

UNIT I:**POLYMER CHEMISTRY**

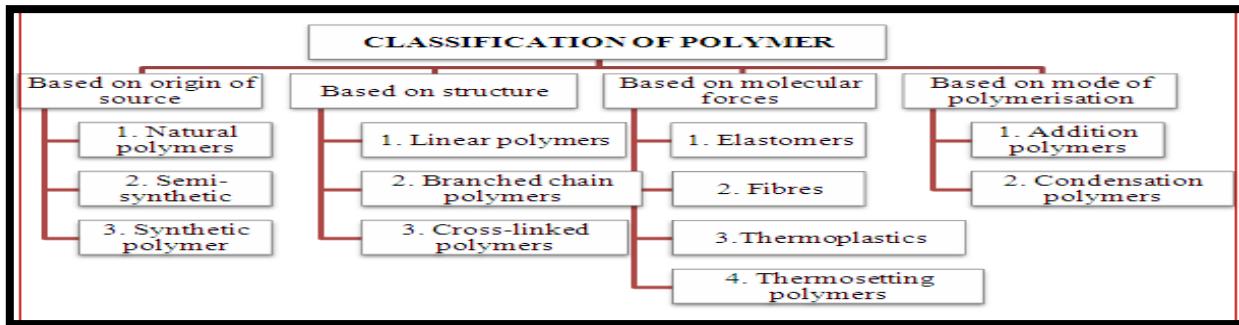
Introduction to polymers, functionality of monomers, co-polymerization, Stereospecific polymerization with specific examples. Plastics - Thermoplastics and Thermosettings, Preparation, Properties and Applications of – Bakelite, Urea Formaldehyde, Nylon-6,6, Carbon fibres. Elastomers–Buna-S, Buna-N– Preparation, Properties and Applications. Conducting polymers - polyacetylene, polyaniline, polypyrroles – Mechanism of conduction and Applications.

Polymers are defined as “high molecular weight molecules formed by resulting linkage of large number of monomers”.

Ex: Poly Vinyl Chloride (PVC).

**CLASSIFICATION OF POLYMERS**

Polymers are classified in different ways based on their physical, chemical, mechanical and thermal characteristics.



Functionality: The functionality of a monomer is the number of sites it has for bonding to other monomers under the given conditions of the polymerization reaction. Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions. A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions.

Definition: The number of bonding sites (or) reactive sites or functional groups present in the molecule.

Ex: The double bond in vinyl monomers ($\text{CH}_2 = \text{CHX}$) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



A). When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.

Ex: (a) vinyl monomers (b) adipic acid (c) hexamethylene diamine

Example for polymer: HDPE (high density polythene)

B). When the functionality of monomer is three (tri-functional), three-dimensional net work polymer is formed. Ex: phenol, glycerol

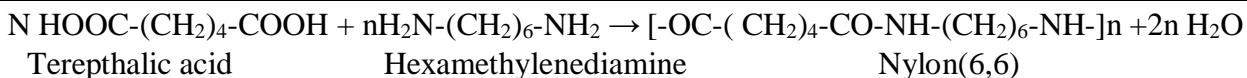
Examples for polymers: Urea formaldehyde, phenol formaldehyde.

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

Ex: LDPE (Low density polyethene)

Copolymerization: Copolymerization is the polymerization of two or more species. It is often used to improve or modify certain properties of plastics. The high molecular weight polymers obtained by copolymerisation are called copolymers. Many commercially important polymers are copolymers. Examples include Nylon (6,6), Nitrile Rubber, and Acrylonitrile Butadiene Styrene (ABS) etc.

Nylon is made from two monomers: dicarboxylic acid, diamine. The monomers combine to form the polymer.



Classification of Copolymers: There classified into Alternating, Block & Random copolymers.

Alternating Copolymers:

- Alternating copolymers contain a single main chain with alternating monomers.
- The formula of an alternating copolymer made up of monomers A and B can be generalized to (-A-B-)_n.
- Nylon (6, 6) is an example of an alternating copolymer, consisting of alternating units of hexamethylene diamine and adipic acid.

An illustration describing the general structure of these polymers is -A-B-A-B-A-B-A-B-A-B-A-B-

Block Copolymers:

- When more than one homopolymer units are linked together via covalent bonds, the resulting single-chain macromolecule is called a block copolymer.
- An example of such a polymer is acrylonitrile butadiene styrene, commonly referred to as ABS polymer.
- An illustration describing the structure of a block copolymer which is made up of the monomers 'A' and 'B' is -A-A-A-B-B-B-A-A-A-B-B-B-

Random Copolymers:

- If the two monomers are randomly ordered then the copolymer is referred to as a random copolymer.
- Styrene-Butadiene copolymer is an example of a random copolymer.

An illustration describing the general structure of these polymers is -A-B-A-B-B-A-A-B-A-B-B-A-

Graft Copolymers:

- In graft copolymerization, the polymer backbone is formed of one monomer and branches are formed of other monomer.
- By grafting polymers onto polymer backbones, the final grafted copolymers gain new properties from their parent polymers like water absorption, improved elasticity and heat resistance etc.
- One of the better-known examples of a graft polymer is high impact polystyrene, which consists of a polystyrene backbone with polybutadiene grafted chains.

An illustration describing the general structure of these polymers is -A-A-A-A-A-A-A-A-A-A-

B
B
B

STEREO CHEMISTRY (TACTICITY) OF POLYMERS

Tacticity: “The stereochemical placement of the asymmetric carbons in polymer chain is called tacticity”. The tacticity has an important bearing on the physical properties like crystallinity, rigidity of the polymer, the temperature at which polymer melts, mechanical properties of polymer etc.

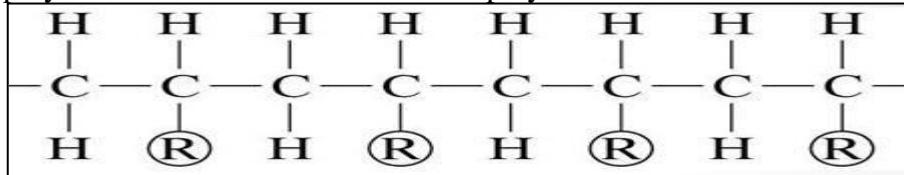
Based on the stereochemical orientation of atoms or groups at asymmetric carbon centers, the polymers can be classified as a) Isotactic polymer b) Syntactic polymer and c) Atactic polymer.

a) ISOTACTIC POLYMERS: The polymers composed of the substituent or groups or atoms at asymmetric carbon on the same side of the polymer chain are known as isotactic polymer.

Ex: Polypropylene formed by

Ziegler-Natta catalysis.

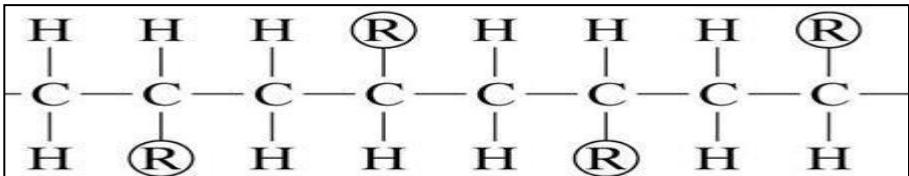
Isotactic polymers are generally semi-crystalline.



b) SYNDIOTACTIC POLYMER: The polymers in which the substituent or groups or atoms of asymmetric carbon are placed in alternative positions along the polymer chain are known as syndiotactic polymers.

Ex: Polystyrene formed by metallocene catalyst and Gutta-percha.

Syndiotactic polymers are generally crystalline in nature.



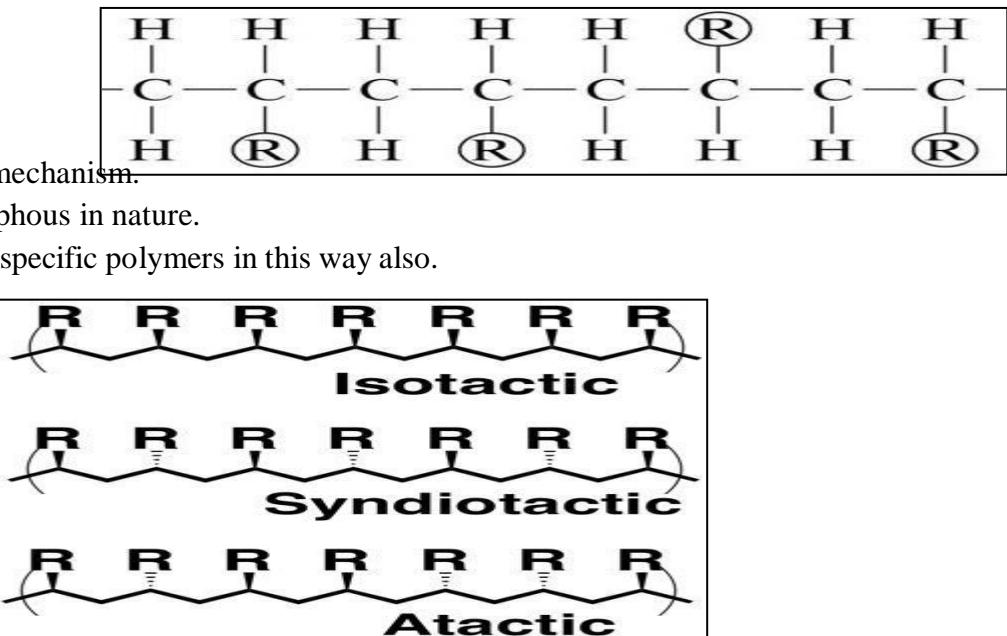
c) ATACTIC POLYMER: In these polymers, the substituent or groups or atoms of asymmetric carbons are placed

randomly along the chain. This type of polymers is formed by free radical mechanism.

Ex: PVC formed by free radical mechanism.

Atactic polymers generally amorphous in nature.

We can represent different stereospecific polymers in this way also.



PLASTICS: The term "plastic" is derived from the Greek word "plastikos", which means easily moulded. The process used to bring plastic into desired shaped is called moulding and it usually happen by the application of heat and pressure in the presence of a catalyst. During moulding, along with polymer, suitable additives are mixed with the polymer and the process is called compounding.

Classification of plastics: They are two types such as 1. Thermoplastics 2. Thermosetting polymers.

Thermoplastics are the plastics that, when heated, do not undergo chemical change in their composition and so can be molded again and again.

Examples include: polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC).

Thermosets, or thermosetting polymers, can melt and take shape only once: after they have solidified, they stay solid. If heated again, they do not melt; they decompose instead. In the thermosetting process, a chemical reaction occurs that is irreversible. Examples include Nylon, Bakelite, U-F resin and Polyesters etc.

DIFFERENCES BETWEEN THERMOPLASTICS AND THERMOSETS

Thermoplastics	Thermosetting plastics
1. These are the products of additionpolymerization.	1. These are the products of condensationpolymerization.
2. They have either linear or branched structures.	2. They have 3D cross linked network structures.
3. They soften on heating and stiffen on cooling.	3. They do not soften on heating.
4. Adjacent polymer chains are held by weak Vander Waal's forces.	4. Adjacent polymer chains are held by strong covalent bonds called cross-links.
5. Soluble in organic solvents.	5. Insoluble in organic solvents.
6. They are soft, weak and less brittle.	6. They are hard, strong and more brittle.
7. They can be remoulded, reshaped & reused.	7. They can't be remoulded & hence can't be reused.
8. They can be recycled.Ex. PE, PP, PS and PVC etc.	8. They cannot be recycled. Ex. Nylon, Bakelite, U-F resin, Polyesters etc.

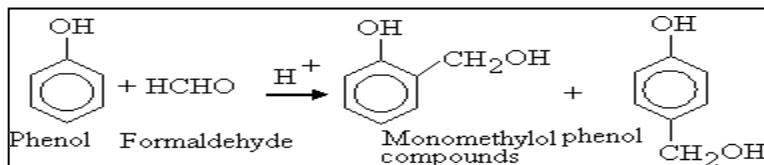
Properties of Plastic:

- 1. Strong and ductile
- 2. Light in weight
- 3. They are available in large number of colours
- 4. Poor conductors of heat and electricity
- 5. Easily moulded into different shape and size
- 6. Resist corrosion and to many chemicals

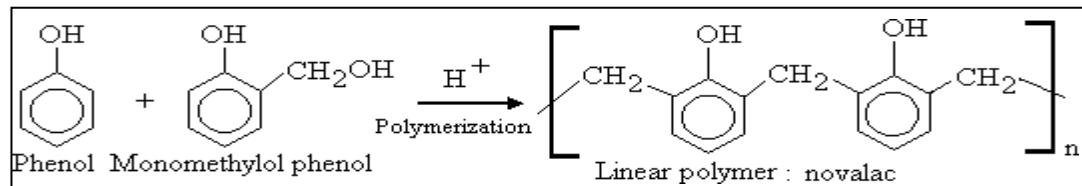
Bakelite (phenol-formaldehyde resin): It is a thermosetting plastic of phenol formaldehyde resin. It has significance as the world's first synthetic preparation, developed by Dr. Leo Baekeland in 1907.

Preparation: Phenol resins are condensed polymerization products of phenol derivatives (phenol, resorcinol) with aldehydes.

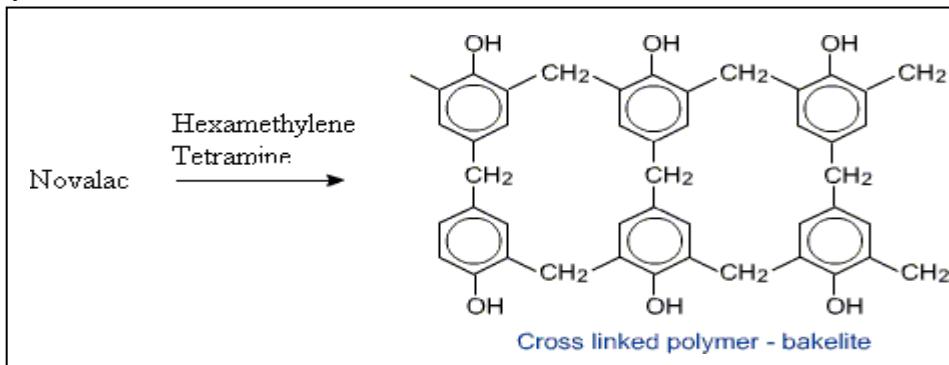
Step 1: By the reaction of phenol with formaldehyde form the methylol derivatives.



Step 2: The methylol derivatives react with phenol to form condensed product when mole ratio of phenol to formaldehyde greater than one (i.e. $p/F > 1$), in the presence of acid catalyst to form Novalac.



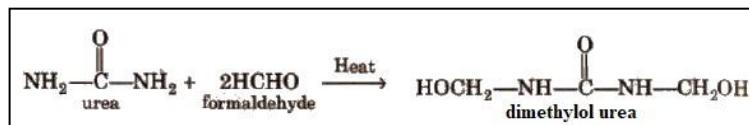
Step 3: Novalac which is on further heating in presence of hexamethylenetetramine (it produces HCHO as curing agent produces Bakelite. It is a three dimensional, cross-linked networked, hard, rigid and infusible solid polymer.



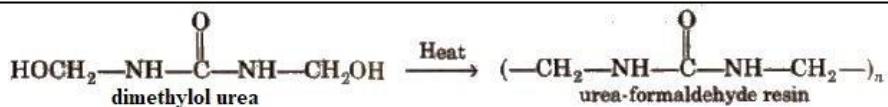
Properties: Bakelite is usually dark coloured (pinkish brown) substance.

- It has excellent heat and moisture resistance.
 - It has good chemical resistance, scratch resistance and good electrical insulator character.
 - It has good acid and salt resistance, but attacked by alkali.
 - It can be manufactured and produced in sheet, rods and tube forms for industrial applications.
- Uses:** Bakelite was used in making electric insulator parts like switches, plugs, switch boards, heater handles etc.
- Used in making saxophone mouth pieces, whistles, cameras, rotary dial telephones, solid bodyelectric guitars, television and radio body parts etc.
 - Used for production of ion-exchange resins.
 - Used in diverse products such as kitchen wares, jewelry, pipe streams and children's toys
 - Used as varnishes, electrical insulators and protective coatings.
 - Used in adhesives for grinding wheels and brake lining.

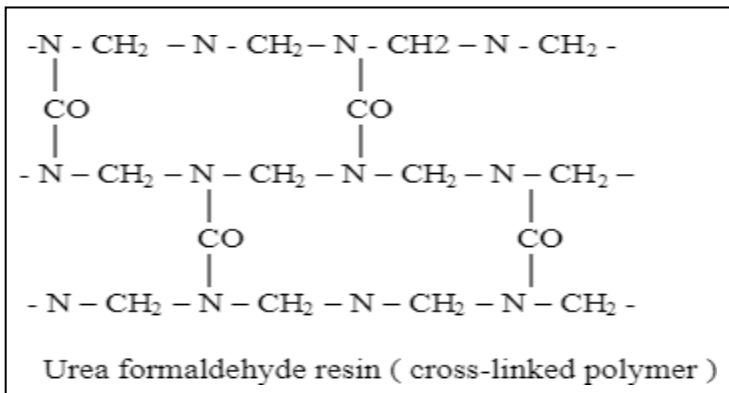
Urea-Formaldehyde resin: Urea-Formaldehyde resin also known as amino resin obtained by reaction of Urea with Formaldehyde. One part of Urea and two parts of formaldehyde react in a steel vessel in basic medium at 50° to form dimethylol urea.



The dimethyol derivative is compounded with fillers, plasticizers, pigments etc., and then cured by applying heat and pressure. During curing, cross-linked urea-formaldehyde polymer is formed.



The structure of cross linked polymer can be represented as-



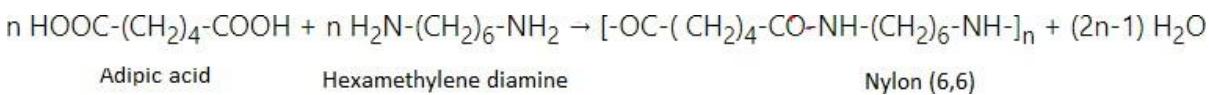
Properties: Urea-Formaldehyde resins give clear, water-white products of good tensile strength

- They have good electrical insulation and chemical resistance
- They also have Great hardness, light stability and good abrasion resistance.

Applications: U-F resins are

- Used for binding grinding wheels
- Binder of glass fibres used for filtration and insulation purpose
- Used for electrical insulation and
- Also used to make decorative articles like plates, drinking glasses and dishes etc.

Nylon (6,6): Nylon (6,6) is a synthetic polymer belonging to polyamide family, with recurring amide groups. It can be obtained by polymerisation of adipic acid and hexamethylene diamine under high pressure and at high temperature.



Removing water drives the reaction towards polymerisation through the formation of amide bonds from acid and amine functions. It can be extruded through a metal plate with fine holes and drawn into filaments.

Properties:

1. Nylon 6, 6 possess excellent abrasion resistance and high melting point.
2. Nylon 6, 6 has high tensile strength and exhibits only half of shrinkage in steam.
3. It also provides a very good resistance to photo degradation.
4. Its chemical properties does not allow it to be affected by solvents such as water, alcohol etc.

Applications:

1. Because Nylon is a light material, it is used in parachutes.
2. Nylon 6, 6 is waterproof in nature so it is also used to make swimwear.
3. Nylon 6, 6 having a high melting point make it more resistant to heat and friction so it is suitable to be used in airports, offices and other places which are more liable to wear and tear.
4. It is also used in airbags, carpets, ropes, hoses etc.
5. Nylon fibers are used to make socks, dresses and filaments for tooth brushes, strings for musical instruments and polymer framed weapons etc.

Carbon fibers: Carbon Fiber is a polymer and is sometimes known as graphite fiber.

It is a very strong material that is also very lightweight.

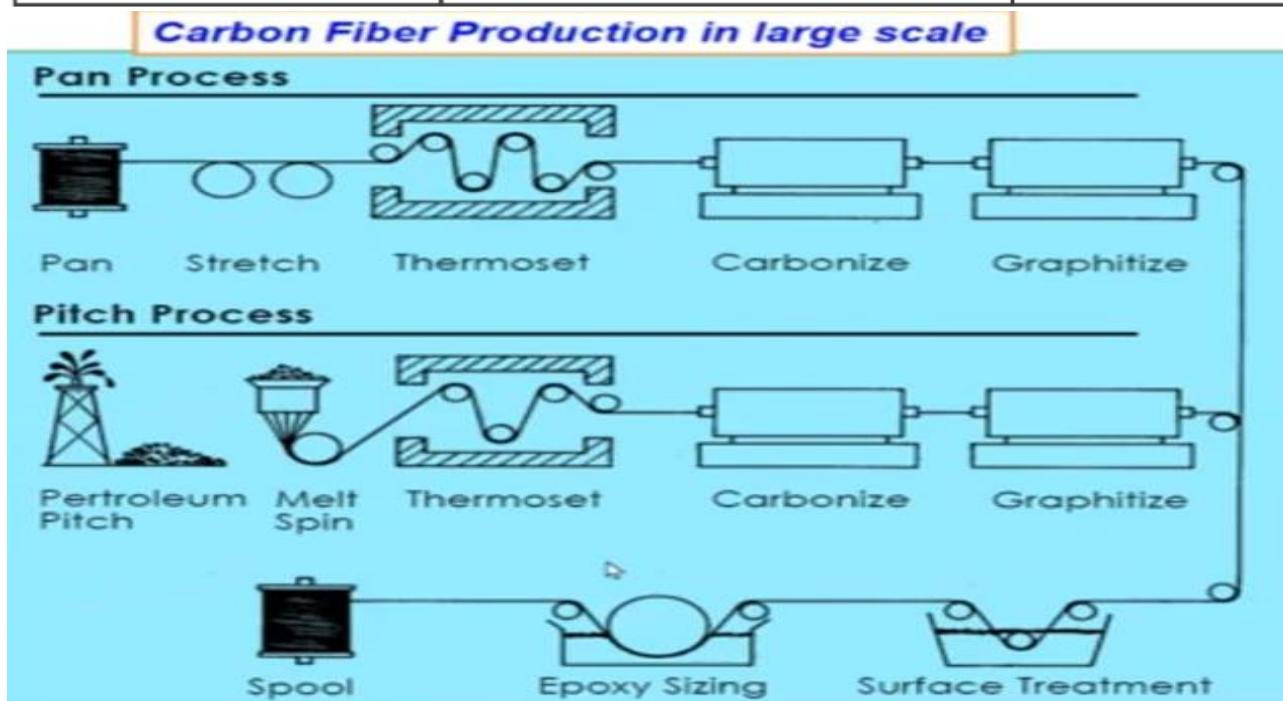
Carbon fiber is five-times stronger than steel and twice as stiff.

Though carbon fiber is stronger and stiffer than steel, it is lighter than steel;

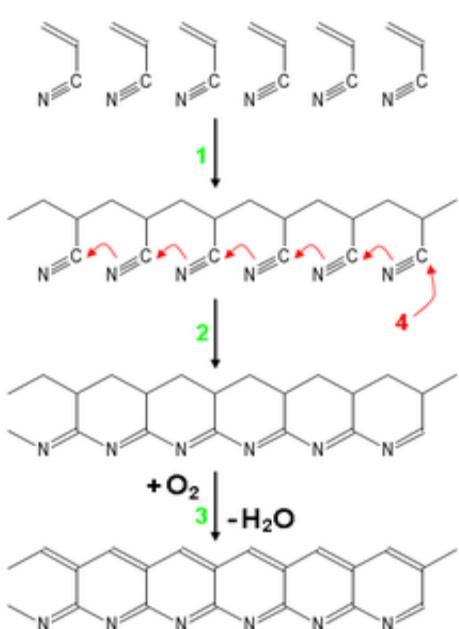
About 90% of the carbon fibers produced are made from polyacrylonitrile (PAN). The remaining 10% are made from rayon or petroleum pitch

Synthesis of carbon Fiber: Carbon fiber is made from a process that is part chemical and part mechanical. It synthesized by following three stages.

First stage	Second stage	Third stage
pretreatment stabilization up to 300°C	carbonization up to 1700°C	graphitization up to 2800°C



Each carbon filament is produced from a polymer such as polyacrylonitrile (PAN), rayon, or petroleum pitch. All these polymers are known as a precursor.



Stage-I Cyclisation: For synthetic, the precursor (PAN or rayon) is first polymers into filament yarns, 180-300 °C in air using chemical and mechanical processes, in this processes plastic to non plastic materials.

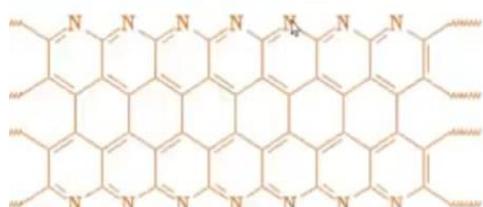
Stage-II Carbonization/Oxidation: The non plastic is then placed into a furnace having an inert atmosphere of a gas such as argon, at 300-1200 °C, which breaks many of the hydrogen bonds and oxidizes the material.

Stage-III Graphitization: The oxidized PAN is then placed into a furnace having an inert atmosphere of a gas such as argon, and heated to approximately 2000 °C, which induces graphitization of the material, changing the molecular bond structure, forming narrow graphene sheets producing the final carbon fiber. The carbon fibers filament yarns may be further treated to improve handling qualities, then wound on to bobbins.^[19]

Properties: Carbon fiber



es.... Graphitization, denitrogenation, fusing chains, 2500 °C



- is high in stiffness
- is high in tensile strength
- has a low weight to strength ratio
- is high in chemical resistance
- is temperature tolerant to excessive heat
- has low thermal expansion

Applications: Carbon fiber is very popular in many industries such as aerospace, automotive, military, and recreational applications.

We can make many different shapes with carbon fiber and other composites, including: Bike frames

- Automotive drive shafts
- Containers
- Car components
- Aircraft Wings
- Tubing
- Propeller blades

CF composites could reduce passenger car weight by 50%, which would improve fuel efficiency by nearly 35% without compromising the performance of the car or the safety of its passengers.

Elastomer: Elastomers are high polymers, which have elastic properties in excess of 300 percent. The elastic deformation in an elastomer arises from the fact that in the unstressed condition, an elastomer molecule is not straight chained but in the form of a coil and consequently, it can be stretched like a spring. The unstretched rubber is amorphous. As stretching is done, the macromolecules get partially aligned with respect to another, thereby causing crystallization and consequent, stiffening of material. On releasing the deforming stress, the chains get reverted back to their original coiled state and the material again becomes amorphous. Natural rubber is an example of elastomer.

Synthetic rubbers (Synthetic Elastomers)

Buna-S (Styrene-Butadiene Rubber or SBR):

Preparation: It is prepared by the free radical polymerization of the two monomers (1, 3-butadiene and Styrene) in the presence of radical initiator like cumene-hydro peroxide.

- This copolymer contains about 75% butadiene and 25% styrene.
- It can also be vulcanized as that of natural rubber.



Styrene

1, 3-Butadiene



Styrene-butadiene rubber

Properties:

- Excellent abrasion resistance and high load bearing capacity.
- Sensitive to oil, wastewater and readily oxidized in presence ozone present in atmosphere.
- Electrical properties good, but not outstanding.

