- When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

➤ **CHROMOPHORE:**

- The term chromophore was previously used to denote a functional group of some other structural feature of which gives a color to compound.
- For example- Nitro group is a chromophore because its presence in a compound gives yellow color to the compound.
- But these days the term chromophore is used in a much broader sense which may be defined as “any group which exhibit absorption of electromagnetic radiation in a visible or ultra-visible region “It may or may not impart any color to the compound.
- Some of the important chromophores are: ethylene, acetylene, carbonyls, acids, esters and nitrile groups etc.

➤ **AUXOCHROMES:**

- It is a group which itself does not act as a chromophore but when attached to a chromophore, it shifts the adsorption towards longer wavelength along with an increase in the intensity of absorption.
- Some commonly known auxochromic groups are: -OH, -NH<sub>2</sub>, -OR, -NHR, and -NR<sub>2</sub>.

➤ **intensity shifts:-**

There are four types of shifts observed in the UV spectroscopy-

a) **Bathochromic effect:-**

This type of shift is also known as red shift.

Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents.

b) **Hypsochromic shift**- This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength. Generally it is caused due to the removal of conjugation or by changing the polarity of the solvents.

c) **Hyperchromic effect** - Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.

d) **Hypochromic effect**- Hyperchromic effect is defined as the effect by virtue of intensity of absorption maximum decreases. Hyperchromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.

➤ **Applications of UV spectroscopy:-**

1. **Detection of functional groups**- UV spectroscopy is used to detect the presence or absence of chromophore in the compound.

This technique is not useful for the detection of chromophore in complex compounds.

The absence of a band at a particular band can be seen as an evidence for the absence of a particular group.

2. **Detection of extent of conjugation**- The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy. With the increase in double bonds the absorption shifts towards the longer wavelength.
3. **Identification of an unknown compound**- An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectrums coincide then it confirms the identification of the unknown substance.
4. **Determination of configurations of geometrical isomers**- It is observed that cis-alkenes absorb at different wavelength than the trans-alkenes. The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances.

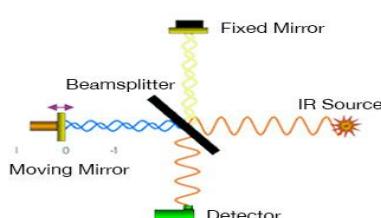
## ➤ FT-IR:-

- FTIR stands for Fourier transform infrared, the preferred method of infrared spectroscopy.
- When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted).
- The resulting signal at the detector is a spectrum representing a molecular 'fingerprint' of the sample.
- The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints.

### So, what is FTIR?

- The Fourier Transform converts the detector output to an interpretable spectrum.
- The FTIR generates spectra with patterns that provide structural insights.

### How does FTIR work and why use it?



The FTIR uses interferometry to record information about a material placed in the IR beam. The Fourier Transform results in spectra that analysts can use to identify or quantify the material.

- An FTIR spectrum arises from interferograms being ‘decoded’ into recognizable spectra
- Patterns in spectra help identify the sample, since molecules exhibit specific IR fingerprints.

➤ **IR of some organic compounds:-**

- IR (infrared) spectroscopy is useful in organic chemistry because it enables you to identify different functional groups.
- This is because each functional group contains certain bonds, and these bonds always show up in the same places in the IR spectrum.
- To generate the IR spectrum, different frequencies of infrared light are passed through a sample, and the transmittance of light at each frequency is measured.
- Different functional groups produce bond absorptions at different locations and intensities on the IR spectrum.
- This table lists the locations and intensities of absorptions produced by typical functional groups.

<b>IR Absorptions of Common Functional Groups</b>		
<b>Functional Group</b>	<b>Absorption Location (cm<sup>-1</sup>)</b>	<b>Absorption Intensity</b>
Alkane (C–H)	2,850–2,975	Medium to strong
Alcohol (O–H)	3,400–3,700	Strong, broad
Alkene (C=C) (C=C–H)	1,640–1,680 3,020–3,100	Weak to medium Medium
Alkyne (C≡C) (C≡C–H)	2,100–2,250 3,300	Medium Strong
Nitrile (C≡N)	2,200–2,250	Medium
Aromatics	1,650–2,000	Weak
Amines (N–H)	3,300–3,350	Medium
Carbonyls (C=O)		Strong
Aldehyde (CHO)	1,720–1,740	
Ketone (RCOR)	1,715	
Ester (RCOOR)	1,735–1,750	
Acid (RCOOH)	1,700–1,725	

➤ **Sampling and applications of FTIR:-**

- FTIR can be a single purpose tool or a highly flexible research instrument. With the FTIR configured to use a specific sampling device – transmission or ATR for instance – the spectrometer can provide a wide range of information:
- Most commonly, the identification of an unknown
- Quantitative information, such as additives or contaminants
- Kinetic information through the growth or decay of infrared absorptions
- Or more complex information when coupled with other devices such as TGA, GC or Rheometry

Ultimately, FTIR can be a cost-effective answer machine.

➤ **Magnetic resonance:-**

- Magnetic Resonance (MR) spectroscopy is a noninvasive diagnostic test for measuring biochemical changes in the brain, especially the presence of tumors.
- While magnetic resonance imaging (MRI) identifies the anatomical location of a tumor, MR spectroscopy compares the chemical composition of normal brain tissue with abnormal tumor tissue.

**How does MR spectroscopy work?**

- MR spectroscopy is conducted on the same machine as **conventional MRI**. The MRI scan uses a powerful magnet, radio waves, and a computer to create detailed images.
- MR spectroscopy analyzes molecules such as hydrogen ions or protons.
- Proton spectroscopy is more commonly used.
- There are several different metabolites, or products of metabolism, that can be measured to differentiate between tumor types:
  - Amino acids
  - Lipid
  - Lactate
  - Alanine
  - N-acetyl aspartate
  - Choline
  - Creatine
  - Myoinositol

➤ **Magnetic Resonance Imaging (MRI) & CT scan**

- MRI is a non-invasive imaging technology that produces three dimensional detailed anatomical images.
- It is often used for disease detection, diagnosis, and treatment monitoring.
- It is based on sophisticated technology that excites and detects the change in the direction of the rotational axis of protons found in the water that makes up living tissues

**How does MRI work?**

- MRIs employ powerful magnets which produce a strong magnetic field that forces protons in the body to align with that field.
- When a radiofrequency current is then pulsed through the patient, the protons are stimulated, and spin out of equilibrium, straining against the pull of the magnetic field.
- To obtain an MRI image, a patient is placed inside a large magnet and must remain very still during the imaging process in order not to blur the image.

**What is MRI used for?**

- MRI scanners are particularly well suited to image the non-bony parts or soft tissues of the body.

- They differ from computed tomography (CT), in that they do not use the damaging ionizing radiation of x-rays.
- The brain, spinal cord and nerves, as well as muscles, ligaments, and tendons are seen much more clearly with MRI than with regular x-rays and CT; for this reason MRI is often used to image knee and shoulder injuries.
- In the brain, MRI can differentiate between white matter and grey matter and can also be used to diagnose aneurysms and tumors.
- Because MRI does not use x-rays or other radiation, it is the imaging modality of choice when frequent imaging is required for diagnosis or therapy, especially in the brain.
- However, MRI is more expensive than x-ray imaging or CT scanning.
- One kind of specialized MRI is functional Magnetic Resonance Imaging (fMRI.)
- This is used to observe brain structures and determine which areas of the brain “activate” (consume more oxygen) during various cognitive tasks.
- It is used to advance the understanding of brain organization and offers a potential new standard for assessing neurological status and neurosurgical risk.

# NON CONVENTIONAL ENERGY SOURCES AND STORAGE DEVICES

Expt:.....

## NON-CONVENTIONAL ENERGY SOURCES : — Introduction

→ Non-conventional energy are those sources which are renewable and ecologically safe. such as solar energy, wind energy, ocean energy, geothermal energy, nuclear energy etc.

→ The importance of using non-conventional or renewable power was recognized in India early 1970.

● 1. Solar energy: It is utilized in India through photovoltaic route and thermal route.

2. Biomass: Power based on biomass were launched in different places in central India.

3. Wind Energy: Wind energy is used for power generation.

4. Geothermal Energy: Geothermal energy generated from hot springs. It is generated in Himachal Pradesh and Jammu & Kashmir.

5. Energy from urban and industrial waste : —

→ Power is generated from urban waste, which is impulsive in Timarpur in Delhi and Tamil Nadu.



## ⇒ SOLAR ENERGY :-

### Introduction :-

- solar energy is a renewable & environment friendly energy.
- The energy received by the earth in the form of electro-magnetic radiation is known as solar energy.
- The solar energy is cheap and pollution free.
- The solar energy is used to generate electricity by using solar cells.
- Solar cell is a form of photovoltaic cell.

Solar cell :- A solar cell is an electrical device that converts the energy of light directly into electricity by photovoltaic cell.

### Photovoltaic cell :-

- The term photovoltaic comes from greek word "Phos" meaning light and volt is the unit of emf. which was named by inventor of the battery the Italian physicist Alessandro Volta.
- This term photo-voltaic is used in since 1849.
- specially, it is used to generate electricity from sun light, lamp light or artificial light.

## Working of photovoltaic cells: -

### Principle:

- Solar cells employ the principle of 'Photovoltaic effect' for energy conversion.
- A material generates electricity when exposed directly to sun light. This is also known as photovoltaic effect.

### Construction:

- Solar cells employ two semi-conductors namely P-type semiconductor and n-type semiconductor.
- P-type semiconductor is usually a silicon doped with Boron impurities.
- n-type semiconductor is a silicon doped with either phosphorous or arsenic.

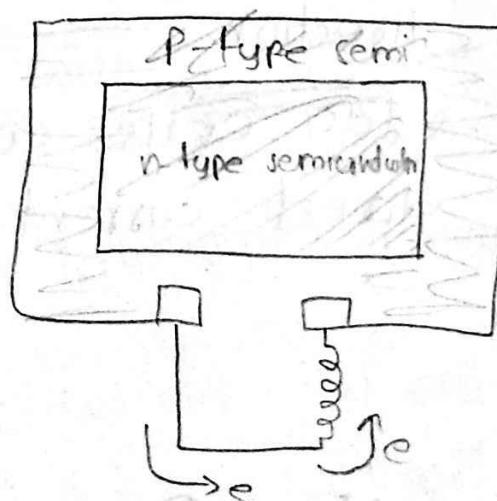
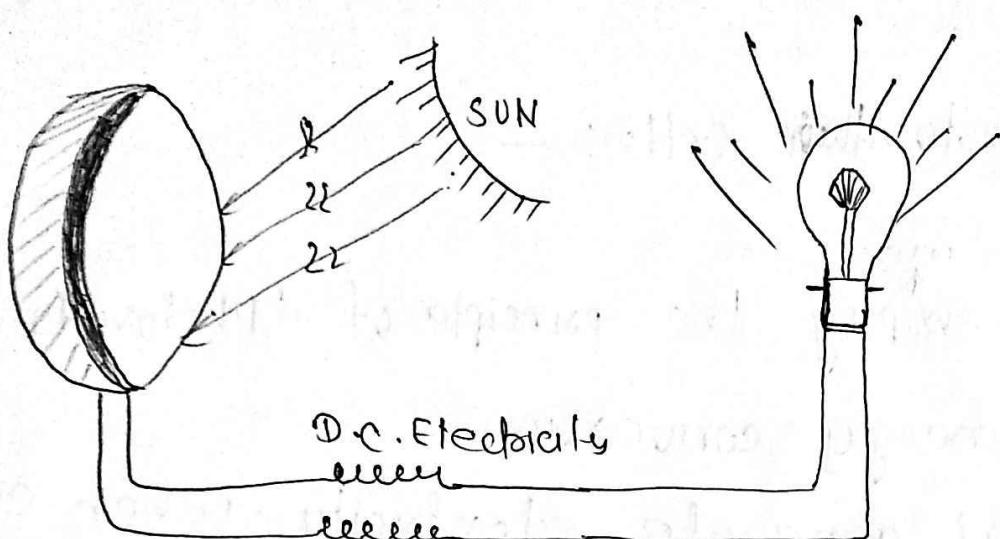


Fig.(1) representation of a solar cell.





Solar cell or photovoltaic cell

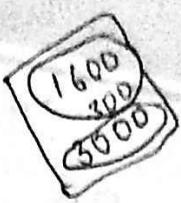
Fig(2): Schematic Diagram of a Solar cell.

\* A solar photovoltaic cell works on the following steps:—

1. Photon in sunlight hits the panel and absorbed by semi conducting material such as silicon.
2. The electrons present in the material are delocalised allowing to flow through the material to produce electricity. Due to spectral composition of solar cells the electrons are allow to move in single direction
3. An array of solar cells converts solar energy into the direct current which can be used.

