UNIT-1

POLYMER CHEMISTRY

Polymers: Introduction, functionality of monomers, chain growth, step growth polymerization, stereo regular polymers.

Plastics: Thermoplastics and thermosetting, preparation, properties and applications of Bakelite, Urea-Formaldehyde & Nylon-66.

Elastomers: Introduction, preparation, properties and applications of Buna-S & Buna-N,

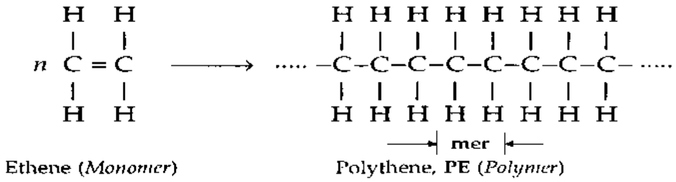
Smart Polymers: Introduction, types of smart polymers and applications of smart polymers.

POLYMERS

Polymers:

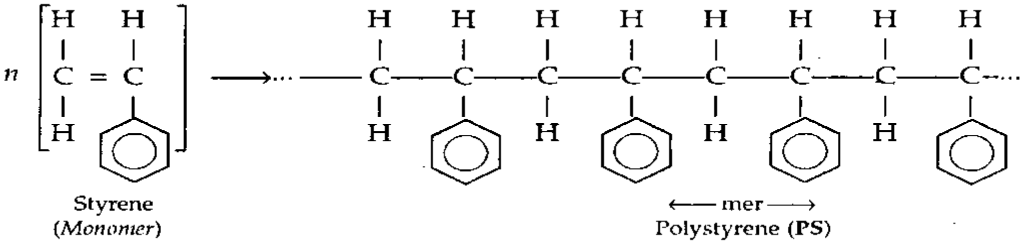
Polymers' (Greek poly - many; mers - units or parts) is 'macromolecules' built-up by the linking together of a large number of small molecules. The repeat units in a polymer chain are linked through strong covalent bonds.

Example: Polythene is a polymer formed by linking together of a large number of ethylene (C_2H_4) molecules.



Monomers:

Small molecules which combine with each other to form polymer molecules are termed **monomers**; and the "repeat unit" in a polymer is called **mer.** Monomers are often called building blocks of polymer chain. The essential requirement of a small molecule to qualify as a monomer is the possession of at least two bonding sites (Bifunctional).



Polymerization:

The fundamental chemical process by which the low molecular weight molecules are converted into high molecular weight molecule, with elimination of small molecules like water, ammonia, alcohol etc. or without such elimination is called the polymerization.

Degree of polymerization" (DP):

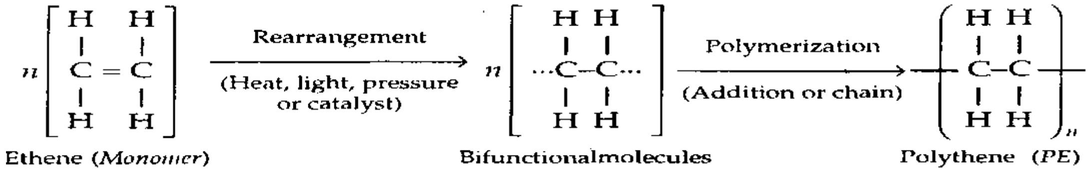
The number of repeating units (n) in polymer chain is known as the "degree of polymerization" (DP). There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule. Most of the polymers, usually, fall into the 5,000—200,000 molecular mass range.

Functionality: The total number of bonding sites or reaction sites present in a monomer molecule is called the functionality of the monomer. Depending on the number of bonding sites, the monomers are called bifunctional, trifunctional and polyfunctional.

Types of Polymerization: On the basis of type of chemical reaction polymerization reactions are classified into three types.

1. Addition or chain polymerization:

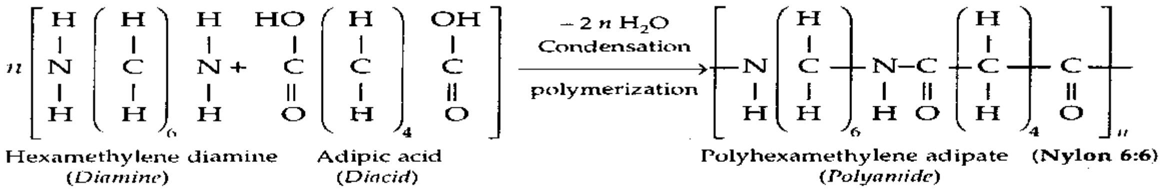
The fundamental chemical process by which the low molecular weight molecules are converted into high molecular weight molecule, without the elimination any small molecules like water, ammonia, ethyl alcohol etc. is called the addition polymerization. A chain polymerization is a reaction that yields a polymer product which is the exact multiple of monomers.



2. Condensation or step growth polymerization:

The fundamental chemical process by which the low molecular weight molecules are converted into high molecular weight molecule with the elimination any small molecules like water, ammonia, ethyl alcohol etc. is called condensation or step growth polymerization.

Example: Nylon 6:6: It is prepared by polymerization of Hexamethylene diamine and Adipic acid.



Difference between addition and condensation polymerization:

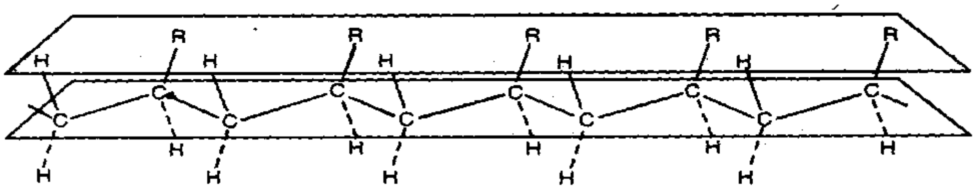
S.NO	Addition Polymerization	Condensation Polymerization
1	It is also known as chain growth polymerization	It is also known as step growth Polymerization
2	The polymerization takes place by self addition of monomers	It is due to slow step wise condensation of the functional groups
2	It takes place only in monomers having multiple bonds	It takes place in monomers having reactive functional groups
3	It takes place without elimination of simpler molecule	It takes place with elimination of simple molecule like H_2O, NH_3, HCl etc
4	High molecular weight polymer is formed soon.	The molecular weight of polymer increases steadily throughout the reaction
5	The product obtained by this Polymerization is thermoplastic.	The product obtained in the polymerization may be either thermoplastic or thermosetting

6	Reaction initiated by initiator(catalyst)	Reaction initiated by heat
7	Reaction proceeds in fast manner	Reaction proceeds comparatively slow.
8	Polyethylene, polystyrene, polypropylene, polyvinyl chloride etc. are its examples	Bakelite, urea formaldehyde resin, epoxy resins, etc. are its examples

Stereo Regular Polymers: The polymer which having specific tacticity is called stereo regular polymer or stereo specific polymer.

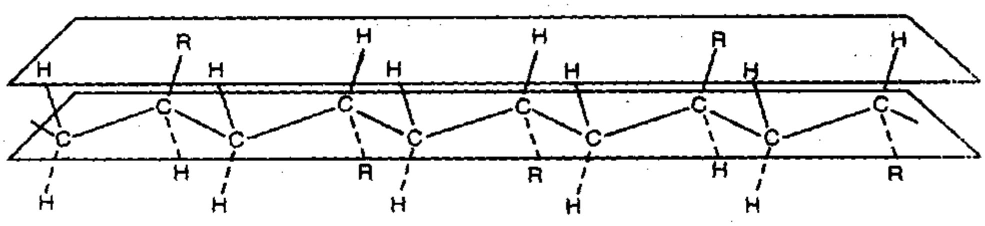
Tacticity of polymers: The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The differences in configuration (tacticity) do affect their physical properties. This orientation results in three types of stereo-regular polymers.

1. **Isotactic Polymer**: The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called **isotactic** polymer. It is Crystalline in nature.



Isotactic

2. **Atactic polymer**: If the arrangement of functional groups is at random around the main chain, it is called **atactic** polymer. It is Amorphous in nature. e.g. polypropylene.



Atactic

3. **Syndiotactic polymer**: If the arrangement of functional groups is in alternating fashion, it is called ‘**syndiotactic**’ polymer. It is semi Amorphous in nature. e.g., gutta percha.

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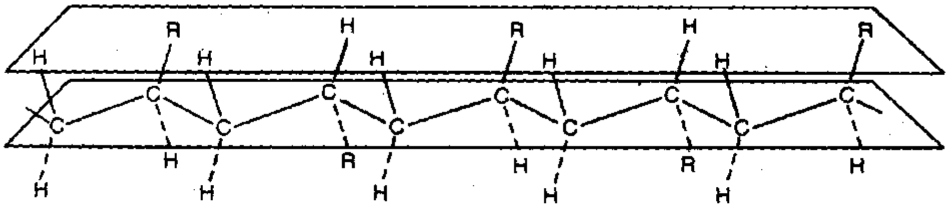


Syndiotactic

Plastics: Plastics are high molecular weight organic Polymers which can be moulded into desired stable shapes by the application of heat and pressure. (Or) Plastics are high molecular weight organic polymers which exhibit the property of plasticity. i.e., ability to get deformed or ‘to undergo change of shape under pressure.

Properties of plastics: In recent years, plastics have attained great importance in every walk of our life, due to their certain unique properties like:

1. Light in weight and have low specific gravity varies from 1 to 2.4.
2. Highly resistant to corrosion.
3. Moulded in to any desired shape.
4. Easy workability, low fabrication cost and low maintenance cost.
5. Shining and glassy surfaces.
6. Good shock-absorption capacity.
7. Good thermal and electrical insulators.
8. Low thermal expansion coefficient.
9. Do not absorb water.
10. Some plastics have high tensile strength
11. Can be made transparent or opaque, brittle, malleable or elastic, hard or soft.
12. Can be obtained any desired colour.

Types of plastics: Plastics are classified into two types:

1. Thermoplastics. 2. Thermosetting

Thermoplastics: Plastics which are softening on heating and harden on cooling are known as thermoplastics.

Thermosetting: The polymers which undergo chemical changes and cross linking on heating and become permanently hard, rigid and infusible are called thermosetting.

Difference between Thermoplastics and Thermosettings

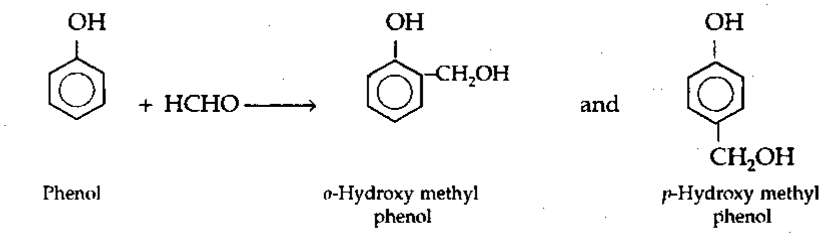
S.No	Thermoplastics	Thermosetting
1	They soften on heating and harden on cooling	Become permanently hard, rigid and infusible product on further heating
2	They are formed by addition polymerization.	They are formed by condensation polymerization.
3	They undergo reversible changes on the application of heat.	They undergo irreversible changes on the application of heat.
4	They can be reshaped and reused.	They cannot be reshaped and reused.
5	They are soft and flexible.	They are hard, rigid and infusible.
6	They have linear structure.	They have three dimensional

7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerization and cross linking during molding process.
8	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
9	They can be reclaimed from waste.	They cannot be reclaimed from waste.
10	Examples: Polyethylene, Polypropylene, Polystyrene, Polyvinyl chloride, Teflon	Examples: Phenol - Formaldehyde resin (PF) Urea - Formaldehyde resin (UF)

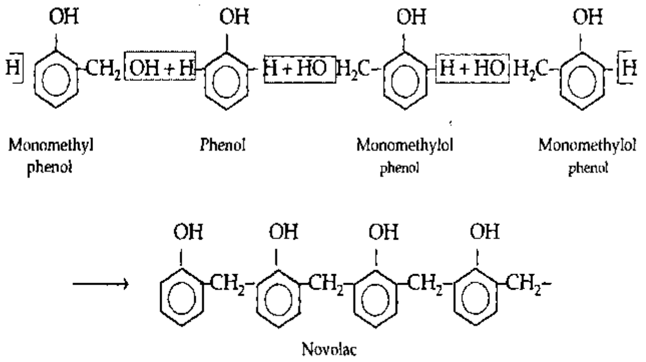
Preparation, Properties and applications of some plastics

1. **Phenol-Formaldehyde Resin (Bakelite):** It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst. The initial reaction results in the formation of o, p - hydroxy methyl phenol, which reacts to form linear polymer, novolac. Thus:

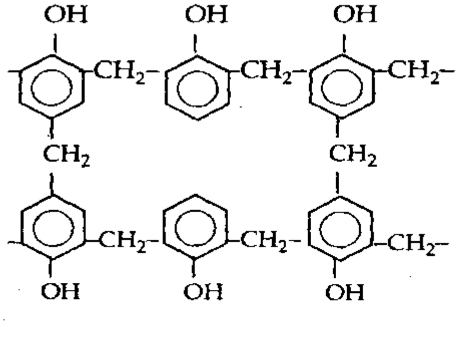
Step-1: formation of o, p methyl phenol:



Step-2: formation of Novalac:



Step-3: formation of Bakelite:



Cross-linked polymer bakelite

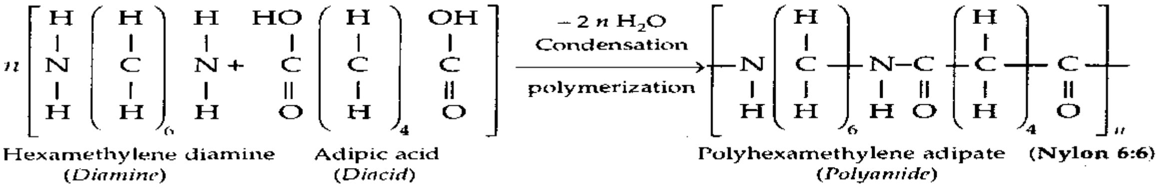
Properties:

- Phenolic resins (bakelite) set to rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids.
- Which are resistant to non-oxidizing acids, and many organic solvents, but are attacked by alkali.
- They possess excellent electrical- insulating character.

Applications:

- For making electric insulator parts like switches, plugs, switch-boards, heater-handles, etc.
- For making moulded articles like telephone parts, cabinets for radio and television.
- For impregnating fabrics, wood and paper.
- As adhesives for grinding wheels.
- In paints and varnishes.
- As hydrogen-exchanger resins in water softening.
- For making bearings, used in propeller shafts for paper industry and rolling mills.

2. **Nylon-6, 6:** It is synthesized by polycondensation of hexamethylenediamine and adipic acid. Equivalent amounts of hexamethylenediamine and adipic acid are combined with water in a reactor. This is crystallized to make nylon salt, an ammonium/carboxylate mixture. The nylon salt goes into a reaction vessel where polymerization process takes place either in batches or continuously.