Uses:

- Mainly used in motor tyres.
- Shoe heels and soles, gaskets and even chewing gum.
- Extensively used in coated papers, being one of the most effective resins to bind pigmented coatings.
- Used in electrical wire and cable insulation, carpet backing and tank lining etc.

Buna-N (or) nitrile rubber: BUNA –N can be prepared by the copolymerisation of 1,3-Butadiene with Acrylonitrile



Properties:

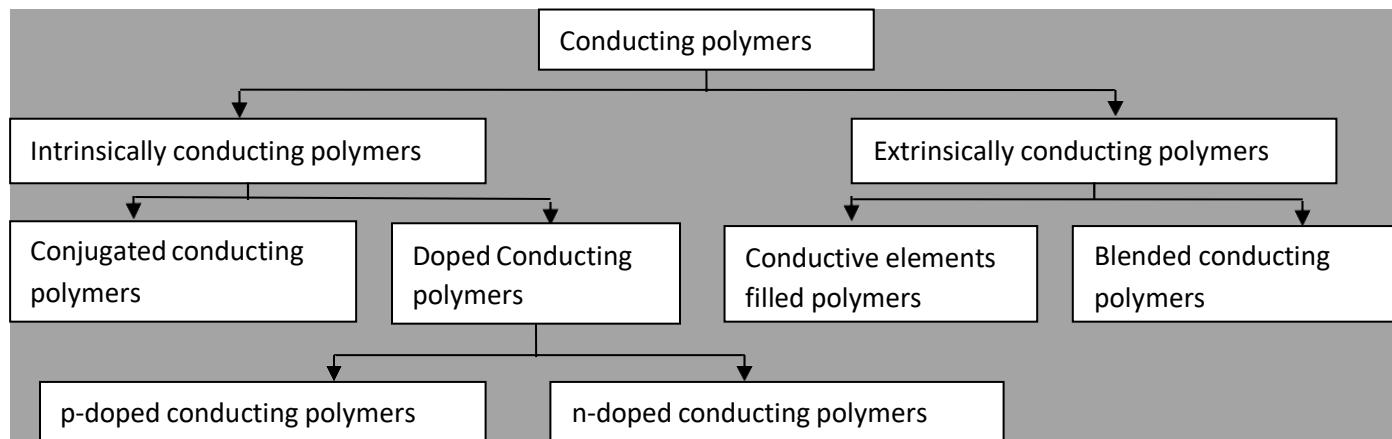
- Nitrile rubbers are stable in oil, heat, sunlight and acids.
- It can withstand scratching and it has good tensile (extension) strength.
- It is not stable in alkalis because of cyano groups.

Engineering applications:

- They are used to make fuel tanks, petrol carrying pipes, rubber sealing joints between metal parts and air craft parts.
- Make tyres along with vulcanized rubber.
- Used in making of automobile parts, hoses, gaskets, printing rollers.

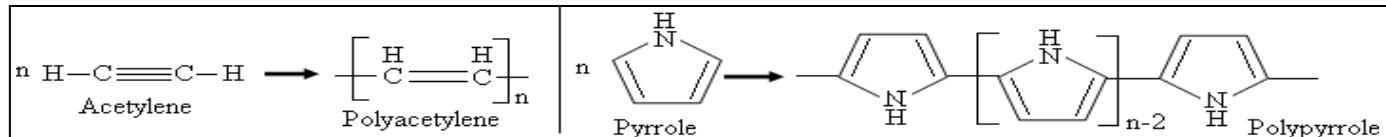
CONDUCTING POLYMERS: Conducting polymers have electrical conductivity in between a standard polymer and a metal.

Classification of conducting polymers



Intrinsically conducting polymers: In this type of polymers, the electrical conductivity is due to repeated double bonds. These are two types.

Conjugated conducting polymers: When bonding and non-bonding orbitals are overlapping over the complete chain of polymer, valence and conduction bands are formed with some band gap. When electric field is applied, the electrons from valence band jumps to conduction band.



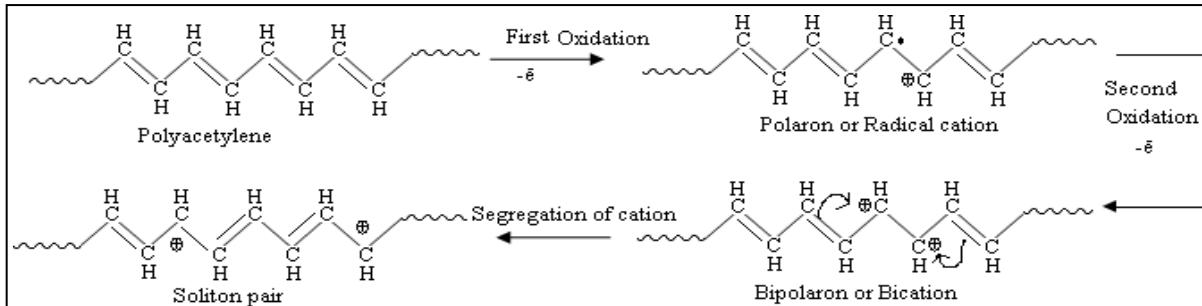
Doped Conducting polymers: The conductivities of general polymers can be increased by inserting either positive or negative charge on the polymer chain with charge transfer agents. There are two types of doping conducting polymers.

a. **p-doped conducting polymers:** These can be gotten by inserting a positive charge on the conducting polymer using an oxidizing agent like Lewis acid or I_2 .



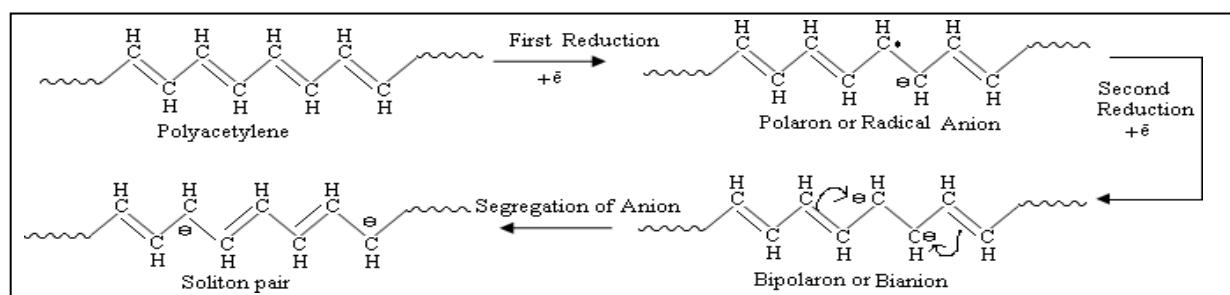
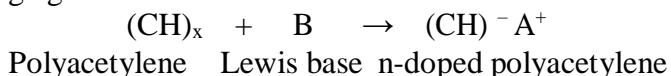
Polyacetylene

Lewis acid p-doped polyacetylene



Two positive charges are formed in the polymer chain from the first and second oxidations by the removal of electrons. These positive charges travel to the nearby carbon atoms along the polymer chain in opposite direction to conduct electricity.

b. n-doped conducting polymers: These can be gotten by inserting a negative charge on the conducting polymer using a reducing agent like Lewis base.



Two negative charges are formed in the polymer chain from the first and second reductions by the addition of electrons. These negative charges travel to the nearby carbon atoms along the polymer chain in opposite direction to conduct electricity.

Extrinsically conducting polymers:

- The polymers show the conductivity due to outside addition of elements into them.
 - There are two types of polymers in this. **i. Conductive elements filled polymers. ii. Blended conducting polymers**
- i. Conductive elements filled polymers:** It is a polymer obtained by filling conducting elements like carbon black, metallic fibers, metal oxides etc. The polymer acts as binder to join the conducting elements. A polymer starts to show the conductivity at minimum concentration of conductive element added. The minimum concentration of this is called Percolation threshold.

Disadvantages: Decrease in the tensile (means extension) strength.

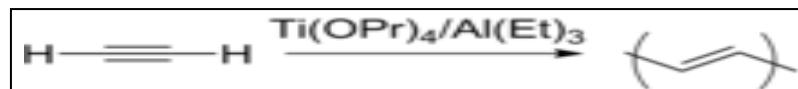
Breaks easily after a fixed length.

ii. Blended conducting polymers: These are prepared by chemical or physical mixing of a general polymer with conducting polymer. The blended conducting polymers have good physical, chemical and mechanical properties and they can be easily processed.

Few important conducting polymers discussed below-

Polyacetylene: Polyacetylene usually refers to an organic polymer with the repeating unit $(C_2H_2)_n$. The high electrical conductivity discovered by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid for this polymer led to intense interest in the use of organic compounds in microelectronics (organic semiconductors). This discovery was recognized by the Nobel Prize in Chemistry in 2000.

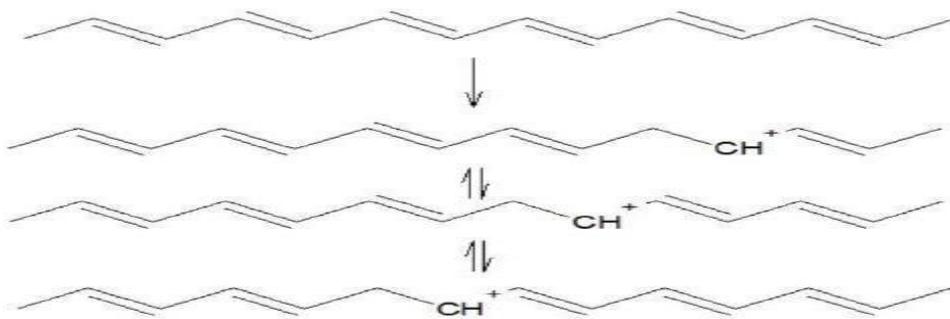
Preparation: Polyacetylene can be synthesized from pure acetylene and other monomers. One of the most common methods uses a Ziegler–Natta catalyst, such as Titanium isopropoxide and triethyl aluminium with gaseous acetylene.



Polyacetylene can also be produced by radiation polymerization of acetylene. γ -radiation, and ultraviolet irradiation have been used. These methods avoid the use of catalysts and solvent, but require low temperatures to produce regular polymers.

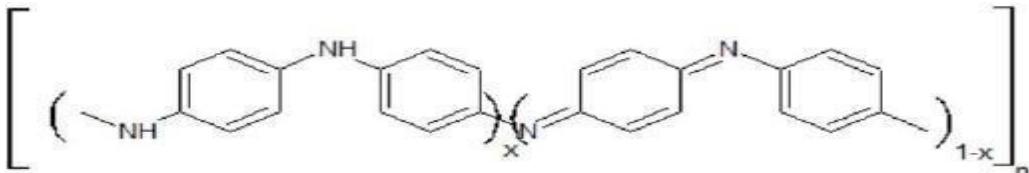
Polyacetylene consists of a long chain of carbon atoms with alternating single and double bonds between them, each with one hydrogen atom. By the early 1970s, this polymer was known to be superconductive at low temperatures. Upon doping polyacetylene with I_2 , the conductivity increased seven orders of magnitude. Similar results were achieved using Cl_2 and Br_2 . These materials exhibited the largest room temperature conductivity and lead to the development of organic conductive polymers.

The polyacetylene is the simplest polymer that shows a great value of conductivity. The alternating double and single bond in the polymer structure is what gives the polymer the ability of resonance. As dopants are inserted in the polymer, the chain of polymers presents charges. The movement of this charge, by resonance when a field is applied, gives rise to the conductivity of the material.



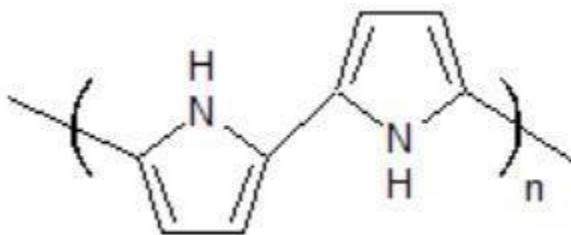
Resonance Mechanism of Polyacetylene: The first step is the formation of the positive soliton (carbocation), followed by the resonance of the compound.

Polyaniline: Polyaniline is one of the most promising conductive polymers and, therefore, one of the most studied one. In this polymer aromatic rings bonded together by nitrogen atoms. Its structure is composed by x units of reduced species alternated with $1-x$ units of oxidized species.



Chemical Structure of the Polyaniline

Polypyrrole: Polypyrrole is one of the conductive polymers studied in the research that resulted in the Nobel Prize. It is obtained by the oxidation of the pyrrole, resulting in the structure shown below.



Chemical Structure of the Polypyrrole

The Redox process of the addition of an anion to the structure that is responsible to the conductive properties of the polypyrrole. Here, the resonance occurs to stabilize the carbocation, moving the charge, resulting in conductivity, mechanism similar as shown for the previous polymers.

Applications

This type of materials has generated interesting in many field of study, due to its conductivity properties as a

metals, but remaining its relatively inert and good mechanical properties.

There are many applications of these materials in electronics, such as batteries, sensors, and microelectronics devices.

These materials are used to make Electromagnetic screening Materials, Transistors, Diodes, PVcells and switches.

The polypyrrole and polyaniline are currently used in protection of metals, as an anti-corrosivecoating. In the medical field, the conductive polymers can be used in the production artificial muscles,biosensors, and drugs controlled-release agents.

QUESTION BANK

ESSAY QUESTIONS

1. Define the term plastic. Differentiate thermoplastics and thermosetting plastics.
2. What is copolymerization? Explain different types of copolymers.
3. Explain the stereochemistry of polymers with suitable examples.
4. Discuss the preparation, properties and uses of Bakelite.
5. Discuss the preparation, properties and uses of Urea-Formaldehyde resin & Nylon 6,6.
6. What are carbon fibers? Explain the properties of and applications of carbon fibers.
7. Define the term elastomer and discuss the preparation, properties and uses of Buna-S &Buna-N.
8. Define conducting polymers. Explain the mechanism of conduction in Polyacetylene.
9. Explain the preparation, properties and applications of Polyacetylene.
10. Explain the preparation, properties and applications of Polyaniline and Ppolypyrrole.

VERY SHORT ANSWER QUESTIONS

1. Define the term “Functionality of polymer”.
2. Nylon 6, 6 is a copolymer. Justify.
3. What is meant by Graft copolymer?
4. Define the term “Tacticity of polymer”.
5. What are the monomers of Bakelite?
6. What are synthetic elastomers? Give examples.
7. What are the monomers of BUNA-S and BUNA-N?
8. What are doped conducting polymers?

UNIT-2:

Electrochemistry and Applications

Electrodes –Reference electrodes (Hydrogen electrode and Calomel electrode), Electrochemical cell, Nernst equation. Concept of pH, pH meter and applications of pH metry, Potentiometry-Potentiometric titrations (Redox titrations),Concept of Conductivity, Conductivity cell, Conductometric titrations (acid-base titrations), Primary cells – Dry cell - Zinc-air battery, Secondary cells – Lead acid battery, Lithium-ion batteries- working of the batteries including cell reactions, and button cells. Fuel cells - Hydrogen-Oxygen and Methanol-Oxygen fuel cells – working of the cells.

Standard electrode (Reference Electrode): An electrode whose electrode potential is known is called standard electrode. These are also called reference electrodes. Important reference electrodes are hydrogen electrode and calomel electrode.

Hydrogen Electrode: It consists of a small platinum foil coated with platinum black to absorb hydrogen gas. A platinum wire is welded to the electrode and sealed through a glass tube makes the contact with the outer circuit. The platinum foil is surrounded by an outer glass tube having an inlet at the top and number of holes at the base. The electrode is placed in 1m solution of hydrochloric acid. Pure hydrogen gas is passed at 1 atm pressure through the inlet of glass tube a small amount of gas is absorbed by the Platinized electrode while the remaining escapes through the lower holes provided at the base of the glass tube.

The electrode is represented as: **Pt, H₂(1atm); H⁺(1M)**.

When in a cell electrode acts as the anode, oxidation takes place.



i.e. some hydrogen gas changes into H⁺ ions which go into the solution.

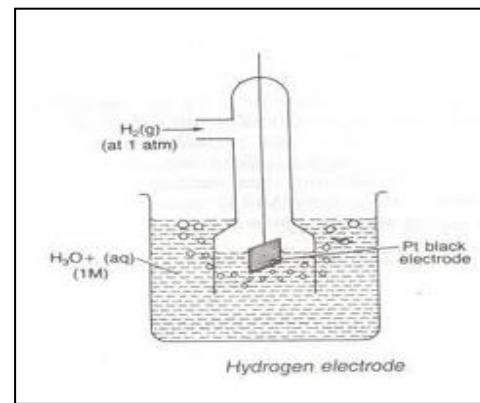
When this electrode acts as a cathode, reduction takes place $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$

i.e., some H⁺ ions from the solution changes to H₂ gas

When hydrogen is passed at 1 atm pressure through a solution of hydrogen ions of unit concentration then the potential of the electrode is arbitrarily fixed as ZERO.

Limitations of S H E:

1. It is not portable
2. Impurities present in the gas affects the activity of platinum foil
3. It is not easy to setup a hydrogen electrode
4. It is readily affected by Hg, As and S and oxidizing agents.
5. It is difficult to maintain the concentration of H₂ at unity and maintaining pressure at 1 atm throughout.

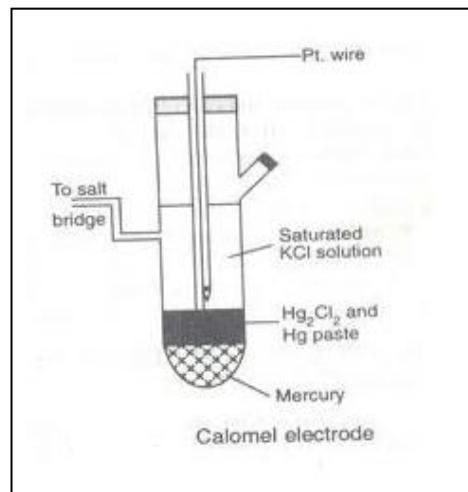


Calomel Electrode: The difficulties encountered with SHE, the use of secondary electrode like calomel electrode is prompted. Calomel electrode consists of mercury, solid mercurous chloride and potassium chloride solution.

It is represented as **Hg, Hg₂Cl₂; KCl (l)**.

Mercury of high degree of purity is placed at the bottom of a glass tube with a side tube on both sides. It is connected to the outer circuit by means of a platinum wire sealed in a glass tube. The surface of the mercury is covered with a paste of mercurous chloride (calomel). A saturated potassium chloride solution is introduced through the side tube present in the right side.

If this electrode acts as <i>anode</i> then	If this electrode acts as <i>cathode</i> then
$2\text{Hg} \rightleftharpoons 2\text{Hg}^+ + 2\text{e}^-$ $2\text{Hg}^+ + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2$ $2\text{Hg} + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$	$\text{Hg}_2\text{Cl}_2 \rightleftharpoons 2\text{Hg}^+ + 2\text{Cl}^-$ $\text{Hg}^{+2} + 2\text{e}^- \rightleftharpoons 2\text{Hg}$ $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$



These overall reactions are just reverse of each other. Hence the calomel electrode is reversible. This electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode whose potential is to be determined.

The standard potential of calomel electrode vary with conc. of KCl.
i.e., for 0.1N KCl - 0.333 V, 1.0 N KCl - 0.2810 V and Saturated. KCl - 0.2422 V.

Electrochemical cell: An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it. These devices are capable of converting chemical energy into electrical energy, or vice versa.

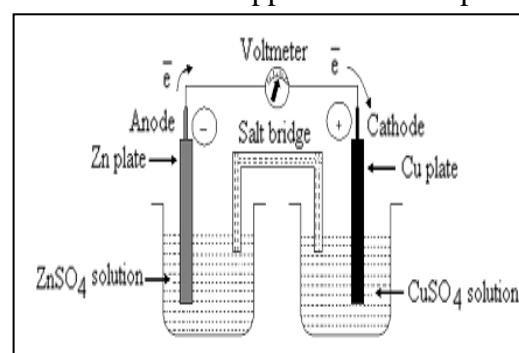
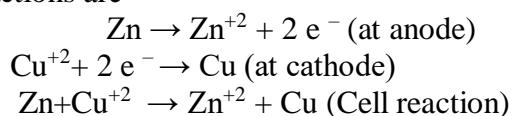
Such cells capable of generating an electric current from the chemical reactions occurring in them are called Galvanic cells or Voltaic cells. Alternatively, the cells which cause chemical reactions to occur in them when an electric current is passed through them are called electrolytic cells.

Galvanic Cell: Galvanic cell is a device which converts chemical energy into electrical energy. Galvanic cell generally consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm (or) connected through a salt bridge.

Ex: Daniel cell

Daniel cell: It consists of two containers one of which is with a zinc rod dipped in zinc sulphate solution and other is with a copper rod dipped in a copper sulphate solution. The solutions are of the two containers are connected by a salt bridge. The salt bridge is a 'u'-tube filled with saturated solution of KCl (or) NH_4NO_3 and both ends of the tube are plugged with porous material. The zinc rod & copper rods are connected extremely through an ammeter by using a wire.

The electrode reactions are



Observations:

1. Zinc starts to dissolve.
2. Copper gets deposited on copper rod.
3. Voltmeter indicates the flow of electrons from zinc to copper.
4. The ZnSO_4 solution becomes richer with Zn^{+2} ions
5. The CuSO_4 solution becomes more diluted with respect to Cu^{+2} ions.

The total cell is represented as $\text{Zn}|\text{ZnSO}_4||\text{CuSO}_4|\text{Cu}$, $E=1.09 \text{ V}$.

At 298K, the Nernst's equation for the Daniel cell can be written as

$$E_{\text{cell}} = \left(E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - E_{\text{Zn}/\text{Zn}^{+2}}^{\circ} \right) - \frac{0.0592}{n} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

Many commercially important batteries (such as the lead-acid battery) are made up of Galvanic cells.

Electrolytic cell: An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds.

For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen. This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction.

The three primary components of electrolytic cells are:

- Cathode (which is negatively charged for electrolytic cells)
- Anode (which is positively charged for electrolytic cells)
- Electrolyte

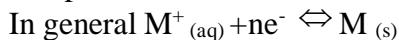
The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.

Applications of Electrolytic Cells

- The primary application of electrolytic cells is for the production of oxygen gas and hydrogen gas from water.
- They are also used for the extraction of aluminium from bauxite.
- Another notable application of electrolytic cells is in electroplating, which is the process of forming a thin protective layer of a specific metal on the surface of another metal.
- Industrial production of high-purity copper, high-purity zinc, and high-purity aluminium is almost always done through electrolytic cells.

Galvanic Cell / Voltaic Cell	Electrolytic Cell
1. Chemical energy is transformed into electrical energy in these electrochemical cells.	1. Electrical energy is transformed into chemical energy in these cells.
2. The redox reactions that take place in these cells are spontaneous in nature.	2. An input of energy is required for the redox reactions to proceed in these cells, i.e. the reactions are non-spontaneous.
3. In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.	3. These cells feature a positively charged anode and a negatively charged cathode.
4. The electrons originate from the species that undergoes oxidation.	4. Electrons originate from an external source (such as a battery).

Nernst equation: Electro chemical cell is a device which a spontaneous redox reaction takes place and electrical energy is obtained



For a reversible reaction, the free energy change (ΔG) and equilibrium constant (K) are related as

$$\begin{aligned}\Delta G &= RT \ln K + RT \ln [\text{Product}] / [\text{Reactant}] \\ &= \Delta G^0 + RT \ln [\text{Product}] / [\text{Reactant}] \quad \dots \dots \dots (1)\end{aligned}$$

Where ΔG^0 is known as the standard free energy change.

The above equation is known as Van't Hoff reaction isotherm.

In an electrochemical cell, the electrical energy is produced at the expense of the free energy decrease. i.e., $-\Delta G = nFE_{\text{cell}}$ and $-\Delta G^0 = nFE^0_{\text{cell}}$

Where E = Electrode potential, E^0 = Standard electrode potential, F = Faraday (96,500 columbs).

Equation (1) can be written as

$$\begin{aligned}-nFE &= -nFE^0 + RT \ln [M/M^{n+}] \\ &= -nFE^0 + RT \ln [1/M^{n+}] \quad (\text{since } [M] = 1) \\ &= -nFE^0 - RT \ln [M^{n+}]\end{aligned}$$

Dividing with ' $-nF$ '

$$\begin{aligned}E &= E^0 + [RT/nF] \ln [M^{n+}] \\ E &= E^0 + [2.303RT/nF] \log_{10} [M^{n+}] \\ E &= E^0 + [0.0591/n] \log_{10} [M^{n+}]\end{aligned}$$

This expression is known as Nernst equation.

Importance: The Nernst equation can be used to calculate-

- Single electrode reduction or oxidation potential at any conditions
- Standard electrode potentials
- Comparing the relative ability as a reductive or oxidative agent.
- Finding the feasibility of the combination of such single electrodes to produce electric potential.
- Emf of an electrochemical cell
- Unknown ionic concentrations

Concept of pH: pH is defined as the negative logarithm of H^+ ion concentration. Theoretically, pH is derived from the word "Pondus Hydrogenii" which means "Potential Hydrogen" or Power of Hydrogen. pH equals the negative logarithmic value of the concentration of hydrogen ion (H^+)

$$\mathbf{pH = -log[H^+]}$$

A pH scale is a tool for measuring acids and bases. The pH of a solution varies from 0 to 14.

- Solutions having a value of pH ranging 0 to 7 on pH scale are termed as **acidic** and for the value of pH ranging 7 to 14 on pH scale are known as **basic** solutions.
- Solutions having the value of pH equal to 7 on pH scale are known as neutral solutions.

Solutions having the value of pH equal to 0 are known to be **strongly acidic solutions**. Further, the acidity decreases as the value of pH increases from 0 to 7 whereas, solutions with the value of pH equal to 14 are termed as **strongly basic solutions**.

Importance of pH:

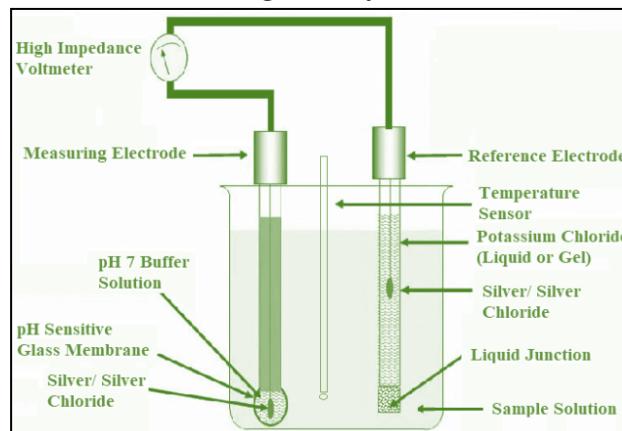
- Only a narrow range of pH change can be sustained by a living organism, any further change in pH can make the living difficult. For example: in the case of acid rain, the pH of water is less than 7. As it flows into a river, it lowers the pH of river water which makes the survival of aquatic life difficult.
- We know that our stomach contains hydrochloric acid which helps in the digestion of food. When the stomach produces too much of hydrochloric acid during indigestion, we feel a lot of pain and irritation. Hence, we generally use antacids or a mild base which increases the pH of the acidic stomach and thus decreases the pain.
- Bacteria present in our mouth sometimes lower the pH of our mouth by producing acids through degradation of the food particle. Hence, we are instructed to clean our mouths with toothpaste (which are generally basic) to prevent their decay by maintaining the pH.