2

## Applications of solar energy:—



1. solar water heating
2. heating and cooling of residential building
3. solar cookers
4. solar engines for water pumping
5. power generation by solar pond
6. solar photo voltaic cell etc

## ⇒ Non-conventional Energy sources :—

### Hydro power :—

- flowing water creates energy that can be captured and turned into electricity.
- The power available depend on the rate at which the water is flowing and the height which it falls down
- The hydro schemes are classified into four types :—

1. Large scale : where power output is about 2mw and above
2. Mini scale : where the output power is 100kw-200kw
3. Micro scale : 5kw-100kw
4. Pico scale : less than 5kw.

- The core of hydro scheme is the turbine, which is rotated by moving water.
- different types of turbines are used depending on the head and flow of the site.
  - Pelton turbines are used for low flow of water
  - Francis turbines are used for high flow and cross flow of water
  - Propeller turbines are used for large flow of water.

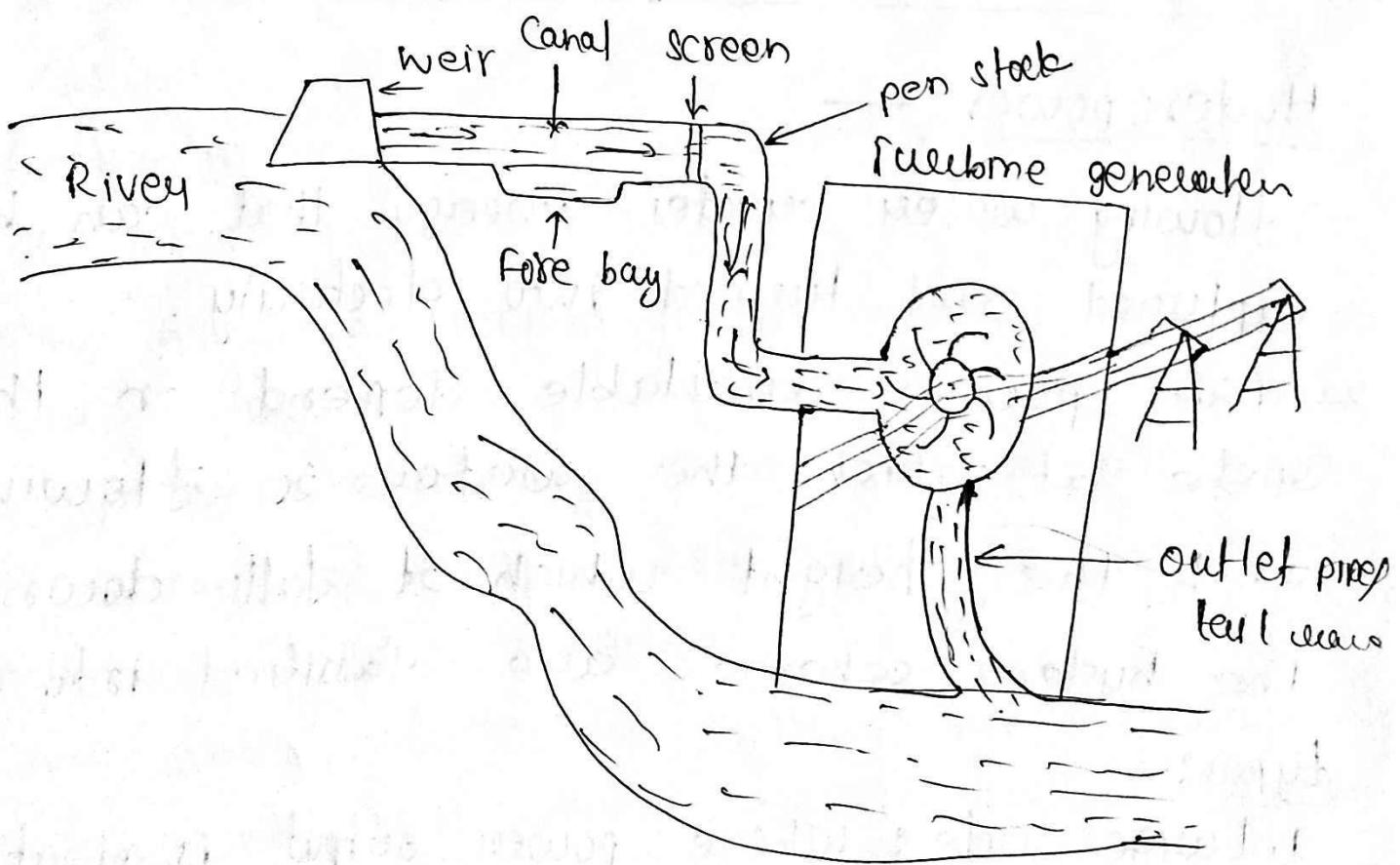


Fig: Generation of hydro power

- A small dam in the river bed directs the water to a settling tank (weir).

- The water and clean water flow in to a canal.
- A pipe to settling tank called forebay.
- water flows out into a pipe called penstock.

## # Geothermal Energy:-

- Geothermal energy is the heat from the earth
- Resources of geothermal energy range from shallow ground to hot water and hot rock
- The first geothermal electricity was produced in Italy in 1904.
- To produce geothermal energy electricity, wells sometimes 1.6 kms deep or more drilled into the underground reservoirs and very hot water that drives turbines and turbines drive electricity generators.

Power  
Three types of geothermal plants : —

- ① dry steam
- ② flash
- ③ binary



1. Dry steam geothermal generator takes steam out of fractures in the ground and uses it directly to drive turbines.

2. Flash geothermal plants pull deep, high pressure hot water into cooler, low pressure water

3. Binary geothermal plants, the hot water is passed by a secondary fluid, with much lower boiling point than water, producing vapour of the secondary fluid, which can drive turbine

→ Most geothermal plant in future will be binary plants

→ Geothermal plants have advantages over other thermal plants, that no fossil fuel is burned, no emission of  $\text{CO}_2$  and other gases and conversion

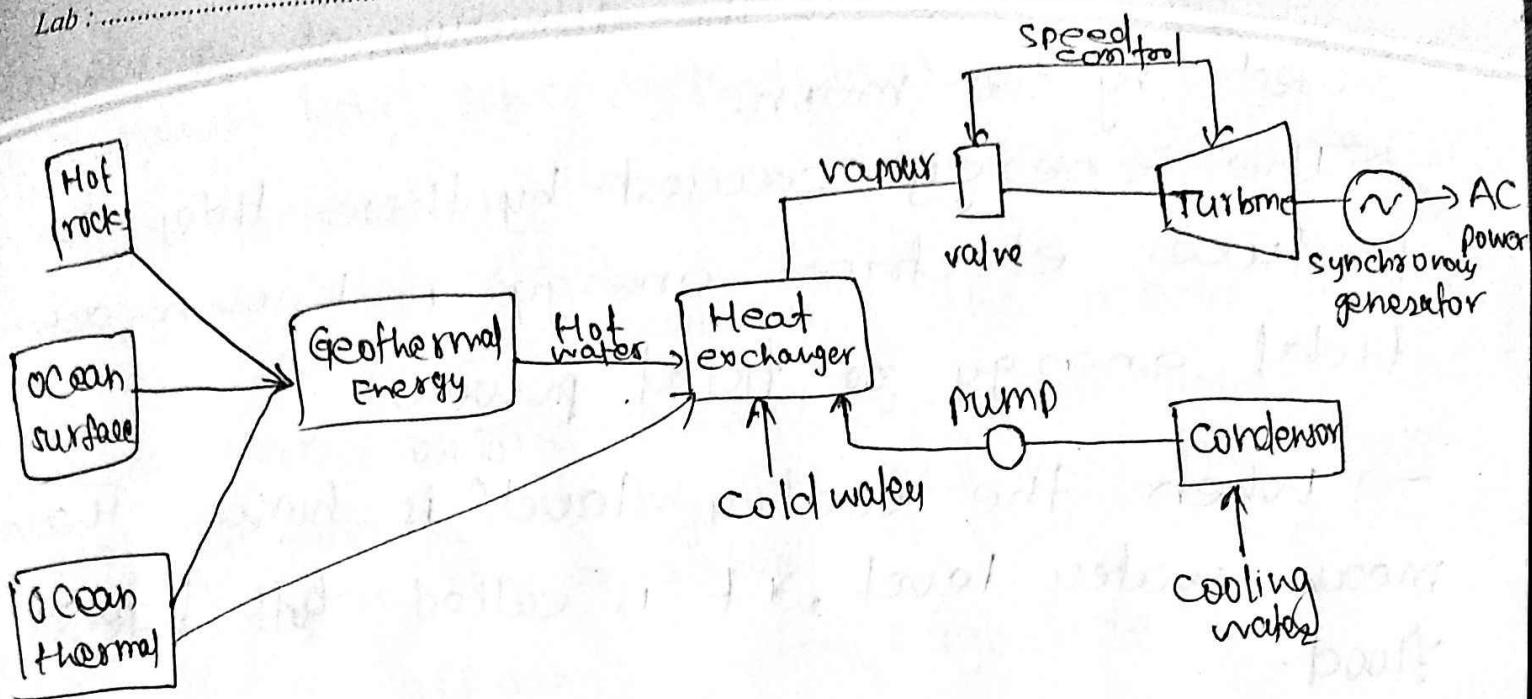


Fig: geothermal power generator (Binary system)

## # Tidal and Wave Power : —

- Tidal power is also called tidal energy.
- It is a form of hydro power that converts the energy obtained from tides into electricity.
- Tidal energy have potential for future electricity generation
- Tides are more predictable than wind energy and solar power, but tidal energy is more costly and limited availability of sites.
- The world largest tidal power plant in France.



→ Tidal is a periodic rise and fall of water level of sea due to the attraction of sea water caused by the moon.

→ The energy caused by these tides to produce electrical energy is known as tidal energy or tidal power.

→ When the water level<sup>of sea</sup> is higher than mean water level, it is called full tide or flood.

→ When the water level is below the mean water level of sea, it is called a Ebb tide.

Tidal power is generated in four methods:

### 1. Tidal steam generator (TSG):

→ This method make use of the kinetic energy of moving water to power turbines in a similar way as wind power turbines.

→ These turbines can be horizontal, vertical, open or ducted and placed near the bottom of the water column.

### 2. Tidal barrage method:

→ Tidal barrage make use of the potential energy difference of high and low tides.

### 3. Dynamic tidal power method (DTP):—

- The interaction between potential and kinetic energy in tidal flow.
- Long dams are built into the ocean without enclosing an area, leading to a significant water level difference producing low and high tides from which power is generated.

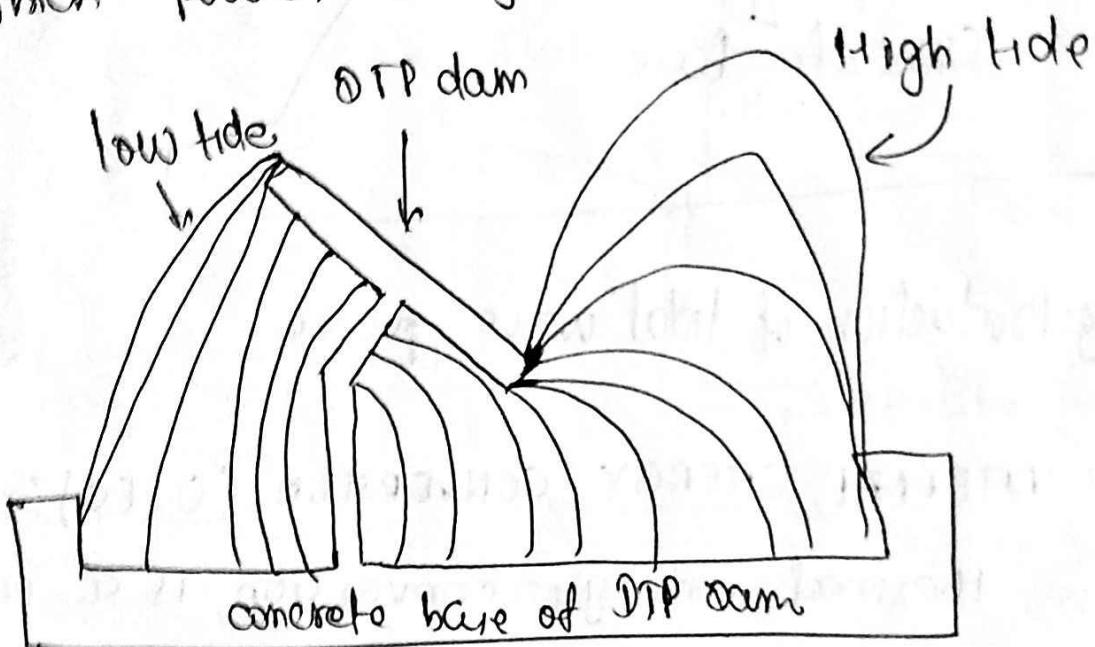


Fig. Top down view of a DTP dam

### 4. Tidal lagoon:

- A newer tidal energy design is to construct circular retaining walls embedded with turbines that can capture the potential energy of tides.