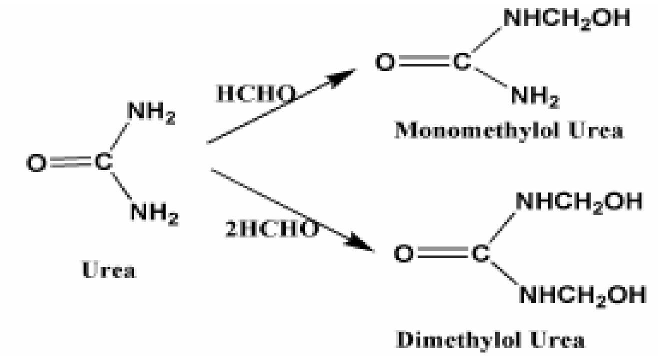
Properties:

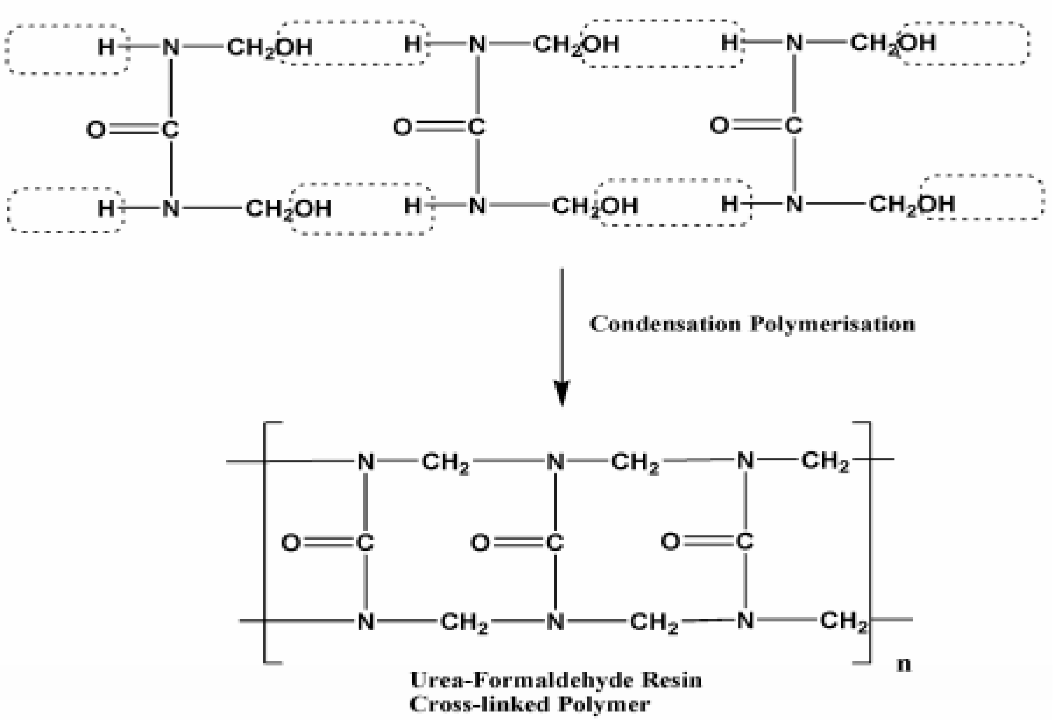
- High mechanical strength, stiffness, hardness and toughness.
- High mechanical damping ability.
- Good sliding properties.
- Excellent wear resistance
- Good electrical insulating properties

Applications:

- It is used in fibers for textiles and carpets and molded parts.
- It has broad use in auto applications; these include "under the hood" parts such as radiator end tanks, rocker covers, air intake manifolds, and oil pans.
- Other applications include electro-insulating elements, pipes, profiles, various machine parts, zip ties, conveyor belts, hoses, polymer-framed weapons, and the outer layer of turnout blankets also a popular guitar nut material

3. Urea-Formaldehyde Resin:





Properties:

- They are clear and white.
- Better hardness and tensile strength than PF resins.
- Resistant to most of the solvents and grease.
- Excellent abrasion resistant and stable to light.
- Good electrical insulators and possess chemical resistance.

Applications:

- These resins are widely used in manufacture of buttons, bottle caps, house hold appliances, surgical items etc.
- They are used as adhesives in plywood industries.
- They are also used in the manufacturing of enamels and other surface coatings.
- Used for the finishing of cotton textiles

ELASTOMERS

Rubbers are high polymers, which have elastic properties in excess of 300 percent. An elastomeric molecule is not straight chained, but in the form of a coil and consequently it can be stretched like a spring. Natural rubber is consists of basic material latex, which is a disperson of isoprene. During the treatment, these isoprene molecules polymerize to form long coiled chains of cis- poly isoprene.

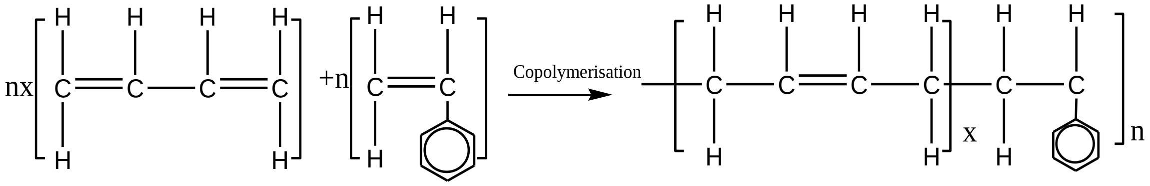
Properties	Raw rubber
Tensile strength	200 Kg/cm ^{2}
Resilience	good
Use full temperature range	10-60 ^0C
Resistance to moisture, oxidation and abrasion	poor
Resistance to organic solvents	poor
Tackiness	marked
Elasticity	Very high
Percent elongation at break	1200
Manipulation to desired shape	Not easy

Buna-S rubber or Styrene rubber or GR-S

Preparation:

It is a synthetic rubber.

It is produced by copolymerization of butadiene (about 75% by weight) and styrene (25% by weight)



Properties:

- It possesses high abrasion resistance
- High load bearing capacity
- But it readily gets oxidized, especially in presence of traces of ozone present in the atmosphere.
- It swells in oils and solvents
- It can be vulcanized by using sulphur

Applications:

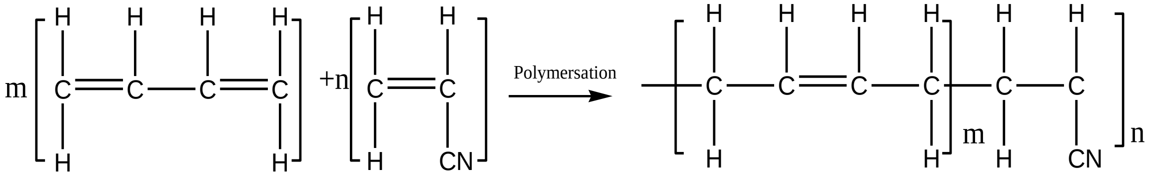
- Manufacture of motor tyres
- Floor tiles, shoe soles, gaskets, foot wear components.

- Wire and cable insulation
- Tank lining etc.

Buna-N rubber or Nitrile Rubber or GR-A

Preparation:

It is a copolymer of butadiene and acrylonitrile



Properties:

- Excellent resistance to heat, sunlight, oils, acids and salts
- Less resistant to alkalis, because of the presence of cyno groups
- Vulcanized nitrile rubber is more resistant to heat

Applications:

- For making
- Conveyor belts
- Tank linings
- Gasket
- Printing rollers
- Auto mobile parts etc.

SMART POLYMERS

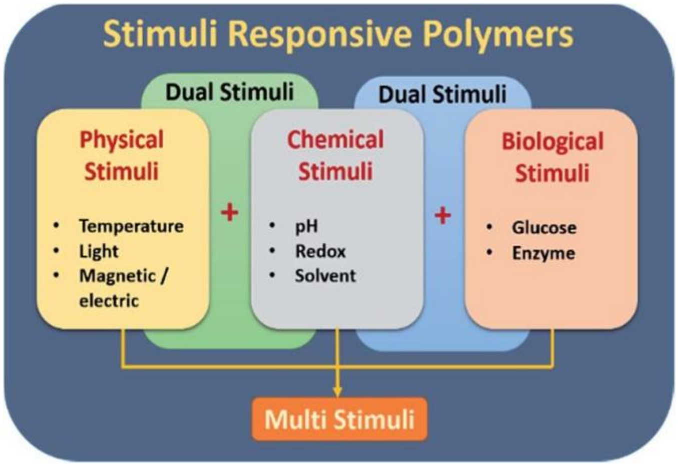
Smart polymers, stimuli-responsive polymers or functional polymers are high-performance polymers that change according to the environment they are in. Such materials can be sensitive to a number of factors, such as temperature, humidity, pH, chemical compounds, the wavelength or intensity of light or an electrical or magnetic field and can respond in various ways, like altering color or transparency, becoming conductive or permeable to water or changing shape (shape memory polymers). Usually, slight changes in the environment are sufficient to induce large changes in the polymer's properties.

“The term smart polymer embraces a wide range of different compounds that can change their color, transparency or shape in response to their environment; they are smart because of their ability to respond in a very dramatic way when small environmental changes are detected”.

It only takes a small variation in temperature, humidity, pH, or light, for example, to induce a large change in smart polymer properties, and this non-linear response makes them unique.

Classification of smart polymers: Stimuli that induce changes in the polymer can be further classified into three categories: physical, chemical and biological stimuli. Polymers respond to physical stimuli (light, temperature, magnetic and electrical) due to the modification of chain dynamics. On the other hand, chemical stimuli modulate molecular interactions between polymer and solvent molecules or between polymer chains to induce changes in the polymer (Fig. 3).10 Biological stimuli correspond to the actual functioning of the molecules such as enzymatic reactions and receptor recognition etc.

1. Physical – temperature, ultrasounds, light, or mechanical strength.
2. Chemical – pH and ionic strength.
3. Biological – enzymes and biomolecules.



Applications of smart polymers

- In Drug delivery System
- As reversible Bio Catalyst
- In textile Engineering
- As glucose Sensor
- In oil Recovery
- In bio separation
- In Protein folding and in purification

UNIT-2

ELECTROCHEMICAL ENERGY SYSTEMS

Batteries: Introduction, classification of batteries, dry cell, lead acid cell, Ni-Cd cell, Lithium cells-Li MnO_2 cell, Lithium-ion cells, Fuel cells – Hydrogen and Oxygen fuel cell, Methanol and Oxygen fuel cell, applications of batteries.

Electrochemistry: Electrochemistry studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus, electrochemistry deals with the interaction between electrical energy and chemical change.

Electrolytic cell (Electrolysis): When a chemical reaction is caused by an externally supplied current, as in electrolysis. Electrolytic cell uses electric current for the propagation of chemical reaction.

Electrochemical cell or Galvanic cell: If an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an electrochemical cell

Redox Or Oxidation – Reduction Reactions: Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or redox reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

Differences between Galvanic cell or electro chemical cell and electrolytic cell

Galvanic cell	**Electrolytic cell**
Spontaneous redox reactions convert the chemical energy to an electric energy	Non-spontaneous redox reactions convert the electric energy to a chemical energy
Electric energy is generated by redox reactions	Electric energy brings about the chemical reaction with the help of an external source
The cathode is the positive electrode and anode is the negative electrode	The anode is the positive electrode and cathode is the negative electrode
The process of oxidation takes place at the anode and the reduction process occurs at the cathode	Here, the oxidation process occurs at the cathode while the reduction process takes place at the anode
Half cells are set up in different containers and are connected through salt bridges	Electrodes are kept in the same container in a molten or solution electrolyte
Application lies in Batteries	Application lies in purifying copper and electroplating

Battery: 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 a term usually applied to a group of two or more electric cells, connected together electrically in series. Batteries are commercial electrochemical cells. These are two types (a) primary cells and (b) secondary cells.

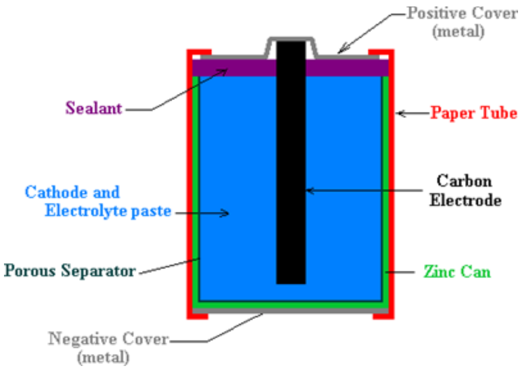
Primary batteries: These are irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means.

Secondary batteries: It can be recharged; in which cell reaction can be reversed by passing direct electric current in opposite direction. Thus, a secondary battery may be used through a large number of cycles of discharging and discharging.

Differences between primary cell (Non-Rechargeable Battery) and Secondary cell (Non rechargeable battery

Primary cell	Secondary cell
Have high energy density and slow in discharge and easy to use	They are smaller energy density
There are no fluids in the cells hence it is also called as dry cells.	There are made up of wet cells (flooded and liquid cells) and molten salt (liquid cells with different composition)
It has high internal resistance	It has a low internal resistance
It has an irreversible chemical reaction	It has a reversible chemical reaction
Its design is smaller and lighter	Its design is more complex and heavier
Its initial cost is cheap	Its initial cost is high

The dry cell or laclanche cell: The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the Centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, Starch and zinc chloride occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.



Anode reaction: $Zn \rightarrow Zn2+ + 2e-$

Cathode reactions: $2MnO2 + H2O + 2e- \rightarrow Mn2O3 + 2\ OH-$

$2\ NH4+ +2\ OH- \rightarrow 2NH3 + 2H2O$

Cathode reaction: $2MnO2 + 2NH4+ + Zn2+ + 2e- \rightarrow Mn2O3 + [Zn\ (NH3)2]2+ + H2O$

Overall reaction: $Zn + 2MnO2 + 2NH4+ \rightarrow Mn2O3 + [Zn\ (NH3)2]2+ + H2O$

Applications:

Dry cells are used in flash light, portable radio, tape recorder, calculators, quartz wall clocks, etc.

Limitations:

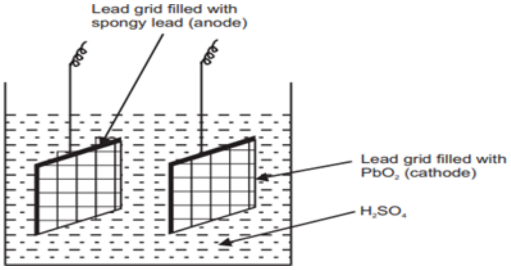
Dry cell gives low voltage when it is used continuously.

The cell gets discharged slowly even if it is not in use. Since Zinc is dissolved acidic electrolyte.

Advantages:

Low price, gives voltage of about 1.5 V; normally works without leaking (leak proof cells); possess high energy density; non-toxic; contains no liquid electrolytes.

Lead storage battery: It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing leaf dioxide, PbO2. These plates are immersed in a solution of about 30% H2SO4. When the cell discharges; it operates as a voltaic cell. The spongy lead is oxidized to Pb2+ ions and lead plates acquire a negative charge.