Limitation of pH Scale:

- pH value of a solution does not instantaneously give us an idea of the relative strength of the solution.

pH Meter: pH Measurement is obtained precisely using a pH Meter. The main components of it are Measuring Electrode, Reference Electrode, and Temperature Sensor. The pH Meter measures the voltage of an electro chemical cell and the pH of a solution. In most of the pH Meters the electrodes and the Temperature Sensor are fabricated into a single body and are called as Combination Electrodes.

The overall potential or the voltage is the algebraic sum of the potentials of the Measuring Electrode, Reference Electrode and the Liquid Junction Potential. The Reference Electrode provides a stable voltage as it has a fixed concentration of Potassium Chloride solution which is a neutral solution. But the potential of the Measuring Electrode depends only on the pH of the solution. The potential difference between a glass membrane of Measuring Electrode and a Reference Electrode which is dipped in the Sample Solution to be tested is measured.



When the two Electrodes are dipped in the Sample Solution, ion-exchange process occurs where in some of the Hydrogen ions move towards the outer surface of the Measuring Electrode and replaces some of the metal ions inside it. Similarly, some of the metal ions move from the Glass Electrode into the Sample Solution. Ion-exchange process also takes place on the inner surface of the Glass Electrode from the sample solution. This creates a potential difference between them. The Liquid Junction potential is usually small and relatively constant which mainly depends on the concentration of the ions in the sample solution. All three potentials are summed up and measured by High Impedance Voltmeter.

To get precise pH measurement, the instrument has to be calibrated by dipping the measuring electrode into buffer solution of known pH.

Applications of pH Measurement

- pH Measurement is very crucial in Agriculture industry for soil evaluation. Major crops require alkaline environment and hence pH Measurement becomes necessary.
- It is also used in Food industry especially for dairy products like cheese, curds, yogurts, etc.
- It becomes mandatory for chemical and pharmaceutical industries.
- It becomes a significant factor in the production of detergents.
- pH level monitoring is essential in water treatment plants and RO water purifiers.

Advantages of pH Measurement

- pH Measurement is inexpensive and robust.
- Pocket size pH Meters are user friendly.
- Readings are accurate and precise.

Disadvantages of pH Measurement

- Temperature impacts the output readings.
- pH Measurement using glass electrodes must be clean as deposition on the electrodes affects the readings.

Potentiometry: A potentiometer consists of two electrodes inserted in two solutions connected by a salt bridge. The voltmeter is attached to the electrodes to measure the potential difference between them. One of the electrodes is a **reference electrode**, whose electrode potential is known. The other electrode is the **indicator electrode/test electrode**.

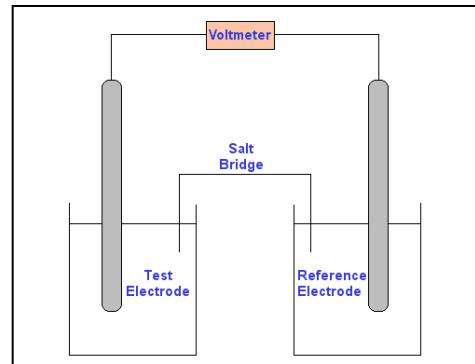
The test electrode is usually either a metal immersed in a solution of its own ions, whose concentration you wish to discover.

The Nernst Equation can be used to find the concentration of the test solution.

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln(K_{\text{eq}})$$

Potentiometric Titrations: Potentiometric titrations involve the measurement of the potential of a suitable indicator electrode with respect to a reference electrode as a function of titrant volume. Potentiometric titrations provide more reliable data than data from titrations that use chemical indicators and are particularly useful with colored or turbid solutions and for detecting the presence of unsuspected species.

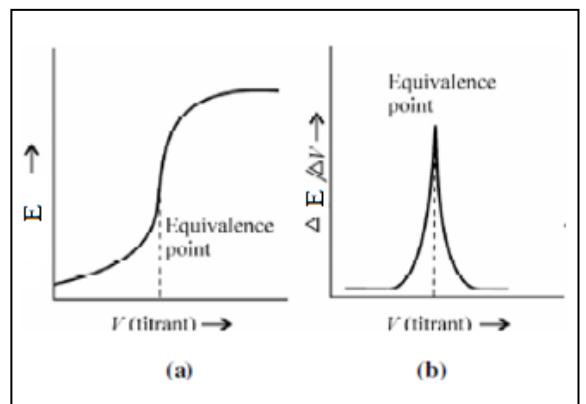
Potentiometric Titration involves measuring and recording the cell potential (in units of millivolts) after each addition of titrant. The titrant is added in large increments at the outset and in smaller and smaller increments as the end point is approached. Sufficient time must be allowed for the attainment of equilibrium after each addition of the reagent by continuous stirring. For this a magnetic stirrer with a stirring magnet bar is used.



Redox titration: Titrations involving oxidising agents (KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) and reducing agents (like ferrous salt) can be followed potentiometrically by using platinum indicator electrode. For example, Fe^{+2} titrated against $\text{K}_2\text{Cr}_2\text{O}_7$. Ferrous iron solution is taken in the beaker and treated with dil. Sulphuric acid. Platinum electrode and calomel electrode are dipped into the solution and they are connected to the potentiometer. On adding $\text{K}_2\text{Cr}_2\text{O}_7$ from the burette, emf of the cell will increase first slowly and at the equivalence point there will be sudden jump in

potential since change in the ratio of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ions concentration. The EMF of the solution after the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ from burette is recorded. A graph is plotted with EMF and volume of $\text{K}_2\text{Cr}_2\text{O}_7$. The steep rise is the end point of titration (a).

The second approach to end-point detection is to plot the derivative curve: Plotting first derivative curve (b) by calculating the change in potential per unit volume of titrant (that is, $\Delta E/\Delta V$). A plot of $\Delta E/\Delta V$ as a function of corresponding reagent volume produces a curve with a maximum that corresponds to the point of inflection.



Conductivity: Conductivity is the ability of a material to conduct electric current. Conductivity (G), the inverse of resistivity (R), is determined from the voltage and current values according to Ohm's law.

$$G = \frac{1}{R} = \frac{I \text{ (amps)}}{E \text{ (volts)}}$$

Since the charge on ions in solution facilitates the conductance of electrical current, the conductivity of a solution is proportional to its ion concentration. The basic unit of conductance is the siemen (S), formerly called the mho.

Conductometry: Conductometric titrations may be defined as those titration in which end-point is detected with the help of conductivity measurements. Conductometric titrations are based on the fact that the conductance of a solution at a constant temperature depends upon the number and mobility of ions present in it.

In practice, Titrant is added from a burette into a known volume of another solution taken in a conductivity cell and the conductivity readings are taken after adding particular amount of Titrant each time. When a Titrant is added to a fixed amount of another solution, some of the ions of the former solution are replaced by those of latter solution causing change in conductance of the resulting solution.

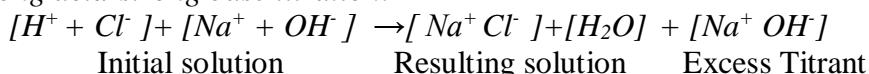
The conductivity reading after adding a particular amount of Titrant is plotted against the volume of Titrant added, two liner curves are obtained the intersection of which gives the end point of titration.

Advantages:

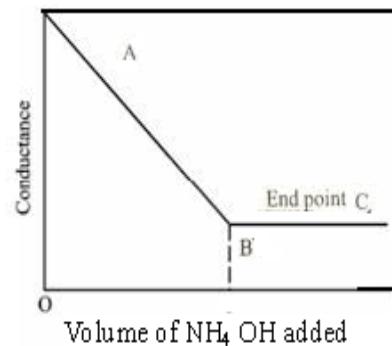
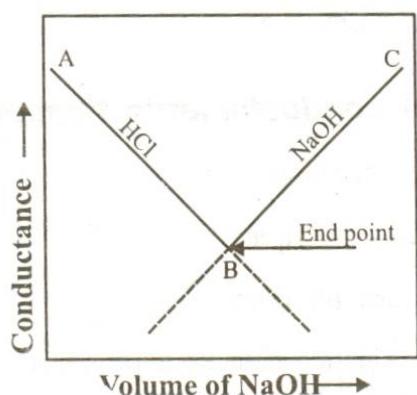
- i. This method gives more accurate results.
- ii. This method is very useful for colour reactants.
- iii. This method can be employed with dilute solutions.
- iv. Result obtained from graphical data so keen observation of end point is not needed.
- v. No need of indicator and the equivalence point can be determined.

Conducotmetric Titrations:

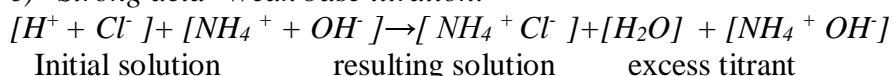
Acid-base titration: Conductometric titrations give excellent results for acid-base titrations, because of fast moving H^+ and OH^- ions.

a) Strong acid-strong base titration:

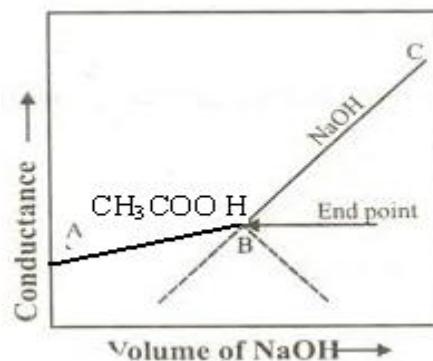
When HCl is titrated against NaOH, initially conductivity of HCl solution is high due to HCl being a strong acid which dissociates easily to give fast moving H^+ ions. But on the addition of certain amount of NaOH to HCl solution, some of the fast moving H^+ ions are neutralized by more OH^- ions. Hence the conductivity keeps on decreasing and all the H^+ ions in HCl are neutralized by OH^- ions from NaOH. Then the resulting neutral solution contains only slow moving Na^+ and Cl^- ions. Further addition of even small amount of NaOH solution; introduce fast moving OH^- in the resulting solution. Hence conductivity of the resulting solution increases.

*b) Weak acid- strong base titration:*

In this titration, initially the conductivity of the solution is low because of its poor dissociation. But on the reaction of acetic acid with NaOH, gives strong conjugate base called sodium acetate which dissociates highly and hence the conductivity of the resulting solution increases slowly. With the progress of the titration, conductance of resulting solution keeps on increasing slowly till the whole acetic acid has been neutralized. At this point neutral solution contains only CH_3COO^- and Na^+ . Further addition of even small amount of highly dissociative NaOH introduces fast moving OH^- ions which increase the conductivity sharply.

c) Strong acid- Weak base titration:

In this titration, initially conductivity of the HCl solution is high, because of its dissociation which gives fast moving H^+ ions. Hence the conductivity is more. But when HCl reacts with $NH_4 OH$, fast moving H^+ ions are replaced by slow moving ions. Hence conductivity of resulting solution decreases. With the progress of titration conductivity of resulting solution keeps on decreasing till the whole HCl has been neutralized. After the end point addition of $NH_4 OH$ does not give any change in the conductance because $NH_4 OH$ dissociate poorly.



Batteries:

- ⊕ Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
 - ⊕ A device which converts chemical energy to electrical energy is called battery.
 - ⊕ Usually in the term applied to a group or two or more electric cells, connected together electrically in series and Batteries are commercial electrochemical cells.
- Batteries are 3 types

1. Primary cells 2. Secondary cell and 3. Fuel cell.

PRIMARY CELLS	SECONDARY CELLS	FUEL CELLS
1. Cell reaction is irreversible. 2. Can't be recharged. 3. Can be used as long as the materials are active in their composition.	1. Cell reaction can be reversed. 2. Can be recharged. 3. Can be used again and again by recharging.	1. Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained. 2. Do not store energy. 3. Cannot be reversed.
E.g.: Lechanche cell.	E.g.: lead storage cell.	E.g.: H ₂ -O ₂ fuel cell.

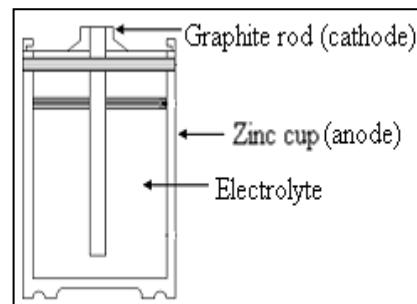
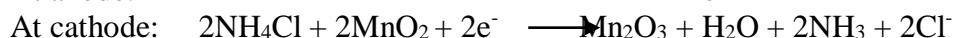
Primary cells: In these the cell reaction is not reversible, when the reactions in the cell are converted to products, no more electricity produced and the battery becomes dead. They can be used once only. In these cells electricity produced at the expense of chemical energy.

Eg: dry cell or leclanche cell.

Dry cell: The dry cell consists of a cylindrical **zinc container acts as the anode and a graphite rod placed at the centre of the cylinder but not touches the bottom acts as the cathode**. Graphite rod is fitted with a metal cap and container is sealed with pitch at the top. The anode is in contact with **a paste of ammonium chloride and zinc chloride as electrolyte**. Cathode carbon rod is surrounded with a paste of manganese dioxide, starch and carbon powder. As the conductivity of MnO₂ is low, granulated carbon is added to increase conductivity. The dry cell can be represented as

**Electrode reactions:**

The electrode reactions are



During the cell reaction the liberated ammonia from ammonium chloride combines with the Zn²⁺ ions to precipitate [Zn(NH₃)₂Cl₂] complex.

These reactions are not involved directly in the electrode reaction and so they do not contribute to the emf of the cell. But these reactions are irreversible and therefore the cell cannot be recharged. A fresh dry cell has a potential of 1.5V. The voltage of the cell decreases gradually with usage and finally it has to be discharged.

Advantages:

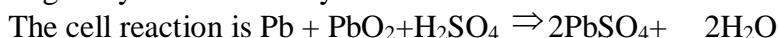
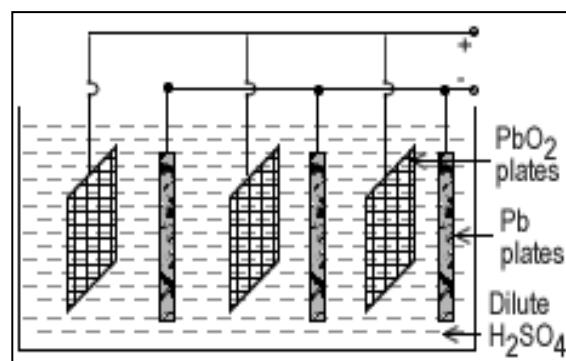
1. They have low price.
2. Dry cells are used in flash light, wall clock, portable radio, tape recorder and similar electronic devices where small amount of current is required.

Secondary cells: Secondary cells are rechargeable cells on exhaustion of reactive chemicals in the cell. They can be classified into two types.

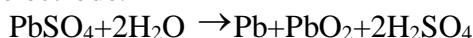
1. Acid storage cell e.g: lead storage cell and 2. Alkaline storage cells e.g: nickel cadmium cell

Acid storage cells (Lead acid battery): In these electrodes are lead grids. The anode grid is filled sponge lead and the cathode grid is filled with lead dioxide. The numbers of electrode pairs with inert porous partitions in between are dipped in 20% H_2SO_4 . The battery is encased in a plastic container.

The product $PbSO_4$ formed during discharge remains adhered on each electrode and these available at the site during recharging. During the discharging sulphuric acid is consumed and water is produced. This results in the decrease in the specific gravity of the electrolyte.

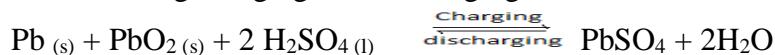


Recharge reactions: When the density of the sulphuric acid in the battery falls below 1.20gcm^{-3} . The battery needs charging. This is done by reversing the discharge reaction by applying extremely a potential higher than that of the cell. The cell acts as an electrolytic cell; depositing lead and lead dioxide electrode.



During charging sulphuric acid is regenerated in the cell.

The net reaction during charging and discharging is

**Applications:**

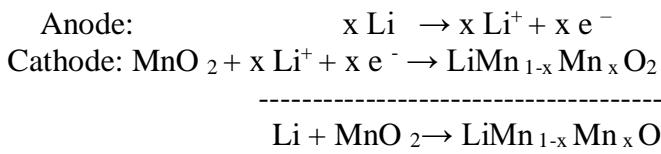
1. Lead storage batteries are extensively used in automobiles to start the engine.
2. They are also used for electric supply in telephone exchanges, railway trains, and hospitals.

b) Lithium batteries: These are of two types. a) lithium batteries and b) lithium ion batteries. Most of the lithium batteries you'll see are in coin/button cell form. Coin cells are small discs often Lithium cells are used.

Lithium batteries: They are primary batteries that use Li metal or Li compounds as anode. One of the common batteries is Li- MnO_2 battery. In this battery solid **Li acts as anode** and **MnO_2 acts as cathode**. The mixture of **propylene carbonate and 1, 2- dimethoxyethane containing dissolved salt such $LiClO_4$ acts as electrolyte**. Lithium battery can be represented as



During the reaction, Mn^{+4} is reduced to Mn^{+3} by intrinsically occupied Li ions in the MnO_2 intercalation compound. $LiMnO_2$ indicates that Li^+ ions remain present in the host MnO_2 lattice. The cell reaction is



Applications: Cylindrical Li-batteries are used in automatic cameras, calculators, security devices, long time memory backup devices and other similar electronic gadgets.

Advantages:

1. They have high charge density (long life).
2. They produce voltage from 1.5 to 3.7 V at operating temperature (-20 °C to 50 °C).

Limitation: The only limitation is their high cost.

Lithium ion batteries (Rechargeable batteries): These cells do not contain metallic lithium hence they are called lithium ion cells and use lithium ions instead. In these cells oxidation and reduction does not take place but transport of Li^+ ions through the electrolyte from one electrode to other electrode take place through the external circuit to maintain electrical balance. In this battery, Li ions interchange between two layers of graphite and $LiCoO_2$.

Fuel cells

A Fuel cell is an electrochemical device that converts chemical energy into electrical energy. In 1932, Francis Bacon developed the first successful FC. He used hydrogen, oxygen, an alkaline electrolyte and nickel electrodes.

Every fuel cell has two electrodes, one positive and one negative, called, respectively, the cathode and anode. The reactions that produce electricity take place at the electrodes.

In all types of fuel cell, hydrogen is used as fuel and can be obtained from any source of hydrocarbon. The fuel cell transforms hydrogen and oxygen into electric power, emitting water as their only waste product.

Every fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which speeds the reactions at the electrodes.

A single fuel cell generates a tiny amount of direct current (DC) electricity. A converter is used to produce AC current. In practice, many fuel cells are usually assembled into a stack. Cell or stack, the principles are the same.

There are different types of fuel cells, differentiated by the type of electrolyte separating the hydrogen from the oxygen.

The types of fuel cells are:

- H₂-O₂ fuel cell, Methanol-oxygen fuel cell and Phosphoric acid fuel cells.

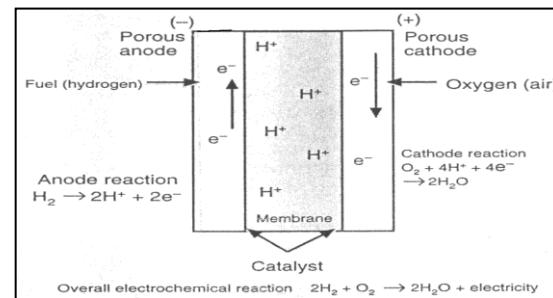
Cell Representation: *fuel/electrode/electrolyte/electrode/oxidant*

In this cell the fuel and oxidizing system are continuously supplied to the electrodes of the cell at which they undergo reaction. Fuel cells are capable of supplying current as long as the reactions are supplied.

$$\text{FUEL} + \text{OXYGEN} \rightarrow \text{OXIDATION PRODUCTS} + \text{ELECTRICITY}$$

Principle, construction and working of H₂-O₂ fuel cell:

- The cell consists of two inert porous electrodes and an electrolyte solution (2.5% KOH).
- Through the anode hydrogen gas is bubbled and through cathode oxygen is bubbled.
- A number of such fuel cells are stacked together in series to make a battery.
- The product is discharged is water.
- The catalysts are made of graphite impregnated with finely divided Pt (or) 75/25 alloy of Pd & Ag or Ni.



Advantages:

- Fuel cells have the big advantage of not requiring charging up, as long as you keep on supplying the fuel and oxidant.
- Hydrogen-oxygen fuel cells create water and since the hydrogen will have to be made from abundant water supplies in the long run, it is effectively a renewable resource, unlike fossil fuels like petrol or diesel.
- Fuel cells do not produce the usual pollutants like sulfur oxides (acid rain), nitrogen oxides and carbon monoxide (harmful gases from traffic pollution).
- Unless an organic fuel like a hydrocarbon or an alcohol is used, there will be no greenhouses gases like carbon dioxide, because hydrogen combustion only produces harmless water.

Disadvantages:

- Hydrogen is a gas and requires a much larger storage volume compared to fossil fuels like petrol.
- Hydrogen is a highly flammable explosive gas – too easily ignited.
- There is no efficient means of mass producing hydrogen.

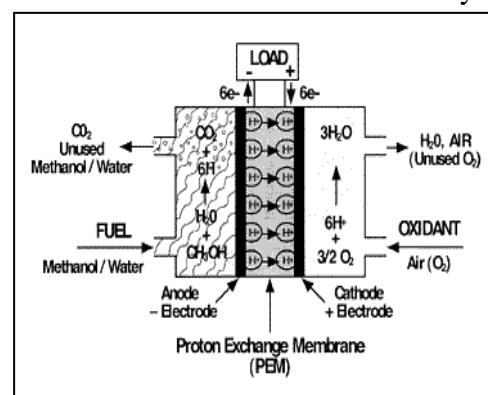
APPLICATIONS: H₂-O₂ fuel cells are used as energy sources in space vehicles, submarines & military vehicles. These fuel cells produce H₂O as a valuable fresh water source for astronauts.

Methanol-Oxygen fuel cell: In this fuel cell, methanol and water are circulated at anode and oxygen or air is circulated at cathode of the cell.

- In this cell electricity is produced at anode by the oxidation of methanol and water on Pt catalyst to form CO₂.
- The water which is formed at cathode is consumed in the reaction migrate towards cathode through the membrane and these H⁺ ions reacts with O₂ at cathode produce water.
- The electrons so produced at anode are transported from anode to cathode through external circuit by producing power.

Advantages:

- Storage of methanol is easy than H₂.
- The energy density of methanol is higher than hydrogen.



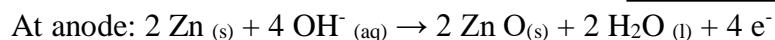
Limitations:

- Methanol is toxic and flammable.
- During oxidation of methanol, CO is formed which is reactive towards Pt and lowering the performance.

Zinc air battery: In zinc air battery, the anode is made of zinc plates. A perforated carbon plate treated with water repellents acts as a cathode. Sodium hydroxide (5M) or potassium hydroxide is used as an electrolyte. The anode, cathode and the electrolyte are contained in an ebonite or polymeric case. At the anode, zinc reacts with electrolyte to form zincate ions which decay into zinc oxide and water. The electrons released at the anode travel to the cathode where oxygen of the air accepts the electrons to form hydroxide ions.

The cell is represented as: **Zn / NaOH (5M) / Air / C**

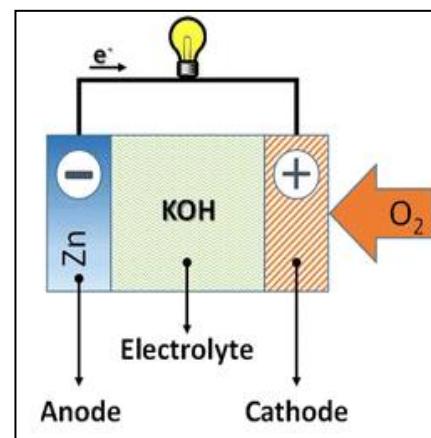
The cell reactions are



They produce 1.65 Volts. Zinc air batteries have the properties of both fuel cell and batteries. Zinc air batteries are electrically non-rechargeable; however they can be recharged mechanically by converting the zinc oxide produced in the battery back into the zinc metal.

Advantages and Applications:

1. This zinc metal can be reused.
2. They are very cheap and are increasingly being used instead of mercury batteries.
3. Their size varies from small button cells that are used in watches and hearing aids to large batteries used in cameras and also for the electric propulsion of vehicles.



QUESTION BANK**ESSAY QUESTIONS**

1. Discuss the construction and working of galvanic cell with a neat Sketch.
2. What is a galvanic cell and how does it differ from electrolytic cell? What are the electrode reactions that take place in Daniel cell?
3. What is meant by Reference Electrode? Discuss the construction and working of Hydrogen Electrode.
4. What is meant by Reference Electrode? Discuss the construction and working of Calomel Electrode.
5. Derive the Nernst equation for the determination of electrode potential.
6. Define pH and explain the construction and working of pH meter.
7. Define potentiometry and explain the potentiometric titration of a redox reaction.
8. Define conductivity and explain the conductometric titration of
a) Strong acid and Strong base b) Weak acid and Strong base.
9. What are batteries? Explain the principle, working and applications of dry cell.
10. Write a short note on
a) Primary and Secondary battery
b) Zinc-air battery.
11. Discuss the working of lead acid battery.
12. What are fuel cells? Explain the construction and working of Hydrogen-Oxygen fuel cell.
13. What are fuel cells? Explain the construction and working of Methanol-Oxygen fuel cell.

VERY SHORT ANSWER QUESTIONS

1. How is a fuel cell better than a battery?
2. Write the cell reactions taking place in dry cell.
3. What are the applications of pH measurement?
4. What are the advantages of conductometric titrations?
5. What is the principle of fuel cell?
6. Dry cell is a primary cell. Why?
7. What are the advantages of methanol-oxygen fuel cell over hydrogen-oxygen fuel cell?
8. Differentiate primary cell, secondary cell and fuel cell.
9. Write the cell reactions of lead-acid battery.
10. Lead-acid battery is a secondary battery. Justify.

UNIT 3

INSTRUMENTAL METHODS AND NON-CONVENTIONAL ENERGY SOURCES

PART-B: NON-CONVENTIONAL ENERGY SOURCES

Introduction – Renewable & Non –Renewable energy sources: **Solar Energy**- Introduction, Applications of Solar energy – Photovoltaic cell: design, working and its importance.

Hydropower plant - schematic diagram. **Geo-Thermal energy**: Introduction-schematic diagram- Design and working. **Tidal power** - Introduction- Design and working. **Biomass energy**.

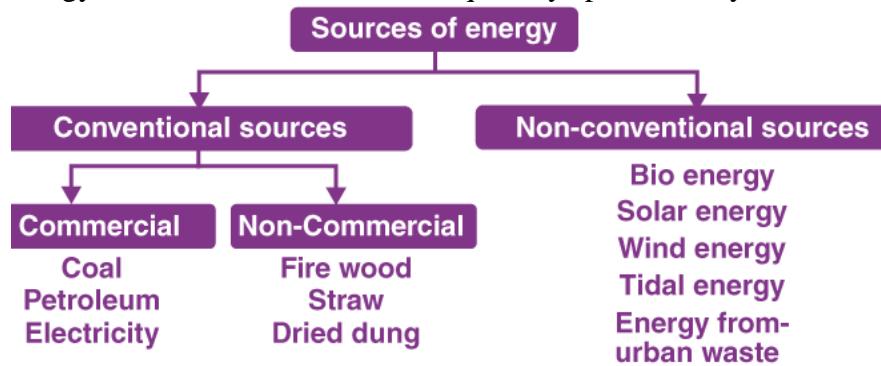
Energy is one of the major parts of the economic infrastructure, being the basic input needed to sustain economic growth. There exists a strong relationship between economic development and energy consumption.