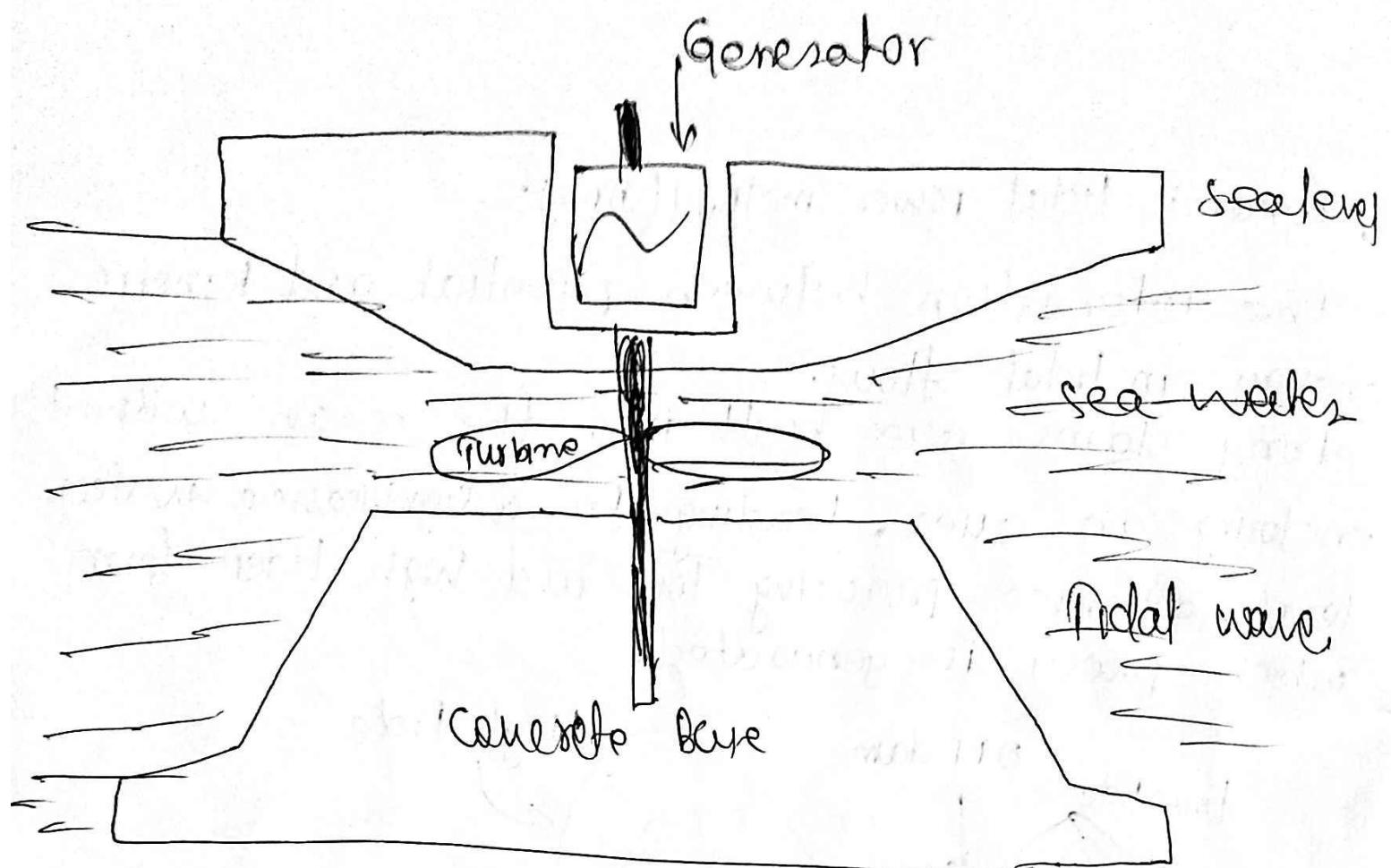


Fig: Production of tidal wave power

### # OCEAN THERMAL ENERGY CONVERSION (OTEC):—

- ocean thermal energy conversion is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water.
- OTEC is base loaded electricity generation
- OTEC theory was developed in 1880 and constructed in 1926.

## Three Types of OTEC:

### 1. closed cycle systems:

→ These systems use fluid with a low boiling point such as ammonia ( $B.P = -33^{\circ}\text{C}$ ) to power a turbine to generate electricity.

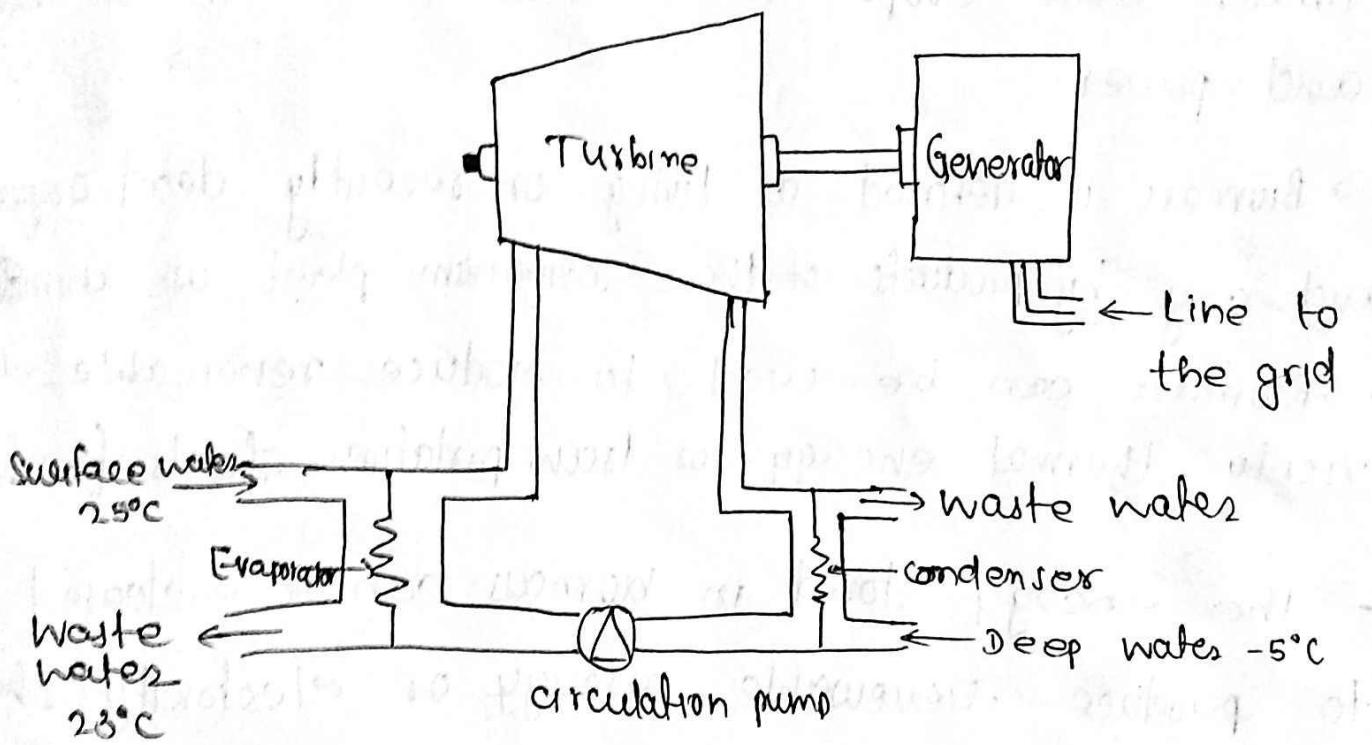


Fig: closed cycle OTEC plant.

### 2. Open cycle OTEC:

→ open cycle OTEC uses warm surface water directly to make electricity

### 8. Hybrid OTEC:

→ A hybrid cycle combines the features of closed and open cycle systems.

### 9. BIOMASS & BY-PRODUCTS.

→ The term biomass refers to organic matter such as timber and crops to be burnt to generate heat and power.

→ Biomass is defined as living or recently dead organisms and any by-products of those organisms plant or animal.

→ Biomass can be used to produce renewable electricity, thermal energy or transportation fuels (biofuels).

→ The energy stored in biomass can be released to produce renewable energy or electricity or heat.

The most common biomass feed stocks are:

1. Grains and starch crops like sugar cane, iron, wheat, sugar beets and industrial sweet potatoes.

2. Food waste

3. Forestry materials

4. Animal by-products

5. Energy crops.

## \*UNIT-V\*

### PART-A

## \*SPECTROSCOPIC TECHNIQUES\*

\*Spectroscopy:- Spectroscopy involves the interaction between electromagnetic radiation and the substance under investigation.

Electromagnetic Spectrum:- The arrangement of all types of electromagnetic radiations in order of their increasing order of frequency and decreasing order of wavelength from Radio waves to Gamma rays is known as electromagnetic Spectrum.

\* Radio waves -  $>0.1\text{ m}$

\* Micro waves -  $0.1\text{ m} - 1\text{ mm}$

\* Infra-Red -  $1\text{ mm} - 700\text{ nm}$

\* Visible Light -  $700\text{ nm} - 400\text{ nm}$

\* ultra Violet -  $400\text{ nm} - 1\text{ nm}$

\* X-rays -  $1\text{ nm} - 10^{-3}\text{ nm}$

\* Gamma Rays -  $<10^{-3}\text{ nm}$

#### \* Uses :-

- Radio waves are used in radio and television signals
- Microwaves are used in cooking and Radar telecommunication purpose.
- Infra-red rays are used to produce over heat to the body.
- Visible light produce Seven different colours to the object like visibility.
- Ultra violet rays are used in Luminiscence lamps and light vision Spectacles.
- X-rays are used in medical purpose to Scan body parts like lungus.
- Gamma rays are used to control the density of Cancerous cells.

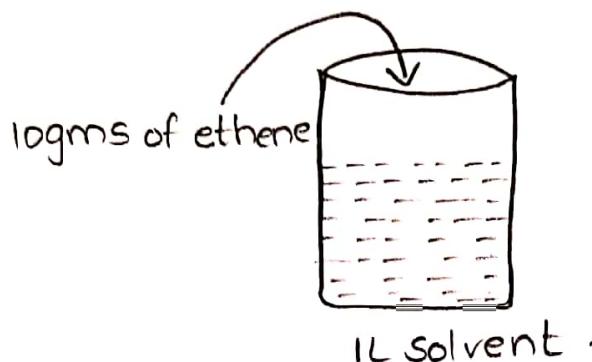
#### \* Uv SPECTROSCOPY :-

UV Spectroscopy is the measurement of the attenuation of a beam of light passing through a Sample or after reflection from Sample Surface.

#### \* ADSORPTION LAWS :-

- i) Beer's Law:- "When a beam of monochromatic light passed through a substance dissolved in a Non-absorbing medium, The adsorption of light is directly proportional to the molar concentration of Solution"

$$\log_{10} \frac{I_0}{I} \propto C.$$



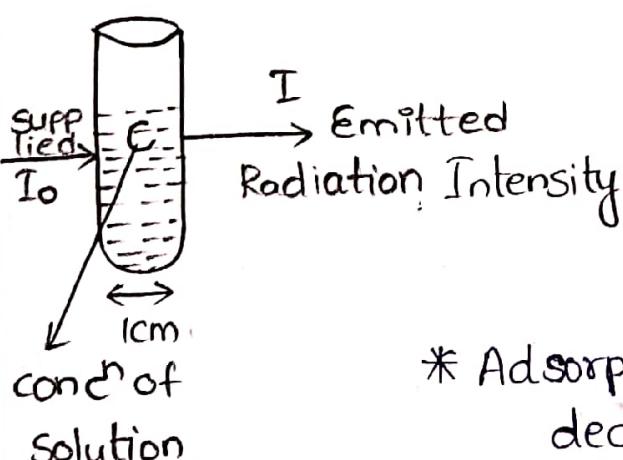
ii) Lambert's Law: "when a beam of light is passed through a substance the absorption of light is proportional to the path length of the substance".

$$\log_{10} \frac{I_0}{I} \propto l$$

From Beer's and Lambert's law,

$$\log_{10} \frac{I_0}{I} \propto cl.$$

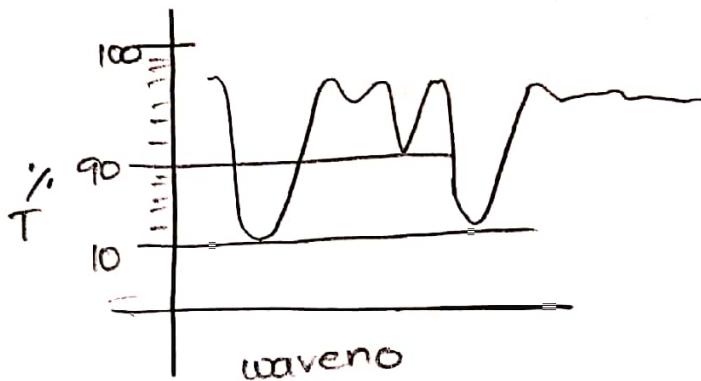
$$\log_{10} \frac{I_0}{I} = Ecl$$



$$\begin{aligned} & (I_0 - I) \\ & (\log I_0 - \log I) \\ & \log \frac{I_0}{I} \end{aligned}$$