Electrode reactions: The electrode reactions that occur during the discharge of the cell, i.e., on drawing current from the cell, are as follows:

At Anode, $Pb \rightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \rightarrow Pb\ SO_4$

$Pb^{2+} + SO_4^{2-} \rightarrow Pb\ SO_4 + 2e^-$

At Cathode,

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \rightarrow Pb\ SO_4$

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

The net cell reaction is,

$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

The product ($PbSO_4$) formed during discharge remains adhered on each electrode and is available at the site during recharging.

From the cell reaction, it is evident that the potential of the lead storage cell is dependent at any given temperature on the activity or concentration of sulfuric acid solution. Thus at 25°c and at a cocentration of 7.4% sulfuric acid the potential devloped by a pair of electrode is 1.90V; at 21.4%, 2.0V and at 39.2% 2.14V. Further , it is evident that sulfuric acid consumed and water is produced during discharge. This result in the decrease in the gravituy of electrolyte.

Recharge reactions: When the density of sulfuric acid in the battery falls below 1.20gcm-3, the battery needs charging . This is done by reversing the discharge reaction by applying extertnally a potntial higher than that of the cell, depositing lead and leaddioxide on the electrodes.

$Pb\ SO_4 + 2e^- \rightarrow Pb^{2+} + SO_4^{2-}$

$PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

During charging sulfuric acid is regenerated in the cell. The net reaction during charging and discharging can be represent as follows:

$$Pb(S) + PbO_2\,(S) + 2H_2SO_{4\,(aq)} \underset{\text{Charging}}{\overset{\text{Discharging}}{\leftrightarrow}} 2PbSO_4 + 2H_2O$$

Advantages

- In expensive and simple to manufacture.
- Mature, reliable and well-understood technology - when used correctly.
- The self-discharge is among the lowest of rechargeable battery systems.
- Capable of high discharge rates.

Disadvantages of Lead Acid Battery:

- Lead is heavier compare to alternative elements.
- It can be charged slowly i.e. fully saturated charge takes 14 to 16 hours.
- It has limited cycle life. Moreover repeated deep cycling reduces battery life.
- It is not environmentally friendly.

Applications:

- Lead–acid batteries are used in emergency lighting and to power sump pumps in case of power failure. Large lead–acid batteries are also used to power the electric motors in diesel-electric submarines and are used as emergency power on nuclear submarines as well.
- These batteries also used in digital cameras, handheld video game, cellphones

Construction of Nickel-Cadmium Battery

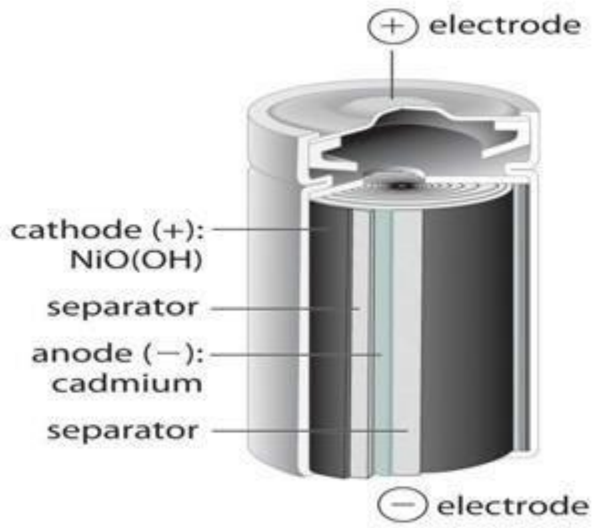
Constructional, the nickel-cadmium battery is the same as lead acid-based batteries. It consists of three fundamental layers. The first one is a nickel layer, then the separator layer, and the cadmium layer. The nickel acts as a positive electrode collector and the cadmium layer acts as a negative layer collector.

The separator layer between the two layers is made up of KOH or NaOH. Its purpose is to provide OH ions. Apart from these, it also consists of a safety valve, sealing plate, insulation ring, insulation gasket, and an outer case. The purpose of the insulator ring is to provide insulation between the two layers. The insulator gasket is the place where the insulation ring is kept nearby. The separator layer is connected to this ring.

The outer case is to provide protection to the inner layers from external factors such as damages and mishandling of the battery. It must be noted that, due to chemical reactions taking place within the batter, it always hazardous to work with the battery. The layers along with the separator layer form the required chemical reaction and form the potential difference.

Nickel Cadmium Battery Working

The Nickel Cadmium batteries have the advantage of being recharged many times and possess a relatively constant potential during discharge and have more electrical and physical withstanding capacity. This battery uses nickel oxide for cathode, a cadmium compound for anode and potassium hydroxide solution as its electrolyte.



Chemical reactions during Discharge process:

At the anode electrode: $Cd+2\,OH^{-} \longrightarrow Cd(OH)_2+2e^{-}$

At the cathode electrode: $2\,NiOOH+2\,H_2O+2e^{-} \longrightarrow 2\,Ni(OH)_2+2OH^{-}$

Overall reaction: $Cd+2\,NiOOH+2\,H_2O \longrightarrow Cd(OH)_2+2\,Ni(OH)_2$

Advantages and Disadvantages

The advantages of Nickel Cadmium Battery are

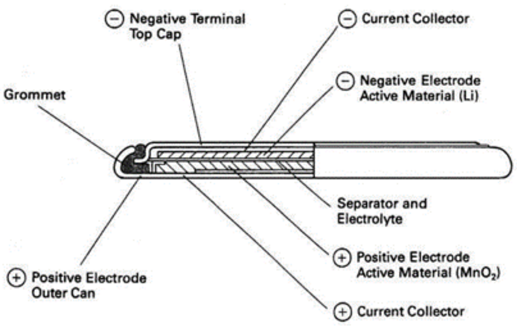
- Delivers high current output
- It tolerates overcharging
- It withstands up to 500 cycles of charging

The disadvantages of Nickel Cadmium Battery are

- Cadmium is not an eco-friendly material
- Less tolerance towards temperature as compared to other batteries.

Lithium Manganese Dioxide (Solid Lthium Battery):

These batteries deliver a voltage of 3.0 V and are cylindrical, button and polymer in shape. The manganese dioxide pellet and lithium anode disc are separated by a non woven polypropylene separator impregnated with the electrolyte. The cell is sealed with the can serving as the cathode terminaal and the cap as the anode terminal.



Electrode Reactions:

At the Anode, $Li \rightarrow Li^{+} + e^{-}$

At the Cathode, $MnO_2 + Li^{+} + e^{-} \rightarrow LiMnO_2$

The net cell reaction is, $Li + MnO_2{}^{-} \rightarrow LiMnO_2$

Mn^{4+} is reduced to Mn^{+3} , with the Li^{+} entering the MnO_2 crystal lattice.

Applications:

As a long time memory backup

In watches, calculators, cameras, lighting equipments, toys and other consumer electronics.

Military radio-communication, Sonbuoys, Emergency location transmitters beacon

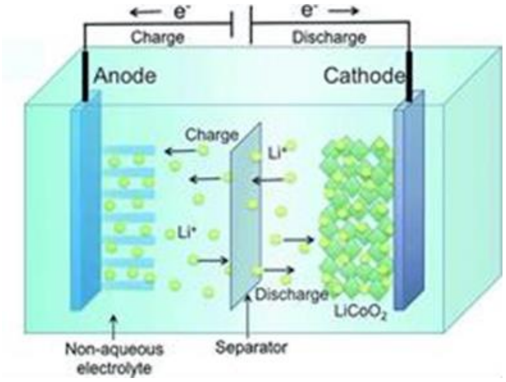
Advantages :

1. Long life expectancy and long operational life.
2. Low self-discharge rate
3. High energy density
4. High cell voltage.
5. High operating Safety
6. Resistance to corrosion
7. Safe and environmentally friendly.

Dis Advantages:

1. LiMnO2 can explode, overheat or leak if not handled appropriately
2. Lithium Manganese oxide batteries are not rechargeable, therefore, these are not ideal for laptops, cellphones and other equipment that needs reliable batteries.

Li-Ion Cell: This cell does not contain metallic lithium hence they called as lithium ion cells and use lithium ions instead. In this cell transport of Li+ ions through the electrolyte from one electrode to other electrode takes place through the external circuit to maintain charge balance. In this battery lithium ions interchanged between two layers of graphite and $LiCoO_2$.



When the cell is in charging Lithium ions leaves $LiCoO_2$ and travel through the electrolyte to the graphite (C6) When the cell is discharges to provide power Li+ ions moved back through the electrolyte to the cobalt oxide while the electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.

Anodic and Cathodic Reactions:

Cathode

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+$$

Anode

$$C + xLi^+ \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC$$

The charging and discharging cycle is simple migration of Li+ ions from one electrode to another electrode with flow of electrons through the external circuit.

Advantages:

1) High energy density

2) Lower self-discharge compared to other rechargeable batteries.

3) Low Maintenance cost

4) Good load characteristics

5) Variety types available

Disadvantages:

1. Requires protection circuit to maintain voltage and current within safe limits.

2. Subject to aging, even if not in use - storage in a cool place at 40% charge reduces the aging effect.
3. Transportation restrictions - shipment of larger quantities may be subject to regulatory control. This restriction does not apply to personal carry-on batteries.
4. Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
5. Not fully mature - metals and chemicals are changing on a continuing basis

Applications:

Pacemakers, defibrillators, watches, meters, cameras, calculators, portable, cell phones, Laptops, low-power use.

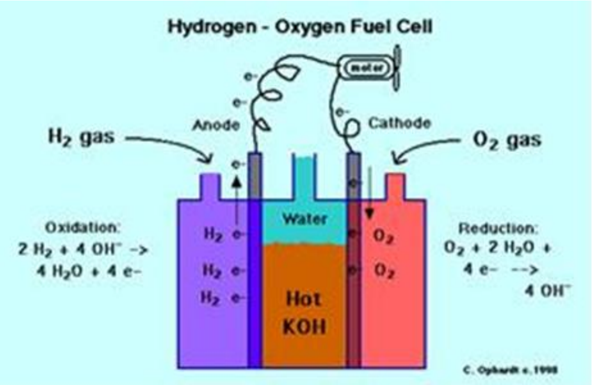
Fuel Cell :

Fuel cell is a device which converts the chemical energy of the fuel directly to electricity. When fuel is burnt, the exchange of electrons takes place only when the atoms oxidizing agent (Oxygen or sir) come in direct contact with the atoms of the substance oxidized (fuel). The energy has generated as heat but the electrical energy obtained the combustion of oxygen and fuel that can be oxidized.

Fuel + Oxygen → Oxidation Product + Electricity

The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidizing agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell.

1. Hydrogen-oxygen fuel: The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution (25%). Hydrogen is oxidized at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:



Anode: $2H_2\ (g) + 4OH^-(aq) \rightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_2\ (g) + 2H_2O\ (l) + 4e^- \rightarrow 4OH^-(aq)$

Overall: $2H_2\ (g) + O_2\ (g) \rightarrow 2H_20(l)$

Applications or advantages over fuel cell:

1.These types of cells are used in space-crafts.

2. Fuel cells are efficient and pollution free.

3. These types of cells are used in sub – marines or other military vehicles.

4. The weight of the fuel battery sufficient for 15 days in space is approximately 250kg.

5. In case of hydrogen-oxygen fuel cells, the produced water is a valuable source of fresh water by astronauts.

Disadvantages:

1. Hydrogen Energy is Expensive.

2. Storage Complications. ...

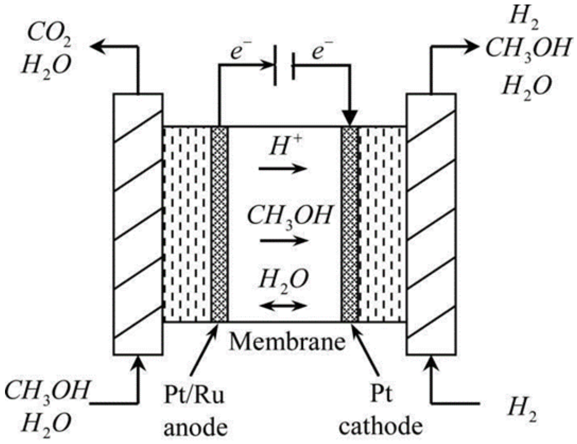
3. It's Not the Safest Source of Energy. ...

4. It is Dependent on Fossil fuels. ...

5. Hydrogen Energy Cannot Sustain the Population.

Methanol-Oxygen Fuel cell:

A fuel cell (FC) is a device where the energy of fuels such as hydrogen, alcohols or hydrocarbons is converted into electricity. It consists of anodic and cathodic compartments. Both the compartments contain platinum electrode. Methanol containing H_2SO_4 is passed through anodic compartment. Oxygen is passed through cathodic compartment. Electrolyte consists of sulphuric acid. A membrane is provided which prevents the diffusion of Methanol into the cathode.



Methyl alcohol –oxygen fuel cell: The half reactions are:

At anode: $CH3OH + H2O \rightarrow CO2 + 6 H+ + 6e-$

At cathode: $3/2O2 + 6 H+ + 6 e- \rightarrow 3 H2O$

Net reaction: $CH3OH +3/2O2 \rightarrow CO2 +2H2O$

Disadvantages of Methanol- Oxygen fuel cell

1. Methanol is toxic and Flammable
2. They produce limited power
3. During the oxidation of methanol, co is formed which is reactive towards pollution and
4. lowering the performance.

Advantages of Methanol- Oxygen fuel cell:

1. Methanol has low carbon content The OH group is easily oxidizable
2. Methanol is highly soluble in water.
3. Storage of methanol is easy than Hydrogen.
4. The energy density of methanol is higher than even highly compressed hydrogen

Applications:

1. Smaller vehicles such as fork lifts and tuggers and consumer goods such as mobile phones, digital cameras or laptops.
2. Military applications of DMFCs are an emerging application since they have low noise and thermal signatures and no toxic effluent.
3. These applications include power for man-portable tactical equipment, battery chargers, and autonomous power for test and training instrumentation.

UNIT-3

SEMICONDUCTORS, STORAGE DEVICES AND LIQUID CRYSTLS

Semiconductors: Introduction-purification of semi conductors-Zone refining, preparation of single crystal semi conductors- Czochralski process, stiochiometric, non stichometric and organic semiconductors-applications.

Storage Devices: Materials used in storage devices, working of floppy, CD, and pen drive.

Liquid crystals: Introduction-types-applications.

SEMICONDUCTORS

Definition semiconductor: A solid is a semiconductor, if its electrical conductivity is in between those of insulators and conductors. The requirements of a material so act as a semiconductor are Almost filled valence band (according to band theory of solids)Almost empty conduction band and a narrow energy gap or forbidden gap (E_g) in between valence band and conduction band. It requires ~1ev to move electron from valence band to conduction band. Ex: Si, Ge etc.

Types of semiconductors: Semiconductors are classified as mainly two types.