The more developed is a country, the higher is the per capita of energy consumption and vice-versa. Human civilization relies on different sources of energy.

The two major sources of energy can be classified under:

1. Conventional Sources (Non renewable Recourses).
2. Non-Conventional Sources(Renewable Recourses)..

Conventional Sources of Energy: These sources of energy are also known as non-renewable sources of energy and are available in limited quantity apart from hydro-electric power. F



urther, it can be classified under

commercial and non-commercial energy.

Commercial Energy Sources: Coal, electricity and petroleum are known as commercial energy since the consumer needs to pay its price to buy them.

a) Coal: Coal is the most important source of energy. There are more than 148790 coal deposits in India. Between 2005-2006, the annual production went up to 343 million tons. India is the fourth-largest coal-producing country and the deposits are mostly found in Bihar, Orissa, Madhya Pradesh and Bengal.

b) Oil and Natural Gas: Today oil is considered to be liquid gold and one of the crucial sources of energy in India and the world. Oil is mostly used in planes, automobiles, trains and ships. It is mainly found in Assam, Gujarat and Mumbai. The total production of oil in India was 0.3 million tons in 1950-51, which increased up to 32.4 million tons in 2000-01.

c) Electricity: Electricity is a common form of energy and used for domestic and commercial purposes. It is mainly utilized in electrical appliances like fridge, T.V, washing machine and air conditioning. The major sources of power generation are mentioned below:

- **Nuclear Power** **Thermal Power** **Hydro-electric power**

Thermal Power: Thermal power is generated at various power stations by means of oil and coal. It is a vital source of electric current and its share in the total capacity of the nation in 2004-05 was 70 percent.

Hydroelectric Power: Hydroelectric power is produced by constructing dams above flowing rivers like Damodar Valley Project and Bhakra Nangal Project. The installed capacity of hydroelectric power was 587.4 mW in 1950-51 and went up to 19600 mW in 2004-05.

Nuclear Power: The fuel used in nuclear power plants is Uranium, which costs less than coal. Nuclear power plants can be found in Kaiga (Karnataka), Kota (Rajasthan), Naroura (UP) and Kalapakam(Chennai).

Non-commercial energy sources: Generally, the energy sources that are freely available are considered non-commercial energy sources. The examples of non-commercial energy sources are straw, dried dung, firewood.

Non-Conventional Sources of Energy

These non-conventional sources are also known as renewable sources of energy. Examples include solar energy, bio energy, tidal energy and wind energy.

1. Solar Energy: This is the energy that is produced by sunlight. The photovoltaic cells are exposed to sunlight based on the form of electricity that needs to be produced. The energy is utilized for cooking and distillation of water.

2. Wind Energy: This kind of energy is generated by harnessing the power of wind and mostly used in operating water pumps for irrigation purposes. India stands as the second-largest country in the generation of wind power.

3. Tidal Energy: The energy that is generated by exploiting the tidal waves of the sea is known as tidal energy. This source is yet to be tapped due to the lack of cost-effective technology.

Difference between Conventional and Non-conventional Sources of Energy

Conventional sources of energy	Non-conventional sources of energy
These sources of energy are also known as a non-renewable source of energy	These sources of energy are also known as a renewable source of energy
They find both commercial and industrial purposes	They are mainly used for household purposes
These can be considered to be one of the reasons for the cause of pollution	These are not responsible for the cause of pollution
Coal, fossil fuels are two examples	Wind, solar energy and Biomass two examples

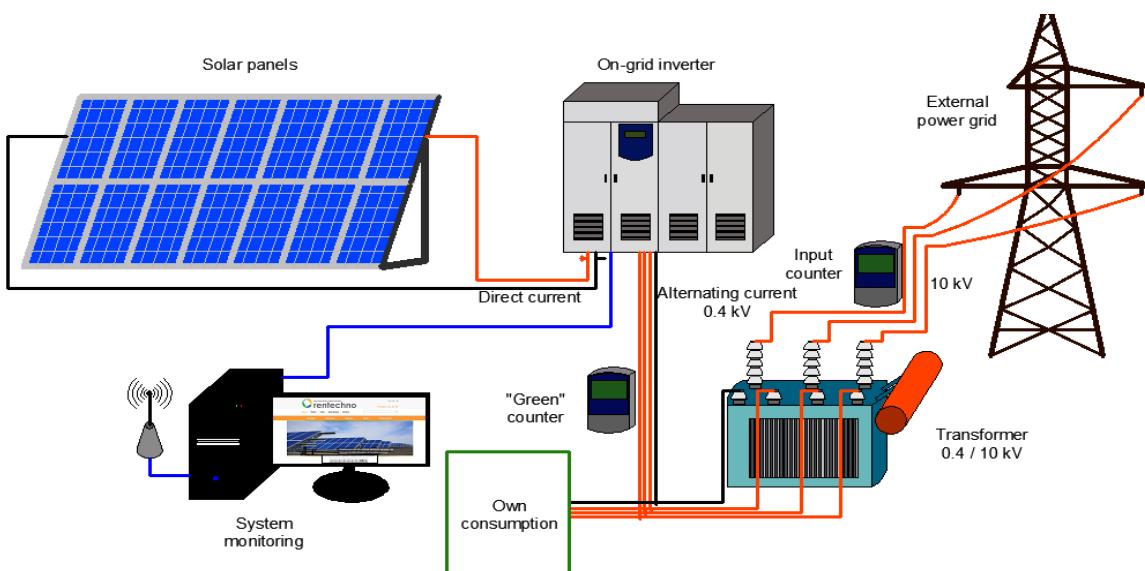
Solar Energy

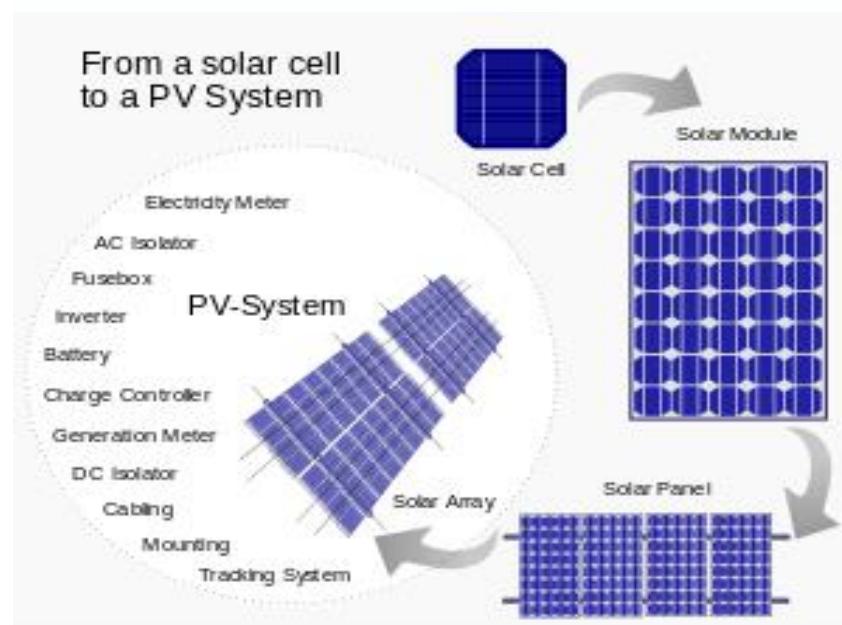
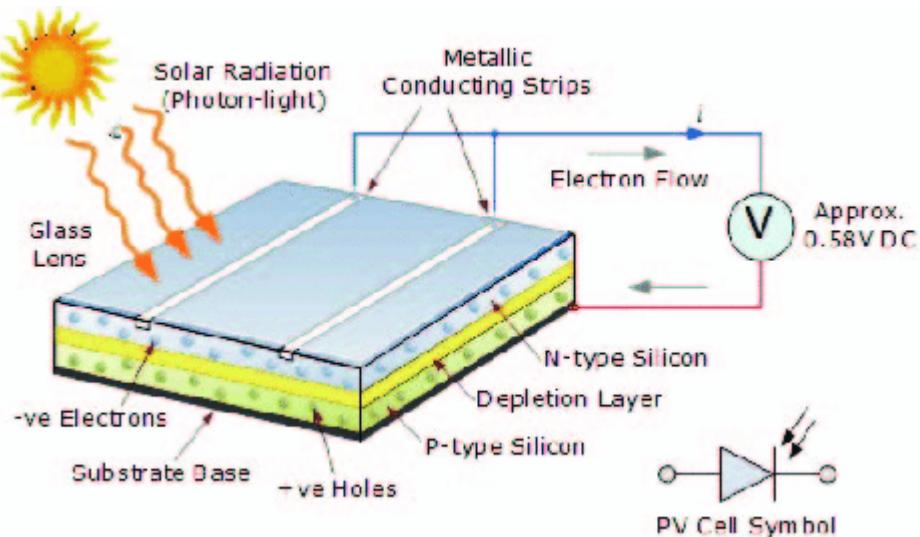
Solar energy refers to capturing the **energy** from the Sun and subsequently converting it into electricity. We can also use the term **solar** power with the same meaning. ... The Sun's **energy** is in the form of **solar** radiation. **Solar** radiation makes the production of **solar** electricity possible.

Applications of Solar energy: Some of the major application of solar energy are as follows:

- | | | |
|--------------------------------|--|-------------------------------------|
| (a) Solar water heating | (e) Solar drying of agricultural and animal products | (h) Solar electric power generation |
| (b) Solar heating of buildings | (f) Solar furnaces | (i) Solar thermal power production |
| (c) Solar distillation | (g) Solar cooking | (j) Solar green houses |
| (d) Solar pumping | | |

Photovoltaic cell or Solar Cell : A **solar cell** (also known as a photovoltaic cell or PV cell) is defined as an electrical device that converts light energy into electrical energy through the photovoltaic effect. A solar cell is basically a p-n junction diode.





Construction of Solar Cell

Solar cell consists of p-type and n-type semi conductors layers and the two layers are sandwiched and there is formation of p-n junction.

The surface is coating with Anti-reflecting coating to avoid the loss of incident light energy due to reflection. A proper **metal contacts** are made on the n-type and p-type side of the semiconductor for electrical connection

Working:

- When a solar panel exposed to sunlight , the light energies are absorbed by a semiconductor materials.
- Due to this absorbed energy, the electrons are liberated and produce the external DC current.

The DC current is converted into 240-volt AC current using an inverter for different applications

Advantages of solar cell

1. It is clean and non-polluting.
2. It is a renewable energy.
3. Solar cells do not produce noise and they are totally silent.
4. They require very little maintenance.
5. They have long life time.
6. There are no fuel costs or fuel supply problems

Disadvantages:

1. Solar cells (or) solar panels are very expensive.
2. Energy has not been stored in batteries.
3. Air pollution and whether can affect the production of electricity.
4. They need large area of land to produce more efficient power supply.
5. Sun does not shine consistently.
6. Less efficient and costly equipment.
7. Reliability Depends On Location

Applications of solar energy:

1. Domestic power supply.
2. Electric power generation in space.
3. Drying Agricultural Products.
4. Solar pumps are used for water supply.
5. Water Heating.
6. Generating Electrical Power.
7. To providing electrical power to satellites

HYDRO-ELECTRIC POWER PLANT

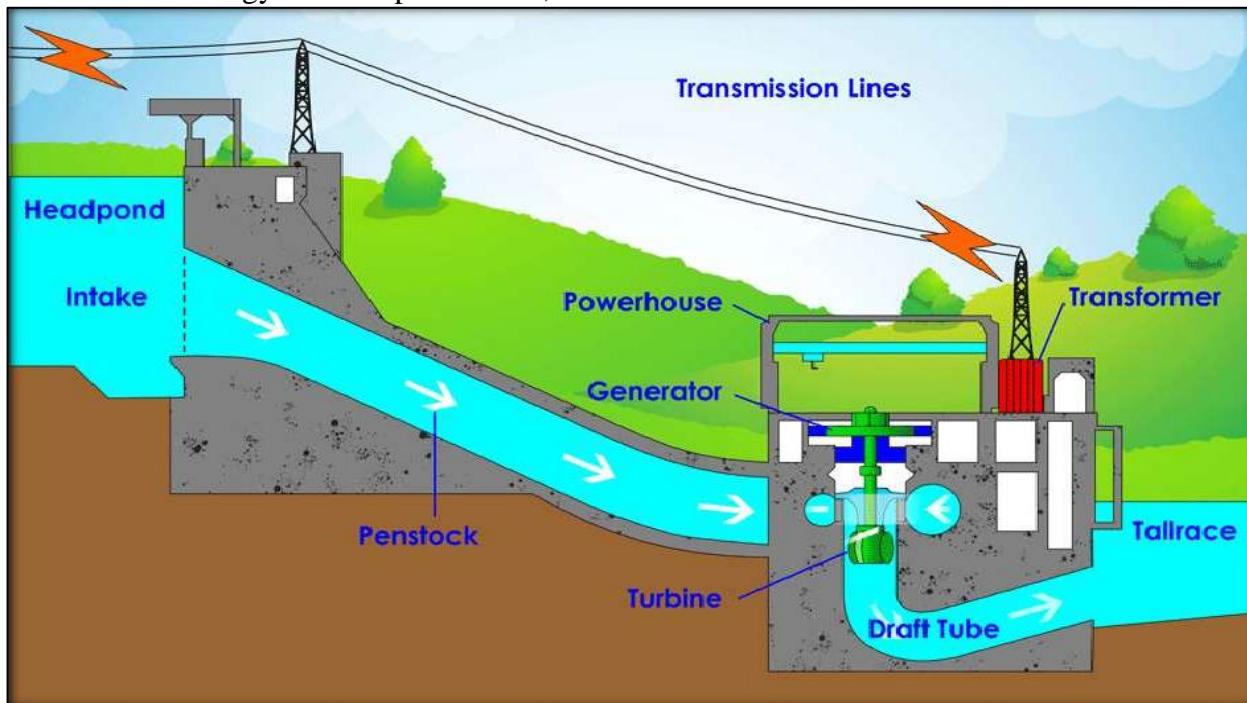
A power plant that produces electricity by using flowing **water** to rotate a turbine (which drives the generator), is called hydro-power plant (or hydroelectric power plant). The electricity produced by using the energy of falling **water** (or flowing **water**) is called hydroelectricity.

PRINCIPAL : A hydraulic turbine converts the energy of flowing water into mechanical energy. A hydroelectric generator converts this mechanical energy into electricity. The operation of a generator is based on the principles discovered by Faraday

The process

- Flowing water is directed toward and used to spin giant turbines.
- Mechanical energy is generated.
- The mechanical energy is converted to electrical energy using generators.

The electrical energy flows to power lines, and from there to consumers as needed



The principal components of H_E power plant are

- | | | |
|---------------------------------|----------------|----------------|
| 1. Dam | 5. Surge tank | 9. Generator |
| 2. Intake structure (Reservoir) | 6. Turbines | 10. Draft tube |
| 3. Spillway | 7. Governor | 11. Tail race |
| 4. Penstocks | 8. Power house | |

Intake structure: Intake structures are used for collecting water from the surface sources such as river, lake, and reservoir.

Spillway: Spillway is used to dispose off excess water in reservoir.

Spillways ensure that the water does not overflow and damage or destroy the dam.

Penstock: The water flow of from dam towards turbine with the help of penstock.

It converts the potential energy of water into kinetic energy.

It is made up of cast iron or concrete material.

Surge Tank: It is connected in between dam & power house.

When water flows from dam towards turbine , it filled the surge tank first , after that valve is open either manually or automatically

This sequence is follow to avoid or to prevent the turbines against water hammer effect.

Due to sudden reduction in water discharge (when load on generator is reduced , governor closes the turbine gates) causes increase in pressure of the water in the penstock.

Due to high pressure penstock may damage. This effect is known as '**Water hammer effect**'.

Turbine or Prime mover: Its main function is to take water from dam at high pressure & start to rotate. It converts kinetic energy of water into mechanical energy.

Types of turbines:

Impulse turbine (Used in high head plants) e.g:- Pelton Wheel, Turgo, Michell-Banki

Reaction Turbine (used in low & medium head plants) e.g:- Francis turbine, Kaplan turbine

Governing system: Governing system or governor is the main controller of the turbine.

The governor varies the water flow through the turbine to control its speed or power output.

Draft Tube: It is used in hydro-electric power plant near the turbine.

It allows the turbine to be set above tail water level, without loss of head.

Generator: It is used to convert the mechanical energy into electrical energy. For that purpose the turbine & generator are mechanically coupled.

Tail race : It is the area where the water leaves the station after generation and it returns to the river.

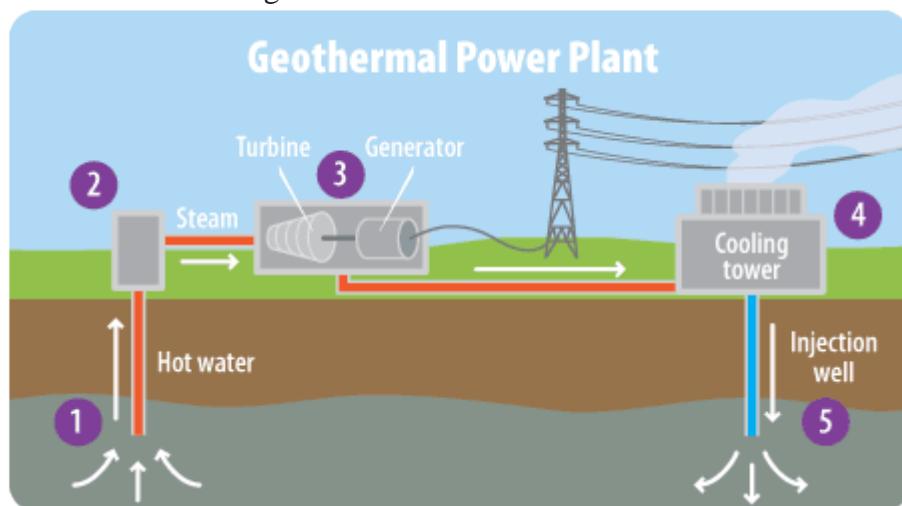
It is designed in such a way that water hammer is minimizes when water leaves the draft tube.

Power house contains the electro mechanical equipment i.e. Hydro power turbin, generator, excitation system, transformers, switchyard, etc.

Advantages: 1. No fuel required 2. No air pollution 3. The life of plant is longest 4. Renewable energy 5. Water supply and flood control 6. Generation cost per unit (KWH) is lowest 7. Can easily work during high peak daily loads

Geothermal power plant

Geothermal power plants are used in order to generate electricity by the use of geothermal energy (the Earth's internal thermal energy). They essentially work the same as a coal or nuclear power plant, the main difference being the heat source



At a geothermal power plant, wells are drilled 1 or 2 miles deep into the Earth to pump steam or hot water to the surface. You're most likely to find one of these power plants in an area that has a lot of hot springs, geysers, or volcanic activity, because these are places where the Earth is particularly hot just below the surface.

Working

1. Hot water is pumped from deep underground through a well under high pressure.
2. When the water reaches the surface, the pressure is dropped, which causes the water to turn into steam.
3. The steam spins a turbine, which is connected to a generator that produces electricity.
4. The steam cools off in a cooling tower and condenses back to water.
5. The cooled water is pumped back into the Earth to begin the process again.

Biomass energy

Biomass energy is **energy** generated or produced by living or once-living organisms.

The most common **biomass** materials used for **energy** are plants, such as corn and soy, above.

The **energy** from these organisms can be burned to create heat or converted into electricity.

Biogas energy plant:

A **biogas plant** can convert animal manure, green **plants**, waste from agro industry and slaughterhouses into combustible gas. The **energy** content of the gas depends mainly on its methane content. High methane content is therefore desirable

Biogas is a clean and efficient fuel. It is a mixture of methane (CH_4), carbon dioxide (CO_2), hydrogen (H_2) and hydrogen sulphide (H_2S). The chief constituent of biogas is methane (65%).

Principle: Biogas is produced as a result of anaerobic fermentation of biomass in the presence of water.

Construction: The biogas plant is a brick and cement structure having the following five sections:

1. Mixing tank present above the ground level.
2. Inlet chamber: The mixing tank opens underground into a sloping inlet chamber.

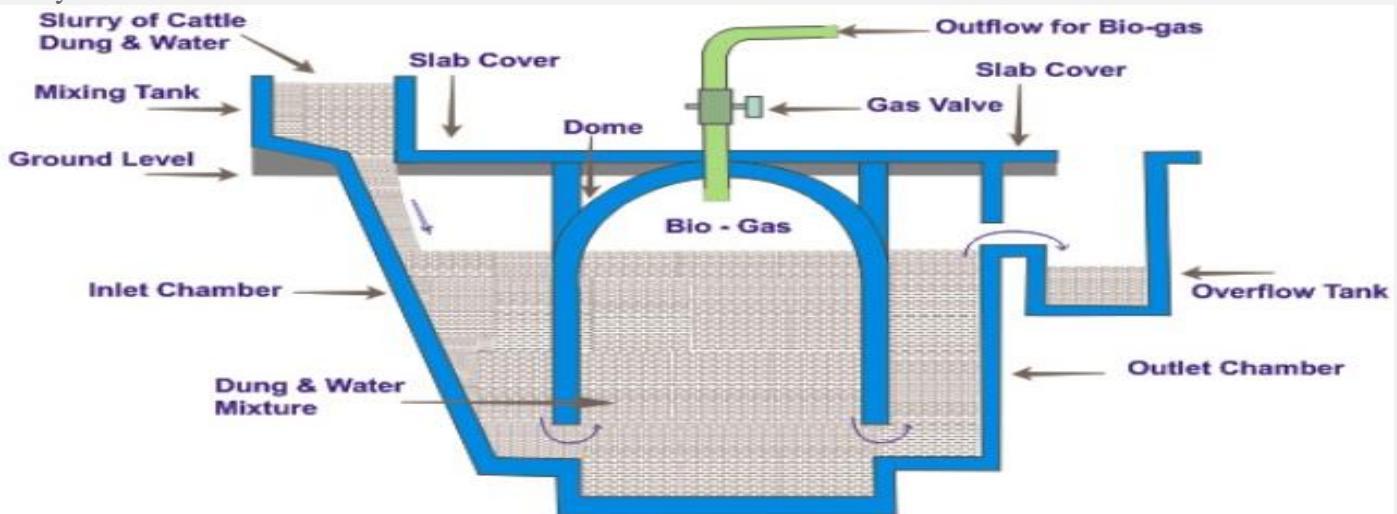
3. Digester: The inlet chamber opens from below into the digester which is a huge tank with a dome like ceiling. The ceiling of the digester has an outlet with a valve for the supply of biogas.

4. Outlet chamber: The digester opens from below into an outlet chamber.

5. Overflow tank: The outlet chamber opens from the top into a small over flow tank.

Working:

1. The various forms of biomass are mixed with an equal quantity of water in the mixing tank.
2. This forms the slurry. The slurry is fed into the digester through the inlet chamber.
3. When the digester is partially filled with the slurry, the introduction of slurry is stopped and the plant is left unused for about two months.
4. During these two months, anaerobic bacteria present in the slurry decomposes or ferments the biomass in the presence of water.
5. As a result of anaerobic fermentation, biogas is formed, which starts collecting in the dome of the digester.
6. As more and more biogas starts collecting, the pressure exerted by the biogas forces the spent slurry into the outlet chamber.
7. From the outlet chamber, the spent slurry overflows into the overflow tank.
8. The spent slurry is manually removed from the overflow tank and used as manure for plants.
9. The gas valve connected to a system of pipelines is opened when a supply of biogas is required.
10. To obtain a continuous supply of biogas, a functioning plant can be fed continuously with the prepared slurry.



Fixed Dome type Bio-gas Plant

The **advantages of biogas** are many and significant:

- It valorizes and exploits **waste biomass** and **by-products** to produce energy, reducing the environmental impact of waste treatment and that caused by the distribution of traditional fossil fuels;
- It contributes to the realization of the **green economy** expected for the future, to the achievement of a **circular economy model** and a more sustainable use of energy, careful to the protection of the environment;
- **Reduces carbon dioxide emissions.** The combustion of biogas does not give rise to additional CO₂ compared to that previously used by vegetable or animal biomass, unlike fossil fuels that produce it from scratch;
- Allows **energy diversification**. The use of biogas reduces dependence on traditional energy sources and is one of the choices of clean and sustainable energy;
- In addition to generating **electricity**, it also produces **heat**. In fact, biogas can be used both to generate electricity and to meet the demand for heating.
- It can be delivered in a **continuous form because the energy from biomass is adjustable at will and can be blocked when desired, as well as fossil fuels.**
- Biogas plants are easier to build and implemented technologies are less sophisticated and easier to find. There is therefore a **reduction in costs** and a lower investment in their construction than other renewable energy plants;
- Biogas, once purified from impurities and CO₂ removed, can **be transformed into biomethane**. Subsequently, it is transported and used through traditional infrastructure, allowing countries to reduce emissions in some difficult sectors, such as heavy industry and freight transport.

What is Tidal Energy?

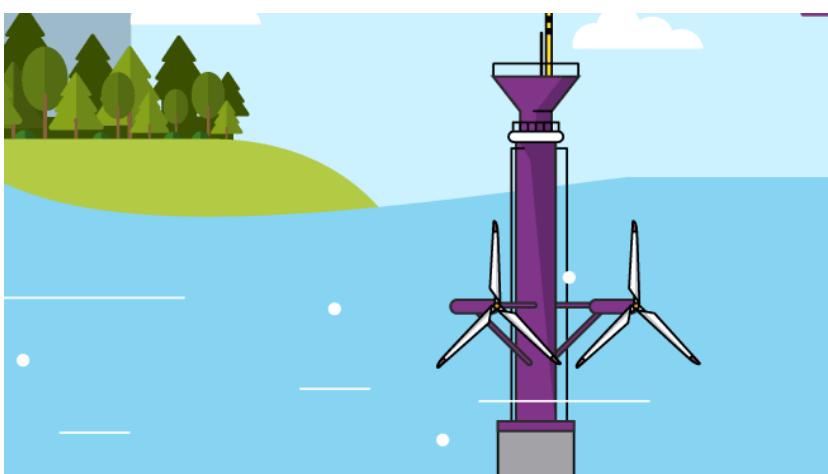
Tides are a regular phenomenon. They can be predicted over months and years in advance. This is why the

energy from this massive movement of water can be harnessed and converted into a usable form of energy.

Tidal Energy Generator

The energy obtained from the rise and fall of tides is called the tidal energy.

Tidal barrages or dams are constructed across a narrow opening to the sea. Water rushes into the dam when the sea level rises. This moves the blades of the turbines which are attached at the opening of the dam. This results in the generation of electricity.



Tidal Energy Generator

shown in figure. The ocean tides rise and fall and water can be stored during the rise period and it can be discharged during fall. A dam is constructed separating the tidal basin from the sea and a difference in water level is obtained between the basin and sea.