\* Adsorption Increases transmission decreases

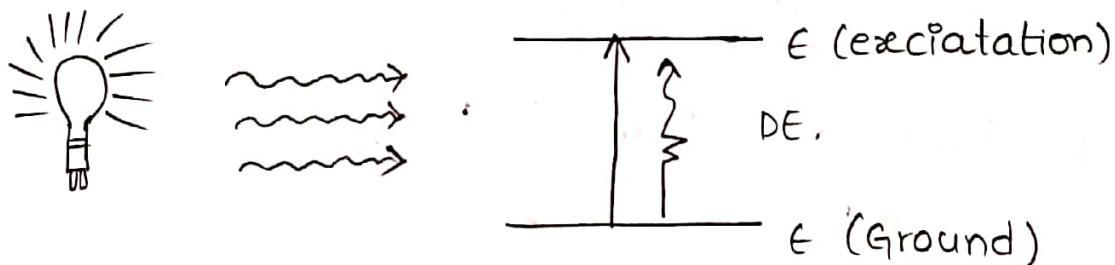
$$\uparrow A \propto \frac{1}{T} \downarrow$$



\* Nature of Solvent:-

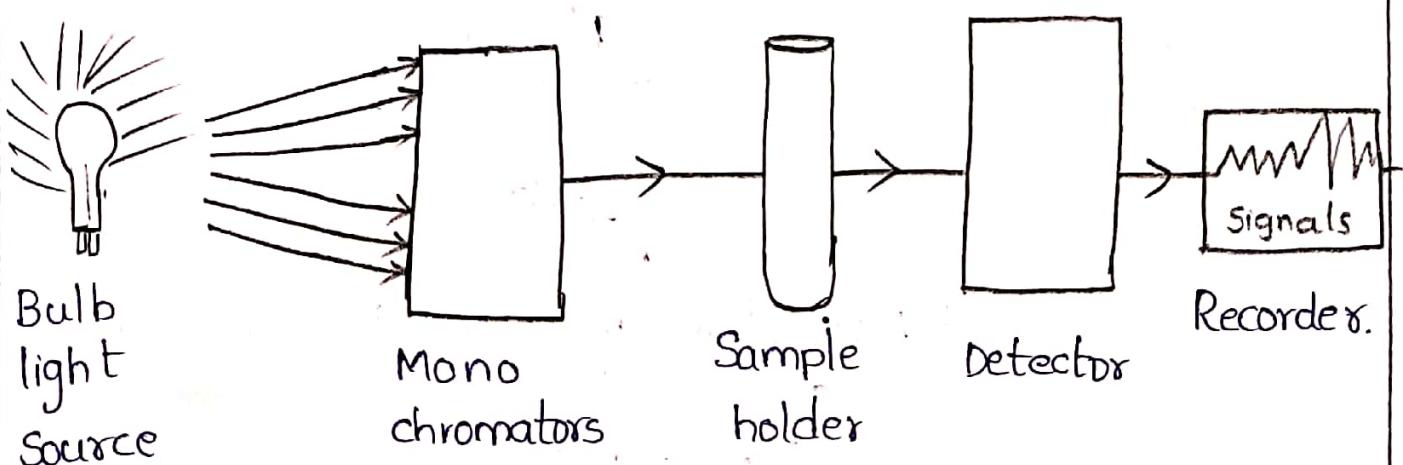
- Solvent should not absorb any kind of Radiation
- It should not be ~~Solvent~~ polar Solvents.

\* Principle of UV-Spectroscopy:-



\* Instrumentation of UV spectroscopy:-

Components.



## 1) Light Source:-

- a) Deutrium lamp - UV region (200-400 nm)
- b) Tungsten halogen lamp - Visible region (400-750 nm)

2) Monochromator:- Monochromator is device use to resolve wide bond of polychromatic light radiation into narrow bond of monochromatic radiation.

Eg:- Filters, prisms, Graftings.

3) Sample holder:- Cuvette is used as Sample holder made up of Quartz.

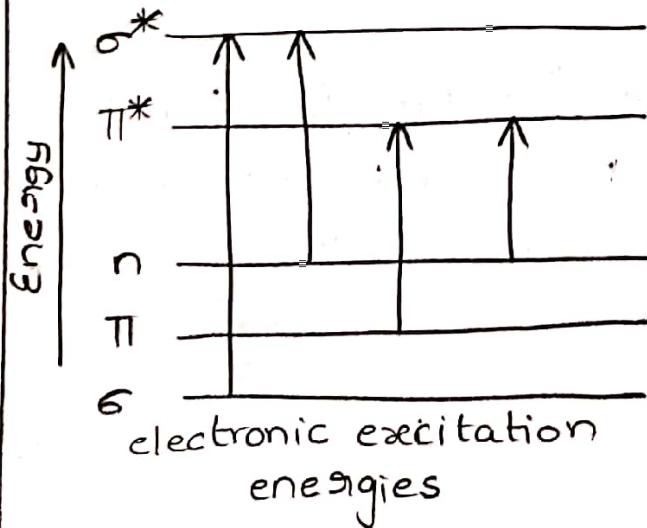
4) Detectors:- It will converts light energy into electrical Signal that are displayed on readout devices

- \* Barrier layer cell
- \* photo tube.
- \* photo multiplier tube (most using)
- \* Thermo couple.
- \* Balo meter.

5) Amplifier & Recorder:- Amplifier Amplifies Signal coming from detector and recorder records them which is displayed on readout device.

## \* Theory of electronic Spectroscopy:-

- when the molecule absorbs UV (or) Visible light, its electrons get promoted from ground state to the higher energy state.
- In the ground state, the spins of electrons in each molecular orbital are essentially paired.
- In the higher energy state, if the spins of electrons are paired is called excited Singlet state.
- On the other hand spins of the electrons excited state are parallel is called excited Triplet state.
- Excited triplet state is more stable than excited Singlet state.
- Excited Singlet state converts to triplet state emission of energy of light.
- The highly probable transition due to absorption of quantised energy involves the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital.



$$\sigma^* > n > \sigma^* \\ > \pi > \pi^* > n > \pi^*$$

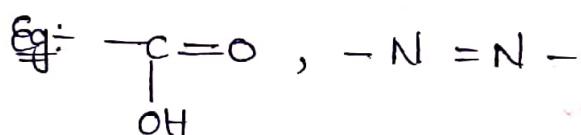
\* **CHROMOPHORES**:- chromophores are covalently bonded moieties with any compound and responsible for absorption of UV-visible radiations.

Eg:- Aldehyde, ethylene, carbonyl etc...

① chromophores with  $\pi-\pi^*$

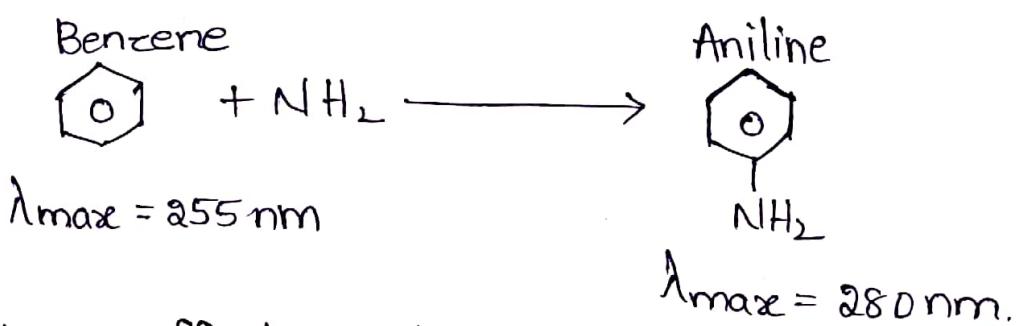


② chromophores with  $n-\pi^*$



\* **AUXOCHROMES**:- Any moiety which does not show any specific colour (or) absorption when separated but when combined with any chromophores it increases the absorption wavelength towards longer wavelength towards by formation of a new chromophore.

Eg:-  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{OR}$ ,  $\text{NHR}$ ,  $-\text{SH}$  etc...



\* Factors effecting absorption:-

1) Absorbing Compounds  
 chromophores, Auxochromes.

2) Solvent effect Benzene 255 nm

CCl<sub>4</sub> 265 nm

chloroform 290 nm

Avoid these  
 Solvents.

3) Temperature.

→ low temp is suitable for UV-spectroscopy.

4) Inorganic Moieties

→ Increases the absorption.

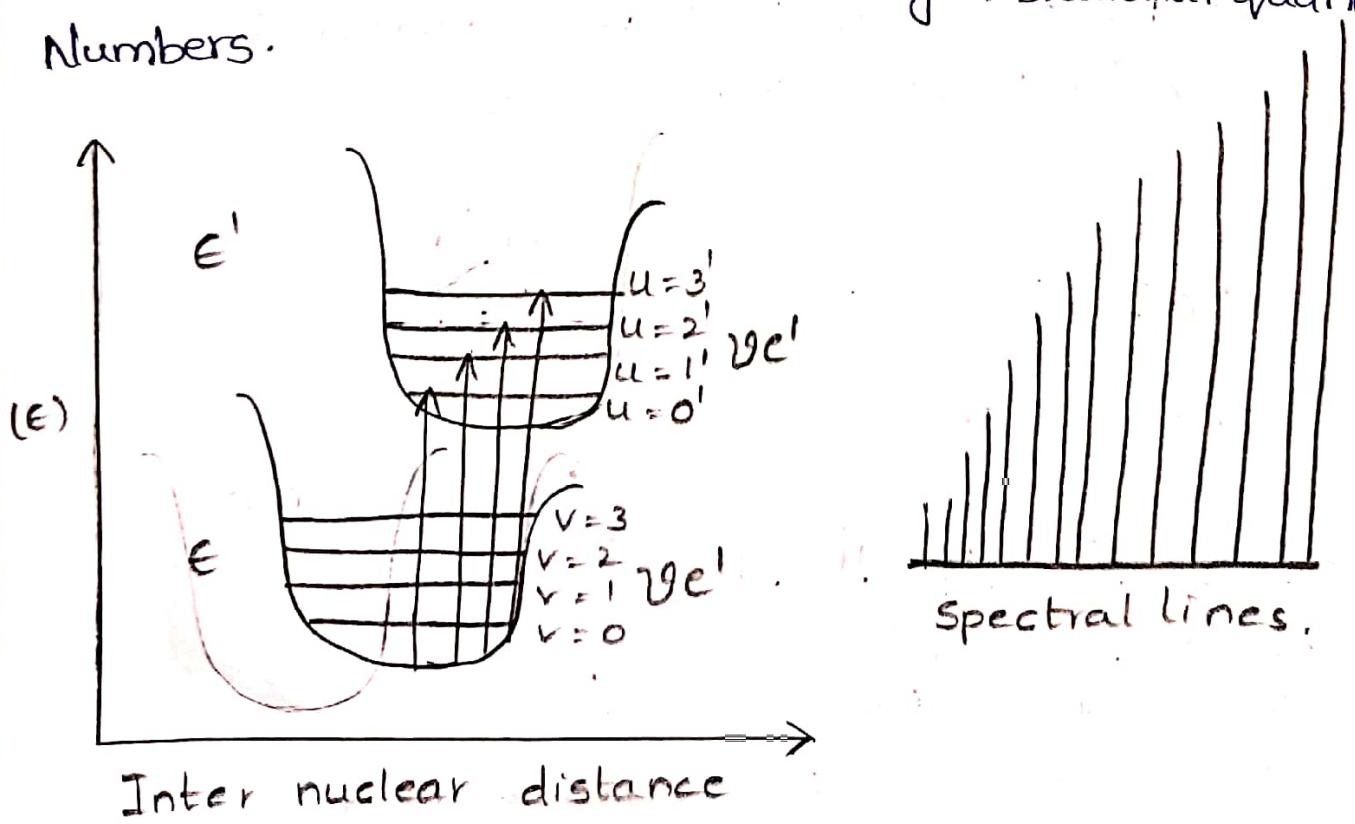
→ Complex Inorganic Moieties →  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$

→ Single inorganic Moieties →  $\text{Ag}$ ,  $\text{Au}$  etc...