1. **Elemental semiconductors:** a) Purer or intrinsic semiconductor b) impure or extrinsic semiconductors
2. **Non-elemental semiconductors**

a) Stoichiometric semiconductors or compound semiconductors

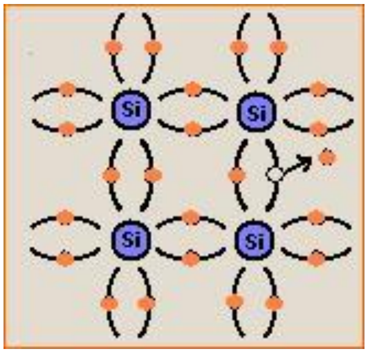
b) Non-stoichiometric semiconductors or defect semiconductors

c) Organic semiconductors

Elemental semiconductors:

Intrinsic semiconductors: These are extremely pure elements like Ge, Si having four valence electrons in their atoms and their forbidden gap is about 1eV.

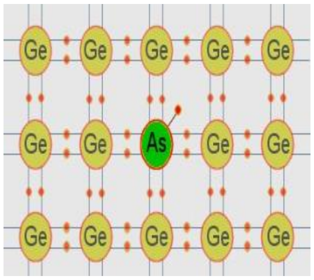
Conduction process: when an e^- from valence band is ejected, a covalent bond is broken and a positively charged hole is left behind the valence band. Consequently, when an electric field is applied across an intrinsic semiconductor at room temperature, electrons in conduction band move to the anode, while the holes in the valence band move to cathode. Hence current in intrinsic semiconductors consist simultaneous movement of holes and e^- s in opposite directions.



Extrinsic semiconductors: Extrinsic semiconductors are basically intrinsic semiconductors, whose conductivity properties by adding small amounts of impurities known as **doping agent**. The addition of doping agent reduces the energy gap, thereby allowing e^- from valence band to conduction band. Usually a part of doping added 106 parts of parent element. Based on the nature of doping agent added, the extrinsic semiconductors are two types.

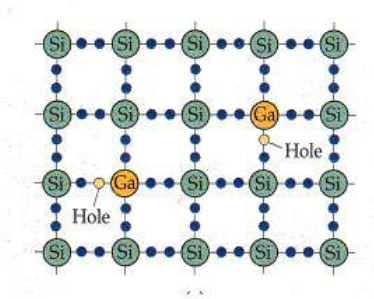
n-type extrinsic semiconductors: It consists of excess negatively charged electrons, obtained by adding extremely small amount of **pentavalent impurity** like P,As,Sb to pure semiconductors Si,Ge crystal lattice.

Conduction process: The doping agent forms four covalent bonds with the surrounding four atoms of intrinsic semiconductors (Ge) with the help of its five valences, while the fifth excess electron remains loosely bound to the donor atom itself. The loosely bound excess electrons are easily excited from valence band to conduction band, when an electric field is applied. The conduction is **due to movement of excess electrons** present in an n-type semiconductor.



p-type extrinsic semiconductors: It consists of excess of positively charged holes containing semiconductor and is obtained by adding an extremely small quantity of **trivalent impurity** like boron, aluminum to pure intrinsic semiconductor silicon, germanium crystal lattice.

Conduction process: All the three valence electrons present in the trivalent atoms form three covalent bonds with surrounding atoms there by one bond in the four of surrounding atoms is left incomplete creates hole. The positive holes so formed in crystal lattice conduct current, when an electric filed.



Non-elemental semiconductors: Stoichiometric or compound semiconductors:

These semiconductors having an average four valence electrons per atom similar to intrinsic semiconductor atoms like silicon and germanium. These compounds having an average of four valence electrons by combing elements of group II with those of group IV, or group III with V such as (CdS,Cdse) and (Gap,GaAs,GaSb). These stoichiometric semiconductors posses widely energy gap from 0.25 to 2.3eV.So they can be employed at a wide range of temperatures than the intrinsic semiconductors. It may be pointed here that these can also be doped to yield n- type and p- type semiconductors.

Compound	**GaP**	**GaAs**	**GaSb**	**InAs**	**InSb**	**CdS**	**CdSe**	**PbS**	**PbTe**
Groups	III-V	III-V	III-V	III-V	III-V	II-VI	II-VI	II-VI	II-VI
Energy gap (E_g) in eV	2.24	1.35	0.67	0.36	0.165	2.42	1.74	0.37	0.25

Non-stoichiometric semiconductors or defect semiconductors

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

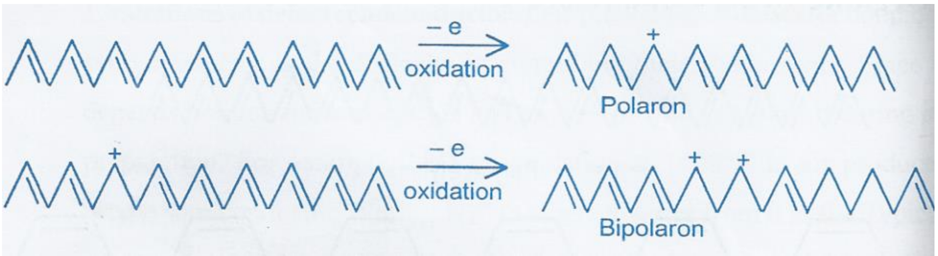
Metals ions defect due to missing cation: Let us consider iron oxide (FeO), which is made up of Fe^{+2} and O^{-2} ions. On heating FeO, some Fe^{+3} ions oxidized to Fe+3ions, thereby giving compounds with composition ranging from $Fe_{0.81}O$ to $Fe_{0.94}O$. These oxides are actually a combination of FeO and Fe_2O_3. For example a crystal compound $Fe_{0.90}$ actually contains $Fe^{2+}_{0.70}Fe^{3+}_{0.20}O^{2-}$. Since Fe^{+3} ion is short by one electron with respective to Fe^{+2} ion, so Fe^{+3} crystal lattice can considered as positive hole. Consequently, under the influence of electric field, the positive holes can move from Fe^{+3} ions to Fe^{+2} ions, thereby producing electrical conductivity. Therefore such non-stoichiometric crystals can be represents as $M_{1-X}Y$ and metal deficient compounds act as p-type semiconductors. **Examples of** such metal ion deficient semiconductors are FeO, Cu_2O, NiO and FeS.

Metal ion excess defect due to extra interstitial cation: On the other hand, when ZnO is exposed to reducing atmosphere, non-stoichiometric compounds such as $Zn_{1.1}O$ are produced by partial removal oxygen. In such compounds, Zn+ ion is rich by one electron with respective to Zn+2 ion. So each Zn^+ ion is capable of donating one electron to the conduction band. Hence, under the influence of electric field, ZnO act as an n-type semiconductor. These metal ion excess non-stoichiometric semiconductors can be represented as $M_{(1+X)}Y$.

Examples of these semiconductors are ZnO, CdO, Cr_2O_3, Fe_2O_3, Pbs, ZnS and CdS

Controlled valence semiconductors: The above limitation of defect-semiconductor is overcome by preparing controlled valencey semiconductor. In order to control the concentration of Ni^{3+} ions in NiO and hence its conductivity, a calculated amount of lithium oxide (Li_20) is reacted with nickel oxide (NiO) and oxygen to form compounds, $Li_x Ni_{1-2x}^{2+} Ni_x^{+3}O$, which exhibit temperature dependent conductivities. Materials with conductivity range 10^{-10} ohm-^{1} cm^{-1}(x =0) to10-^{11} ohm^{-1} cm-^{1} (x 0.1) at 25°C can be obtained.

Organic semiconductors: Organic semiconductors are nothing but conjugated polymers. Conjugated polymers are organic polymeric materials having very high conductivity due to the presence of conjugated double bond sequence. Conducting polymers which all become conducting upon doping with oxidizing and reducing agent. The doping agent concentration is very high. The doping agents used as $AlCl_3$, I_2, $FeCl_3$ etc. These are the materials, with intrinsic semi conductivity with an energy gap of 1.0 to 2.0eV.



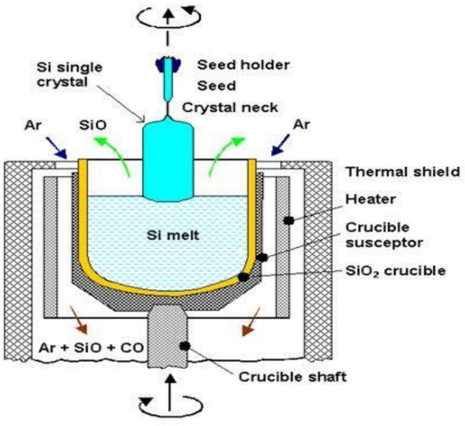
The Czochralski process is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium and arsenide), metals (e.g. palladium, platinum, silver, gold), salts and synthetic gemstones.

High-purity, semiconductor-grade silicon (only a few parts per million of impurities) is melted in a crucible at 1,425 °C (2,597 °F; 1,698 K), usually made of quartz. Dopant impurity atoms such as boron or phosphorus can be added to the molten silicon in precise amounts to dope the silicon, thus changing it into p-type or n-type silicon, with different electronic properties. A precisely oriented rod-mounted seed crystal is dipped into the molten silicon. The seed crystal's rod is slowly pulled upwards and rotated simultaneously. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt. Occurrence of unwanted instabilities in the melt can be avoided by investigating and visualizing the temperature and velocity fields during the crystal growth process. This process is normally performed in an inert atmosphere, such as argon, in an inert chamber, such as quartz.

The process begins when the chamber is heated to approximately 1500 degrees Celsius, melting the silicon. When the silicon is fully melted, a small seed crystal mounted on the end of a rotating shaft is slowly lowered until it just dips below the surface of the molten silicon. The shaft rotates counterclockwise and the crucible rotates clockwise. The rotating rod is then drawn upwards very slowly about 25 mm per hour when making a crystal of ruby allowing a roughly cylindrical boule to be formed. The boule can be from one to two metres, depending on the amount of silicon in the crucible.

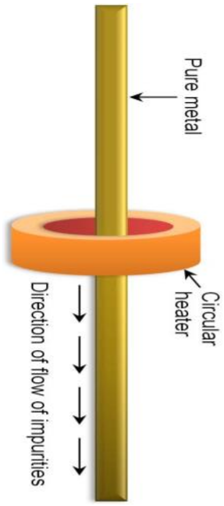
Czochralski Process

The **Czochralski process** is a method of crystal growth used to obtain single crystals of semiconductors (e.g), metals (e.g. palladium, platinum, silver, gold), salts and many oxide crystals (LaAlO3, YAG, .and GGG etc) The most important application may be the growth of large cylindrical ingots, or boules, of single crystal silicon. High-purity, semiconductor-grade silicon (only a few parts per million of impurities) is melted down in a crucible , which is usually made of Quartz. Dopant impurity atoms such as boron or phosphorus can be added to the molten intrinsic silicon in precise amounts in order to dope the silicon, thus changing it into n-type or p-type extrinsic silicon. This influences the electrical conductivity of the silicon. A seed crystal, mounted on a rod, is dipped into the molten silicon. The seed crystal's rod is pulled upwards and rotated at the same time. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt. This process is normally performed in an inert atmosphere, such as argon, and in an inert chamber, such as quartz.



Zone refining Process

Zone refining refers to the method of purifying a crystal wherein a thin region of the crystal undergoes melting. This ‘molten zone’ is now moved across the crystal. The impurities in the metal are melted at the forward edge by the molten zone and move through the block of metal, leaving the solidified pure element behind. The principle of zone refining is that the impurities in an ingot or ore of metal are more soluble in the melt state when compared to the corresponding solid state of the impurities. In the zone refining process, a circular mobile heater is fixed at one end of the metal rod which is made up of the impure metal. Now, the circular mobile heater is moved slowly across the metal rod. The metallic impurities melt at the temporary position of this heater. The melt containing the impurities moves forward along with the heater through the entirety of the metal rod. The pure metal is left to solidify as the heater moves along the rod, as the heater moves forward, the concentration of the impurities in the melt increases. This is because the impurities are more soluble in their corresponding melt state. Finally, the impurities are accumulated at one end of the metal rod. The process described above is repeated many times in the same direction. The end of the rod in which the impurities have now accumulated in is cut off, leaving behind the pure metal.



Applications of semiconductors:

1. Semiconductor devices are all around us. They can be found in just about every commercial product we touch, from the family car to the pocket calculator. Semiconductor devices are contained in television sets, portable radios, stereo equipment, and much more.

2. Semiconductors are extensively used in electronic devices to perform specific functions by replacing old-fashioned vacuum tubes (small size, low power consumption and no warm up time)
3. Semiconductor devices can and do perform all the conventional functions of rectification, amplification, oscillation, timing, switching, and sensing. Simply stated, these devices perform the same basic functions as the electron tube; but they perform more efficiently, economically, and for a longer period of time
4. The various types of modem military equipment are literally loaded with semiconductor devices. Many radars, communication, and airborne equipment are transistorized.
5. Data display systems, data processing units, computers, and aircraft guidance-control assemblies are also good examples of electronic equipments that use semiconductor devices.
6. Science and industry also rely heavily on semiconductor devices. Research laboratories use these devices in all sorts of electronic instruments to perform tests, measurements, and numerous other experimental tasks.
7. One of the first applications of conducting polymers was that of light-weight batteries.
8. Polyphenylene have been very effectively used as anode materials in batteries that exhibit much higher energy densities, of around 65mWH/g (compare with standard nickel–cadmium batteries which have about 39mWH/g).
9. Light Emitting Diodes: Other exciting phenomena, that have caught the imagination of both scientists and technologists alike, are the phenomena of Photoluminescence and electroluminescence in conjugated polymers. Emission of light upon irradiation is termed as photoluminescence, while the emission on application of a voltage is termed electroluminescence.
10. Biosensors: Conducting polymers have also touched the arena of biomedical applications. One such application is the fabrication of a glucose biosensor. Such a device can not only sense the presence of glucose but can also estimate its concentration.

STORAGE DEVICES

Definition: A hardware device is designed to store information is called storage device. There are two types of used in computer.

1. Primary storage device or internal memory or main memory.
2. Secondary storage device or external memory or auxiliary storage.
3. **Primary storage device or internal memory or main memory**:

   It is a storage location that holds memory for short periods of times while the computer is on. It is also internal or main memory. Example of a primary memory storage devices are computer RAM and cache. This type storage is the fastest type of memory in a computer and it is used to store data while it is being used. For, example when a program is opened data is moved from the secondary storage into the primary storage.

1. **Secondary storage device or external memory or auxiliary storage**:

It is storage medium that holds information until it is deleted or overwritten regardless if the computer has power. It is also known as external memory and auxiliary storage. Examples of secondary storage devices are floppy disk drive and hard disk drive. The primary storage is accessed much faster than secondary storage. Secondary storage is used with today's computers to store all the programs and personal data.

Floppy:

A floppy disk is a portable computer storage device that permits easy handling of data. Commonly used with personal computers, note book computers and word processors. This disc consists of flat, circular plates made of metal or plastic and coated with iron oxide. When disk is inserted into the disk drive of a computer, information can be magnetically imprint this coating, which will thereafter permit easy location and retrieval of same data. Magnetic disks first used to store data in 1962, initially provided supplemental memory in high speed computer system. They were ideal for this type of retrieval. Floppy disks – smaller, more flexible, portable versions were introduced in 1970s. Although they cannot store as much as conventional disk.