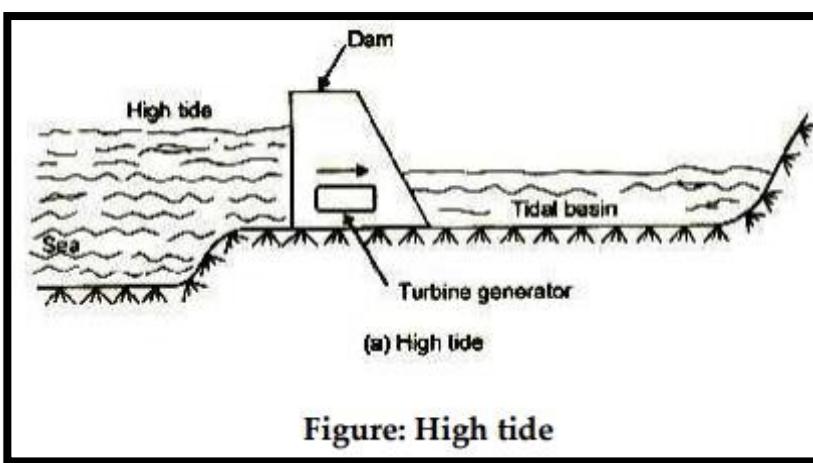


Figure: High tide

Working: The arrangement of this system is

Figure: High tide

During high tide period, water flows from the sea into the tidal basin through the water turbine. The height of tide is above that of tidal basin. Hence the turbine unit operates and generates power, as it is directly coupled to a generator.

Figure: Low tide

During low tide period, water flows from tidal basin to sea, as the water level in the basin is more than that of the tide in the sea. During this period also, the flowing

water rotates the turbine and generator power.

The generation of power stops only when the sea level and the tidal basin level are equal. For the generation of power economically using this source of energy requires some minimum tide height and suitable site. Kislava power plant of 250 MW capacity in Russia and Rance power plant in France are the only examples of this type of power plant.

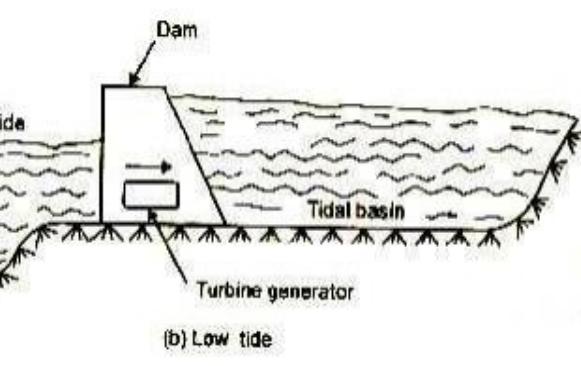
Advantages and Disadvantages of Tidal Energy

Some advantages of tidal energy are:

- Environment-friendly
- A highly predictable energy source
- High energy density

Some of the disadvantages of tidal energy are:

- High tidal power plant construction costs
- Negative influence on marine life forms



- Operational and maintenance costs are low
- An inexhaustible source of energy

- Location limits
- The variable intensity of sea waves

Although not widely used, tidal energy has the potential for future electricity generation. Among other sources of renewable energy tidal energy has suffered due to the relatively high cost and limited availability of sites for construction. However, due to the recent technological developments indicating that the economic and environmental costs can be brought down to competitive levels, there seems to be a bright future for tidal energy generation.

QUESTION BAN
ESSAY QUESTIONS

1. Explain the principle, construction, working and applications of photo voltaic cell (**solar energy**). 7M
2. Which type of non conventional energy source you prefer for the generation of energy?
How to construct it and its importance? (**Hydropower plant**) 7M
3. What is tidal energy? Write any two conditions to generate **tidal energy**. 7M
4. What are the non-conventional energy sources? Discuss about **geothermal energy** 7M
5. How do non-conventional energy sources differ from conventional energy sources?
Write about **tidal wave power**. 7M

VERY SHORT ANSWER QUESTIONS

1. What are the advantages of Hydro power? 2M
2. What are the drawbacks of geothermal power plants? 2M
3. Name the raw materials used for the production of bio fuels. 2M
4. What are the constituents of biogas? 2M
5. What are the different steps involved in the production of bio ethanol? 2M
6. What are the advantages of non conventional energy sources? 2M

UNIT IV: SOLID STATE CHEMISTRY

Types of solids – Crystal defects- Frenkel and Schottky defects – Spinel and Inverse spinel.
Hall Effect and Applications.

Semiconductors: Preparation of pure semiconductors by Zone refining, Distillation and Czochralski crystal pulling technique, Doping- Epitaxy, Diffusion and Ion-implantation technique- Intrinsic and Extrinsic semiconductors - Applications.

Insulators: Electrical Insulators and their Applications.

Solids are characterized by definite shape, strength and rigidity. They are used in architecture, conductors and semi-conductors.

Types of solids: Based upon atomic arrangement, binding energy, physical & chemical properties, solids can be classified into Crystalline & Amorphous solids.

Crystalline solids: The building constituents arrange themselves in regular manner throughout the entire three dimensional networks. The characteristic features are

- Existence of crystalline lattice. i.e., a solid figure which has a definite geometrical shape, with flat faces and sharp edges.
- Long range order
- Definite sharp melting point.
- Anisotropy, i.e., their physical properties are different in different directions.
- Give x-ray diffraction bands.
- Regarded as True solids

Examples: NaCl, CsCl, etc.

Amorphous Solids: The term Amorphous is derived from Greek word ‘Omorphe’ meaning shapeless. The characteristic features are

- No regular arrangement of atoms or molecules.
- Short range order
- No definite sharp melting point.
- Isotropy i.e., their physical properties are same in different directions.
- Do not give x-ray diffraction bands.
- Considered as non-crystalline solids or super-cooled liquids.

Examples: Glass, Rubber and Plastics etc.

Crystal Defect or Imperfection:- Any departure from perfectly ordered arrangement of the constituent particles in the crystal called imperfection or defect.

The defects in the crystal arise when crystallization takes place at the fast or moderate rates because the constituent particles do not get sufficient time to arrange in perfect order.

Point defect:- When the deviation or irregularities exists from ideal arrangement around a point or an atom in a crystalline substance the defect is called the point defect or atomic imperfection.

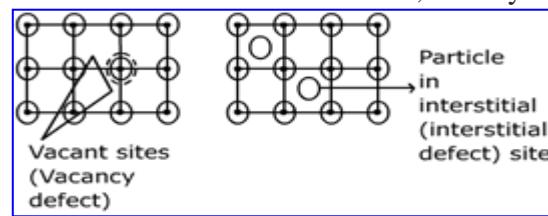
Types of the point defects:-

1. Stoichiometric defects
2. Non stoichiometric defects
3. Impurity defects

I. Stoichiometric defect:- If imperfections in the crystal are such that the ratio between cations and anions remains same, and stoichiometry of substance do not disturbed, the defect is called stoichiometric defect. These defects are of the following types.

1. Vacancy defect:- In a crystalline substance, if some of the lattice sites are vacant, the crystal is said to have vacancy defect. It results in decrease of density of substance.

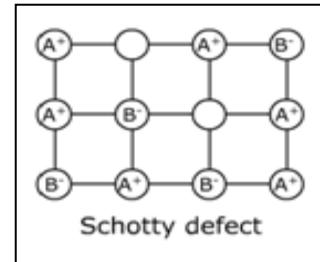
2. Interstitial defect:- When some constituent particles are present in the interstitial site the crystal is said to have interstitial defect. This defect generally results no change in density of crystal.



Schottky defect:- If in an ionic crystal of the type A^+B^- equal number of cations and anions are missing from the lattice site so that electrical neutrality is remained is called Schottky defect.

This type of defect is shown by highly ionic compounds which have- High Co – ordination number (6 or 8) and small difference in the sizes of cations and anions.

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.



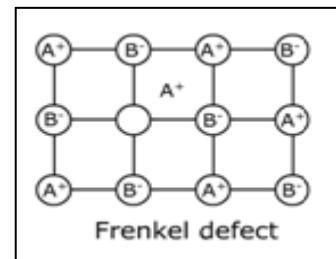
Consequences of Schottky Defect

As the number of ions decreases, as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases.

The crystal begins to conduct electricity to a small extent by ionic mechanism.

The presence of too many voids lowers lattice energy and the stability of the crystal.

Frenkel defect:- If an ion is missing from its lattice site and occupies the interstitial site, electrical neutrality as well as stoichiometry of the compound are maintained. This type of defect is called Frenkel defect. Mostly cations are relatively smaller in size and therefore it is easier to place cations in interstitial positions.



This type of defect is present in ionic compounds which have- Low co ordinations number and larger difference in size of cations and anions and also in compounds having highly polarizing cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.

Consequences of Frenkel defect

As no. of ions missing from the crystal lattice as a whole is zero, therefore density of the solid remains the same.

The closeness of like charges tends to increases the dielectric constant of the crystal.

The crystal conducts electricity to a small extent by ionic mechanism.

II. Non stoichiometric defects:- Due the result of the imperfections in the crystal, if the ratio of the cations and anions becomes different from that indicated by ideal chemical formula, the defects are called non-stoichiometric defects. They are of two types

i. Metal excess defects:- A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, thereby maintain the electrical neutrality.

The interstitial sites containing the electron thus trapped in the anion vacancies are called the F – centers. This name comes from the German word **Farbe** meaning **colour**.

They are responsible for imparting colour to the crystals.

Example:- When NaCl is heated in an atmosphere of Na vapours, the excess of Na atoms

deposit on the surface of NaCl crystal. Cl^- ions then diffuse to the surface where they combine with Na^+ ions formed from Na atoms due to loss of electrons. These electrons lost by Na atoms diffuse back into the crystal and occupy the vacant sites created by Cl^- ions and imparts Yellow colour to NaCl crystal.

By presence of extra cation in interstitial sites:- Metal excess may also be caused by an extra cation occupying the interstitial site. For example when ZnO is heated, it loses oxygen and turns yellow due to following reaction



The excess cations and the electrons will be in neighboring interstitial sites.

ii. Metal deficiency defect:- This defect occurs when the metal shows the variable valency. Due to metal deficiency the compounds obtained are non stoichiometric. For example it is difficult to prepare ferrous oxide with ideal composition because Iron exists as both Fe^{+2} and Fe^{+3} ions thus we obtain $\text{Fe}_{0.95}\text{O}$ or Fe_xO with $x = 0.93$ to 0.96 .

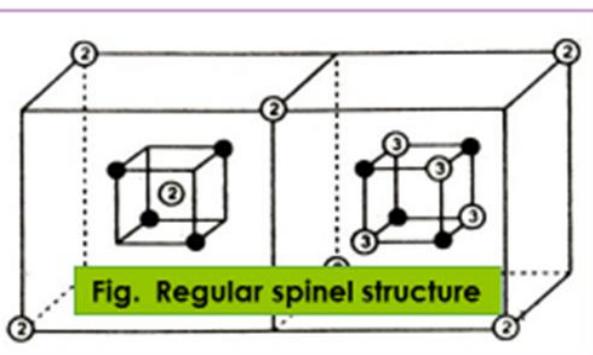
III. Impurity defects:- These defects are arises when foreign atoms are present at the lattice site in place of the host atom or it is present at the vacant interstitial site.

Example n – type semi conductor, p – type semi conductor.

Structure of normal Spinel and inverse spinels: The spinels are a class of minerals of general formulation $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4^{2-}$ which crystallises in the cubic crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice.

Regular or Normal spinel structures are usually cubic close-packed oxides with two tetrahedral and one octahedral sites per formula unit. Mineral spinel MgAl_2O_4 has a normal spinel structure.

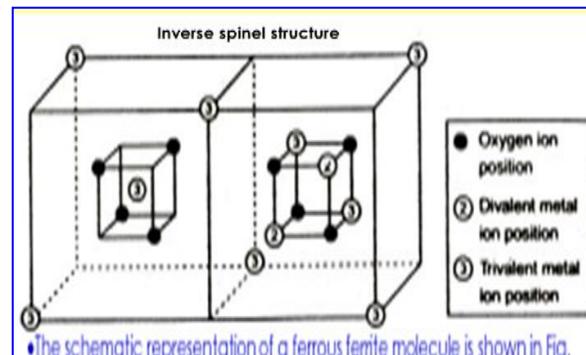
Inverse spinel structures have a different cation distribution in which the entire A cations and half of the B cations occupy octahedral sites, while the other half of the B cations occupy tetrahedral sites. An example of an inverse spinel is Fe_3O_4 .



In this type, each divalent metal ion occupies 1 tetrahedral site and each trivalent metal ion occupies 1 octahedral site. Totally in an unit cell, there will be **8 tetrahedral (8 A sites) and 16 octahedral (16B sites)**.

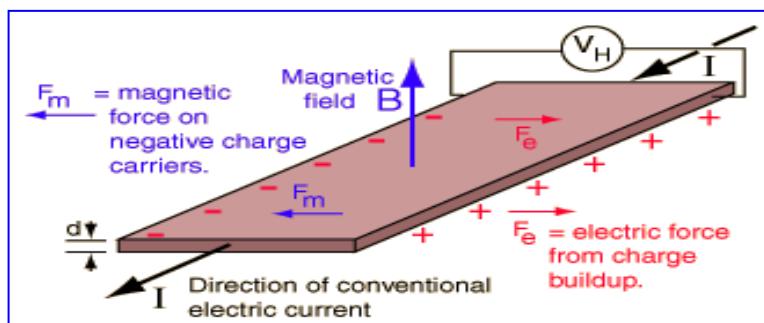
Hence, the sites A and B combined to form a regular spinel ferrite structures as shown in Fig.

The schematic representation of zinc ferrite molecule as shown in Fig.



In this type half of the B sites (8sites) are occupied by divalent metal ions and the remaining half of the B sites (8 sites) and all the A sites are occupied by the trivalent metal ions, as shown in Fig.

Hall Effect: If an electric current flows through a conductor in a magnetic field, the magnetic field exerts a transverse force on the moving charge carriers which tends to push them to one side of the conductor. This is most evident in a thin flat conductor as illustrated in the diagram.



A buildup of charge at the sides of the conductors will balance this magnetic influence, producing a measurable voltage between the two sides of the conductor. The presence of this measurable transverse voltage is called the Hall effect after E. H. Hall who discovered it in 1879.

Hall Effect in semiconductors: When a current carrying semiconductor is kept in a magnetic field, the charge carriers of the semiconductor experience a force in a direction perpendicular to both the magnetic field and the current. At equilibrium, a voltage appears at the semiconductor edges.

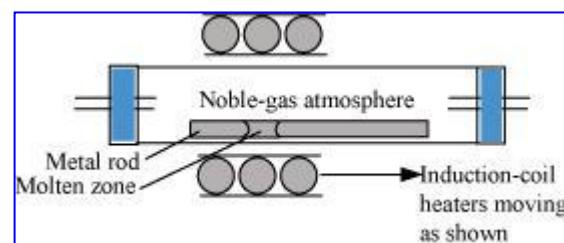
Applications: Hall probes are often used as magnetometers, i.e. to measure magnetic fields, or inspect materials (such as tubing or pipelines) using the principles of magnetic flux leakage.

Hall Effect devices are immune to dust, dirt, mud, and water. These characteristics make Hall effect devices better for position sensing than alternative means such as optical and electromechanical sensing.

Preparation of Semiconductors: Silicon of extreme purity (99.9999%) is required for the preparation of semiconducting materials. It is achieved through the following steps.

[a] Zone Refining: This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

A circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concen-



This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

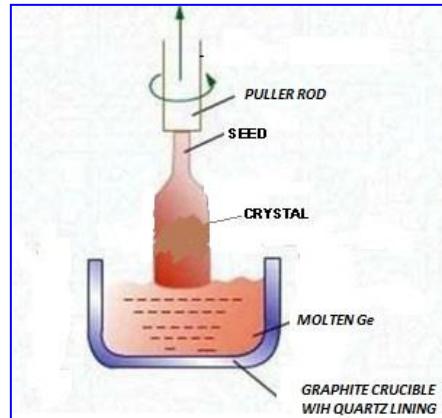
[b] Distillation: Distillation is based on the separation of materials due to difference in boiling point. Trichlorosilane (SiHCl_3) is taken in a series of distillation stills and a layer of HCl is kept over it to remove arsenic impurity. Chlorine gas is then passed through the charge, which is kept heated electrically. The emerging vapours are passed through a fractionating column and collected finally in an ice-cold receiver.

Pure SiCl_4 so obtained is then treated with extra pure water to get SiO_2 , which is then reduced, in an atmosphere of hydrogen to obtain elemental silicon.

Similarly Ge Cl_4 is employed to get germanium of high degree purity.

[c] Czochralski crystal pulling technique: Ge and Si obtained by Czochralski crystal pulling technique give crystal with regularity in crystal structure. This method involves growing crystal on a single crystal seed; thereby the atoms reproduce identical atomic arrangement as that of the seed crystal.

In this process, solid polycrystalline semiconducting material (say Ge) taken in a quartz chamber is heated till it melts. Then, the temperature is lowered to just above the m.p. of Ge. At this stage properly oriented single crystal seed of Ge is carefully lowered into the melt, till it is in contact with the surface of the charge. Thereafter, the crystal is rotated slowly and then gradually pulled out. It will be noticed that the melt in contact with the seed crystal starts solidifying producing the orientation identical on that of the seed crystal. After this, the pull rate is kept at about 1.5 to 5 cm per minute and the rotation speed is maintained at about 100 ppm. Finally, an intrinsic crystal of Ge of 5cm diameter and 25 cm length is obtained. The crystal is cut into wafers (0.25mm thick) with the help of a diamond-tipped saw. One side of each wafer is then rubbed against a metal surface with fine abrasive until it is flat and smooth.



Doping Techniques: For getting doped material, calculated quantity of dopant (B or P) is added to the melt before crystal pulling stage. Usually, dopant atoms added are of the order of 1 atom of B or P per 10^8 atoms of Ge or Si. Other techniques for doping are:

a) Epitaxy: Epitaxy refers to a type of crystal growth or material deposition in which new crystalline layers are formed with a well-defined orientation with respect to the crystalline substrate. The new layers formed are called the epitaxial film or epitaxial layer.

The term *epitaxy* comes from the Greek roots *epi*, meaning "above", and *taxis*, meaning "an ordered manner". Epitaxy involves in unified crystal growth or deposition of a thin crystal layer on another substrate, often with added dopants. The material in the epitaxial layer must have a lattice spacing and structure close to that of the substrate, e.g., Si on Ge or Ge on Si.

The Ge or Si wafer is placed in a long cylindrical quartz tube reactor, which is then heated by RF coil. Then, the gases containing compounds of Ge or Si mixed with calculated quantities of Dopant are introduced into the reactor. The process of heating is continued, till a thin film of Dopant over the wafer results. The doped wafer so obtained is ready for the fabrication of semiconductor devices.

For getting Si epitaxial film, SiCl_4 , H_2 , and N_2 mixture is used. For carrying out n-type doping, the mixture is mixed with a calculated amount of phosphine and for p-type doping, diborane is employed.

One of the main commercial applications of epitaxial growth is in the semiconductor industry.

b) Diffusion technique: Diffusion technique involves in conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atoms into the crystalline lattice of the semiconductor material without any melting. The process consists of heating a p-

type Dopant (Sb or P). This causes some of the impurity atoms to condense on the surface of wafer and diffuse, thereby resulting in a p-type semiconductor material.

By this technique, the extent of impurity atoms penetration can be controlled, even less than a few millionths of a centimeter by controlling the concentration of dopant atoms and temperature. This technique is employed for preparing n or p-type semiconductor, used in high frequency devices and to prepare n-p-n type transistor with a base width of even 5μ .

c) Ion implantation technique: In the ion implantation charged dopants of B or P are accelerated in an electric field and irradiated onto the wafer. This causes the implantation of some Dopant atoms into the crystal lattice of semiconductor. The penetration depth can be set very precisely by reducing or increasing the voltage needed to accelerate the ions. Since the process takes place at room temperature, previously added dopants cannot diffuse out. Regions that should not be doped can be covered with a masking photo resist layer.

The major advantages of this process are

- i) The process occurs at room temperature.
- ii) Extremely precise control of the dopant amount on specific area of semiconductor
- iii) Obtaining deep regions of very precise and required penetration depth having high or low concentration of dopant.

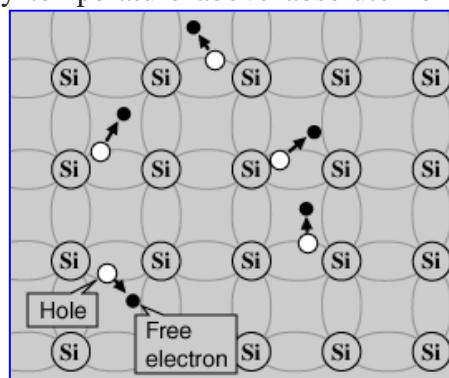
This technique is especially employed for the fabrication of high frequency devices.

The wafers obtained by above methods are then cut into chips by using chemical etching, ultrasonic vibrations, laser beams etc.

Semiconductors: Semiconductors are materials which have a conductivity between conductors (generally metals) and nonconductors or insulators (such as most ceramics). Semiconductors can be pure elements, such as silicon or germanium, or compounds such as gallium arsenide or cadmium selenide. The important types of semiconductors are discussed here.

Intrinsic Semiconductor: An intrinsic semiconductor material is chemically very pure and possesses poor conductivity. It has equal numbers of negative carriers (electrons) and positive carriers (holes).

A silicon crystal is from an insulator because at any temperature above absolute zero temperature, there is a finite probability that an electron in the lattice will be knocked loose from its position, leaving behind an electron deficiency called a "hole". If a voltage is applied, then both the electron and the hole can contribute to a small current flow. The band model of a semiconductor suggests that at ordinary temperatures there is a finite possibility that electrons can reach the conduction band and contribute to electrical conduction. The term intrinsic here distinguishes between the properties of pure "intrinsic" silicon and the dramatically different properties of doped n-type or p-type semiconductors.



Extrinsic Semiconductor: An extrinsic semiconductor is an improved intrinsic semiconductor with a small amount of impurities added by a process, known as doping, which alters the electrical properties of the semiconductor and improves its conductivity. Introducing impurities into the semiconductor materials (**doping process**) can control their conductivity.

Doping process produces two groups of semiconductors: the negative charge conductor (**n-type**) and the positive charge conductor (**p-type**).

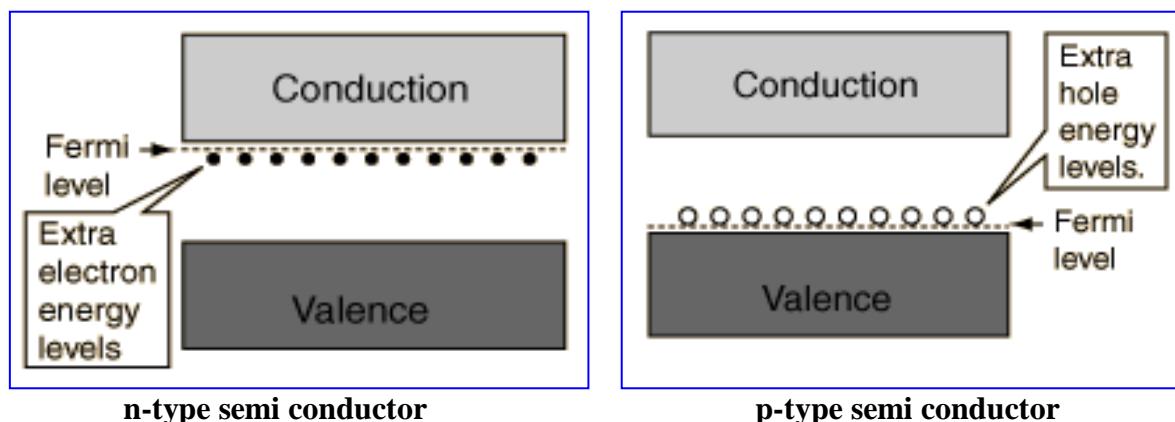
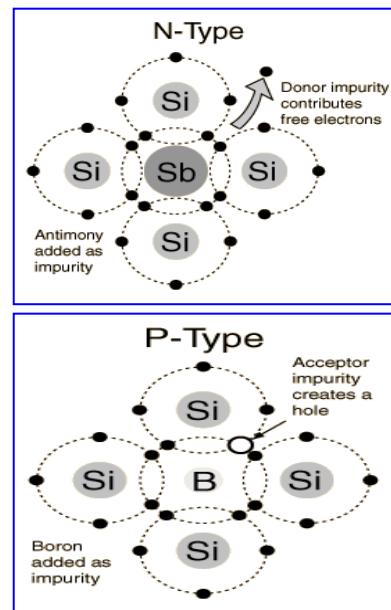
N-Type Semiconductor: The addition of pentavalent impurities such as antimony, arsenic or phosphorous contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor. Holes are said to be the **minority carriers** whereas electrons are the **majority carriers**. When the donor density is increased, the Fermi level moves closer to the edge of the conduction band.

Phosphorous may be added by diffusion of phosphine gas (PH_3).

P-Type Semiconductor: The addition of trivalent impurities such as boron, aluminum or gallium to an intrinsic semiconductor creates deficiencies of valence electrons, called "holes". Electrons are said to be the **minority carriers** whereas holes are the **majority carriers**.

When the acceptor density is increased, the Fermi level moves closer to the edge of the valence band.

It is typical to use B_2H_6 diborane gas to diffuse boron into the silicon material.



Electrical Insulators: Electrical insulators are those materials through which electrical charges cannot pass through. In insulators, no free electrons are available for conduction. They are non metallic materials. Important characteristics of electrical insulators are:

1. The electrical charges cannot pass through the insulator.
2. They possess low conductivity i.e., high resistivity ($10^9 - 10^{20}$ ohm-cm at room temp.)
3. They should be resistant to chemicals, solvents, acids, alkalis, oils and organic solvents.
4. They should have low thermal contraction and expansion.
5. They should have low dielectric constant.
6. The electrical properties of insulators should not be altered by change in chemical composition.

Solid Insulators: Synthetic resins, glass, polyester resins, paper and press boards are the common examples of solid insulators. Generally solid insulators are thermally and chemically stable and possess excellent dielectric properties. Some of commonly used solid insulators and their applications are-

Silicone rubber-Used in aircraft cables and motor winding insulations.

Butadiene rubber- Used in low voltage domestic cables, insulating wires.

Teflon- Used as insulator for all kinds of windings.

PVC-For insulation of flexible wire covering and insulating electric wires.

Polyethylene- High frequency insulator in radio, TV, communication circuit cables and power submarine cables

Liquid Insulators: Mineral oils and synthetic hydrocarbons are most commonly used liquid insulators. They can be used in temperature range of -50 to 100°C and possess low dielectric count, good thermal, chemical and electrical stability.

Some of commonly used liquid insulators and their applications are-

Mineral oils- Used in oil filled high-voltage cables, in transformers to allow cooling by convection.

Chlorinated hydrocarbons- Used in transformer fluids.

Gaseous Insulators: Air, Nitrogen, Hydrogen and SF₆ etc. are used as gaseous insulators. They are non-inflammable and chemically inert.