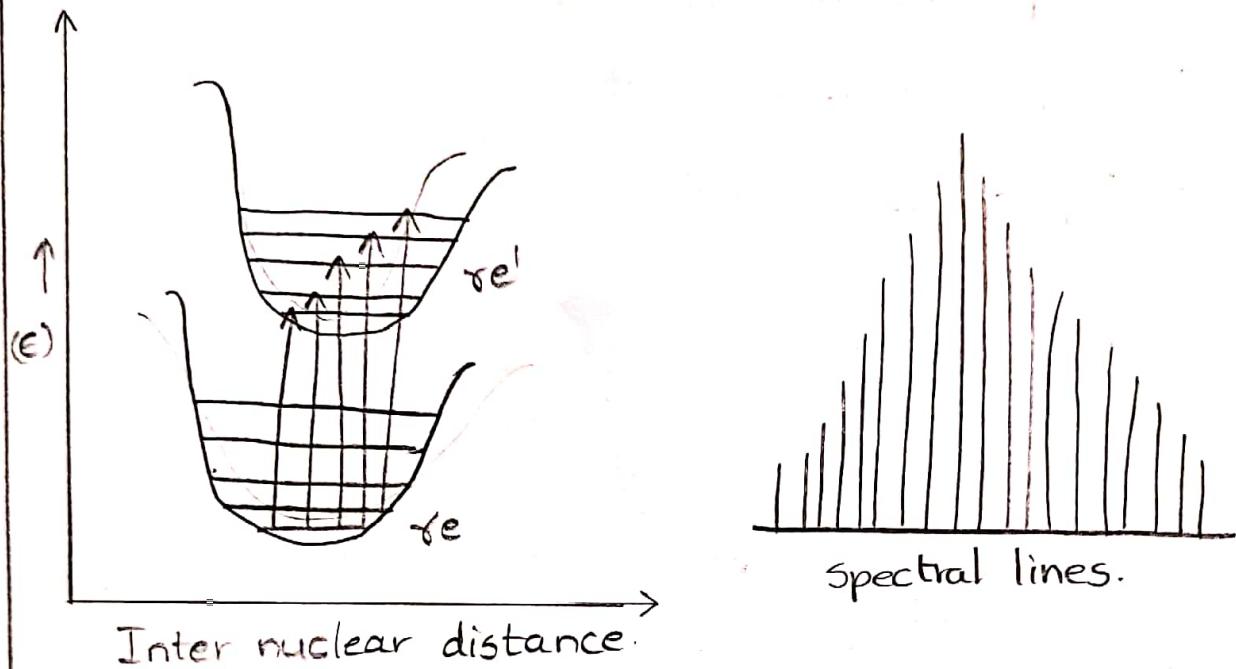
\* Franck Condon Principle:-

"An electronic transitions takes place so rapidly that a vibrating molecule does not change its inter-molecular distance during the transitions"

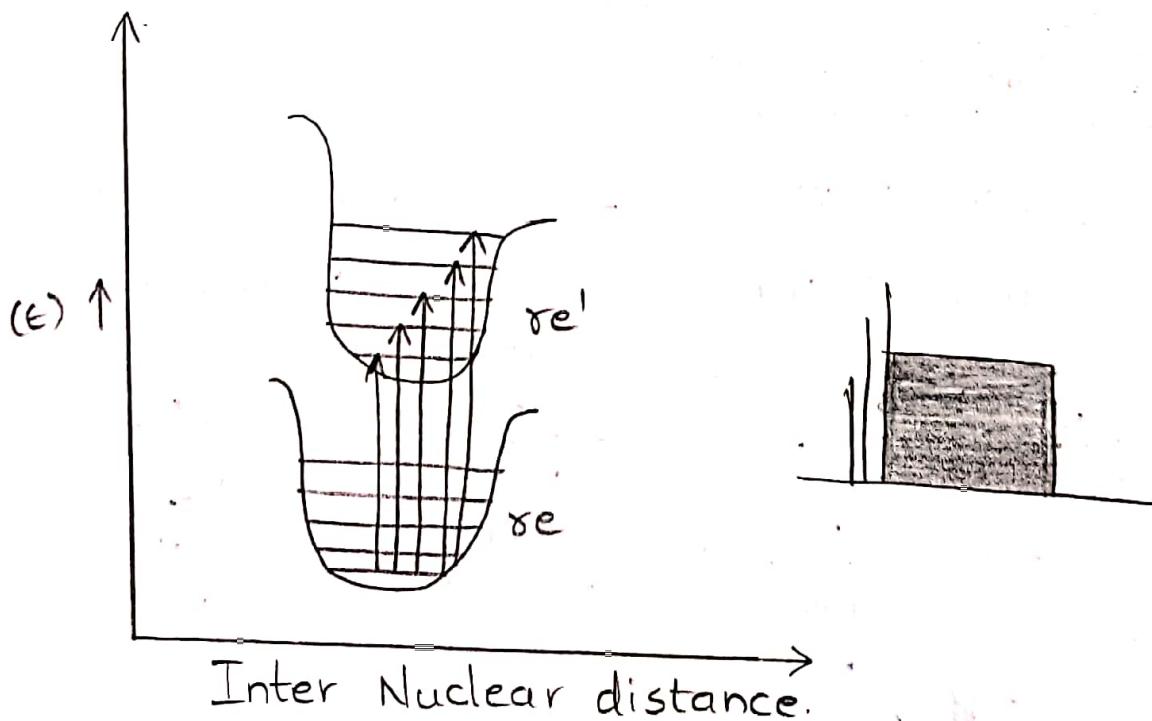
Case i:- when  $\nu e = \nu e'$  the intensity of the spectral lines increases with increasing vibrational quantum numbers.



Case - ii :- When  $r_e' > r_e$ . The intensity of the spectral lines for intermediate vibrational levels is very high compared to the lower and higher vibrational levels.

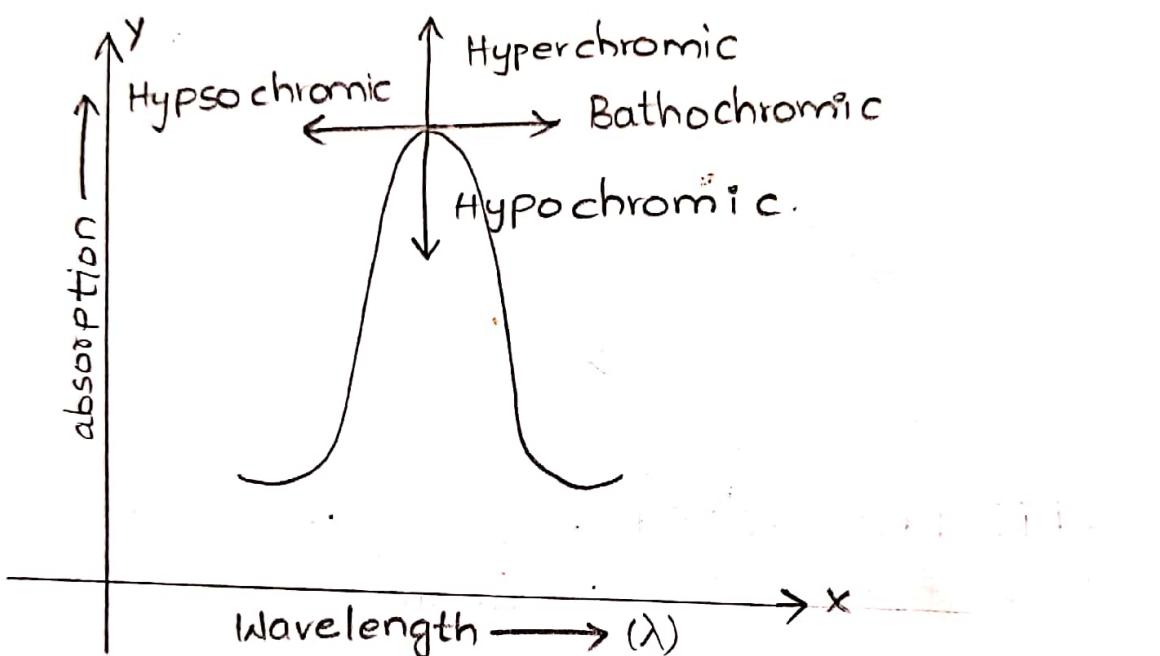


Case - iii :- When  $r_e' \gg r_e$ . we can observe only one (or) two lines followed by continuum.

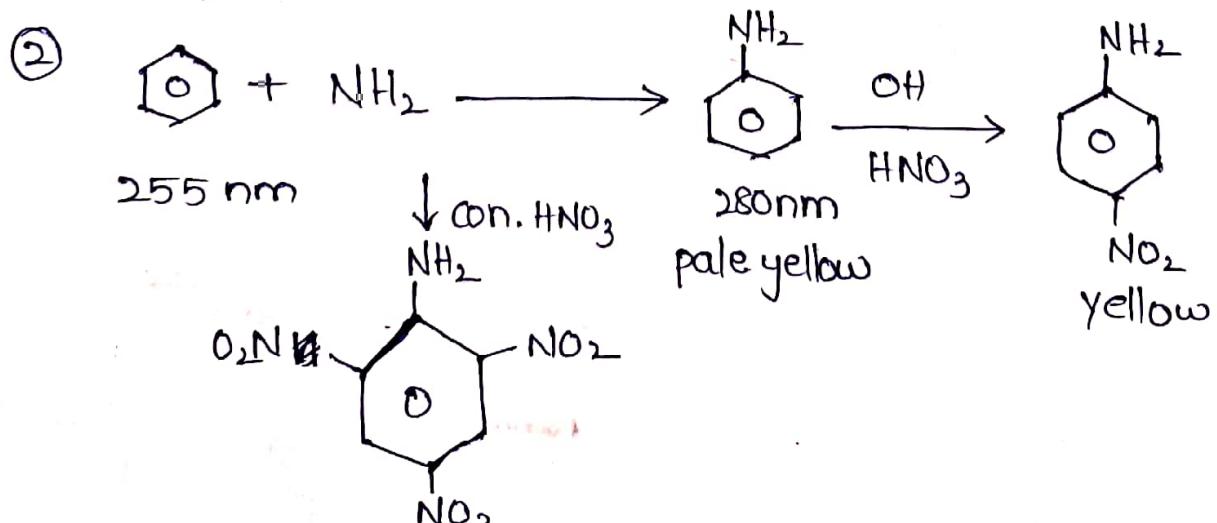
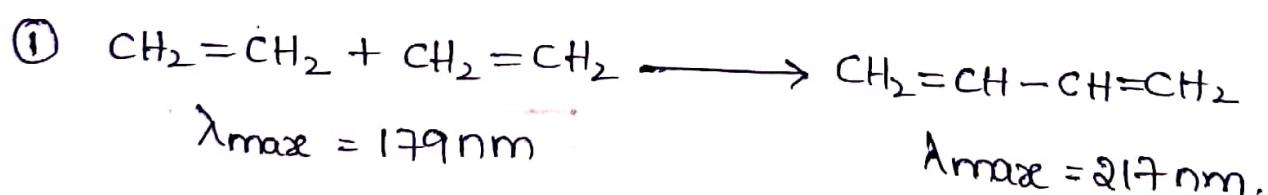


## \* INTENSITY SHIFTS:-

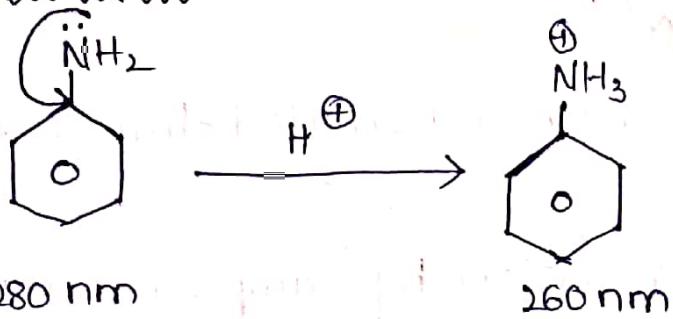
- \* Bathochromic effect (or) Red shift.
- \* Hypsochromic effect (or) Blue shift.
- \* Hyperchromic effect.
- \* Hypochromic effect.