Raw materials:

1. All 8-inch and 5 1/4 disks have three major components 1. The jacket 2. The liner 3. The recording media.
2. The jacket is made of a vinyl polymer, poly vinyl chloride (PVC), to protect media against physical damage due handling and storage.
3. Inside the jacket the liner consists of special purpose, non- woven anti static fabric that is laminated to the PVC during manufacture.
4. The liner continually cleans the disk by removing debris from the surface of media.
5. The recording media is a pliable layer of Mylar – a polyester film that trade mark of the Du Pont Corporation – that is only 0.007 cm thickness.

Compact disc or CD:

The **Compact Disc**, or **CD** for short, is an optical disc used to store digital data. It was originally developed to store and play back sound recordings only, but the format was later adapted for storage of data (CD-ROM), write-once audio and data storage (CD-R), rewritable media (CD-RW), Video Compact Discs (VCD), Super Video Compact Discs (SVCD), Photo CD, Picture CD, CD-i, and Enhanced CD. Audio CDs and audio CD players have been commercially available since October 1982.Standard CDs have a diameter of 120 millimeters (4.7 in) and can hold up to 80 minutes of uncompressed audio or 700 MB (700 × 10^6 bytes) of data. The Mini CD has various diameters ranging from 60 to 80 millimeters (2.4 to 3.1 in); they are sometimes used for CD singles, storing up to 24 minutes of audio or delivering device drivers.CD-ROMs and CD-Rs remain widely used technologies in the computer industry. The CD and its extensions are successful in 2004; worldwide sales of CD audio, CD-ROM, and CD-R reached about 30 billion discs. By 2007, 200 billion CDs had been sold worldwide. Compact Discs are increasingly being replaced or supplemented by other forms of digital distribution and storage, such as downloading and flash drives OR pendrives , with audio CD sales dropping nearly 50% from their peak in 2000.

Raw materials:

1. CD consists of three layers of materials.
2. A base layer made of a poly carbonate plastic.
3. A thin layer of aluminum coating over the poly carbonates plastic.
4. A clear protective acrylic coating over the aluminum layer.
5. Some manufactures use a silver or even gold layer instead of the aluminum layer.

Pendrive or USB flash drive:

A **USB flash drive** is a data storage device that includes flash memory with an integrated Universal Serial Bus (USB) interface. USB flash drives are typically removable and rewritable, and physically much smaller than a floppy disk. Most weigh less than 30 g. As of September 2011 drives of up to 256 gigabytes (GB) are available. Storage capacities as large as 2 terabytes are planned, with steady improvements in size and price per capacity expected. Some allow up to 100,000 write/erase cycles, depending on the exact type of memory chip used, and a 10 year shelf storage time. USB flash drives are often used for the same purposes for which floppy disks or CD-ROMs were used, i.e. for storage, back-up and transfer of computer files. These are smaller, faster, have thousands of times more capacity, more durable and reliable because they have no moving parts . Most of pendrives draw their power from the USB connection and don't require battery.

Raw materials:

A flash drive consists of a small printed circuit board carrying the circuit elements and a USB connector, insulated electrically and protected inside a plastic, metal, or rubberized case which can be carried in a pocket or on a key chain, for example. The USB connector may be protected by a removable cap or by retracting into the body of the drive, although it is not likely to be damaged if unprotected. Most flash drives use a standard type-A USB connection allowing plugging into a port on a personal computer, but drives for other interfaces also exist.

LIQUID CRYSTALS

Substances that are not as ordered as a solid, yet have some degree of alignment, are properly called Liquid Crystals. The characteristic orientation order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term Mesogenic State.

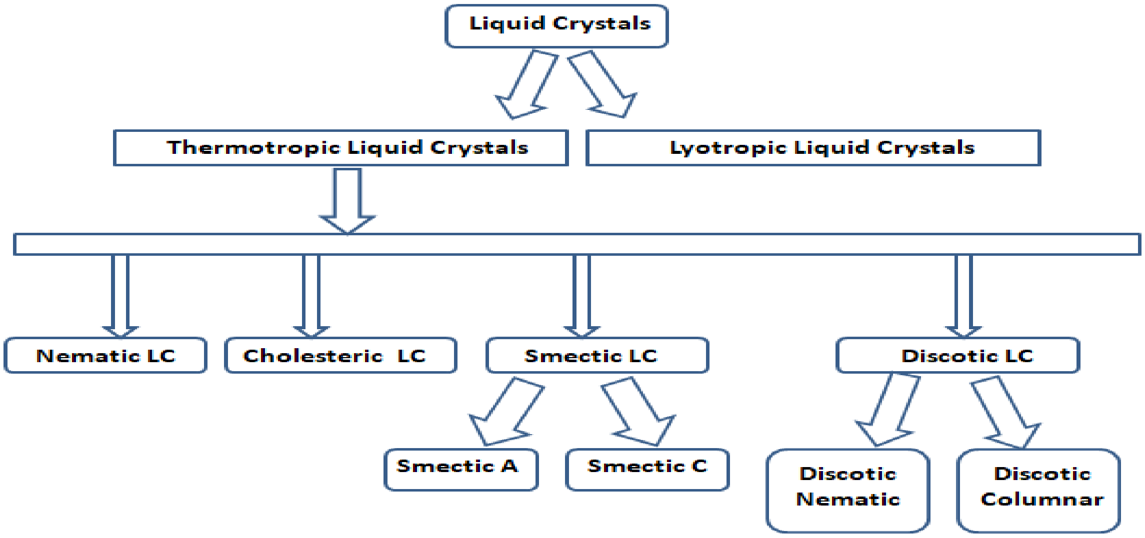
Characteristics of Liquid Crystals:

1. Positional order refers to the extent to which an average molecule or group of molecules show translational symmetry.
2. Orientation order represents a measure of the tendency of the molecule to align along the director on a long-range basis.

Classifications of Liquid Crystals:

Liquid crystals may be divided into two broad categories Thermotropic and Lyotropic based on the breaking of the order of the solid state.

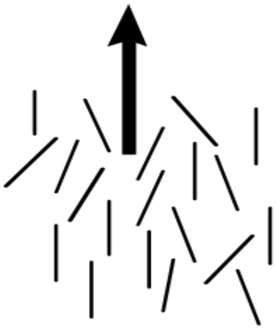
Thermotropic Liquid Crystal: These are established slowly by the adjustment of temperature. Thermo tropic liquid crystals are of three types. They are Nematic, Cholesteric, Smectic and Discotic



Thermotropic Liquid Crystals

Nematic Liquid Crystals: Nematics (from the Greek: nematon- thread-like). The nematic phase has no positional order, but has orientational order. The nematic phase is the simplest form of liquid crystal and is the phase in which the crystal molecules have no orderly position and are free to move any which way. However, while they have no specific order, during this phase the molecules do tend to point in the same direction, which is what differentiates it from a pure liquid. Liquid crystal in this phase can be characterized by its thread-like appearance when looked at under a microscope.

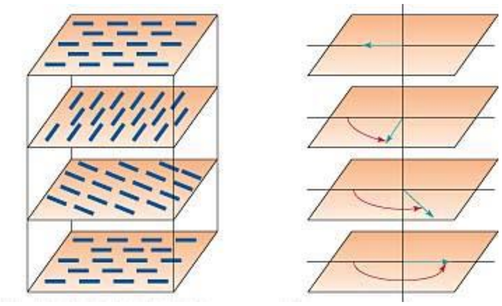
Example: p-Azoxyanisole



Nematic Liquid Crystals

Cholesteric Liquid Crystals: Cholesteric LC have temperature dependent optical properties. The Cholesteric phase, also known as chiral nematic phase, is characterized by the molecules being aligned and at a slight angle to one another, stacked within very thin layers. This type of liquid crystal also has the characteristic of changing color when it is exposed to different temperatures. It is for this reason that Cholesteric liquid crystal is used in common household items such as thermometers and mood rings. Positional order and orientational order of molecules present with in a layer, but on whole it does not possess positional order and orientational order.

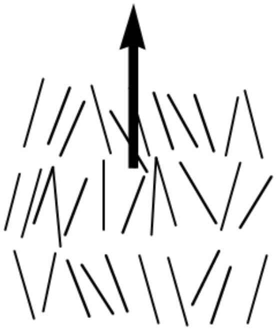
Example: Cholesteryl Benzoate



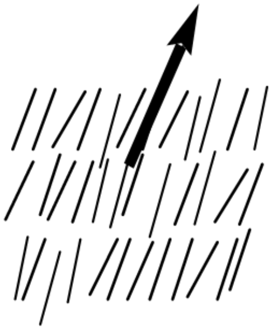
Cholesteric Liquid Crystals

Smectic Liquid Crystals: Smectic phases have orientational order, and some degree of positional order. These phases are distinguished by the presence of layers perpendicular to the director. Smectic phases have more positional order perpendicular to the director resulting in a "bookshelf "ordering. The smectic phase of liquid crystal, which is defined as being equivalent to the slippery, thick residue found at the bottom of soap dishes, is characterized by a slight degree of translational order in the crystal molecules which is not found in the nematic phase. Smectic liquid crystal has been found to have fast electro-optical response time and because of this is used, along with nematic liquid crystal, in producing liquid crystal display (LCD) screens.

Example: Ammonium Oleate



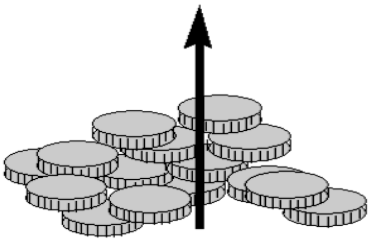
Smectic A



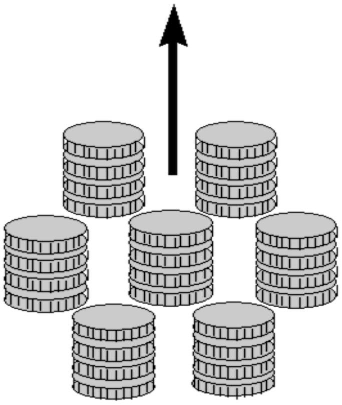
Smectic C

Discotic Liquid Crystals: A Discotic phase in one is which flat molecules typically with threefold or four fold symmetry. In nematic discotics phases there is no positional order between the molecules, only orientational order. In the case of columnar Discotic phases the molecules themselves lie roughly on top of each other, so there is some degree of positional order.

Example: Benzene-hexa-n-alkanes

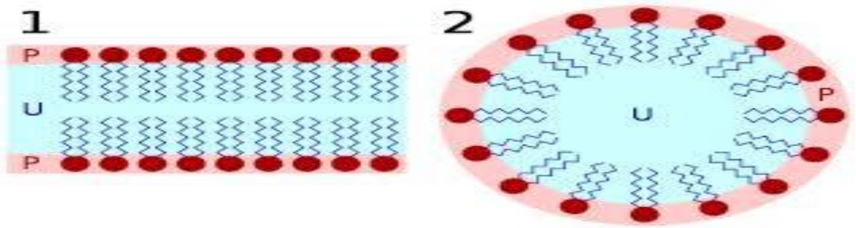


Discotic Nematic



Discotic Columnar

Lyotropic Liquid Crystal: Lyotropic mesophases occur in concentrated solutions of rod like molecules in an isotropic solvent (usually water). The stability of these mesophases is a readily influenced by concentration of solute as by temperature. Example: Sodium laurate in water and Di phosphatidyl chlorine in water. Lyotropic mesophases are important in soaps, gels and colloids.



Lyotropic mesogens are typically Amphibilic, meaning that they are composed of both lyophilic (solvent-attracting) and lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophobic ends extend outward towards the solution.

Applications of Liquid Crystals: Liquid crystals have wide application due to two main properties Dynamic and scattering effect.

1. Field effect Cooperated at low pressure, less power consumption and clarity of display in presence of light.
2. Display of pocket calculations is a field effect, when displays hours and minutes.
3. Electronics for the wrist watches display contains 1,500 transistors which are connected. The oscillations are controlled at low voltages by silica.
4. Cholesteric substances exhibit same color at the same temperature, by the temperature variation color of substance changes.
5. Color change can be visualized up to 0.01^0C visually using temperature sensors.
6. The liquid crystal substances when applied to the surface of the skin, so as to locate the veins, arteries, infections, tumors and the fetal placenta which are warmer than surrounding tissues.

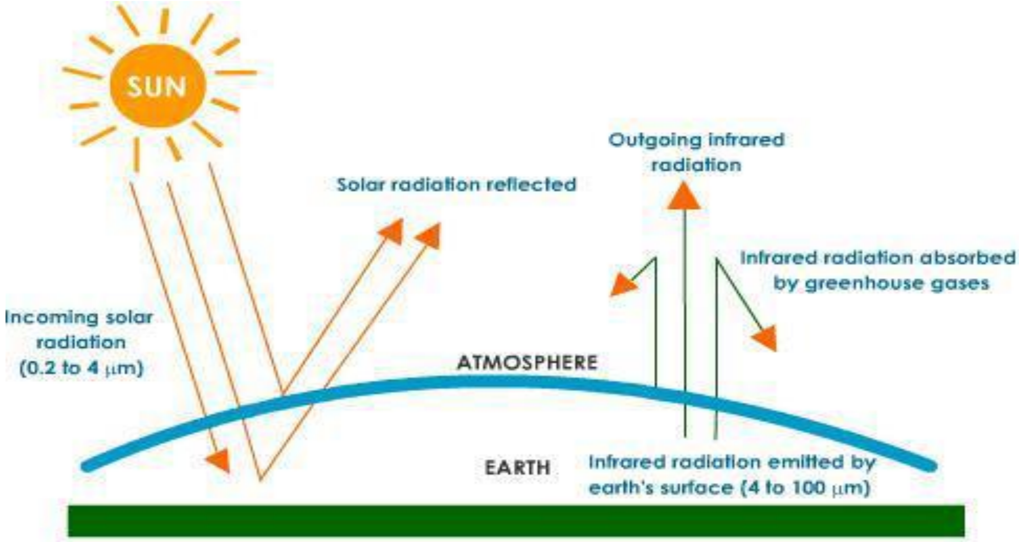
UNIT-4

ENERGY SOURCES

Solar Energy: Introduction- greenhouse effect-causes, consequences, and remedies, harnessing of solar energy, thermal conversion-solar water heater, parabolic dish parabolic trough and solar tower, solar power plant-construction and working, photo voltaic conversion- construction and working of Photo voltaic cell, applications of solar energy.

Ocean thermal energy: Introduction, closed-cycle ocean thermal energy conversion (OTEC), open cycle OTEC-schematic diagram and explanation.