Some of commonly used gaseous insulators and their applications are-

Air- Provides insulation between overhead transmission lines.

Nitrogen- Used in transformers to replace harmful oxidizing atmosphere. Also used under high pressure as dielectric in electrical capacitors.

SF₆- Used in electrical devices such as capacitors and cables.

Hydrogen- Used as coolant in electrical machines such as turbo generators.

QUESTION BANK

ESSAY QUESTIONS

1. Explain a) Hall Effect and its applications b) Schottky defect.
2. Write short note on Crystal defects.
3. What are insulators? Write about electrical applications of insulators.
4. What are semi conductors? Explain different types of semi conductors.
5. Explain Zone refining and Distillation for the preparation of semiconductors.
6. Explain a) Frenkel defect b) Czochralski crystal pulling technique.
7. Explain Epitaxy and Diffusion Doping techniques.
8. Explain a) Structures of Spinel and Inverse Spinel b) Intrinsic semiconductor.
9. Explain a) Doped semiconductors and b) Crystalline and Amorphous solids.

VERY SHORT ANSWER QUESTIONS

1. Define Hall Effect.
2. What are the consequences of Frenkel defect?
3. What are the consequences of Schottky defect?
4. What are the elements used to employ doping?
5. What are the applications of insulators?
6. Give examples for different types of insulators.
7. What do you understand by the term Doping?
8. What is the principle involved in Zone refining method?

UNIT 4: SOLID STATE CHEMISTRY

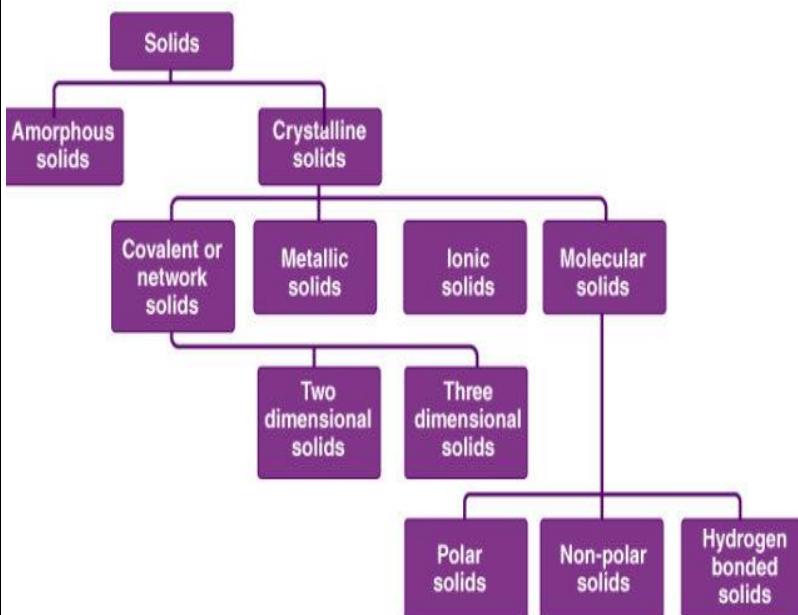
Types of solids – Crystal defects- Frenkel and Schottky defects – Spinel and Inverse spinel. Hall Effect and Applications.

Semiconductors: Preparation of pure semiconductors by Zone refining, Distillation and Czochralski crystal pulling technique, Doping- Epitaxy, Diffusion and Ion-implantation technique- Intrinsic and Extrinsic semiconductors - Applications.

Insulators: Electrical Insulators and their Applications.

Matter may exist in three different phases namely solid, liquid and gas. Solids differ from liquids and gases by possessing **definite volume and definite shape**. In the solids the atoms or molecules or ion are tightly held in an **ordered arrangement**. Understanding the relation between the structure of solids and their properties is very much useful in synthesizing new solid materials with different properties.

Types of solids: Categories of Solids Based on the Solid Pack



Classification of Solids: Based on their crystal structures, solids can be classified into the following categories:

1. Crystalline solids 2. Amorphous solids

Crystalline Solids: A crystal or crystalline solid is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. Examples: Sodium chloride, diamond, and sodium nitrate.

Amorphous Solids: The solids in which the particles are not arranged in any specific order or lack the overall order of a crystal lattice are called amorphous solids. The term ‘amorphous’, means “without form”. Examples: Polymers (rubber, plastic, and gels) and nano structured materials.

Categories of Solids Based on Bonds that Hold the Solid Together

However, crystalline solids can be further classified into

1. Molecular Solids (soft , low mp, electrical insulators, Van der Waals)

2. Covalent Solids (hard, high mp, electrical, Covalent)

3. Ionic Solids (high mp, brittle, poor conductor, electrostatic forces)

4. Metallic Solids (high melting points and brittleness and good conductors)

1. Molecular solids: A molecular solid is composed of molecules held together by van der Waals forces. Its properties are dictated by the weak nature of these intermolecular forces. Molecular solids are soft, often volatile, have low melting temperatures, and are electrical insulators.

Examples Dry Ice (CO_2), I_2 , sugar, polyethylene and bromine. Br_2 is liquids that form molecular solids when cooled slightly; Br_2 freezes at -7°C . The van der Waals forces holding the CO_2 molecules together are weak enough that dry ice *sublimes* — it passes directly from the solid to the gas phase — at -78°C .

2. Covalent solids: Covalent Solids Such as diamond, form crystals that can be viewed as a single giant molecule made up of an almost endless number of covalent bonds. Each carbon atom in diamond is covalently bound to four other carbon atoms oriented toward the corners of a tetrahedron; covalent solids are very hard and high melting point (4027°C).

3. Ionic solids: Made up of positive and negative ions and held together by electrostatic attractions. They're characterized by very high melting points and brittleness and are poor conductors in the solid state. An example of an ionic solid is table salt, NaCl .

4. Metallic solids: Made up of metal atoms that are held together by metallic bonds. Characterized by high melting points, can range from soft and malleable to very hard, and are good conductors of electricity.

Examples copper, gold, zinc, Aluminium, Iron

Crystal defects

The missing and lacking of atoms or ions in an ideal or imaginary crystal structure or lattice of unit cells in real crystals are called **crystal defects** or **solid defects**

Defects in crystalline solid can be divided into four groups namely 1. **line defects**, 2. **point defects**, 3. **volume defects** and 4. **surface defects**

In a crystalline **solid**, when the ideal arrangement of **solids** Atoms/ ions are distorted around a **point**/ atom it is called a **point defect**. There are **3 types of point defects**:

1. **Stoichiometric defect**
2. **Frenkel defect**
3. **Schottky defect**

1. Stoichiometric Defect (or) Intrinsic (or) Thermodynamic defects (Non ionic)

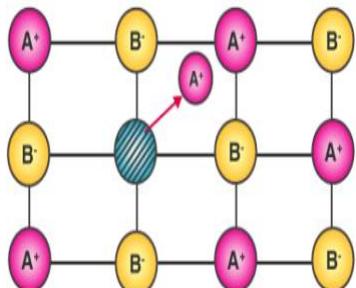
In this kind of point defect, the ratio of positive and negative ions (Stoichiometric) and electrical neutrality of a solid is not disturbed. Sometimes it is also known as intrinsic or thermodynamic defects. e.g., ZnS, AgCl and AgI etc

Fundamentally, they are of two types:

Vacancy defect: When an atom is not present at their lattice sites, then that lattice site is vacant and it creates a vacancy defect. Due to this, the density of a substance decreases. Eg Sulfur vacancies in a monolayer of molybdenum disulfide.

Interstitial defect: It is a defect in which an atom or molecule occupies the intermolecular spaces in crystals. In this defect, the density of the substance increases.

A non-ionic compound mainly shows vacancy and interstitial defects. An ionic compound shows the same in Frenkel and Schottky defect.



Frenkel Defect

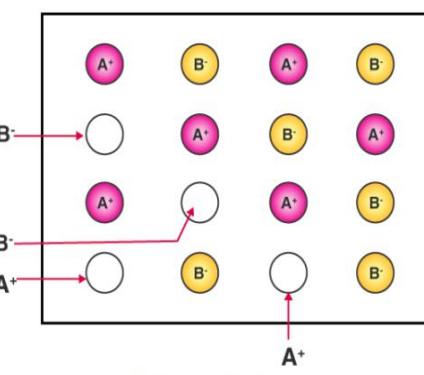
2. Frenkel Defect (or) Dislocation defect (ionic compound)

A Frenkel defect is a type of point defect in crystalline solids named after its discoverer Yakov Frenkel. The defect forms when an atom or smaller ion leaves its place in the lattice, creating a vacancy, and becomes an interstitial by lodging in a nearby location; this type of defect is called Frenkel Defect.

Mostly Cations are smaller in size and therefore it is easier to move to interstitial position. In this case, a vacancy defect is created on its original position and the interstitial defect is experienced at its new position. It is also known as dislocation defect. **Example:** ZnS, AgBr, AgI, AgCl etc

Consequences of Frenkel defect

1. As no ions are missing from the crystal lattice as a whole, therefore density of the solid remains the same.
2. The closeness of like charges tends to increases the dielectric constant of the crystal.
3. The crystal conducts electricity to a small extent by ionic mechanism.
4. Electrically neutrality.
5. It happens when there is a huge difference in the size of anions and cations.



Schottky Defects

Here two cations (A^+) and anions (B^-) are missing from the lattice

3. Schottky Defect (or) Valency Defect (ionic compound)

This kind of vacancy defects is found in highly Ionic Solids.

In ionic crystals, this defect forms when oppositely charged ions leave their lattice sites and become incorporated for instance at the surface, creating oppositely charged vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid. (An equal number of anions and cations will be missing from the compound.)

Examples: NaCl, KCl, KBr, CsCl, AgBr, CeO₂, cubic ZrO₂, UO₂, ThO₂ and PuO₂.

Consequences of Schottky defect

1. As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases
2. The crystal begins to conduct electricity to a small extent by ionic mechanism
3. The presence of too many voids lowers lattice energy and the stability of the crystal
4. In this, the size of cations and anions are of almost the same.

Spinel and Inverse spinel

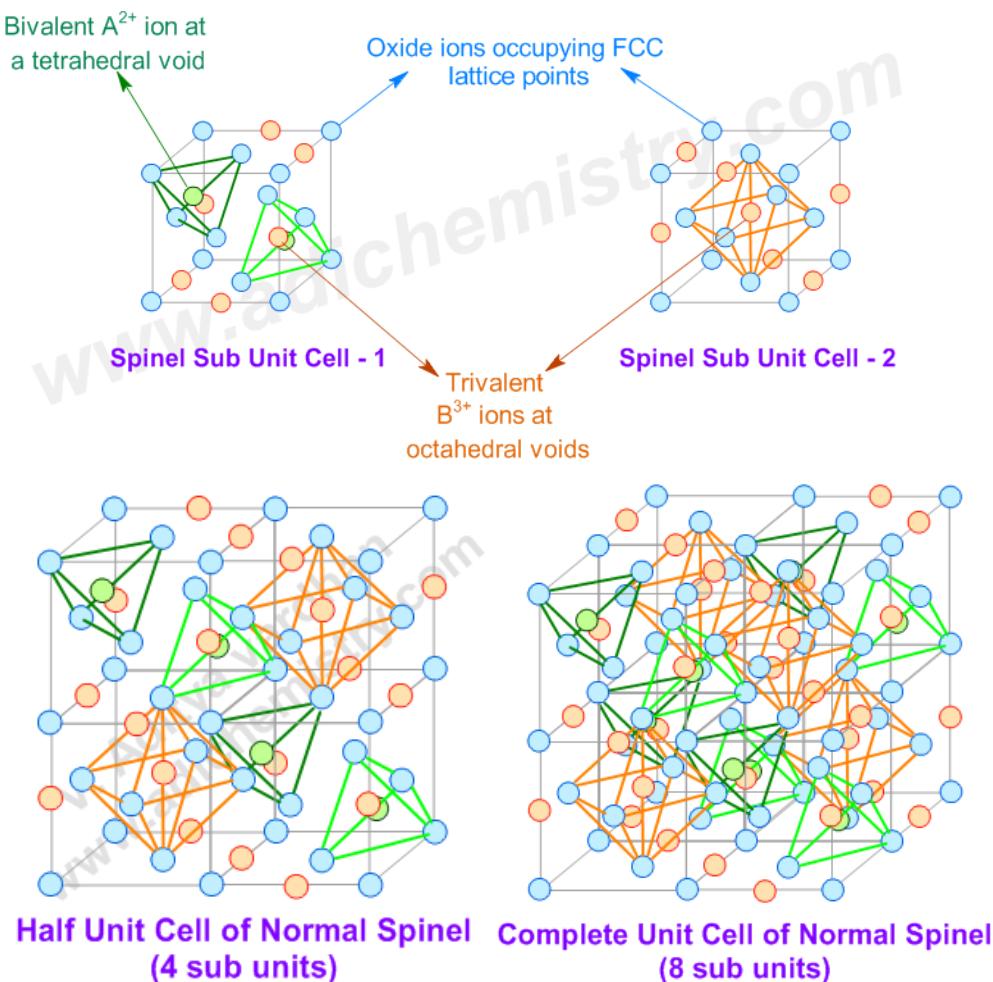
The **spinels** are any of a class of minerals of general formulation AB_2X_4 which crystallises in the arranged in a cubic close-packed lattice, with the X anions (typically chalcogens, like oxygen and sulfur) and the A and B are tetrahedrally and octahedrally coordinated cations.

oxide spinels have the general formula AB_2O_4

Depending on how cations occupy different interstices, spinel structure can be Normal or Inverse.

Normal Spinel

- In the **normal spinel** structure, there is a close-packed array of anions. And it is made up of 8 FCC cells, The A-site cations fill 1/8 of the tetrahedral holes and the B-site cations fill 1/2 of the octahedral holes.
- The anions (usually oxide ions: O^{2-}) occupy the FCC lattice points.
- Examples Aluminates such as $MgAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$ and Ferrites such as $ZnFe_2O_4$ and $CdFe_2O_4$.
- In this, all the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.
- We know that in one FCC lattice unit cell, the effective number of atoms (or ions) occupying the lattice points is $4(8x (1/8) + 6x (1/2))$.
- At the same time, the effective number of tetrahedral voids (holes) = 8 and that of octahedral voids = 4.
- That means, in a normal spinel,
- The number of anions occupying the lattice points of 8 FCC unit cells = $8 \times 4 = 32$.
- Whereas, the number of divalent A^{II} cations occupying 1/8th of tetrahedral voids = $8 \times 1/8 \times 8 = 8$
- and the number of trivalent B^{III} ions occupying the half of octahedral voids = $8 \times 1/2 \times 4 = 16$.
- i.e. The ratio of $A^{II} : B^{III} : O^{2-} = 8 : 16 : 32 = 1:2:4$ which confirms with the formula of normal spinels.
- Thus a normal spinel can be represented as: $(A^{II})_{tet}(B^{III})_2^{oct}O_4$



Inverse Spinel $B(AB)O_4$

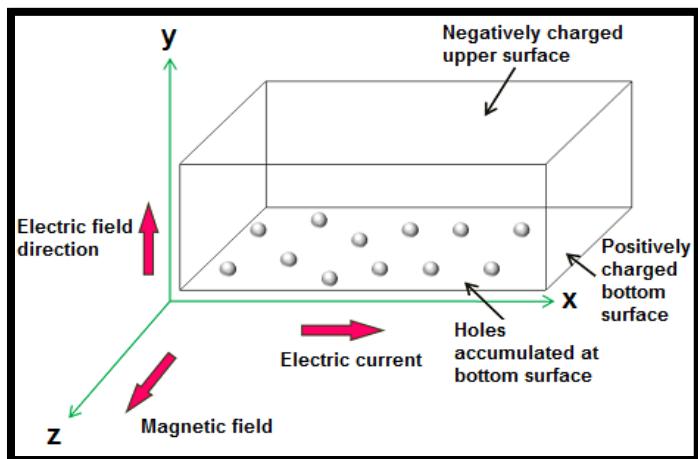
- **Inverse spinels** have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places.
- Inverse spinels are thus formulated $B(AB)O_4$, where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intermediate between the **normal** and **inverse** spinel structure.
- Some spinel and inverse spinel AB combinations are:
- $A^{4+}B^{2+}$, e.g., $Pb_3O_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$ (inverse spinel)
- $A^{2+}B^{3+}$, e.g., $MgAl_2O_4$ (normal spinel)
- $A^{6+}B^+$, e.g., Na_2WO_4 (normal spinel)

- Many magnetic oxides, such as Fe_3O_4 (or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and CoFe_2O_4 , are spinels.
- In this structure, $\frac{1}{2}$ of the B^{3+} ions occupy the tetrahedral sites and remaining $\frac{1}{2}$ B^{3+} and all A^{2+} ions occupy the octahedral sites.
 - The A^{II} ions occupy the $1/4$ th of octahedral voids, whereas one half of B^{III} ions occupy the $1/8$ th of tetrahedral voids and the other half occupies $1/4$ th of octahedral sites. It can be represented as: $(\text{B}^{\text{III}})^{\text{tet}}(\text{A}^{\text{II}}\text{B}^{\text{III}})^{\text{oct}}\text{O}_4$.
 - Anions occupying the lattice points of 8 FCC unit cells = $8 \times 4 = 32$.
 - Divalent A^{II} cations occupying $1/4$ th of octahedral voids = $8 \times 1/4 \times 4 = 8$
 - Trivalent B^{III} ions occupying the $1/4$ th of octahedral voids = $8 \times 1/4 \times 4 = 8$.
 - Trivalent B^{III} ions occupying the $1/8$ th of tetrahedral voids = $8 \times 1/8 \times 8 = 8$.
 - The ratio of $\text{A}^{\text{II}} : \text{B}^{\text{III}} : \text{O}^{2-} = 8 : (8+8) : 32 = 1:2:4$ which confirms with the formula of inverse spinels.
 - Thus an inverse spinel can be represented as: $(\text{B}^{\text{III}})^{\text{tet}}(\text{A}^{\text{II}})^{\text{oct}}(\text{B}^{\text{III}})^{\text{oct}}\text{O}_4$

Hall Effect

Principle of Hall Effect: When magnetic field is applied perpendicular to a current-carrying conductor, then a voltage is developed in the material perpendicular to both magnetic field and current in the conductor. This effect is known as Hall effect and the voltage developed is known as Hall voltage (V_H).

Hall effect is useful to identify the nature of charge carriers in a material and hence to decide whether the material is n-type semiconductor or p-type semiconductor, also to calculate carrier concentration and mobility of carriers.



Theory: Hall effect can be explained by considering a rectangular block of an extrinsic semiconductor in which current is flowing along the positive X-direction and magnetic field B is applied along Z-direction as shown in Fig. In the n-type semiconductor, **free electrons** are the majority carriers and **holes** are the minority carriers. That means most of the current in the n-type semiconductor is conducted by free electrons. In the p-type semiconductor, holes are the majority carriers and free electrons are the minority carriers. That means most of the current in the p-type semiconductor is conducted by holes.

by using Hall Effect we can easily identify whether the semiconductor is a p-type or n-type.

When a voltage is applied to a conductor or semiconductor, electric current starts flowing through it. In conductors, the electric current is conducted by free electrons whereas in semiconductors, electric current is conducted by both free electrons and holes.

Due to the distortion in the magnetic field of the charge carriers, the negatively charged electrons will be deflected to one side of the plate and positively charged holes to the other side. A potential difference, known as the Hall voltage will be generated between both sides of the plate which can be measured using a meter.

The Hall voltage represented as V_H is

$$V_H = \frac{IB}{qn d}$$

Here, I = the current flowing through the sensor

B = the magnetic Field Strength

n = the number of charge carriers per unit volume

q = the charge

d = the thickness of the sensor.

Applications of Hall Effect

Hall Effect principle is employed in the following cases:

1. It is used to determine if the given material is a type semiconductor or insulator.
2. **Calculate the Carrier Concentration**
3. **Used as Magnetometers:** It is used to measure the magnetic field and is known as a magnetometer
4. **The Hall sensor is used in some automotive fuel-level indicators.**
5. They find applications in position sensing as they are immune to water, mud, dust, and dirt.
6. For the measurement of direct current, Hall Effect Tong Tester is used.
7. They are used in integrated circuits as Hall Effect sensors.
8. It is used in phase angle measurement
9. **Hall Effect Sensors is also used as Current Sensors.**

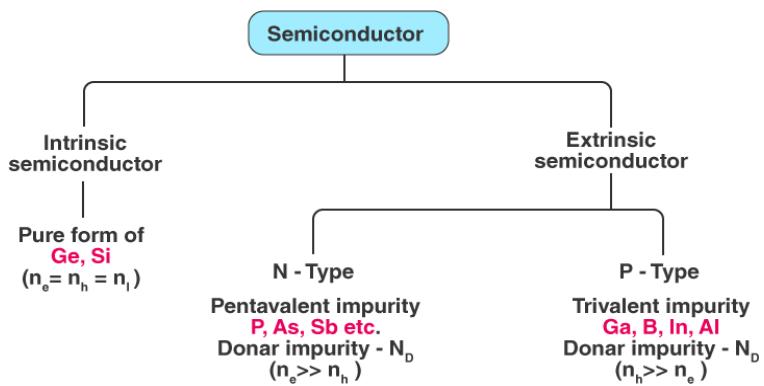
10. For detecting wheel speed and accordingly assist the anti-lock braking system.

Semiconductors

Semiconductors are materials which have a conductivity between conductors (generally metals) and non-conductors or insulators (such as most ceramics). **Semiconductors** can be pure elements, such as silicon or germanium, or compounds such as gallium arsenide or cadmium selenide. **Semiconductors** are an essential component of electronic devices, enabling advances in communications, computing, healthcare, military systems, transportation, clean energy, and countless other applications.

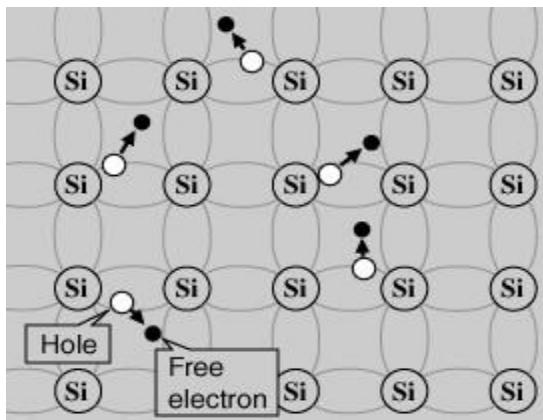
Types of semiconductors:

Intrinsic Semiconductor: An intrinsic semiconductor material is chemically very pure and possesses poor conductivity. It has equal numbers of negative carriers (electrons) and positive carriers (holes). A silicon crystal is different from an insulator because at any temperature above absolute zero temperature, there is a finite probability that an electron in the lattice will be knocked loose from its position, leaving behind an electron deficiency called a "hole". This hole can travel from one atom to the adjacent atom by accepting an electron from later one.



This process involves formation of new covalent bond and breaking an existing bond by filling up the hole and creating a new hole. In this way, the holes travel from one atom to the adjacent atoms in crystal lattice.

If a voltage is applied, then both the electron and the hole can contribute to a small current flow.



Extrinsic Semiconductor: Extrinsic semiconductor is an improved intrinsic semiconductor with a small amount of impurities added by a process, known as doping, which alters the electrical properties of the semiconductor and improves its conductivity. Introducing impurities into the semiconductor materials (**doping process**) can control their conductivity.

Doping process produces two groups of semiconductors: the negative charge conductor (**n-type**) and the positive charge conductor (**p-type**). Semiconductors are available as either elements or compounds. Silicon and Germanium are the most common elemental semiconductors. Compound Semiconductors include InSb, InAs, GaP, GaSb, GaAs, SiC, GaN.

Si and Ge both have a crystalline structure called the diamond lattice. That is, each atom has its four nearest neighbours at the corners of a regular tetrahedron with the atom itself being at the centre. In addition to the pure element semiconductors, many alloys and compounds are semiconductors. The advantage of compound semiconductor is that they provide the device engineer with a wide range of energy gaps and mobilities, so that materials are available with properties that meet specific requirements. Some of these semiconductors are therefore called wide band gap semiconductors.

How doping of semiconductors is done?

The Doping of Semiconductors: The addition of a small percentage of foreign atoms in the regular crystal lattice of silicon or germanium produces dramatic changes in their electrical properties, producing n-type and p-type semiconductors.

Pentavalent impurities: (5 valence electrons)

Produce n-type semiconductors by contributing extra electrons.

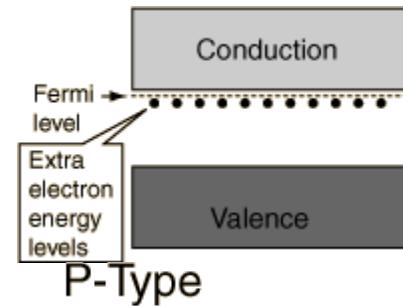
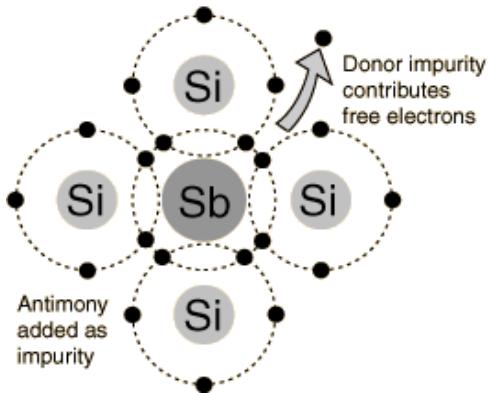
Trivalent impurities: (3 valence electrons)

Produce p-type semiconductors by producing a "hole" or electron deficiency.

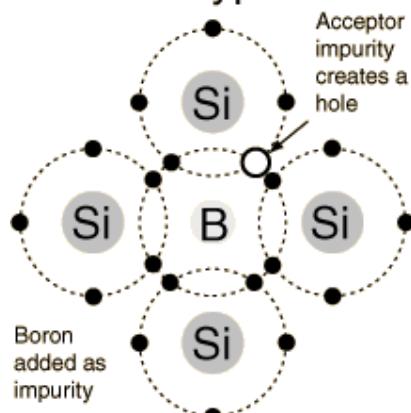
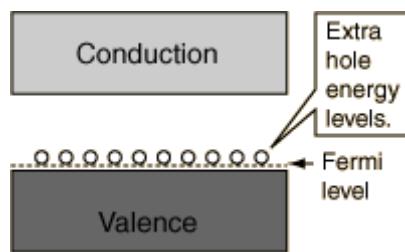
N-Type Semiconductor:

The addition of pentavalent impurities such as P, As or Sb to an intrinsic semiconductor creates contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor.

N-Type



P-Type



P-Type Semiconductor

The addition of trivalent impurities such as B, Al or Ga to an intrinsic semiconductor creates deficiencies of valence electrons, called "holes".

Note: positive holes are less mobile than free electrons so the conductivity of a P-type semiconductor is inherently less than that of N-type semiconductor.

What are the differences between p-type and n-type semiconductors?