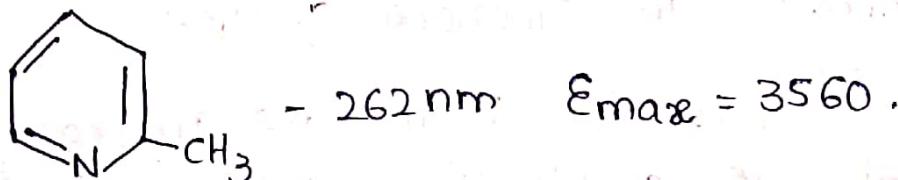
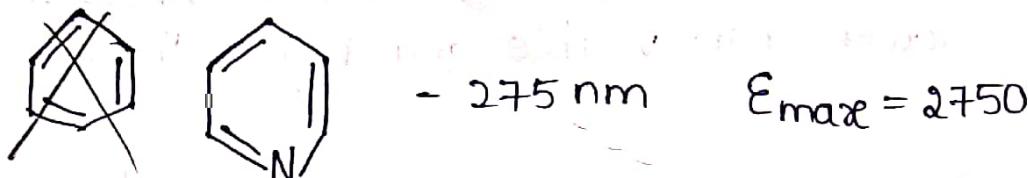
## \* Bathochromic shift:-



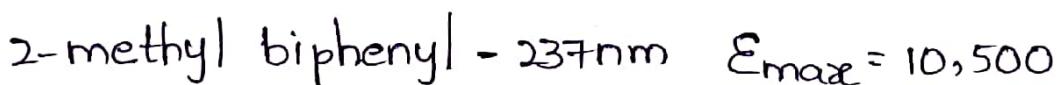
### \*Hypsochromic Effect:-



### \*Hyperchromic Effect:- (Increasing Intensity)



### \*Hypochromic effect:- (Decreasing Intensity)



### \* Applications of Uv Spectroscopy:-

- 1) Determination of Molecular weight of a molecule.
- 2) Determination of impurities present in the sample.
- 3) Unknown concentration of a solution can be determined by this Spectroscopy.
- 4) characterisation of aromatic compounds and in detect -ion of  $\pi$  Conjugation.

## \* FT-IR SPECTROSCOPY:-

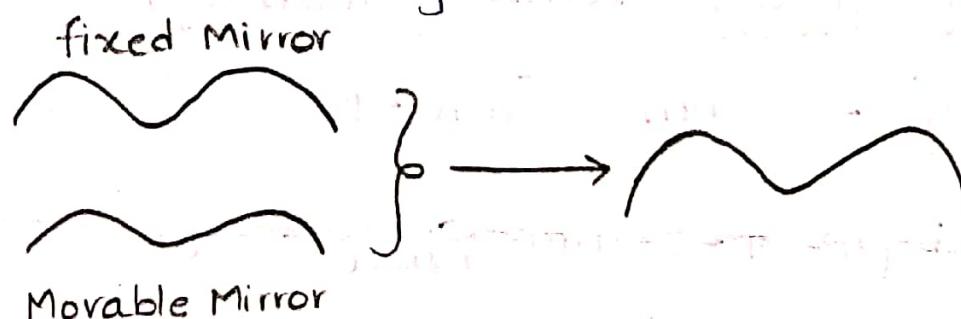
→ FT-IR means Fourier transmitted - Infra red Spectroscopy.

Absorption of IR radiation by Sample result in vibration transition.

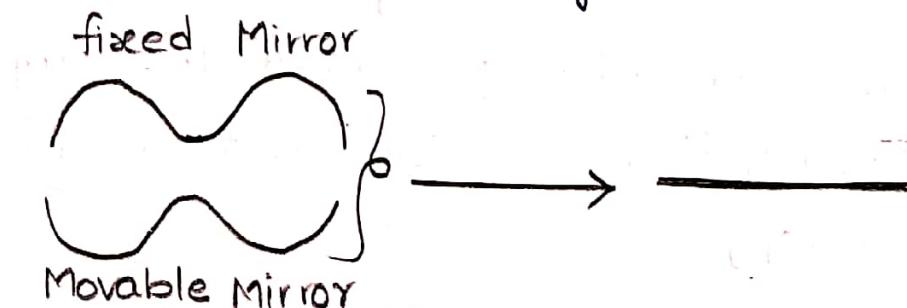
→ Infrared waves have wavelengths longer than visible and shorter than micro waves, and have frequencies which are lower than visible and higher than micro-waves.

→ IR spectra are mainly used in structure elucidation to determine the functional groups.

→ If the radiation beams are in phase the beams will interfere constructively and resultant amplitude will be twice as high.



→ If the radiation beams are out of phase the beams will interfere destructively and cancelling out each other.



## \* Instrumentation of FT-IR Spectrometer Components:-

① Source

② An optical System which uses Interferometer.

    (a) Beam splitter.

    (b) stationary Mirror.

    (c) Moving Mirror.

③ Sample

④ Detector

1) Source:- Nernst glower, Global source, Tungsten lamps, Mercury arc.

2) Beam splitter:- It is made of material which has 50% refractive index.

a) For Far IR:- Nylar film sandwiched between halide plate of low refractive index solid used.

b) For Middle IR:- Thin film of Ge-(or)Si deposited on CSI (or) CSBR (or) KCL (or) NaCl.

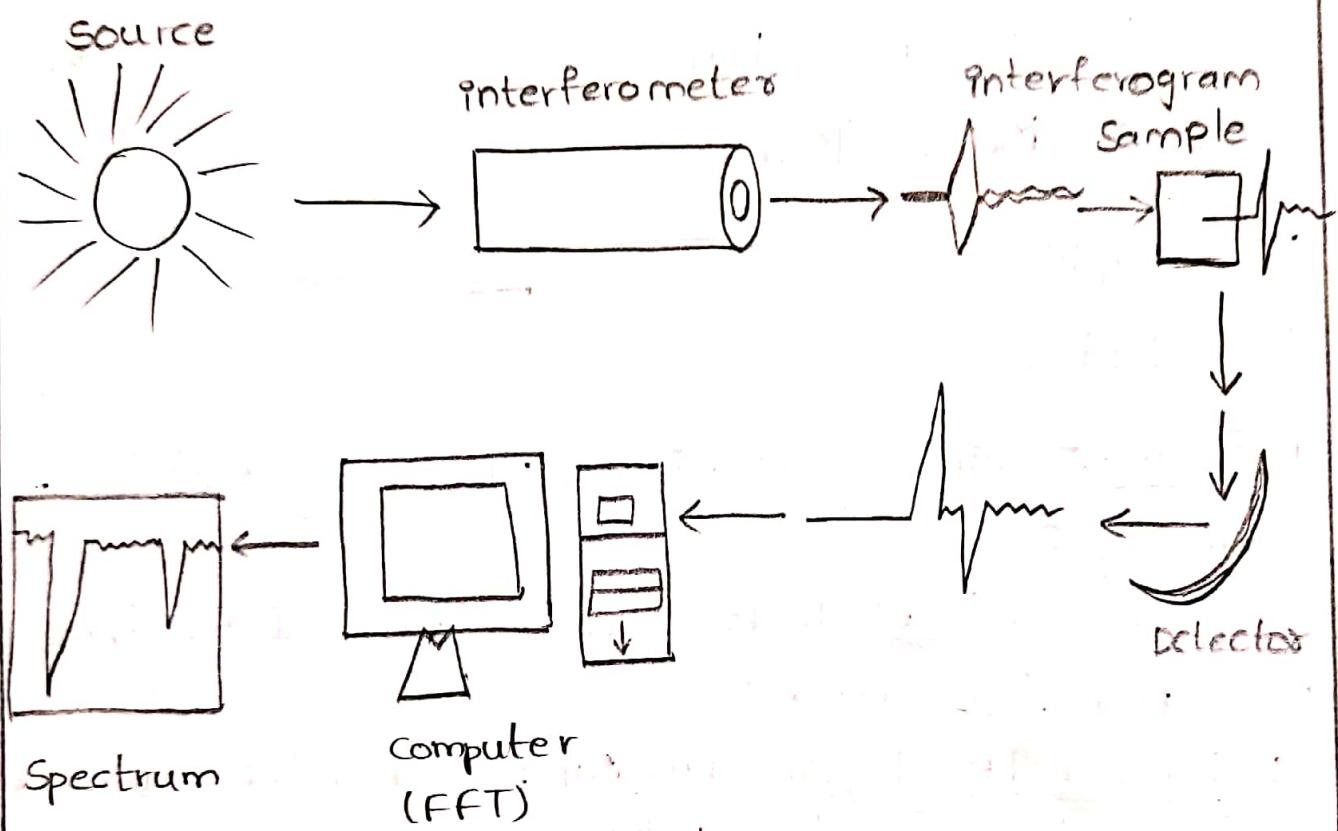
c) Near IR:- Thin film of ferric oxide deposited on calcium chloride.

3) Detector:- pyro electric detector used

It consists of two perpendicular mirrors. One is stationary other is movable.

→ Movable Mirror is controlled by 'HeNe laser (632.8 nm)

- Between these mirrors set a beam splitter at  $45^{\circ}$  from the initial position of the movable mirror.
- A parallel beam of radiation from the IR Source is passed on for the mirror through the beam splitter.

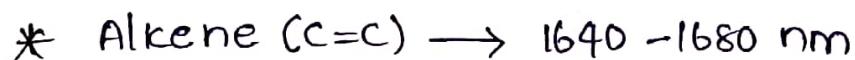
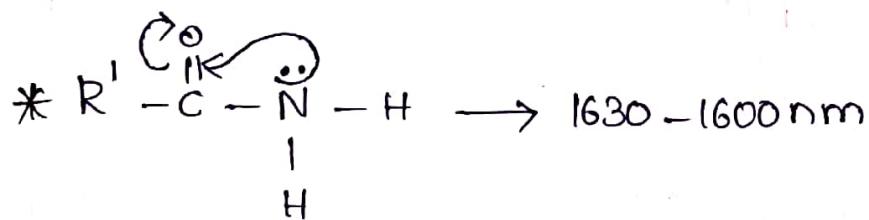
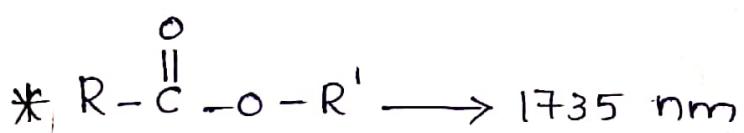
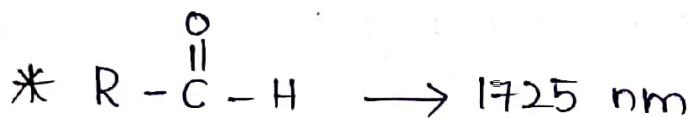
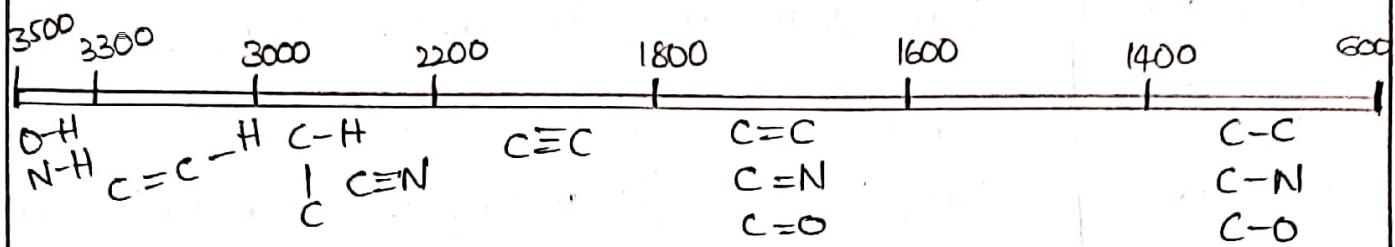


### \*Advantages:-

- 1) Better Sensitivity and brightness
- 2) Allows Simultaneous measurement over the entire wave number range.
- 3) Requires no slit device.
- 4) We can determine even Small Quantity of analyte.
- 5) Structural studies of cells & Bacterial.
- 6) Identify chemicals from paints, polymers, coatings, drugs, and contaminants.

→ Identify types of chemical bonds in functional groups.

\* IR of Organic Compounds:-



## \* MAGNETIC RESONANCE IMAGING:-

\* felix block & Edward purcell - 1946.

\* Raymond Damadian used in medical purpose.

MRI:- "MRI is ideal for diagnosis of conditions in tissues or ligaments. Any type of soft injury in the brain including Tumor and in the spine would be better spotted using an MRI"

Primary Magnetic field

Gradient coil.

RF coil

PATIENT

RF coil

Gradient coil

Primary magnetic field

## \* MRI Components:-

### Super Conducting Magnet:-

They are large magnets that takes most of the space in the MRI machine. It creates a powerful magnetic field, strength of Super conducting magnetic field is 5000 - 20,000 gauss.

Gradient Magnets:- Variant Magnetic field which allows different parts of the body to be scanned the ray from 180 Gauss to 270 gauss.

Coils:- Coils that transmit radiofrequency waves into the patient's body these are different for different body parts.

\* Teeth - Bone  $\rightarrow$   $H_2O$  poor tissue because of these are prepared by calcium.

\* Procedure:-

- 1) patient reclines on the table and is moved into MRI machine.
- 2) patient is moved into active magnetic field.
- 3) Hydrogen atom with in patient's body align in response to magnetic field.
- 4) Radio frequency pulse is directed through coils into body part being scanned.
- 5) Radio frequency causes protons in certain hydrogen atoms to spin at a specific frequency.
- 6) Gradient magnets after the magnetic field following the machine to scan very precise sections of the body
- 7) Radiofrequency pulse is turned off causing hydrogen protons to release absorbed energy.
- 8) Coils detect the energy released and sends the data to the computer which generates MRI Images.