Green House Effect: The process of heating of globe is called ‗Global warming'. This phenomenon is similar to that of green house or glass house in which glass roof allows solar radiation inside but prevents the escape of the terrestrial radiation (heat) generated inside the green house. As a result, inside temperature of the green house will rise and allow tropical plants to grow on temperature soils without any discomfort hence; it takes the name of green house effect‖. J.FOURIER – a French scientist first recognized in 1827. But ANTHES differ to use the name green house effect as there was no perfect analogy between CO2 and glass. They preferred to call ‗atmospheric effect to green house effect'. The earth's surface partly absorbs sun rays, while emits long wave infrared radiation. CO2 and water vapour in the atmosphere strongly absorb infrared radiation and effectively block a large fraction of the earth's emitted radiation. The radiation thus absorbed by carbon dioxide and water vapour is partly returned to the earth's surface. The net result is that the earth's surface gets heated and the phenomenon is known as Green house effect. The gases which are cause for the global warming are known green house gases. Surface of the earth is about 15°C; this is about 33° C higher than it would be in absence of greenhouse effect. Without this background temperature, our earth would have remained as any other lifeless cold planet with —18°C.



a) Carbon dioxide (CO_2):It is the most important green house gas. It contributes more than 60 per cent to the warming of the globe. It stays in the atmosphere, on average, for about 500 years. Prior to industrial revolution, the CO2 concentration in the earth's atmosphere was 280 ppm and by 1994 it was 358 ppm with an annual increase of 1.5 ppm. If the same trend continues it is estimated that by the end of the 21st century the carbon dioxide concentrations may cross 600 ppm mark.

b) Methane (CH_4): It is estimated that domestic cow can produce 73,000 liters of methane per year. Its concentration is around 1 .7 ppm and increasing at a rate of 1.1% each year. Though one molecule of Methane is 25 times as effective as CO2 molecule at trapping heat, it contributes around 15% of the total global warming. It stays in the troposphere for7- 10 years.

C) Nitrous oxide (N_2O):Unlike other oxides of nitrogen N2O has longer life span (140 – 190 years) and its concentration in the atmosphere is 380 pp is rising at a rate of about 0.3 % per year, because of the increased use of fossil fuels and chemical fertilizers. One molecule of N2O is 250 times as effective as CO2 molecule at trapping heat. It accounts for 4% of the total global warming.

d) Chlorofluorocarbons (CFCs):These are man-made, long-lived, stable and inert wonder chemicals, which are responsible for the majority of the modern man‘s comforts. Now these are mainly blamed for the destruction of protective ozone layer in the stratosphere. In addition to this, they can act as GHGs and can bring about 11% of total global warming. They are rising at the rate of 5% in the atmosphere. One molecule of CFC is 20,000 times as effective as CO2 molecule at trapping heat.

e) Troposphere ozone (0_3):It is produced through photochemical reactions involving Hydrocarbons and Nitrogen oxides that are coming from automobile exhaust gases. It concentration in the atmosphere is about 0.02 ppm. It is 2000 times as effective as CO2, in heat retention property. This gas along with water vapour and other gases may contribute 9% of the total global warming effect.

Consequences of global warming:

1. Melting of polar ice caps, glaciers.
2. Sea level rise, submergence of low-lying areas — sinks coastal cities and islands. Maldives may vanish by the end of this century.
3. By the year 2080, Manhattan and Shanghai could be underwater.
4. Salt water inundation, intrusion into fresh water aquifers, Water crisis.
5. Shift in rainfall pattern, Change in cropping pattern.
6. Crop failures, Starvation, hunger deaths.
7. Beach erosion, Loss of biodiversity (species extinction).
8. Corals bleaching.
9. Coastline change-disputes with maritime boundaries.
10. 1°C rise is equal to a change in latitude by 100km.
11. 2-5 rises is enough to have in Europe the climate of Africa today.
12. Drought, Desertification, Climate change, Severe storms, floods, winters, heat waves,

Green solutions to control global warming:

1. Greening of the globe can save the planet and its life: 600 million forests are necessary to prevent global warming.
2. Enriching oceans with iron could help to absorb phytoplankton more carbon dioxide.

3. Locking carbon in tropical forest biomass is the only cost effective remedy. Seriously think about Carbon capturing and Carbon burying.

4. Switching over to carbon free fuels. Car pooling, Mass transport, Cycle and recycle. Create market to C02. Carbon trading

5. Adopting low carbon lifestyles and economies. Promote Veg. diets, No car days, No-car incentives, No night time crickets.

6. Alternative energy sources or Renewable energy.

7. Solar and Nuclear power rather than thermal power.

8. Less Carbon intensity of fossil fuels.

9. Installing fluorescent lights or natural skylights. evelopment of new technologies, such as hydrogen cars, may reduce the consumption of petroleum and emissions of carbon dioxide.

10. Increased use of biofuels (such as ethanol fuel and biodiesel.

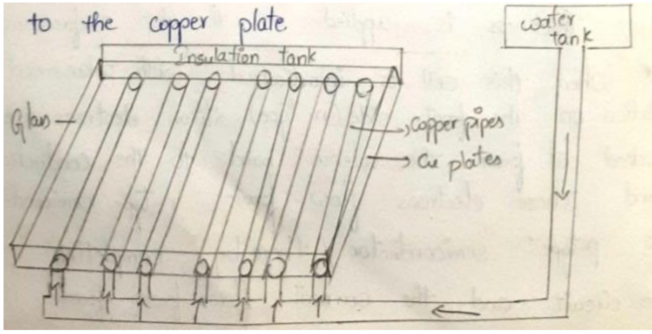
11. New buildings can be constructed using passive solar building design, using renewable heat sources.

12. Reforestation and avoided deforestation.

Solar Energy:

Introduction: Solar energy is the most readily available source of energy. It is also the most important of the non-conventional sources of energy because it is non-polluting and, atherefore, helps in lessening the greenhouse effect. When we hang out our clothes to dry in the sun, we use the energy of the sun. In the same way, solar panels absorb the energy of the sun to provide heat for cooking and for heating water.

1. A flat plate made up of copper is coated with black colour placed in presence of sunlight
2. Due to copper which is good conductor of heat and black being a good absorbent, the plate is heated quickly Copper plates coated with black colour are welded to the copper plate. Through the pipes water (or) gas is passed.
3. The transfer of heat takes place between the pipes and water. The water gets heated The hot water is stored in a insulatory tank
4. During the process high frequency radiation is emitted. To prevent this the arrangement is protected with glass.
5. It is non-concentrating heat collector
6. It is most economic design



Uses

1. Used in hotels, hostels, hospitals, apartments
2. Used in domestic purposes

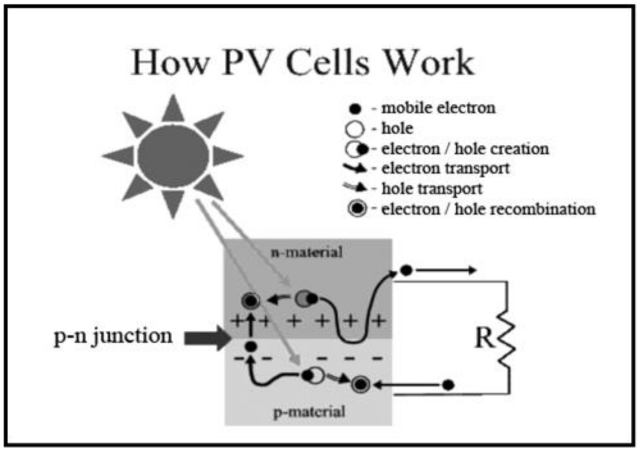
Harnessing The Sun's Energy: Solar energy can be converted to electricity in two ways:

1. **Solar photovoltaic cells (SPV):** Solar power is the conversion of sunlight into electricity, either directly using solar photovoltaic cells (SPV). Photovoltaic cells convert light into electric current using the photoelectric effect.

2. Concentrated solar power plants (CSP): Concentrated solar power systems use lenses or mirrors and tracking systems to reflect and concentrate slight on to receivers. That collects solar energy and converts into heat. This thermal energy can then be used to produce electricity via a steam turbine driving a generator. Two draw backs of solar energy: 1. The amount of Sunlight that arrives at the Earth‘s surface is not constant. It depends on location, time of day, time of year and weather conditions. 2. Because the Sun doesn‘t deliver large amount of energy to any one place at any one time, a large surface area is required to collect the energy at a useful rate.

Photovoltaic Cell or Solar Cell:

A photovoltaic cell, commonly called a solar cell or PV, is the technology used to convert solar energy directly into electrical power. A photovoltaic cell is a non mechanical device usually made from silicon alloys. The photo diode is made up of semiconductor materials like silicon, cadmium, telluride, gallium, arsenide etc which are capable of absorbing the photons of sunlight. A p-n junction diode is formed by doping a portion of this wafer with a trivalent impurity (for p- type) and another portion with a pentavalent impurity (for n-type). The n-type silicon is on the front side and the p-type silicon is on the backside. An anti-reflection coating of silicon nitrade or titanium oxide of abou 0.1um thickness is applied on the top surface. When photons strike a photovoltaic cell, only the absorbed photons provide energy to generate electricity. When enough Sunlight (energy) is absorbed by the material (a semiconductor), electrons are dislodged from the material‘s atoms, Special treatment of the material surface during manufacturing makes the front surface of the cell more receptive to free electrons, so the electrons naturally migrate to the surface. When the electrons leave their position, holes are formed. When many electrons, each carrying a negative charge, travel toward the front surface of the cell, the resulting imbalance of charge between the cell‘s front and back surfaces creates a voltage potential like the negative and positive terminals of a battery. When the two surfaces are connected through an external load, such as an appliance, electricity flows. The photovoltaic cell is the basic building block of a photovoltaic system. Individual cells can vary in size from about 0.5 inches to about 4 inches across. However, one cell only produces 1 or 2 watts. To increase power output, cells are electrically connected into a packaged weather-tight module. Modules can be further connected to form an array. Array is made up of one or several thousand modules. Most modern modules are about 10% efficient in converting Sunlight. Further research is being conducted to raise this efficiency to 20%.



Some advantages of photovoltaic systems are:

I. Conversion from Sunlight to electricity is direct, so that bulky mechanical generator systems are unnecessary.

2. PV arrays can be installed quickly and in any size.

3. The environmental impact is minimal.

4. Requiring no water for system cooling.

5. Generating no by-products

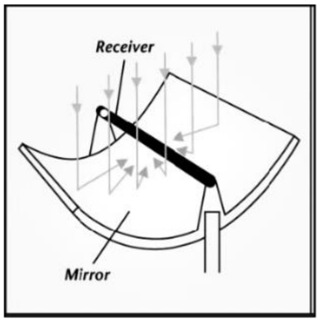
SPV can be used for a number of applications such as:

1. Domestic lighting. Street lighting.
2. Village electrification.
3. Water pumping.
4. Desalination of salty water.
5. Powering of remote telecommunication repeater stations.
6. Railway signals.

Solar thermal power plants: It uses the Sun‘s rays to heat a fluid to very high temperatures. The fluid is then circulated through pipes so it can transfer its heat to water produce steam. The steam, in turn, is converted into mechanical energy in a turbine and into electricity by a conventional generator coupled to the turbine. The three main types of solar thermal power systems are:

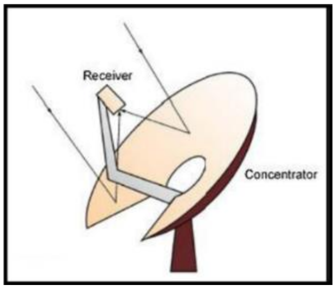
1. Parabolic trough (the most common type of plant).
2. Solar dish.
3. Solar power tower.

1. A parabolic trough: It is a type of solar thermal energy collector. It is constructed as a long parabolic mirror (usually coated silver or polished aluminum) with a Dewar tube running its length at the focal point. Sunlight is reflected by the mirror and concentrated on the Dewar tube. The trough is usually aligned on a north-south axis, and rotated to track the sun as it moves across the sky each day. Heat transfer fluid (usually oil) runs through the tube to absorb the concentrated sunlight. This increases the temperature of the fluid to some 400°C. The heat transfer fluid is then used to heat steam in a standard turbine generator. The temperature of the heat transfer fluid quickly reaches 750 degrees as the sun's energy is captured by the Parabolic Troughs. The overall process is very economical and thermal efficiency ranges from about 60% to as high as 80%.



2. Parabolic Dish Systems:

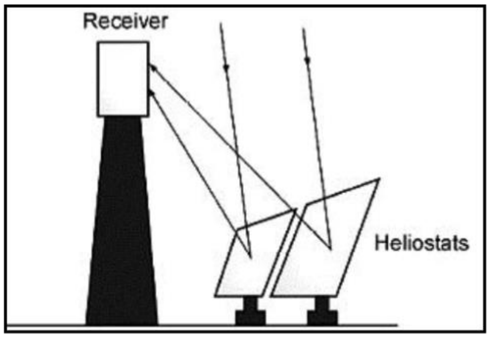
1. A polished aluminium sheet shaped into a parabolic dish and placed in sunlight.
2. Due to its reflecting surface and parabolic shape the rays gets reflected to a point foci.
3. A metal box coated with black colour is placed at the foci of the parabolic dish, water is filled in the box and gets heated and converted into steam.
4. This steam used to run turbine and electricity is generated.
5. During this process high frequency radiation is emitted to prevent this the box is covered with a glass material.
6. Most loss of energy in this collector is due to imperfection in the shape and imperfect reflection.
6. In these heat collectors it is very difficult to track the sun. If we're able to track the sun by the position, then the efficiency of this heat collector is high.



3. Solar Power Tower:

Solar power towers generate electric power from sunlight by focusing concentrated solar radiation on a tower-mounted heat exchanger (receiver). The system uses hundreds to thousands of sun-tracking mirrors called heliostats to reflect the incident sunlight onto the receiver. In a molten-salt solar power tower, liquid salt at 290ºC

(554ºF) is pumped from a Cold storage tank through the receiver where it is heated to 565ºC (1,049ºF) and then on to a hot‘ tank for storage. When power is needed from the plant, hot salt is pumped to a steam generating system that produces superheated steam for a conventional Rankine- cycle turbine/generator system. From the steam generator, the salt is returned to the cold tank where it is stored and eventually reheated in the receiver.



Applications of Solar Energy:

- As heat for making hot water, heating buildings and cooking.
- To generate electricity with solar cells or heat engines
- To take the salt away from sea water.
- To use sun rays for drying clothes and towels.
- It is used by plants for the process of photosynthesis.
- To use in cooking (Solar cookers).

OCEAN THERMAL ENERGY CONSERVATION

Ocean thermal energy conservation is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water. OceanThermal Energy Conversion (OTEC) is to turn the solar energy trapped by the ocean into useable energy. This kind of energy is found in tropical oceans where the water temperature differs from surface to deeper into the sea. On the ocean surface it can be at least 20°C hotter or cooler than the temperature at a deeper sea level. OTEC plant pump large quantities of deep cold sea water and surface sea water to run a power cycle and produce in 1880 and constructed in 1926. An amount of large quantity of cold water is a by – product, that can be used for air conditioning and refrigeration.

Working Principle: -

OTEC generates electricity by using the temperature difference of 20°C(36°F) or more than that exists between the warm tropical waters at the sun warmed surface, and cold water drawn from the depth of 1000 meters. To convert this thermal gradient into electrical energy, the warm water can be used to heat and vaporize a liquid. The working fluid develops pressure as it is caused to evaporate. This expanding vapor runs through a turbine generator and is then condensed back into a liquid by cold water brought up from depth and the cycle is repeated.