Differences between p-type and n-type semiconductors:

N-type Semiconductor	P-type Semiconductor
It is an extrinsic semiconductor which is obtained by doping the impurity atoms such as P, As or Sb to the pure Ga or Si semiconductor	It is an extrinsic semiconductor which is obtained by doping trivalent impurity atoms such as B, Ga, In to the pure germanium or silicon semiconductor.
The impurity atoms added, provide extra electrons in the structure, and are called donor atoms.	The impurity atoms added, create vacancies of electrons (i.e. holes) in the structure and are called acceptor atoms.
The electrons are majority charge carriers and holes are minority charge carriers.	The holes are majority charge carriers and Electrons are minority carriers.

Preparation of pure semiconductors

Preparation of Semiconductors: For preparing semiconducting devices, the basic materials such as Si and Ge must at least 99.99% pure. Consequently extreme precautions have to be taken during the preparation of these elemental semiconductor materials. Various steps followed during the preparation of highly pure materials are as follows

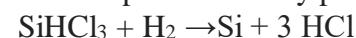
Preparation of pure Ge/Si: This is carried by using the following methods:

Zone refining, 2. Distillation 3. Czochralski crystal pulling technique

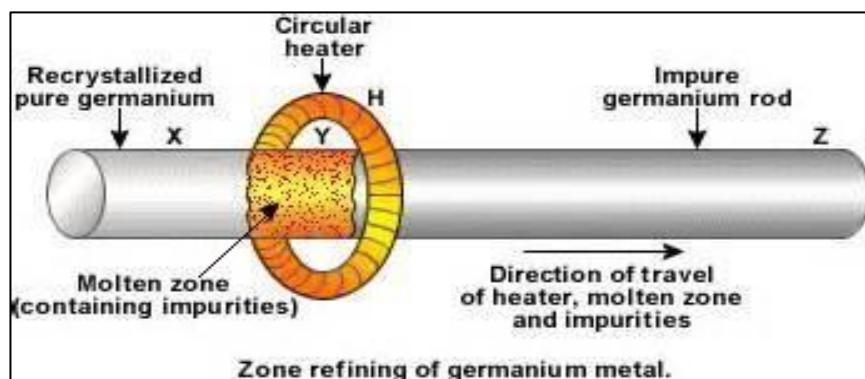
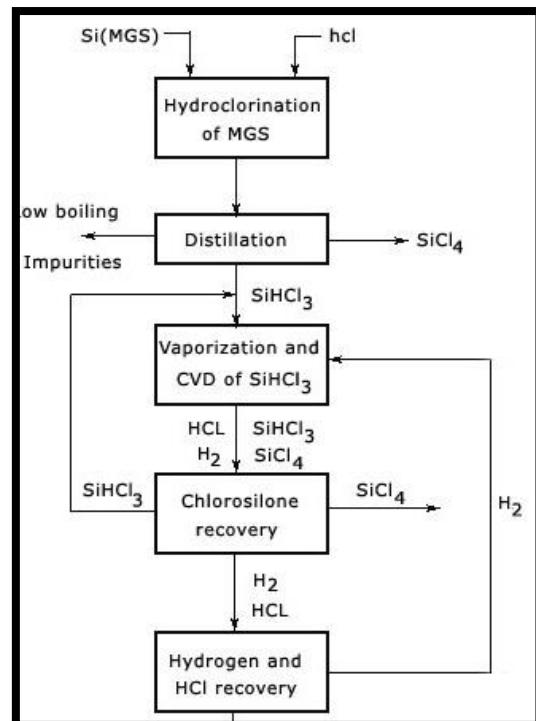
Distillation: is based on the separation of materials due to difference in boiling points. The starting raw materials employed are GeCl_4 and SiCl_3 for the preparation of pure Ge and Si respectively. The process was first developed by Siemens (Siemens process)

A small amount of the metallurgical grade silicon is further refined for the semiconductor industry. Powdered MG-Si is reacted with anhydrous HCl at 300°C in a fluidized bed reactor to form SiHCl_3 . $\text{Si} + 3\text{HCl} \rightarrow \text{SiHCl}_3 + \text{H}_2$

During this reaction impurities such as FeCl_3 , AlCl_3 , BCl_3 etc. The SiHCl_3 has a low boiling point of 31.8°C and distillation is used to purify the SiHCl_3 from the impurity halides. Finally, the pure SiHCl_3 is reacted with H_2 at 1100°C for $\sim 200 - 300$ hours to produce a very pure Si (99.9999%).



The reaction takes place inside large vacuum chambers and the silicon is deposited onto thin polysilicon rods (small grain size silicon) to produce high-purity polysilicon rods of diameter 150-200mm.



Zone refining:

The zone refining technique involves melting a narrow zone of long ingot of the material to be processed. This molten zone is then slowly moved by moving the heater gradually along the length of the ingot in one direction. This process is repeated multiple times till the required purity level is reached.

In this process difference between solubility of impurities in the molten and solid phases is used to concentrate impurities at the end section of the ingots.

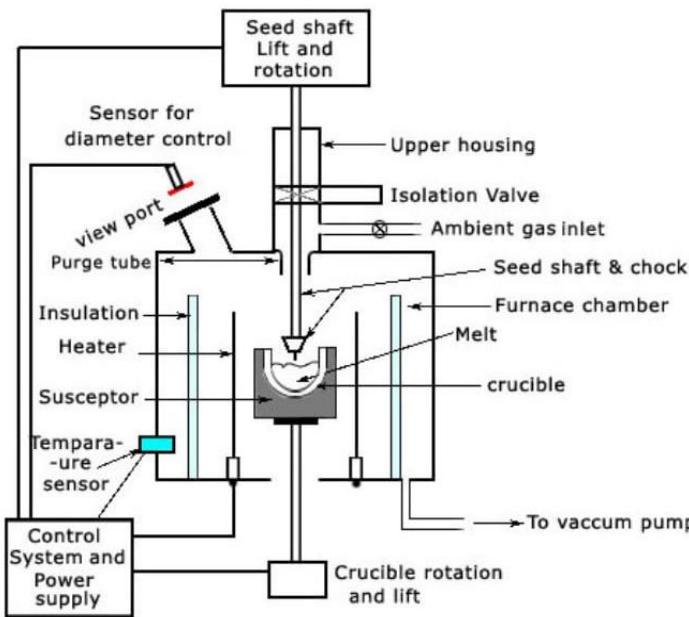
This method is particularly used when metals are required in high degree of purity. It is based on the principle that when an impure metal in a molten state is allowed to cool, only the metal crystallizes while the impurities remain present in the molten state (mass) or melt.

The impure metal converted into a rod which is heated at one end with a circular heater. A narrow zone of metal is melted. The heater is slowly moved along the rod. The pure metal recrystallizes out of melt while the impurities remain in the melt which moves along with the melted zone of the rod with the movement of heater. The process is repeated several times. The end of rod where impurities have collected is cut off. This method is employed for the purification of germanium, silicon, gallium etc, which are used in semi – conductors.

Czochralski Crystal pulling Technique:

Ge or Si obtained by zone refining method is polycrystalline, i.e., there is no regularity in their crystal structure and crystals contain different sizes. But fabrication of most of the Semiconductor devices require single crystal of semi conducting materials. Consequently, they are grown in the form of single crystals.

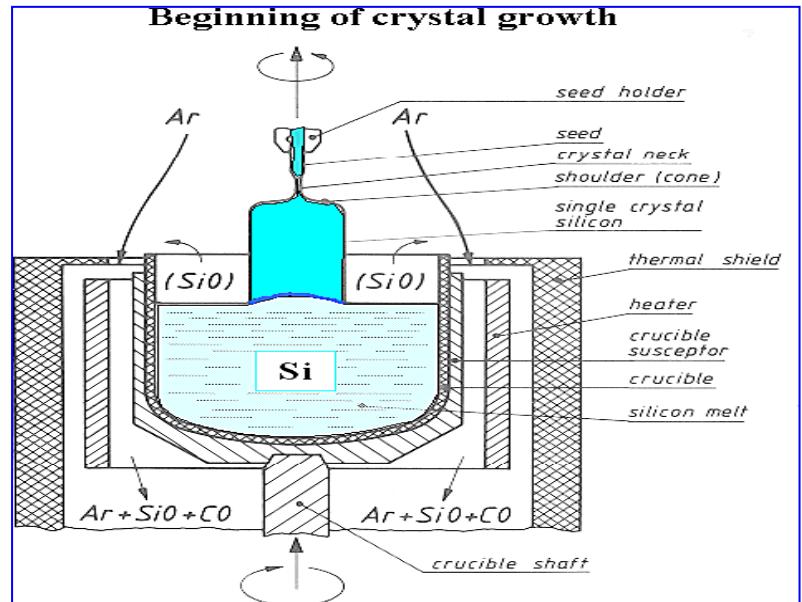
This method involves growing the single crystal on a crystal seed; thereby the atoms reproduce identical atomic arrangement as that of the seed crystal. In this process, solid polycrystalline semiconducting material is taken in a quartz chamber and heated by using RF power source, till it melts. Then the temperature is lowered to just above the m.p of Ge.



At this stage, properly oriented single crystal of Ge, attached to a puller rod is carefully lowered into the melt, till it is in contact with the surface of the charge. Then the crystal is rotated slowly and then gradually pulled out so that the melt in contact with the seed crystal starts solidifying producing the orientation identical as that of the seed crystal. After this, the pull rate is kept at about 1.5 to 5 cm/minute and the rotation speed is maintained at about 100rpm. Finally, an intrinsic crystal of Ge of 5cm diameter and 25 cm length is obtained. This crystal is tested for its conductivity and cut into wafers with the help of a diamond-tipped saw.

Doping techniques: For getting a doped material, calculated quantity of dopant (Boron or Phosphorus) is added to the melt before crystal pulling stage. Usually dopant atoms added are of the order of one atom of B or P per 10^8 atoms of Ge or Si. Other methods of doping are:

Epitaxy: Involves in unified crystal growth or deposition of a thin crystal on another substrate, often with added dopants. The material in the epitaxial layer must have a little spacing and structure closed to that of the substrate. ex. Si on Ge or Ge on Si. The Si or Ge wafer (kept in graphite boat) is placed in a long cylindrical quartz tube reactor, which is then heated (by RF induction coil). Then gases containing compounds of Ge or Si mixed with calculated/appropriate quantities of dopant over the wafer results. The doped wafer so obtained is ready for the fabrication of semiconductor devices. It may be pointed out that for getting Si epitaxial film, SiCl_4 , H_2 and N_2 mixture is used. For carrying out n-type doping, this mixture is mixed with a calculated amount of phosphine (PH_3) and for p-type doping; Diborane (B_2H_6) is employed.



Diffusion technique: Involves in conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atom into the crystal lattice of the semiconductor material without any melting and it consists of heating a P-type dopant (Phosphorus or Stilbium). This causes some of the impurity atoms to condense on the surface of water and diffuse thereby resulting in a P-type semiconductor material. By this technique, the extent of impurity atoms penetration can be controlled even less than a few millions of a centimetre by controlling the concentration of dopant atoms and temperature. This technique is especially employed for preparing n or p type semiconductors, used in very high frequency devices. This doping technique can also be used to prepare n-p-n type transistor with a base width of even 5 microns.

Ion implantation technique: Involves in bombarding the semiconductor material with an electrically controlled beam of high energy ions of B or P of 10000ev. This causes the implantation of some dopant atoms into the crystal lattice of semiconductor.

Main advantages of this technique are: 1. Implantation at low temperature 2. Extremely precise control of the dopant amount on desired specific semiconducting material 3. Obtaining deep or shallow regions of very precise and required penetration depths having high or low concentration of dopant. This technique is especially employed for the fabrication of high frequency devices.

Cutting into chips: the wafers obtained by above methods are then cut into chips by using methods such as chemical etching, ultrasonic vibrations, laser beams etc.

Applications of Semiconductors

Let us now understand the uses of semiconductors in daily life. Semiconductors are used in almost all electronic devices. Without them, our life would be much different.

Their reliability, compactness, low cost and controlled conduction of electricity make them ideal to be used for various purposes in a wide range of components and devices. transistors, diodes, photosensors, microcontrollers, integrated chips and much more are made up of semiconductors.

Uses of Semiconductors in Everyday life

- Temperature sensors are made with semiconductor devices.
- They are used in 3D printing machines
- Used in microchips and self-driving cars
- Used in calculators, solar plates, computers and other electronic devices.
- Transistor and MOSFET used as a switch in Electrical Circuits are manufactured using the semiconductors.

Industrial Uses of Semiconductors

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

The microprocessor used for controlling the operation of space vehicles, trains, robots, etc is made up of transistors and other controlling devices which are manufactured by semiconductor materials.

Importance of Semiconductors

Here we have discussed some advantages of semiconductors which makes them highly useful everywhere.

- They are highly portable due to the smaller size
- They require less input power
- Semiconductor devices are shockproof
- They have a longer lifespan

They are noise-free while operating

Insulators: Electrical Insulators and their Applications.

An **insulator** is a material that does not conduct electrical current. Insulating materials include paper, plastic, rubber, glass and air. Vacuum is also an **insulator**, but is not actually a material. Most electrical conductors are covered by insulation.

An **electrical insulator** (also referred to as an insulator) is used in an electrical system to prevent unwanted flow of current to the earth from its supporting points. The **insulator** plays a vital role in the electrical system. An electrical insulator is a very high resistive path through which practically no current can flow.

Characteristics of a Good Insulating Material:

A good insulating material should possess the following characteristics:

1. High dielectric strength.
2. High mechanical strength.
3. High thermal conductivity (High thermal strength).
4. Uniform viscosity—it gives uniform electrical and thermal properties.
5. Least thermal expansion.
6. Low permittivity.
7. Should be resistance to oils or liquids, gas fumes, acids and alkalies.
8. Should be resistant to thermal and chemical deterioration.

Applications

The various materials which can be used as solid insulators are given below:

i. Asbestos: Chemically it is a hydrated magnesium silicate. It is very useful inorganic material. Chrysotile $3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$ belongs to the group of fibers in nature.

Asbestos combined with its non-inflammability, makes it particularly suited for thermal as well as electrical insulation.

ii. Bakelite :(a) It is heat proof, acid proof and mechanically strong.

(b) It is commonly used for manufacture of electrical fittings— lamp-holders, switches, plugs etc.

iii. Paper: (a) It is prepared from wood pulp and manila fibers beaten and rolled into sheets.

(b) The paper is used for winding and cable conductor insulation, primary dielectrics in capacitors, backing for mica insulation, slot insulation of electrical machines, transformer insulation.

(c) The low density paper is preferred in high frequency capacitors and cables as the electric loss

Medium density paper is used in power capacitors.

High density papers are preferred in DC and energy storage capacitors and other DC insulation.

iv. Waxes: Waxes are used as impregnating compounds in condensers and in the radio coils used in the tropics and paper and cloth insulation, as a dipping medium, and as a directly applied coating on conductors.

v. Rubber: The materials used in cable insulation are – (i) pure rubber, (ii) impregnated paper, and (iii) vulcanised bitumen. Raw rubber cannot be used as an insulating material directly because it is brittle and hard when cold but soft and stiff when hot. Sulphur addition makes the product harder material with excellent insulating properties.

vi. Ceramics: (a) The ceramics used as dielectric may be broadly described as clay containing porcelains, alumina ceramics, talc containing steatites.

(b) Ceramics with dielectric constant below 12 are more advantageously used in bulk as insulator, bushing, housing and the like. Materials with $\epsilon < 12$ are porcelains, steatite, torsterit, wollastonite, alumina ceramics etc. Other applications of low permittivity ceramics include suspension insulators for high voltage lines and pin insulators for low voltage lines, station insulators and bushing for transformers, oil breakers, disconnecting switches. At high temperature they are used for support of heaters and furnace windings, wire wound power resistor, insulators for thermocouples, cathode heaters, insulation in valves and sparking plugs.

vii. Resins or Polymers: (a) Resins are organic substances with very high molecular weight. Synthetic resins are synthetic polymers known as plastics and form an important group of insulating materials.

(b) They are bad conductors of electricity and unsuitable for high temperature service.

viii. Glass: (a) Ordinary glass is a good insulator but it is too brittle to be used for anything; scientific instrument parts, containers etc.

(b) It is widely used as an insulating material to form the envelop and for internal supports in electric light bulbs, electronic valves, X-ray tubes etc.

QUESTION BANK ESSAY QUESTIONS

1. Explain a) Hall Effect and its applications b) Schottky defect.
2. Write short note on Crystal defects.
3. What are insulators? Write about electrical applications of insulators.
4. What are semi conductors? Explain different types of semi conductors.
5. Explain Zone refining and Distillation for the preparation of semiconductors.
6. Explain a) Frenkel defect b) Czochralski crystal pulling technique.
7. Explain Epitaxy and Diffusion Doping techniques.
8. Explain a) Structures of Spinel and Inverse Spinel b) Intrinsic semiconductor.
9. Explain a) Doped semiconductors and b) Crystalline and Amorphous solids.

VERY SHORT ANSWER QUESTIONS

1. Define Hall Effect.
2. What are the consequences of Frenkel defect?
3. What are the consequences of Schottky defect?
4. What are the elements used to employ doping?
5. What are the applications of insulators?
6. Give examples for different types of insulators.
7. What do you understand by the term Doping?
8. What is the principle involved in Zone refining method?

UNIT 5: MATERIAL CHEMISTRY

Nano materials—Introduction- Top-down and Bottom- up approaches, Sol-gel method. Characterization by BET and TEM methods. Carbon nano tubes and fullerenes - Types, Preparation (Arc discharge Laser ablation and Chemical Vapour Deposition methods) Properties and Applications.

Liquid crystals - Introduction – Types – Applications.

Superconductors - Type-I & Type-II, Properties & Applications.

Green chemistry- Principles and Applications.

NANO MATERIALS

Introduction: Nano materials (Nano particles) are the materials or particles like metals, ceramics, polymeric materials or composite materials with dimensions in the range of 1 nm to 100 nm.

$$1 \text{ Meter} = 100 \text{ cm} = 10^3 \text{ mm} = 10^6 \text{ micro meters} = 10^9 \text{ nm} \quad \& \quad 1 \text{ nm} = 10^{-9} \text{ m}$$

The significance of nano material is due to their small size.

A nano particle is defined as a small object that behaves as a whole unit in terms of its transport properties and exhibits a number of special properties relative to bulk materials.

Synthesis of Nanomaterials: There are two general approaches for the synthesis of nanomaterials.

a) Top- down approach b) Bottom-up approach.

Top-down – Breaking down matter into more basic building blocks.

Frequently uses chemical or thermal methods.

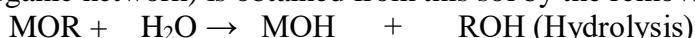
- Top-down approach means Big to Small.
- They aren't cheap and slow.
- They are not suitable for large scale preparation
- Lithography, Etching, Cutting, Grinding are examples of Top down approach.
- Nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on its surface.

Bottom-up – Building complex systems by combining simple atomic-level components.

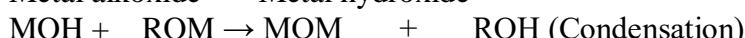
- Bottom-up approach refers Small to Big.
- They are cheap methods
- They are suitable for large scale preparation
- Chemical synthesis and self assembly are examples for bottom up approach.
- It is with the better possibilities to obtain nanostructures with less defects and more homogeneous chemical compositions.

Sol-gel method: It is very popular wet chemical technique used for the preparation of oxide nano materials. The Sol-gel process involves hydrolysis followed by condensation. A metal or metalloid employed as a precursor is dispersed in acid or water to form a sol (colloidal suspensions) by hydrolysis.

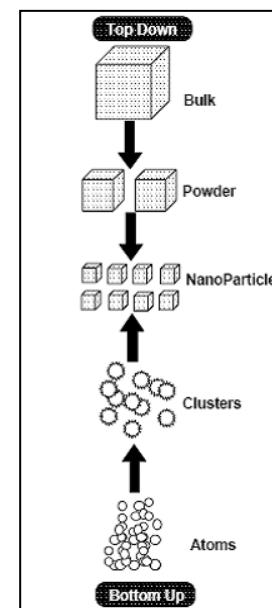
Gel (inorganic network) is obtained from this sol by the removal of water (poly condensation).



Metal alkoxide Metal hydroxide



Metal hydroxide Metal-oxo polymers



The various steps involved are as follows:

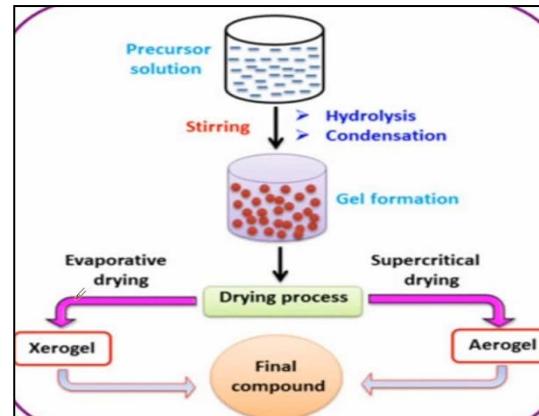
1. Hydrolysis of precursor (sol formation): The precursor is an aqueous solution of metal alkoxide ($M-OR$), where R is the alkyl group (e.g., C_2H_5). The metal alkoxide reacts with the surrounding water and forms the colloidal suspension (sol) of metal hydroxide.

2. Polycondensation (Gelation): This stage results in a formation of the Gel - a rigid 3-D network built of polymeric molecules and surrounded with the solvent.

3. Aging: During the aging stage the poly condensation reactions continue completing the formation of the gel. The gel structure is reinforced with additional cross-links, which cause contraction of the gel matrix and expulsion of the solution from the shrinking pores.

4. Drying: The water and other liquids entrapped within the pores of the gel structure are removed during this stage. Drying is performed at a temperature of about $200^{\circ}C$. After drying the gel it converts into a monolith micro-porous structure called Xerogel. Drying at super-critical conditions preventing collapsing of the gel network results in a formation of a macro-porous low density structure called Aerogel.

5. Calcination: Calcination is performed at increased temperatures varying within the range $400-800^{\circ}C$. During the calcination stage the dry gel structure is dehydrated.



Advantages:

- ✓ The size, shape and chemical composition of the nano materials can be easily controlled.
- ✓ Substance produced is of high degree of purity.
- ✓ Sol-gel approach is interesting in that it is a cheap and low-temperature technique.
- ✓ The reaction mechanism is easily controllable.

Limitations:

- ✓ Controlling the growth of particles is difficult.
- ✓ Production rates of nano powders are very low.

Applications: Sol gel derived materials have diverse applications in optics, electronics, space, energy, medicine and chromatography etc.

CHARACTERISATION OF NANO MATERIALS:

Surface Area: The most common technique is the nitrogen adsorption technique based on the BET isotherm, and is routinely carried out in many laboratories.

BET Method: The theory of multilayer adsorption proposed by Brunauer, Emmett and Teller in 1938. This theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a nano material.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

- a. Gas molecules physically adsorb on a solid in layers infinitely;
- b. There is no interaction between each adsorption layer; and
- c. Langmuir theory can be applied to each layer.

In BET surface area analysis, known amounts of nitrogen gas are released stepwise into the sample cell. Relative pressures less than atmospheric pressure are achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure.

The resulting **BET equation** is expressed by (1):

$$\frac{1}{v[(P_0/P) - 1]} = \frac{c - 1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c} \quad (1)$$

Where P = Equilibrium Pressure of adsorbate

P_0 = Saturation pressure of adsorbate at the temperature of adsorption,

V = the adsorbed gas quantity,

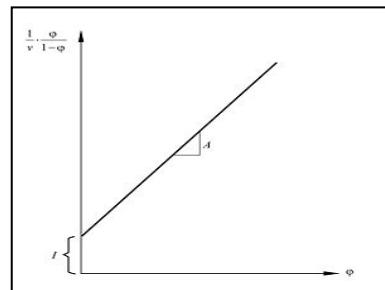
V_m = the monolayer adsorbed gas quantity and

C = the BET constant.

Eqn. (1) is an adsorption isotherm and can be plotted as a straight line with $1/v [(P_0/P) - 1]$ on the y-axis and $\varphi = P/P_0$ on the x-axis according to experimental results.

This plot is called a **BET plot**.

For example, activated carbon, which is a strong adsorbate and usually has an adsorption cross section of 0.16 nm^2 for nitrogen adsorption at liquid nitrogen temperature, is revealed from experimental data to have a large surface area around $3000 \text{ m}^2 \text{ g}^{-1}$.



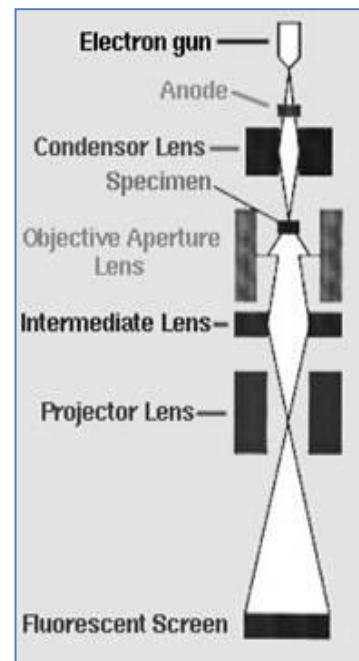
Transmission electron microscope (TEM): Transmission electron microscope (TEM) is type of electron microscope. It uses a beam of electrons to focus on a specimen producing a highly magnified and detailed image of the specimen. It has four working parts which include:

1. Electron gun
2. Condenser lens system
3. Image producing system and
4. Image recording system

1. Electron gun & condenser system: Electron gun responsible for producing the electron beams. Typically, Electrons are produced by a cathode that is a tungsten filament. When electrons are transmitted from the cathode, they pass through the columnar aperture (hole) to the anode at high voltage with constant energy, which is efficient for focusing the specimen to produce an accurately defined image.

2. Condenser lens system: Condenser lens system which works to focus the electron beam on the specimen by controlling the energy intensity and the column hole of the electron gun.

3. Image producing system: The image-producing system, consisting of the objective lens, movable specimen stage, and intermediate and projector lenses, which focus the electrons passing through the specimen to form a real, highly magnified image. Here, the electron beam strikes the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens



into an imageon screen.

4. Image recording system: The image-recording system, which converts the electron image into some form perceptible to the human eye. The image- recording system usually consists of a fluorescent screen for viewing and focusing the image and a digital camera for permanent records.

Characterization of nano materials by TEM: The transmission electron microscope (TEM) is the perfect instrument for structural and chemical characterization of material at the nano scale. The quantitative measures of particle size, grain size, size distribution, size homogeneity, lattice type, morphological information, crystallographic details, chemical composition of phase distribution, and parameters can obtain by transmission electron micrographs.

Advantages: In addition to the capability of structural characterization and chemical analyses, TEM also has been used for other applications like determination of melting points of nano crystals and measurement of mechanical and electrical properties of individual nano wires and nano tubes can also be done.

Drawbacks: One drawback of TEM is its limited depth resolution.

CARBON NANOTUBES (CNTs):

- CNTs are made up of carbon and look like a long, thin cylinders.
- In CNT, each carbon atom is covalently bonded to three other nearby carbon atoms.
- CNTs are molecules having very small size, shape and rare physical properties.
- CNT is one of the allotropes of carbon and others are diamond, graphite, fullerenes etc.
- Length to diameter ratio of a CNT is greater than 100,000.
- CNT is formed, when hexagonal graphene sheet is turned around into a cylinder and its edges joined
- So the CNTs are longer tubes of graphite sheet.