### \* Advantages:-

- 1) Sectional Images in any plane heart vessels, chambers and valves.
- 2) Sensitive to grey & white matter.
- 3) No use of Ionising radiation.

### Disadvantages:-

- 1) Expensive Machine.
- 2) No Image for Bones & Teeth.
- 3) Not suitable for cardiac pacemakers implants.

### \* COMPUTED TOMOGRAPHY (CT):-

CT Scan is ideal for any type of skeletal injuries. If there are bone injuries in the head, spine (or) chest then CT Scan is the best way to identify problem.

⇒ X-ray Images are taken from different angles.

### \* Procedure:-

- 1) The patient will need to lie down on a motorized examination table that slides into a doughnut shaped CT scanner machine.
- 2) In most cases the patient will lie on their back, facing up, but sometimes they may need to lie facedown (or) sideways.
- 3) After one x-ray picture the couch will move slightly and then machine will take another image and so on. The patient needs to lie very still for the best result.

- 4) During the scan, everybody except for the patient will leave the room. An intercom will enable two-way communication between the radiographer and the patient.
- 5) If the patient is child, a parent (or) adult might be allowed to stand (or) sit near by but they will have near a lead apron to prevent radiation exposure.

\* Uses:-

- 1) Soft tissues.
- 2) The pelvis.
- 3) Blood vessels
- 4) lungs.
- 5) Brain
- 6) abdomen.
- 7) Bones.

\* Disadvantages:-

- 1) There is a chance to develop cancer less than 1 in 2000.
- 2) Pregnant, breast feeding womens avoided
- 3) Claustrophobia patients avoided.

prepared by

Sarveshelli Venkata Rao

M.Sc B.Ed

# NON CONVENTIONAL ENERGY SOURCES AND ① STORAGE DEVICES

## Non conventional energy sources:-

Non conventional energy sources are those energy sources which are renewable and ecologically safe such as solar energy, wind energy, biomass energy, ocean energy, geothermal energy etc. The importance of increasing the use of non-conventional (or) renewable power was recognized in India in the early 1970.

\* Solar energy:- Solar energy in India is utilized through photovoltaic route and thermal route

\* Biomass:- power generating systems based on biomass combustion as well as biomass gasification were launched in different places in central India.

\* Wind energy:- Wind energy is used for power generation. Wind generator is used to generate power.

\* Geothermal energy:- Geothermal energy generated from hot springs. It is generated in H.P and Jammu & Kashmir.

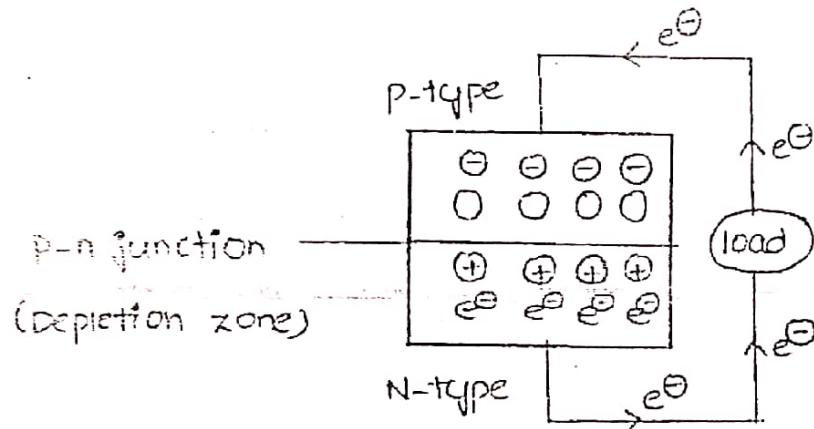
\* Energy from urban & industrial waste:- power is generated from urban waste, which is an practice in Timarpur, Delhi and Tamilnadu.

## Solar cell / photo voltaic cell:-

A device which converts from sun rays into electricity is known as solar cells.

\* solar cells are prepared from semiconductor material like silicon.

\* silicon is doped with 15<sup>th</sup> and group 13<sup>th</sup> elements to produce p-type and n-type semiconductor materials



N-type semiconductor materials results in an excess of electrons and p-type semiconductor materials results in an excess of holes.

Elections diffuse across the p-N junction from the n-type material creating positive charges in the n-type material.

Holes diffuse across the p-N junction from the p-type material creating negative charge in the p-type material.

### Depletion of ozone:

The area near the p-N junction is called depletion ozone because there are no charge carries present.

The separated the positive and negative charge created on electric field across the depletion ozone

→ When light is absorbed by the semiconductors extra free electrons and holes are created in the electric field makes the electron flow to the n-type material and holes flow to the p-type material.

\* The separation of charges creates a potential difference across the p-n junction electrons flow through an external wire to the p-type material to unite with the holes producing an electric current.

$$I = I_p - I_D - I_{sh}$$

where  $I$  = output current in amperes

$I_p$  = light produced current in amperes

$I_D$  = Diode junction produced current in amperes

$I_{sh}$  = short current released in amperes

Materials used in the preparation of solar cells:-

1. crystalline silicon [like - poly silicon, ribbon silicon, mono crystalline silicon]
2. cadmium telluride
3. copper, Indium, Gallium, selenides [CuInGaSe] ie [CIGS]
4. cadmium, Arsenide multi-function material
5. dye sensitized cells  $\rightarrow$  Ru (Ruthenium), Arsenic
6. organic polymers like poly vinylene, poly propylene, carbon fullerenes

Applications of solar cells:-

1. To generate electricity

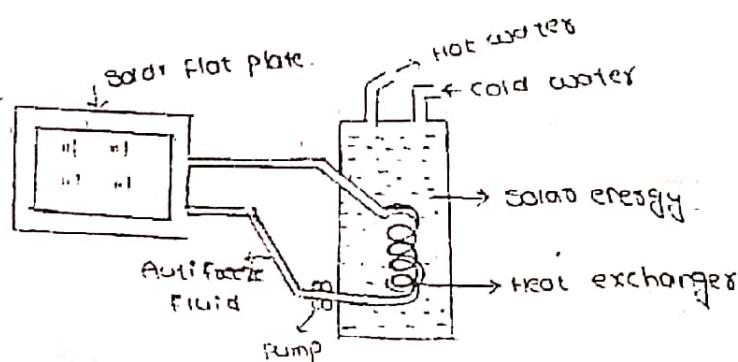
2. To prevent carbon foot print
3. These are used in agriculture sector to supply water from wells.
4. These are used as a water heaters
5. These are also used as a cooling of the water by using evaporation and condensation techniques
6. These are ecologically friendly resources.

### Solar Heaters:

Solar water heaters consists of a storage tank placed above the cylinder at a certain height. The cylinder is connected to copper pipes, which are able to absorb the solar radiations resulting in the heating of the water passing through the copper pipes.

### Working:

Water from the storage tank fills into the cylinder and reaches into the copper pipes, which are heated by solar radiations and there will be the formation of hot water. The hot water from the pipes enters the lower portion of the cylinder and reaches to the different sites.

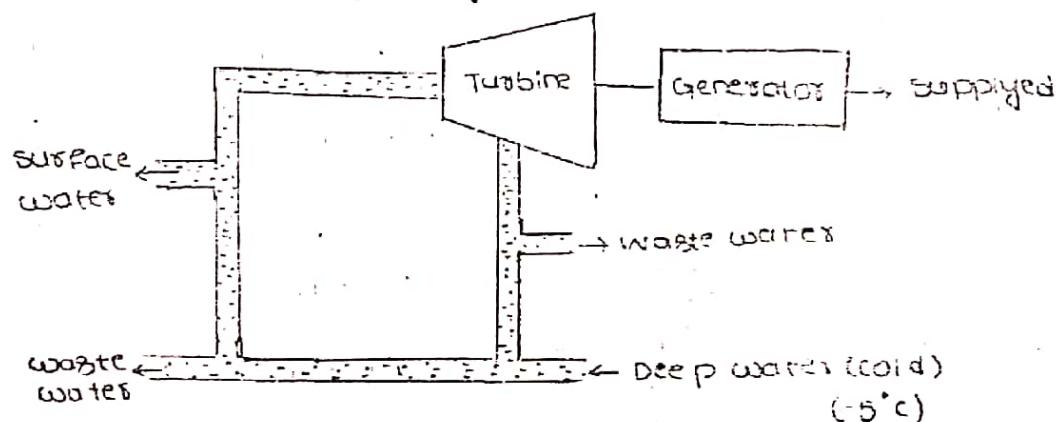


## Ocean Thermal Energy conversion (OTEC):

It is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water. OTEC plant pump large quantities of deep cold sea water and surface seawater to run a power cycle and produce electricity. This theory was developed in 1880 and constructed in 1926.

An amount of large quantity of cold water is a by-product, that can be used for air conditioning and refrigeration. There are three types of OTEC systems

- 1) closed cycle
- 2) open cycle
- 3) hybrid.



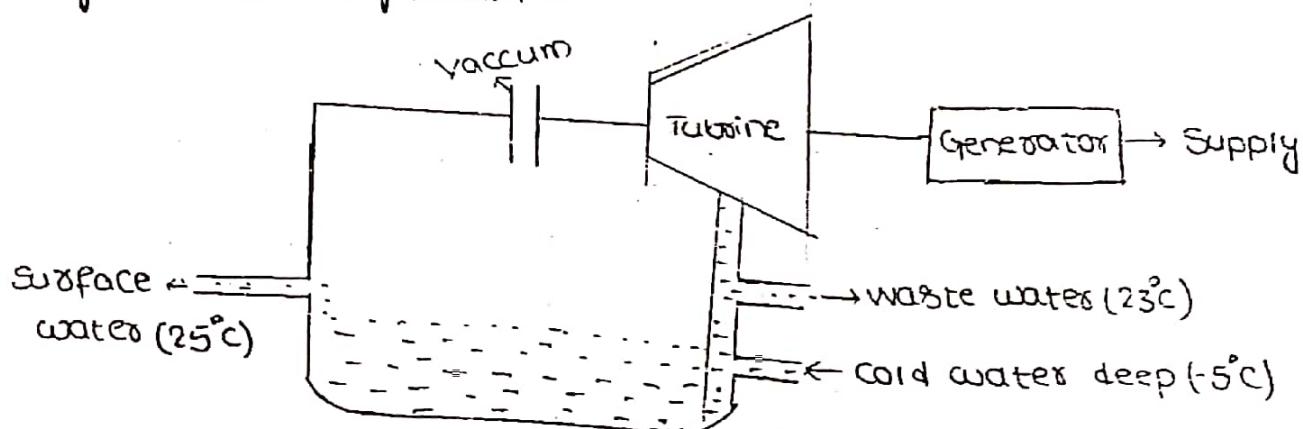
Here in the closed cycle, working fluid is ammonia used to power a turbine to generate electricity.

Warm sea water is pumped to heat exchanger, here the ammonia is vapourised and vapours of ammonia rotates the turbine and generates the electricity. The vapours with of ammonia is converted into liquid in the bottom heat exchanger by passing deep cold water and the liquid

ammonia again enters into the top heat exchanger and finally we will get cold water as byproduct coming from the bottom heat exchanger.

### Open cycle OTEC:

Open cycle OTEC uses warm surface water directly to make electricity. The warm sea water is first pumped into a low pressure container which causes it to boil. In some processes, the expanding steam drives low pressure turbine attached to an electrical generator. The steam leaves its salt and contaminates in the low pressure container to give pure fresh water. It is condensed to a liquid by exposure to cold temperatures from deep-ocean water. This method produces desalinated fresh water suitable for drinking, irrigation and agriculture.



### Hybrid OTEC:

A hybrid cycle combines the features of closed and open cycle systems. In a hybrid warm sea water enters a vacuum chamber & flash evaporated similar to open

cycle evaporation process. The steam vaporizes the ammonia working fluid of closed cycle loop on the other side of an ammonia vaporizer. The vaporized fluid then drives a turbine to produce electricity. The steam condenses with in the heat exchanger and provides desalinated water.

#### \* Tidal And wave power:-

Tidal power is also called tidal energy is a form of hydro power that converts the energy obtained from tides into useful forms of power mainly electricity. The world's first large scale power plant is the Rance tidal power plant in France.

The ocean tides on the earth are ultimately due to gravitational interactions with the moon and sun and the earth's rotation. Tidal power is practically inexhaustible. Movement of tides causes a loss of mechanical energy in the earth moon system due to the pumping of water through natural restriction around coastlines and consequent viscous dissipation at the seabed and turbulence.

This loss of energy has caused the rotation of the earth to slow in the 4.5 billion years since its formation during the last 620 million years. The period of rotation of the earth is slower than the rotation of earth since its formation.

Tidal power is taken from earth's oceanic tides.