There are three types of OTEC

1. Closed Cycle OTEC

2. Open Cycle OTEC
3. Hybrid Cycle OTEC

Closed Cycle OTEC employs a low-boiling-point liquid like propane or ammonia (B.P=-33℃) as an intermediate fluid. In OTEC plant first warm surface sea water is pumped through a heat exchanger to vaporize the fluid. The expanded vapour turns the turbo generator. Cold water pumped through a second heat exchanger condenses the vapour into a liquid which is then recycled. The first closed cycle OTEC.

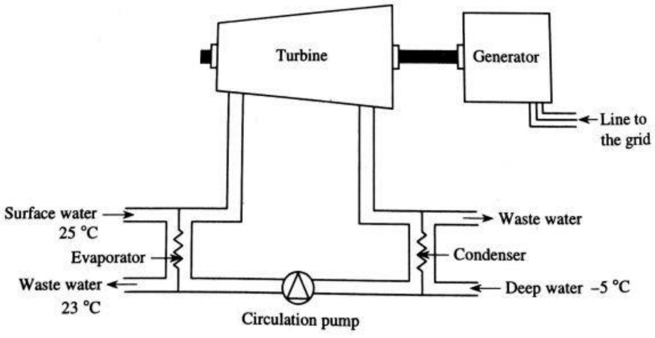


Diagram of closed cycle OTEC plant

Open cycle OTEC uses warm surface water directly to make electricity. The warm sea water is first pumped into a low-pressure container, which causes it to boil. In some processes, the expanding steam drives low pressure turbine attached to an electrical generator. The steam leaves its salt and contaminants in the low pressure container to give pure fresh water. It is condensed to a liquid by exposure to cold temperatures from deep–ocean water. This method produces desalinated fresh water, suitable for drinking, irrigation and agriculture.

In other systems the rising steam is used in a gas lift technique of lifting water to significant heights. Depending on the embodiment such steam lift pump techniques generate power from a hydro electric turbine either before or after the pump is used.

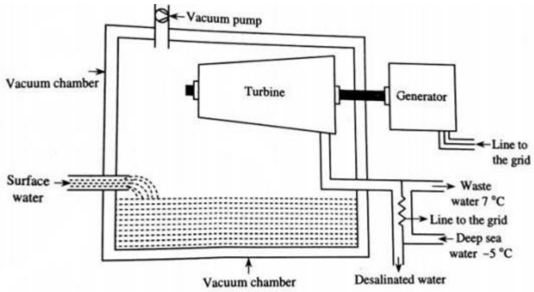


Diagram of Open cycle OTEC plant

constructed in 1926. An amount of large quantity of cold water is a by – product, that can be used for air conditioning and refrigeration.

An OTEC system application

1. Hydrogen can be produced via electrolysis using electricity generated by the OTEC process.
2. Desalination of seawater
3. It reduces the financial & energy coasts of pumping large volumes of water from Deep Ocean.

4. Deep ocean water contains high concentration of essential nutrients that are depleted in surface water due to biological consumption.
5. Mineral Extraction

Advantages of OTEC

1. Warm surface sea water and cold water from the ocean from the ocean depths replace fossil fuels to produce electricity.
2. OTEC plants will produce little or no carbon dioxide or other polluting chemical
3. OTEC systems can produce fresh water as well as electricity. A lot of fish & other nutritious sea-food will be collected in outlet flow.
4. OTEC can also be used to produce ammonia, hydrogen, aluminium, chlorine and other chemicals.

Disadvantages of OTEC

1. OTEC produced electricity at present would cost more than electricity generated from fossils fuels at their current costs.
2. No energy company put money in this project because it only had been tested in a very small scale.
3. Construction of OTEC plants and lying of pipes in coastal waters may cause localized damage to reefs and near-shore marine ecosystem.

UNIT-5

NANOMATERIALS AND COMPUTATIONAL CHEMISTRY

Introduction, preparation of nanomaterials-sol-gel method, characterization by scanning electron microscopy (SEM), Types of nanomaterials-Carbon Nano Tubes (CNT's) and fullerenes, preparation, properties and applications of CNTs and fullerene, applications of Nanomaterials.

Computational Chemistry: Introduction to computational chemistry, molecular modeling and docking studies.

Introduction to Nano materials

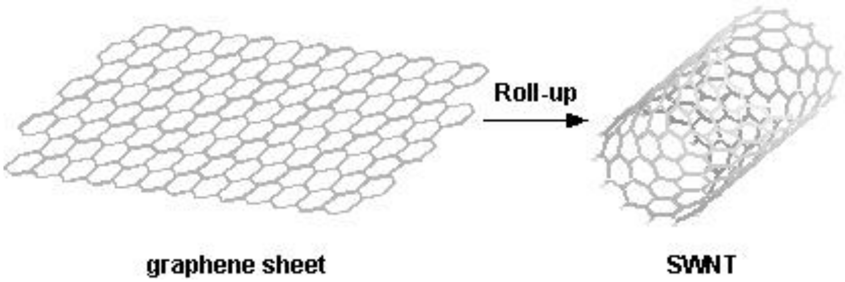
Nano means one billionth i.e. $\frac{1}{1000000000}$ or 10^{-9} and therefore a nano meter is just one billionth of a meter. **Nano materials** are those which possess at least one dimension in the nano scale i.e. 1 to 100 nm. Nanotechnology is a field of applied science focused on the design, synthesis and application of materials and devices on the nanoscale. When a bulk material is changed into nanosized particle, the properties also change. The properties that are changed at nano scale are:

PROPERTIES OF NANO MATERIALS

1. **The physical properties** like melting point, adsorption and catalytic activity are dependent on the surface area or more precisely the surface to volume ratio. As the size of the particle decreases, the surface to volume ratio increases tremendously. More atoms are on the surface rather than in the bulk (inside of a particle). Therefore, the melting point decreases, the catalytic activity, adsorption increases as the particle size decreases.
2. **The optical properties and electric properties** depend on the band structure or density of states. As the particle size decreases, the band gap increases in semiconducting materials and therefore shows different colors with different sizes. (Ex. CdTe particles in solution show colors from blue, green, yellow red as the size increases from 1 to 50 nm.
3. **The magnetic properties** of magnetic (Ferro, anti Ferro, Para and dia) materials change with size of the particles i.e. as the size approaches individual domain size, they can be magnetized to a great extent and multi domain structure disappears and we get single domain structure. Ex. Fe particles of size below 16 nm can be magnetized to more than the bulk iron.
4. **The mechanical properties** of ceramics which are usually brittle can be enhanced to a large extent if the crystallite sizes are small in the nano-range rather than highly crystalline nature. Because of the small crystallites embedded in amorphous matrix, they get more malleability (less brittle) and still have high tensile strength. Carbon nanotubes have high mechanical strength because of rigid structure of hexagonal carbon atoms.
5. **Chemical Properties** Based on the surface area to volume effect, nanoscale materials have
   a) Increased total surface area.
   b) Increased number of atoms accessible on the surface.
   c) Increased catalytic activity of those large number surface atoms.
   d) Different/tunable surface catalytic properties by the change in shape, size and composition. Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.

Introduction to Nano materials - Carbon Nano Tubes (CNTs)

- Carbon Nano Tubes (CNTs) were discovered by S. Iijima in the year 1991.
- They are long, thin tube like cylinders made of hexagonal rings of carbon atoms, Bonded covalently by sp^2 hybridization



- A sheet of graphite is rolled into a cylinder or twisted to make a tube of few nm in diameter and upto hundreds of micrometers long (length to diameter ratio 28,000,000 :1)
- These nano tubes have a hemispherical "cap" at each end of the cylinder (closed CNTs) And they can be open also (open CNTs)
- CNT diameter = ~1.2 nm

CNTs are two types depending upon the way in which they are arranged.

(a) A single walled nanotube (SWNT)

(b) A multi walled nanotubes (MWNT)

Single Walled Nano Tubes (SWNT)

SWNTs have a diameter of close to 1nm, with a tube length that can be many millions of times longer. The structure of SWNT can be obtained by wrapping a one-atom thick layer of graphite called ‘graphene’ into a seamless cylinder.

Multi Walled Nano Tubes (MWNTs)

The structure of MWNT can be obtained by wrapping few layers of graphite (‘graphene’ layers) into a concentric cylinders with the small diameter CNT lying inside the large diameter CNT and so on. The gap between two layers is of the order of 1.33 $A^{0.}$

Preparation of Carbon Nano Tubes:

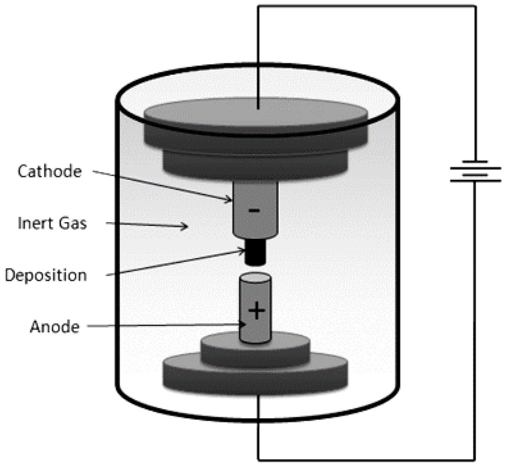
1. Arc discharge method (Krotschmer and Huffman method, 1990)

- Electrical discharge between graphite electrodes (mixed with metal catalyst like (Fe, Co, Ni etc.) in an atmosphere of Helium, argon at low pressure 50 -700 mbar produces carbon nano tubes along with other carbon mass.
- A direct current of 50-100 A and voltage of 20V creates high temperature arc between the electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
- The resulting soot (on the graphite cathode, inner walls of evaporation chamber) is scraped and dissolved in polar organic solvents. The metal catalysts are separated by treating with mild acid/base and then dissolved in aromatic organic solvent (colored solution).

- The colored solution is separated from the black insoluble soot (settling at the bottom) and then CNTs are isolated by column chromatography.
- Depending on the exact technique, it is possible to selectively grow SWNTs, or MWNTs.

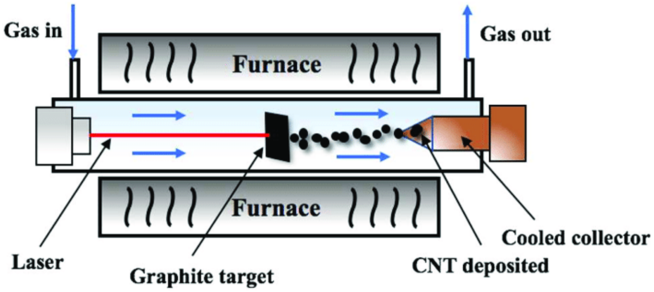
Control factors

Pressure of Helium & Argon, their ratio, the current & voltage, the catalyst type, size and content, the distance between electrodes etc. determine the type of CNTs their quality, quantity and diameter.



2. Laser ablation method

- In this method, a high energy pulsed laser vaporizes a graphite target in a high temperature reactor, while an inert gas like He or Ar is fed into the chamber (500 Torr)
- A pulsed or continues laser is used to vaporize a graphite target in an oven at 1200°C
- The main difference between continues and pulsed laser, is that the pulsed laser demands much higher intensity.
- A very hot vapour forms, then expands and cools rapidly.
- The nano tubes develop on the cooler surface (water cooled copper collector) of the reactor as the vaporized carbon condenses
- This method has an yield of 70 % and mainly produces SWNTs with controllable diameter depending on reaction temperature
- However, it is more expensive than arc discharge or CVD



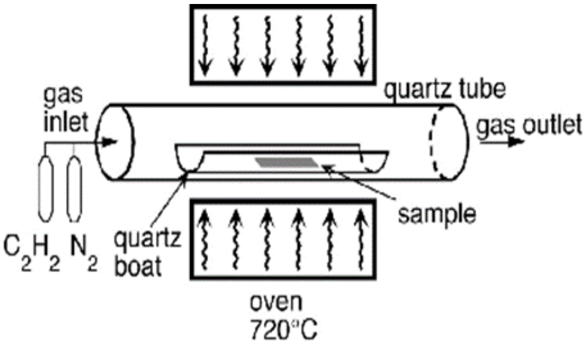
3. Chemical Vapour Deposition

- A substrate is prepared with metal catalyst particles (Ni, Co, Fe or a combination). The diameter of CNTs will depend on size of metal particles. This can be achieved by patterned or masked deposition of metal, annealing or etching of a metal layer
- The substrate is heated to approximately 700^0 C
- To initiate growth of CNTs, two gases are fed into the reactor

Process gas: ammonia, nitrogen and hydrogen

Carbon containing gas: CO, acetylene,
methane, ethanol etc.

- Using thermal annealing or chemical etching results in cluster formation on the substrate.
- The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900^{o}C range.
- The typical yield for this CVD method approximately 20-100%



Properties of CNTs

Mechanical properties:

- It is the strongest, stiffest in terms of tensile strength and elasticity property. This strength results from the covalent sp2 bonds formed between the individual carbon atoms (a strong chemical bond). CNTs have a low density – 1.3 – 1.4 g/cm^3
- The tip of CNT will bend on pressing without damage and return to its original state when force is removed. Thus CNTs are used as probe tips for high resolution scanning probe microscopy.
- High Electrical Conductivity
- Very High Tensile Strength
- Highly Flexible- can be bent considerably without damage
- Very Elastic ~18% elongation to failure
- High Thermal Conductivity
- Low Thermal Expansion Coefficient
- Good Field Emission of Electrons
- Highly Absorbent

- High Aspect Ratio (length = ~1000 x diameter)

Engineering Applications of Carbon Nanotubes:

The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of applications

- They find application in conductive and high strength composites, energy storage and energy conversion devices, sensors and nano meter sized semi conductor devices.
- They are used as nanoprobes in meteorology and biological and chemical investigations.
- CNT can be functionalized with bio active peptides, proteins, nucleic acids and drugs.
- Functionalized CNT display low toxicity and are used in the field of nanobiotechnolgy and nano medicine.
- Hydrogen can be stored in the carbon nanotubes, which is in turn used for the fuel cells. The SWNTs are effective as a hydrogen-storage material for fuel cell electrical vehicle.
- CNTs can replace **platinum** as the catalyst in fuel cells, which could reduce fuel cells overall cost. Since CNTs could be resistant to corrosion.
- These fuel cell CNT electrodes are very light weight and thin.
- A catalyst having CNTs makes a reaction safer and selective.
- CNTs are used for the electrochemical reaction of oxygen
- CNTs along with ruthenium (Ru) metal used as catalyst in the hydrogenation reaction of cinnamldehyde.
- Carbon nano tubes are being highly used in the fields of efficient drug delivery and biosensing methods for disease treatment and health monitoring.
- Carbon nanotubes can be used as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction.
- Due to high electrochemically accessible surface area, high electrical conductivity and useful structural properties, SWNT and MWNTs in highly sensitive glucose detectors.