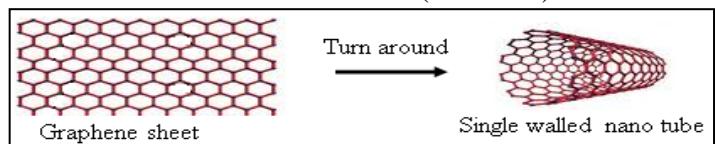
Types of CNTs: There are two types of CNTs depend on their arrangement. Single walled nano tubes (SWNTs) & Multi walled nano tubes (MWNTs).

Types of CNTs: There are two types of CNTs depend on their arrangement.

1. Single walled nano tubes (SWNTs)
2. Multi walled nano tubes (MWNTs)

- **Single walled nano tubes (SWNTs):**

SWNT is formed, when single one atom thick graphene sheet is turned around into a cylinder and its edges joined. SWNTs have a diameter of 1 nm. The length of SWNT is many millions times of its diameter. SWNT show electrical conductivity.



- It is used to make field effect transistors (FETs).

SWNTs are three types of SWNTs based on the arrangement of single one atom thick graphene sheet. 1. Armchair, 2. Zigzag 3. Chiral

- Graphene sheet is represented by a pair of indices (n,m) called Chiral vector. Where n and m are number of unit vectors along two directions in the hexagonal crystal lattice of graphene.
 - If $n = m$, the nano tubes are called “armchair”.
 - If $m = 0$, the nano tubes are called “zigzag”.
 - Otherwise, they are called “Chiral”. It has a bend shape around the nano tube.

(Diagrams for understanding purpose only)

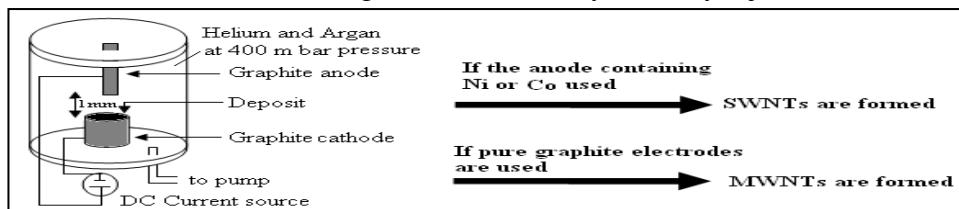
Multi walled nano tubes (MWNTs):

- MWNT is formed, when more than two one atom thick graphene sheets are turned around into a cylinder and its edges joined.
- These are concentric tubes of graphene.
- The distance between graphene layers of MWNT is $\approx 3.3 \text{ \AA}^0$.
- They have metallic and semi conducting properties.
- New function groups are inserted on the surface of DWNTs to add new properties to it.
- This type of DWNTs shows both metallic and semiconducting properties.
- In the **Russian doll model**, sheets of graphene are arranged in concentric cylinders, for example: a large (0, 10) SWNT in a small (0, 8) SWNT.
- In the **parchment** (means animal skin) **model**, a single sheet of graphene is turned around itself, like a roll of news paper.

SYNTHESIS OF CARBON NANOTUBES:

1. Arc-discharge method: The carbon arc discharge method initially used by Iijima in 1991 for producing C₆₀ fullerenes.

- This technique produces a mixture of components and requires separation of nanotubes.
 - In this method two carbon rods placed end to end, separated by approximately 1mm in an enclosure.
 - A direct current of 50-100A driven by approximately 20v creates a high temperature discharge between two electrodes.
 - The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
 - Different diameter distributions are found depending on the mixture of He & Ar.
 - These mixtures have different diffusion co-efficient and thermal conductivities.
- These properties affect the speed with which the carbon and catalyst molecules diffuse and cool. Mostly produce MWNTs but can also produce SWNT with Ni-Co, Co-Y or Ni-Y on either the anode or the cathode.
- Depending on the exact technique, it is possible to selectively grow SWNT's (or) MWNT's.



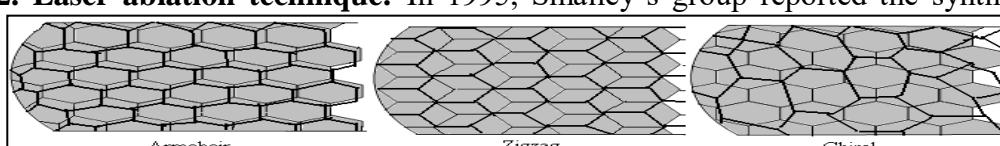
Advantages of Arc discharge method: Simple procedure

High quality product is obtained

The process is relatively inexpensive.

Disadvantages: Require further purification and tubes tend to be short with random sizes.

2. Laser ablation technique: In 1995, Smalley's group reported the synthesis of carbon nano tubes by laser ablation technique. This method is similar



to arc discharge method.

- A pulsed or continuous laser is used to vaporize a graphite target in an oven.
- The oven is filled with helium or argon gas in order to keep the pressure at 500Torr.
- As the vaporized species cool, small carbon molecules and atoms quickly condense to form large clusters.
- The catalyst also begins to condense, but more slowly at first, and attached to carbon clusters and prevent their closing into cage structures.

From these initial clusters, tubular molecules grow into single-wall carbon nano tubes until the catalyst particles become too large. The SWNT's formed in this case are bundled together by Vander walls forces.

Advantages of Laser ablation method: yield up to 70%.

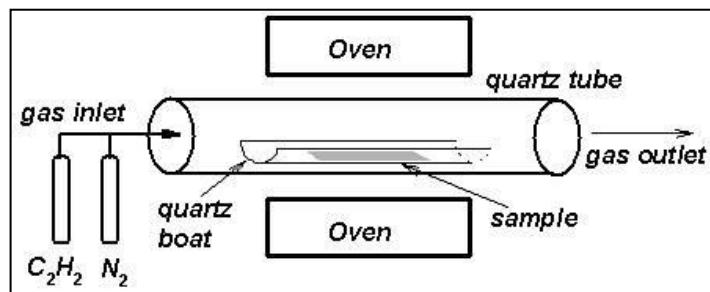
This method produces CNTs with good diameter control and pure product.

Disadvantage: The method is expensive because of lasers and high power equipment.

3. Chemical vapour deposition:

Chemical vapour deposition (CVD) synthesis is achieved by using a carbon source in the gas phase and an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule.

- Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene.
- The energy source is used to “crack” the molecule into reactive atomic carbon (usually a first row transition metal such as Ni, Fe or Co).
- Control over the diameter, as well as the growth rate of the nano tubes can also be maintained.
- The temperatures for the synthesis of nano tubes by CVD are generally within the 650-900 °C range. Typical yields for CVD are approximately 30%.



Advantages of CVD: Simple method and product is pure. The method can be increased to industrial production.

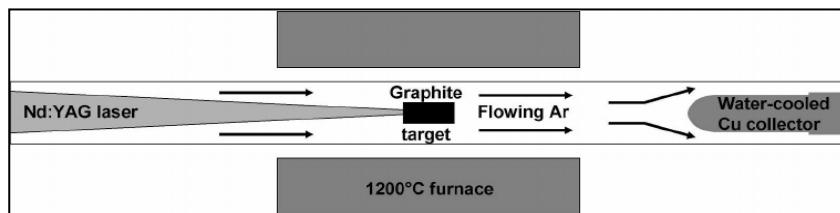
Disadvantage: Few defects are common.

PROPERTIES OF CARBON NANOTUBES (NANOMATERIALS): CNTs have several unique mechanical, electrical, vibrational, optical and sterical properties that make them attractive as drug delivery and bio-sensing platforms for the treatment of various diseases and the noninvasive monitoring of blood levels and other chemical properties of the human body, respectively.

Mechanical Properties:

i. **Strength:** The strength of the sp^2 carbon-carbon bonds gives CNTs amazing mechanical properties.

- CNTs are the strongest and stiffest materials in terms of tensile strength and elastic modulus respectively.
- This strength results from the covalent sp^2 bonds formed



between the individual carbon atoms.

- Since CNTs have a low density for a solid of $1.3\text{-}1.4\text{ g cm}^{-3}$, its specific strength is up to 48,000 kNmkg^{-1} .

ii. Hardness: One study succeeded in the synthesis of a super-hard material by compressing SWNTs to above 24GPa at room temperature.

- The hardness of this material was measured with a nano indenter as 65-152GPa.
- The bulk modulus of the compressed SWNTs was 462-546GPa.

Electrical Properties: CNTs can be metallic or semi conducting depending on their structure.

- This depends on the symmetry and unique electronic structure of graphene.
- For a given (n, m) nanotube, if $n = m$, the nanotube is metallic; if $n-m$ is a multiple of 3, then the nano tube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor.

Vibrational Properties: Atoms in CNT are continuously vibrating back and forth. They have two normal modes of vibrations.

- A_{1g} mode: It involves ‘in’ and ‘out’ oscillation.
- E_{2g} mode: Here squashing of the tube takes place(oscillation between sphere and an ellipse).

The frequencies of two modes of vibrations are Raman active.

Optical properties: Spectral shift of optical absorption and fluorescence properties

- Increased quantum efficiency of semi conductor crystals.

Sterical Properties:

- Increased selectivity for specific drug transportation and controlled release.

APPLICATIONS OF CNTs: The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications.

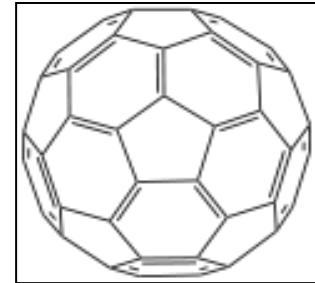
- The SWNTs are effective as hydrogen -storage material for fuel cell electric vehicles.
- Carbon nano tubes can replace platinum as the catalyst in fuel cells, which reduces the overall cost and CNTs are resistant to corrosion.
- CNTs are be used in electronics such memory, semiconductor components and conducting films for touch screens, displays and solar cells.
- CNTs as drug delivery vehicles have shown potential in targeting specific cancer cells with a dosage lower than conventional drugs used, does not harm healthy cells and significantly reduces side effects.
- CNTs are used in the preparation of structural materials such as-
Textiles-Water proof and tear resistant fabrics
Body armor- Jackets that use CNT fibers to stop bullets
Concrete- CNT in concrete increase tensile strength
Sports equipment- Stronger and lighter tennis rackets, bicycle parts etc.
Bridges- CNT may be able to replace steel in suspension and other bridges.
- CNTs are increasingly recognized as materials for catalyst, either as catalyst themselves, as catalysts additives or as catalysts supportive. Some chemical reactions are carried out inside the nano tubes like
Reduction of nickel oxide (Ni O) to the base metal Ni. $\text{Ni O} \rightarrow \text{Ni}$
Reduction of AlCl_3 to its base metal. $\text{AlCl}_3 \rightarrow \text{Al}$

FULLERENES: A third newly discovered allotrope of carbon is Buckminster fullerene named in the honor of the American architect Buckminster Fuller. The shape of C₆₀ resembles with the domes designed by Fuller. Fullerenes were discovered as an unexpected surprise during laser spectroscopy experiments at Rice University.

Types of Fullerenes: Fullerenes are the family of carbon allotropes, molecules entirely composed of Carbon, in the form of hollow, sphere, ellipsoid, tube or plane.

Thus fullerenes are of the following types:

1. Spherical fullerenes: They look like a soccer ball, and are often called Bucky balls.
2. Cylindrical fullerenes: These are called carbon nanotubes or bucky tubes.
3. Planar fullerenes: Graphene is an example of planar fullerene sheet.



Preparation: Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixtures of fullerenes like C₆₀, C₇₀, etc. are formed which are separated by solvent extraction.

C-60 is gotten from this mixture by column chromatography using alumina and hexane.

Structure: Fullerenes are a class of closed-cage carbon molecule, C_n, characteristically containing 12 pentagons and a variable number of hexagons.

- C₆₀ is a spherical crystal of carbon atoms with an arrangement of even number of sp² atoms over the surface of a closed hollow cage.
- Each atom is trigonally linked to its three neighboring atoms by bonds and thus forms a polyhedral network. The C₆₀ molecule has a truncated icosahedron structure.
- An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagons and 20 hexagons.

Properties:

1. C₆₀ is a mustard colored solid. When the thickness of the film increases, it appears brown to black.
2. It is moderately soluble in the common organic solvents, specially aromatic hydrocarbons.
3. It dissolves in benzene forming a deep magenta solution.
4. It is very tough. It can be accelerated to 1500 miles/hour and can be pushed against a tough surface without damaging it.
5. It is thermally stable up to 600°C. It undergoes sublimation under vacuum at 600°C.

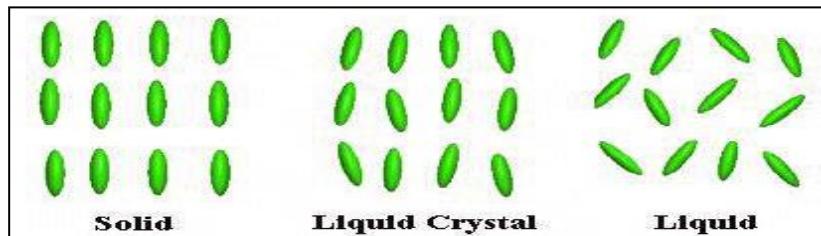
Applications:

1. Fullerenes can easily accept electrons; therefore, they may be used as charge carrier in batteries.
2. Fullerene can be used as organic photovoltaics.
3. Alkali metal fullerides are superconductors.
4. It can also be used as a soft ferro magnet.
5. Its spherical structure makes it suitable for the use as lubricant.
6. Researchers have found that water soluble derivatives of fullerenes inhibit the HIV-1 protease.
7. Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death.

8. Major pharmaceutical companies are exploring the use of fullerenes in controlling the neurological damage of such diseases as Alzheimer's disease and Lou Gehrig's disease (ALS).

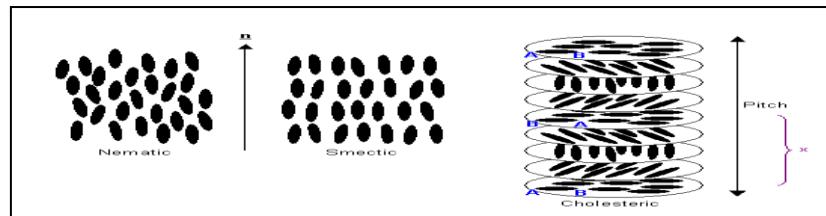
9. They are used as catalyst as they have marked ability to accept and to transfer hydrogen atoms; hydrogenation and hydro-dealkylations.

10. Due to their extremely resilient and sturdy nature, fullerenes are being considered for use in combat armour.



LIQUID CRYSTALS

Liquid crystals usually have rod like structure, rigidity of the long axis, and strong dipoles and sometimes easily polarisable substituent. The general orientation of solids, liquids and liquidcrystals are as shown here.



CLASSIFICATION OF LIQUID CRYSTALS: Depending on the conversion from solid state to liquid crystalline state, the liquid crystals can be divided in to two major categories.

These are 1. Thermotropic and 2. Lyotropic.

1. Thermotropic Liquid Crystals: When a solid is heated to a certain temperature, if changes to liquid crystal then such liquid crystals are called Thermotropic liquid crystals. These are further classified in to three major categories viz i. Nematic
ii. Cholesteric and iii. Smectic.

These will have different kinds of molecular order.

Nematic liquid crystal: In this, molecules are parallel to each other along the long molecular axes. They are moved in three directions and can rotate about one axis. They have one-dimensional structure. So, small amount of energy is enough to spoil the order of a nematic liquid crystal.

Cholesteric liquid crystal: Many compounds of cholesterol show nematic liquid crystal structure. Hence it is called Cholesteric liquid crystal. This structure can be seen like thin nematic layers are placed on top of the one below as shown in diagram. This structure can be visualized as a stack of thin nematic – like layers. In this structure, the directions actually form in a continuous helical pattern about the normal.

Smectic liquid crystal: The word "smectic" is derived from the Greek word for soap.

A thick,oily substance seen at the bottom of a soap dish is an example of smectic liquid crystal. In the Smectic liquid crystal, the molecules have the same order of nematic liquid crystal. But the molecules are not moved and hence there are eight smectic structures. These are named as A to H.

2. Lyotropic Liquid Crystals: In concentrated solutions, lyotropic mesophases can be formed. The solvent should be isotropic.

Examples: 1. Sodium laurate in water and 2. Dhosphatidyl choline in water.

Lyotropic mesophases are found in soaps, gels and colloids, and in biological systems. Soap films are constituted by multi component lyotropic systems.

Applications: Liquid crystal technology is a very useful technology in areas of science, medicine and engineering.

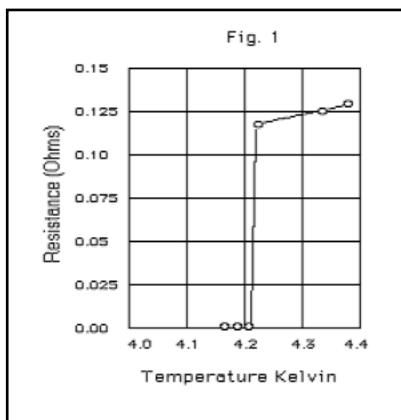
A. These are mainly used as displays in many instruments and devices (LCD i.e., liquid crystal display), used in digital wrist – watches, calculators, television screens, computer monitors.

B. Thermometers: Cholesteric substances exhibit one colour at a particular temperature. But by changing the temperature, the colour also changes. So these are useful to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissue.

C. Radiation and Pressure sensors: Cholesteric liquid crystals are also used in radiation and pressure sensors.

D. In research work: Nematic liquid crystals are good solvents for NMR spectra. Some liquid crystals can also be used as chromatographic separations. of chemical reactions and enable rearrangements and kinetics.

E. Other applications: Liquid applications also. For example, transmitted by a walking foot on by using low molar mass (LMM) changes with rise in temperature.



These can direct the course us to study the molecular

crystals have medical the transient pressure the ground can be measured liquid crystals whose colour

Material	T _c
Aluminum	1.2K
Tin	3.7K
Mercury	4.2K
Niobium	9.3K
Niobium-Tin	17.9K
Tl-Ba-Cu-oxide	125K

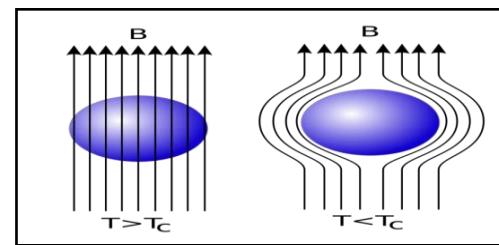
SUPER CONDUCTORS

Superconductors are the material having almost zero resistivity and behave as diamagnetic below the superconducting transiting temperature

o Superconductivity is the flow of electric current without resistance in certain metals, alloys, and ceramics at temperatures near absolute zero, and in some cases at temperatures hundreds of degrees above absolute zero.

- o The temperature at which a material at normal conducting state changes into super conducting state is known as transition temperature or critical temperature (T_c).
- o Below critical temperature, material is said to be in superconducting and above this it is said to in normal state. Below this temperature the superconductors also exhibits a variety of several astonishing magnetic and electrical properties
- o **Zero electrical resistance:** The electrical resistance of the superconductors of the superconductor is zero below the transition temperature (T_c). This property of Zero electrical resistance is known as ‘defining property’ of a super conductor.

- Effect of Magnetic Field:** Below T_c superconductivity can be destroyed by the application of a strong magnetic field. Minimum magnetic field strength required to destroy the super conducting property at any temperature is known as Critical magnetic field (H_c).
- Effect of impurities:** When impurities are added to superconducting elements, the superconductivity is not lost but the T_c is lowered.
- Effects of pressures and stress:** Certain materials exhibits superconductivity on increasing the pressure in superconductors, the increase in stress results in increase of the T_c value.
- Isotope Effect:** In most of the cases, the isotope of a super conducting element is also a super conductor. T_c of a heavier isotope is lower than that of a lighter isotope.



Meissner effect: The complete expulsion of all magnetic field by a superconducting material is called “Meissner effect”. The Meissner effect is a distinct characteristic of a superconductor from a normal perfect conductor. In addition, this effect is exhibited by the superconducting materials only when the applied field is less than the critical field H_c .

Normal state: $T > T_c$

Superconducting state : $T < T_c$

Types of Super conductors: Two types of super conductors are differentiated as below.

S. No.	Type – I super conductors.	Type – II super conductors.
1.	The material loses its magnetization suddenly.	The material loses its magnetisation gradually.
2.	They exhibit complete Meissner effect i.e. they are completely diamagnetic	They do not exhibit complete Meissner effect
3.	There is only one critical magnetic field (H_c)	There are two critical magnetic field (H_c) i.e., lower critical field (H_{c1}) and upper critical field (H_{c2})
4.	No mixed state exists.	Mixed state is present.
5.	Also known as soft super conductors.	They are called Hard super conductors.
6.	Ex: Lead, Tin, Mercury etc.,	Ex: Nb_3Ge , Nb_3Si , $Nb-Ti$ etc.

High T_c Super conductors: In a super conductor if the transition temperature is high i.e., greater than 20K, then it is called as high-temperature super conductors. Some of them are shown here.

Applications of Super conductors:

1. SQUID: SQUID stands for Superconducting QUantum Interference Device. It is an ultra-sensitive instrument used to measure very weak magnetic field of the order of 10^{-14} tesla Application:

- SQUID can be used to detect the variation of very minute signals in terms of quantum flux.
- It can also be used as storage device for magnetic flux.
- SQUID is useful in the study of earth quakes, removing paramagnetic impurities, detection of magnetic signals from the brain and heart.

2. Magnetic levitation: When a super conducting material shows the Meissner effect. Due to this effect, super conducting materials strongly repel external magnets. This leads to a levitation effect.

When a magnet is placed over a super conductor, it floats. This phenomenon is known as Magnetic Levitation. Magnetic levitated Train (Maglev train) works on this principle.

3. Medical applications: MRI (Magnetic Resonance Imaging) scans produce detailed images of soft tissues. The superconducting magnet coils produce a large and uniform magnetic field inside the patient's body. So it is used to study the patient.

4. Additional applications:

- Super conducting Magnets.
- Electrical Machines.
- Power cables to reduce transmission losses.
- Computer memory devices and super computers

GREEN CHEMISTRY

Green chemistry also called **sustainable chemistry**. Basic idea of Green Chemistry is a new approach which provides the design of chemical products and process that minimize the use and generation of hazardous substances so that it is inherently of less risk to human health and the environment. Green chemistry is needed in the design and attainment of sustainable development. Green Chemistry is an important area for science and technology to pursue for the benefit of the environment, industry and the general public.

The need of Green Chemistry:

- Industrial discharges, pesticides and herbicides fill the skies and seas.
- The technological power is increased day by day but the side effects and potential hazardous also increased.
- To maintain our current standard of living and improve our quality of life, society has come to depend on the products of chemical industry.
- The public is equally aware of the hazardous substances used and generated by the chemical processes.

S.No	High T_c Super conductors	T_c in K
1.	$\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$	36
2.	$\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$	90
3.	$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125
4.	$\text{HgBa}_2\text{CaCu}_2\text{O}_6$	133

THE PRINCIPLES OF GREEN CHEMISTRY: Chemistry is determinant to understand and protect our environment, as the world's future is strongly dependent on the chemical process adopted.

Green chemistry is considered as science based non-regulatory, economically driven approach and essential piece of a comprehensive program to achieve the goals of environmental protection, human health, and sustainable development eco-efficiency.

Paul T. Anastas and *John Warner* proposed twelve principles of green chemistry.

1. Waste prevention: It is better to prevent waste than to treat or clean up waste after it is formed.

2. Atom economy: Synthetic materials should be designed maximize the incorporation of all materials used in the process into the final product.

3. Use of less hazardous and toxic chemicals: Where ever possible synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing of safer chemicals: Chemical products should be designed to preserve efficiency of function while reducing toxicity.

5. Safer solvents and auxiliaries: The use of auxiliary substances should be made unnecessary wherever possible, when used and innocuous.

6. Design for Energy efficiency: Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of renewable raw materials: A raw material or feedstock should be renewable rather than depleting, wherever technically and economically practicable.

8. Reduce Derivatives: Unnecessary derivations (blocking groupings etc.) should be avoided whenever possible.

9. Catalysis: Catalytic reagents are superior to stoichiometric reagents.

10. Design for degradation: Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Real-time analysis for pollution prevention: Analytical methodologies need to be further developed to allow for real time, in-process monitoring and control prior to formation of hazardous substances.

12. Inherently safer chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires, i.e., plants should be designed as to eliminate the possibility of accidents during operations.

APPLICATIONS OF GREEN CHEMISTRY

1. Applications of engineering ecofriendly principles to the design of manufacturing and combusting processes to reduce air pollutant emissions to acceptable levels.
2. Perchloroethylene (PERC), $\text{Cl}_2\text{C}=\text{CCl}_2$ is commonly being used as a solvent for dry cleaning. It is now known that PERC contaminates ground water and is a suspected carcinogen. Use of liquid CO₂ and a surfactant for dry cleaning clothes, thereby replacing PERC is a Green Chemistry pathway.

3. For obtaining good quality of paper, lignin in the raw material wood is removed by harmful Cl_2 gas. A versatile agent involves the use of H_2O_2 as a bleaching agent in the presence of some activators as catalysts which promote the conversion of H_2O_2 into hydroxyl radicals that are involved in bleaching.
4. Green Solution to turn turbid water clear tamarind seed kernel powder, discarded as agriculture waste, is an effective agent to make municipal and industrial waste water clear. This is best practice than the presently used Alum treatment of water which increases toxic ions in treated water and could cause diseases like Alzheimer's.
5. Adipic acid, the starting material for the preparation of Nylon generally prepared from Benzene, which is a carcinogenic. A green chemistry biological pathway established i.e., from D-Glucose, which is harmless.
6. Aqueous phase method was introduced which use water as solvent instead of harmful volatile organic solvents.
7. Developing of various processes to remove nitrogen oxides, sulphur oxides, volatile organic compounds (VOC), reactive organic gases and other air pollutants from fuel gases.
8. Improving industrial processes to eliminate waste and reduce consumption of organic solvents. Similarly, super critical fluid extraction method was used for extraction of caffeine and other flavanoids instead of organic solvents like chloroform and benzene.
9. A new commercialized and greenery processes in biomass conversion used in synthetic fabric in furniture industry and water based paints in auto industry.
10. New methodology has developed by engineers that the conversion of lignin into useful chemicals, antioxidants medicinal compounds.
11. By using biotechnology processes. The biomass converted to fermentable sugars in presence of enzymes from crop residues such as corn stover and stalks, wheat straw and rice straw.
12. The engineers established chemical production processes, which have led to reduce energy, water consumption, minimized by products and even noise reduction.

QUESTION BANK
ESSAY TYPE QUESTIONS

1. Write a note on a) Top down and Bottom up approaches
b) Arc discharge method.
2. Explain a) Laser ablation method
b) Transmission Electron Microscopy (TEM)
3. Explain a) Chemical vapour deposition method
b) BET method for characterisation of nano materials.
4. Explain a) Sol-gel method for preparation of nano particles
b) Properties and Applications of Fullerenes
5. Discuss a) SWNT and MWNT
b) Type – I and Type II superconductors.
6. What are superconductors? Write their properties and applications.
7. What are liquid crystals? Discuss the types and any five applications of liquid crystals.
8. Explain the principles and applications of green chemistry.