The tidal forces are periodic variations in gravitational

attraction exerted by celestial bodies. Due to strong attraction to the oceans, a bulge in the water level is created, causing temporary increase in sea level when sea level is raised, water from the middle of the oceans is forced to move towards the shorelines creating a tide in an unfailing manner, due to consistent pattern of the moon's orbit around the earth.

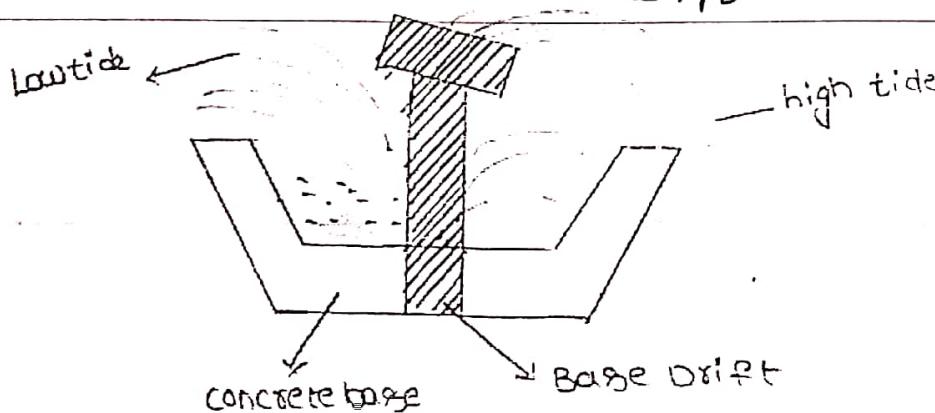
### Tidal steam generator (TSG):-

This method make use of the kinetic energy of moving water to power turbines. These may be horizontal, vertical, open etc. placed near the bottom of the water column.

### Tidal barrage method:-

Tidal barrage is a dam like structure used to capture the energy from masses of water moving in and out of a river due to tidal forces. The temporary increase in the level of the tide is channeled into a large base behind the dam & the potential energy of the tide is converted into mechanical energy to produce electric power through the use of generators.

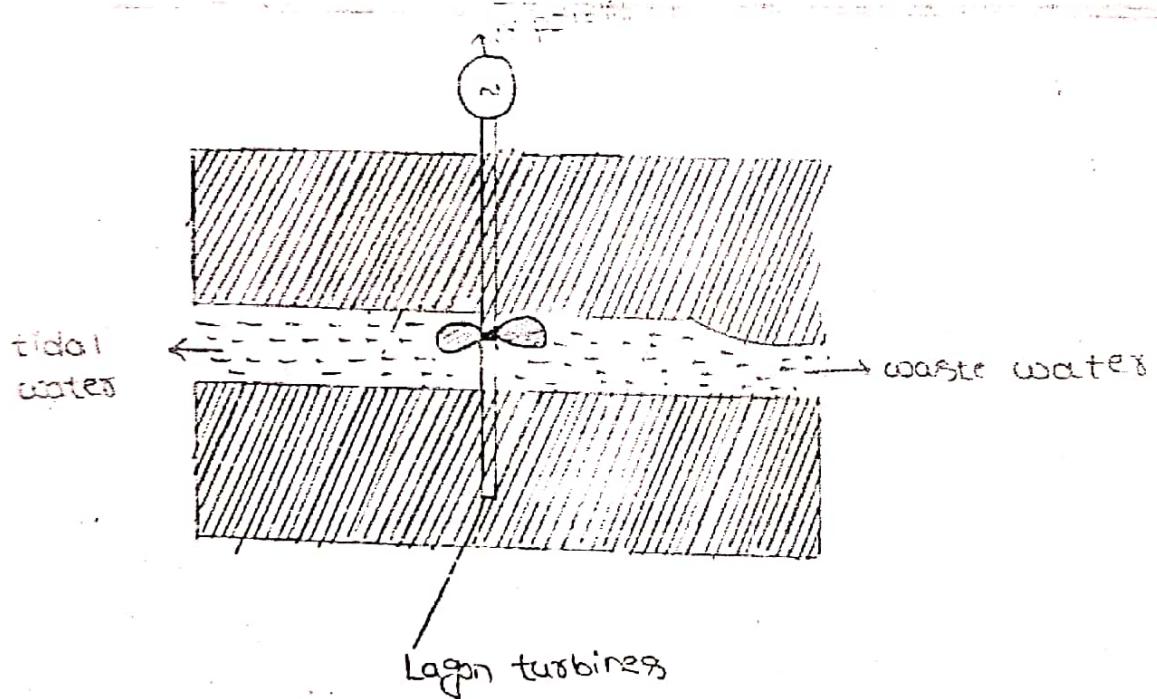
### Dynamic tidal power method:- (DTP)



The interaction between potential and kinetic energies in tidal flows. Long dams are built into the ocean without enclosing an area, leading to a significant water level difference producing low and high tides from which power is generated.

### Tidal lagoon method [74] :

The reservoirs similar to tidal barrages are created called lagoon which can be in double format without



## Hydro power:-

Flowing water creates energy, that can be captured and turned into electricity. The power available in a river (or) stream depends on the rate at which the water is flowing and the height which it falls down. The hydro schemes are classified into four groups but the basic principle of operation are the same for all.

\* Large scale :- Where power output is about 2 MW

\* Mini scale :- Where the power output is about and above 100 kW - 2 kW

\* Micro scale :- The power output is 5 kW - 100 kW

\* Pico scale :- Where the power output is less than 5 kW.

The core of a hydro scheme is the turbine, which is rotated by the moving water. Different types of turbines are used depending on the head and flow at the site.

Pelton turbines - for low flow of flowwater.

Francis turbines - high flow & cross-flow

Propeller turbines - large flow of water

River current turbines are like a wind turbines immersed in water and used to extract power from a large flow of water in river.

River



weir



canal



screen



pen stock

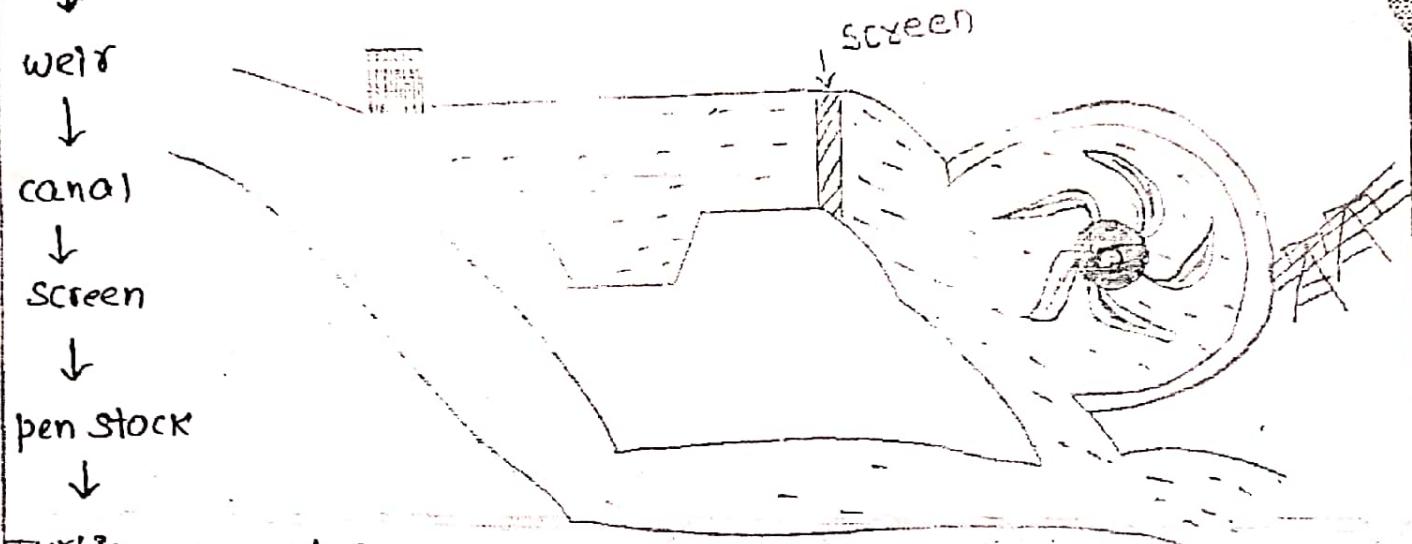


Turbine generator



electricity production.

A small dam in the river bed directs the water to a settling tank (weir), which allows the silt to settle out of water and the clean water flow into a canal (or) a pipe to a settling tank called forebay which is sited above the power house. The canal can be long. The outlet from the forebay has a screen to trap silt and floating debris. Water flows out into a pipe called penstock, which is made as steep as possible to transfer water to the turbine. Water leaving the turbine is led into the stream through the outlet pipe.



## Geothermal Energy:-

It is the heat from the earth. It is clean and sustainable. Resources of geothermal energy range from shallow groups to hot water and hot rock found few miles beneath the earth's surface and deeper extremely high temperature molten rock called magma. The first geothermal electricity was produced in Italy in 1904.

To produce geothermal generated electricity wells of 1.6 Kms deep (or) more are drilled into the underground reservoirs to tap steam and very hot water that drive turbine which inturn drive electricity generators.

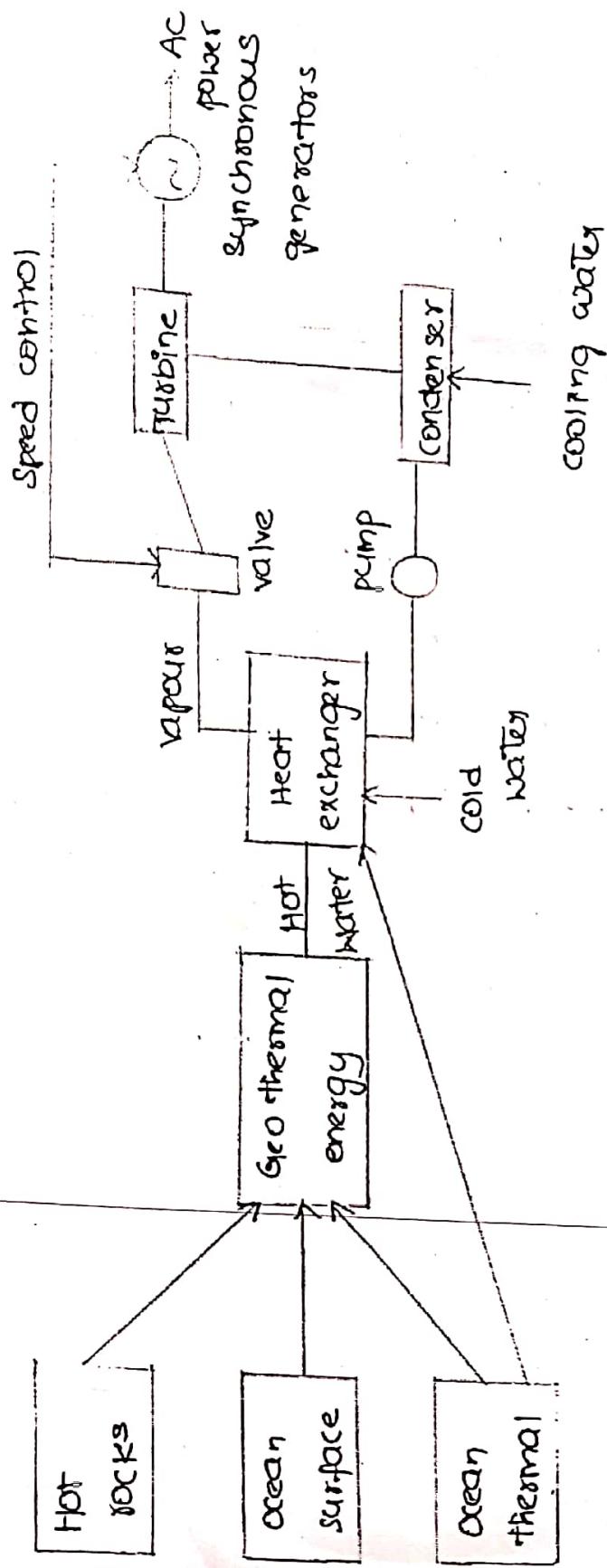
There are 3 types of geothermal power plants

\* Dry steam:- Dry steam geothermal generator takes steam out of fractures in the ground and uses it directly to drive turbines.

\* Flash geothermal plant:- It pulls deep, high pressure hot water into cooler, low pressure water. The steam that is produced is used to drive the turbine

\* Binary geothermal plant:- The hot water is passed by a secondary fluid with much lower boiling point than water, producing vapors of the secondary fluid, which can drive a turbine

Geothermal plants have advantages over other thermal plants that no fossil fuel is burned, no emission of  $\text{CO}_2$ , and other gases etc.



Prepared by  
Sarveshelli. Venkata Rao  
M.Sc B.Ed