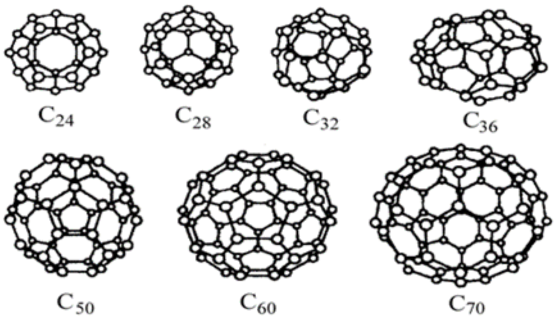
Introduction to Nano materials - Fullerenes

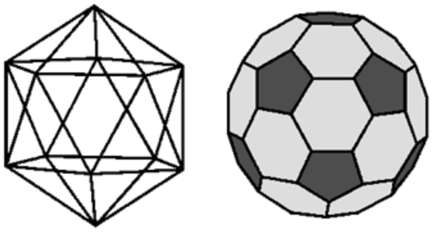
Fullerenes are CNTs are allotropic forms of carbon. The diamond and graphite structures of carbon are well known and main allotropes of carbon with tetrahedral and planar arrangement of carbon atoms respectively.

Fullerenes (C_{60} and others) were discovered by R. F. Curl., H. W. Kroto, R. E. Smalley in 1985 and they were awarded Nobel Prize in Chemistry 1996.

- They are closed structures of only carbon atoms, each bonded covalently by sp^2 hybridization (one double bond, two single bonds)
- The double bonds are usually given for hexagons only

- C_{60} is a polygon (truncated icosahedron) with 12 pentagons and 20 hexagons (like a soccer ball). Diameter = 1 - 2 nm (Icasohedron)

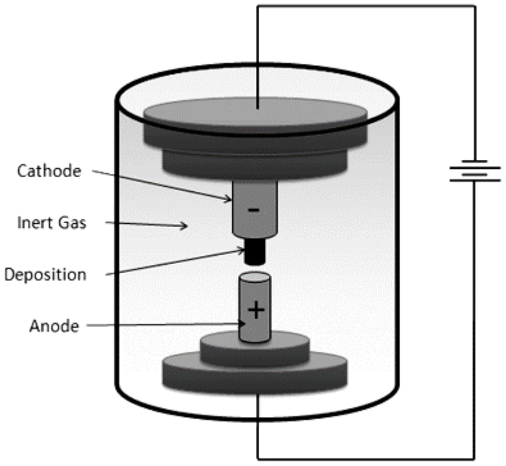




Preparation of Fullerenes:

1. Arc discharge method (Krotschmer and Huffman method, 1990)

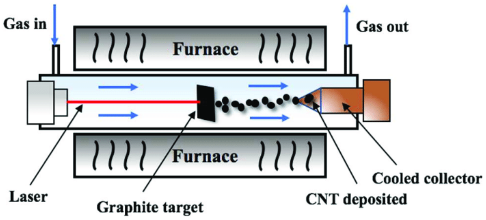
- Electrical discharge between graphite electrodes (mixed with metal catalyst like (Fe, Co, Ni etc.) in an atmosphere of Helium, argon at low pressure 50 -700 mbar produces carbon nano tubes along with other carbon mass.
- A direct current of 50-100 A and voltage of 20V creates high temperature arc between the electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
- The resulting soot (on the graphite cathode, inner walls of evaporation chamber) is scraped and dissolved in polar organic solvents. The metal catalysts are separated by treating with mild acid/base and then dissolved in aromatic organic solvent (colored solution).



2. Laser ablation method

- In this method, a high energy pulsed laser vaporizes a graphite target in a high temperature reactor, while an inert gas like He or Ar is fed into the chamber (500 Torr)
- A pulsed or continues laser is used to vaporize a graphite target in an oven at 1200^{o}C

- The main difference between continues and pulsed laser, is that the pulsed laser demands much higher intensity.
- A very hot vapour forms, then expands and cools rapidly.
- The nano tubes develop on the cooler surface (water cooled copper collector) of the reactor as the vaporized carbon condenses
- However, it is more expensive than arc discharge or CVD



Properties of Fullerenes

- **Physical properties:** C_{60} is a mustard colored solid. When the thickness of the film increases, it appears brown to black
- It is moderately soluble in the common organic solvents, especially aromatic hydrocarbons.
- **Mechanical Properties:** It has high tensile strength and also highest packing density of all known structures
- **Thermal properties:** Thermally stable upto 600 ^{o} C. it undergoes sublimation under
- **Electrical Properties:** It has high electrical conductivity, when doped with alkali metals; they show even superconductivity (Eg. KC_{60})
- They are difficult to oxidize
- They are good acceptors of electrons (used in polymer solar cells) and electronic energy

Engineering applications of fullerenes:

- Fullerenes can easily accept electrons; hence they may be used as charge carrier in batteries.
- Fullerenes can be used as organic photovoltaic.
- Alkali metal fullereids are super conductors.
- It can also be used as a soft ferromagnetic.
- Its spherical structure makes it suitable for the use as lubricant.

COMPUTATIONAL CHEMISTRY

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids

The term theoretical chemistry may be defined as a mathematical description of chemistry, whereas computational chemistry is usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer

Examples of such properties are structure (i.e., the expected positions of the constituent atoms), absolute and relative (interaction) energies, electronic charge density distributions, dipoles and higher multipole moments, vibrational frequencies, reactivity, or other spectroscopic quantities, and cross sections for collision with other particles

In theoretical chemistry, chemists, physicists, and mathematicians develop algorithms and computer programs to predict atomic and molecular properties and reaction paths for chemical reactions.

Computational chemists, in contrast, may simply apply existing computer programs and methodologies to specific chemical questions.

Computational chemistry has two different aspects:

- Computational studies, used to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.
- Computational studies, used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanisms not readily studied via experiments.
- Thus, computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical objects.
- Several major areas may be distinguished within computational chemistry:
- The prediction of the molecular structure of molecules by the use of the simulation of forces, or more accurate quantum chemical methods, to find stationary points on the energy surface as the position of the nuclei is varied.
- Storing and searching for data on chemical entities.
- Identifying correlations between chemical structures and Computational approaches to help in the efficient synthesis of compounds.
- Computational approaches to design molecules that interact in specific ways with other molecules (e.g. drug design and catalysis).

Molecular Modelling:

1. Molecular modelling encompasses all methods, theoretical and computational, used to model or mimic the behaveiour of molecules. The methods are used in the fields of computational chemistry, drug

design, computational biology and materials science to study molecular systems ranging from small chemical systems to large biological molecules and material assemblies.

2. Modeling is a tool for doing chemistry. Models are central for understanding of chemistry. Molecular modeling is a discipline concerned with developing models of molecular system, chemical reactions. Models are some kind of representation of a system, usually simplified, that allows for description and prediction of properties of interest Molecular modeling can be performed by currently available software.
3. Molecular modeling allows us to do and teach chemistry better by providing better tools for Investigating , Interpreting, Explaining, and Discovering new phenomena (for Drug) Due to the advance in methodology and computer technology an alternative approach become feasible namely molecular simulation. Fluids consist of molecules and their thermo physical properties are determined by the molecular interaction. Molecular models describe these molecular interactions by means of parameterized potential function.
4. To help with analysis and interpretation of experimental data .To uncover new laws and formulate new theories. To help solve problems and hint solutions before doing experiments. To help design new experiments. To predict properties and quantities that is difficult or even impossible to observe experimentally.
5. Important characteristics of models are: a) Level of simplification: very simple to very complex b) Generality: general or specific, i.e. relate only to specific systems or problems c) Limitations: one must always be aware of the range of applicability and limits of accuracy of any model. d) Cost and efficiency: CPU time, memory, disk space.

Molecular Modeling Tools:

1. The tools of the trade have gradually evolved from physical models and calculators, including the use of programmable calculators as visualization aids, computers running analysis pack.
2. Various classes of computers are required formolecular modeling. • For chemical information systems the choice of a computer is generally larger, and many packages run on VAX, IBM, or PRIME machines.
3. The computational chemistry programmes allow scientists to generate and present molecular data including geometries, energies and properties.

7. Molecular Modeling Strategies

a) Direct drug design

b) Indirect drug design

A) Direct Drug Design:

1. In the direct approach, the three dimensional features of the known receptor site are determined from X-ray crystallography to design a lead molecule.
2. In direct design the receptor site geometry is known; the problem is to find a molecule that satisfies some geometry constraints is also a good chemical match.
3. After finding good candidates according to these criteria a docking step with energy minimization can be used to predict binding strength.

B) Indirect Drug Design:

The indirect drug design approach involves comparative analysis of structural features of known active and inactive molecules that are complementary with a hypothetical receptor site. If the site geometry is not known, as is often the case, the designer must base the design on other ligand molecules that design on the other ligand molecules that bind well to the site.

8. Molecular modeling properties

a) Molecular mechanics: Molecular mechanics describes the energy of a molecule in terms of a simple function which accounts for distortion from "ideal" bond distances and angles, as well as and for nonbonded van der Waals and Columbic interactions.

b) Quantum mechanics: In this process properties of the molecules are calculated by equations of quantum Physics involving interactions between electron and nuclei.

c) Geometry: All geometric data of the molecular models, i.e. bond length and bond angles were determined based on calculations.

d) Electrostatics: Intermolecular electrostatics and interactions are mainly occurring due to static polarities of single molecules that can well be obtained by quantum chemistry.

9) Molecular simulation method

a) Molecular dynamics

b) Periodic boundary condition

a) Molecular dynamics

Molecular dynamics is an approach to mimic the movement of molecule in an ensemble.

b) Periodic boundary condition

Periodic boundary condition by applying PBC the amount of interaction partners of a molecule in a simulation theoretically rises to infinity

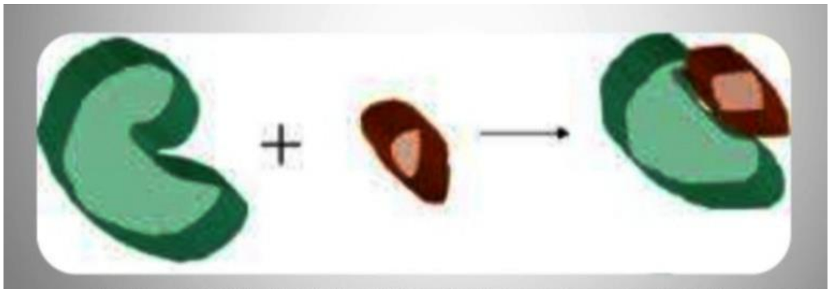
Applications:

1. Generation of Chemical Structures
2. Molecular Structure Visualization
3. Modeling of Drug Receptor Interactions

Molecular Docking

Introduction:

1. Docking is an attempt to find the best matching between two molecules.
2. Docking is a method which predicts the preferred orientation of one ligand when bound in an active site to form a stable complex.



Docking of small molecule ligand (brown) with a protein receptor (green) to produce a complex.

Lock and Key: Finding the correct relative orientation of the “key” which will open up the “lock”. On the surface of the lock is the key hole. In which direction to turn the key after it is inserted.

The protein can be thought of as the “lock” and the ligand can be thought of as a “key”.

Aim: To achieve an optimized conformation for both receptor and ligand & the relative orientation between protein and ligand such that the free energy of the overall system is minimized. Successful docking methods search high-dimensional spaces effectively and use a scoring function that correctly ranks candidate dockings.

Importance:

1. Molecular Docking Prediction of the binding affinity (Scoring Function)
2. Identification of the ligand’s correct binding geometry (pose) in the binding site (Binding Mode)
3. Rational Design Of Drugs

Types of docking:

a) Rigid Docking (Lock and Key): In rigid docking, the internal geometry of both the receptor and ligand are treated as rigid.

b) Flexible Docking (Induced fit): An enumeration on the rotations of one of the molecules (usually smaller one) is performed. Every rotation the energy is calculated; later the most optimum pose is selected.

Docking can be between

- Protein - Ligand
- Protein – Protein
- Protein – Nucleotide

Types of Interactions:

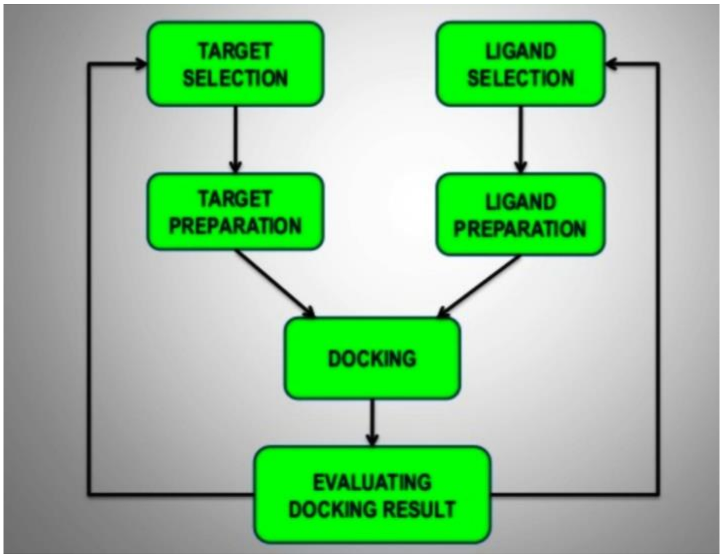
Electrostatic forces - Forces with electrostatic origin are due to the charges residing in the matter. • Electrodynamics forces - The most widely known is probably the van der Waals interaction. • Steric forces - These are caused by entropy. For example, in cases where entropy is limited, there may be forces to minimize the free energy of the system.

Solvent-related forces – These are due to the structural changes of the solvent. These structural changes are generated, when ions, colloids, proteins etc, are added into the structure of solvent. The most commonly are Hydrogen bond and hydrophobic interactions

Key stages in docking

1. Target/Receptor selection and preparation
2. Ligand selection and preparation
3. Docking • Evaluating docking results

A typical docking workflow:



_Receptor selection and preparation Building the Receptor

1. The 3D structure of the receptor should be considered which can be downloaded from PDB.
2. The available structure should be processed.
3. The receptor should be biologically active and stable.

Identification of the Active Site

1. The active site within the receptor should be identified.
2. The receptor may have many active sites but the one of the interest should be selected.

Ligand selection and preparation

1. Ligands can be obtained from various databases like ZINC, PubChem or can be sketched using tools like Chemsketch.
2. Docking The ligand is docked onto the receptor and the interactions are checked. The scoring function generates score, depending on which the best fit ligand is selected.

Software’s

SANJEEVINI

GOLD

AUTODOCK

Hex Protein Docking

GRAMM

Applications:

1. Virtual screening (hit identification).
2. Docking with a scoring function can be used to quickly screen large databases of potential drugs in silico to identify molecules that are likely to bind to protein target of interest.
3. Drug Discovery (lead optimization)
4. Docking can be used to predict in where and in which relative orientation a ligand binds to a protein (binding mode or pose). This information may in turn be used to design more potent and selective analogs.
5. Bioremediation.
6. Protein ligand docking can also be used to predict pollutants that can be degraded by enzymes.