Sir C R Reddy College of Engineering, Eluru

Applied chemistry material

Course : I/IV B.E/B.Tech
Regulation: **R20**

UNIT I: POLYMER TECHNOLOGY

Polymers are macromolecules (giant molecules of high molecular masses) built-up by the linking together of a large number of small molecules (called monomers).For example, polythene is a polymer formed by linking together of a large number of ethene molecules.

The number of repeating units (n) in chain formed in a polymer,is known as the **degree of polymerization.**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: For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. The number of **bonding sites** in a monomer is referred to as its functionality.

Methods of polymerization:

Emulsion polymerization: In emulsion polymerization, the monomer is dispersed in aqueous phase as fine droplets which is stabilized by adding surfactant or protective colloids. The surfactants lead to the formation of micelles when their concentration exceeds critical micelle concentration. Addition of water-soluble initiator at this stage initiates the polymerization reaction in the micelles which ultimately increase the micelle size. For continuation of the reaction, monomers diffuse from its droplets to the micelle. The process continues till the size of polymer is big enough to come out of the micellies. The probability of termination is less in this process as the active sites remain isolated from each other. Thus, high molecular weight polymers can be formed.

Suspension polymerization: In suspension polymerization, the monomer is dispersed as large droplets in water and is kept in suspension by mechanical agitation using stabilizers such as gelatin or water-soluble cellulose derivatives. The initiator used remains soluble in monomer which initiates polymerization in each droplelt. The polymer is obtained as spherical beads. This technique is cheap as it involves water instead of solvent. The method is limited to water-insoluble monomers such as vinyl chloride, vinyl acetate, and styrene.

Compounding of plastics:

Usually, the high-polymer material is mixed with 4 to 10 ingredients, each of which imparts some useful property to the plastics. The main types of compounding ingredients and their functions are described below:

1.**Resin** is the binder,which holds the different constituents together.
2.**Plasticizers** are materials that are added to resins to increase their plasticity and flexibility. Most commonly used plasticizers are vegetable oils, camphor and some phosphates.
3.**Fillers** are added to give to the final plastic better hardness, tensile strength.

Most commonly used fillers are wood-flour, asbestos, china clay, talc, gypsum, saw-dust, marble flour, paper pulp, mica, carbon black, metallic oxides(like ZnO,PbO) and metal powders(like Al,Cu,Pb).
4.**Lubricants** like waxes,oils,stearates,oleates and soaps are employed to make the moulding of plastic easier and to impart a glossy finish to the products. Lubricants reduce friction and increase flow with in a machinery.
5.**Stabilizers:** The purpose of adding stabilizers is to improve the thermal stability during processing. Stabilizers commonly used are amines, epoxides, organometallic compounds etc.
6.**Colouring materials:** These provide desired colours to the plastics. For example carbon-black for black colour, iron-oxide for red colour , chromium-oxide for green colour etc.

Fabrication methods of plastics:
Many methods of fabricating platics into desired-shaped articles are employed.The methods,usually,depend upon the type of resins used , i.e., whether thermo setting or thermoplastic.Commonly used plastic fabrication methods are a) compression moulding b) injection moulding c) blown film and d) extrusion moulding.

Compression moulding is a method applied to both thermoplastic and thermosetting resins.The plastic ingredients in proper proportions get filled between the two half-pieces of mould ,which are capable of being moved relative to each other. Heat and pressure are then applied according to specifications. The cavities get filled with fluidized plastic. Two halves are closed very slowly. Finally, curing is done either by heating(in case of thermosetting) or cooling(in case of thermoplastics).After curing, the moulded article is taken out by opening the mould parts. This method is used for moulding the resins into shapes like plastic buttons, telephone parts, furniture handles etc.

Injection moulding is applicable mainly to thermoplastic resins. The plastic ingredients in proper proportions get filled between the two half-pieces of mould ,which are capable of being moved relative to each other. Heat and pressure are then applied according to specifications. The cavities get filled with fluidized plastic. Two halves are closed very slowly. Finally, curing is done either by heating(in case of thermosetting) or cooling(in case of thermoplastics).After curing, the moulded article is taken out by opening the mould parts.
This method is used for moulding the resins into shapes like buckets, bowls etc.

Extrusion moulding: Extrusion moulding is used for moulding of thermoplastic materials into articles of uniform cross section like tubes, rods, wires, cables etc. The thermoplastic ingredients are heated to plastic state(semi solid state) and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be fabricated. The extruded article gets cooled due to atmospheric exposure or artificially by air jets, or by water sprayer in a long conveyor which carries away the cooled product.

Blown-film: Blowing otherwise known as bubble casting is used for fabricating hollow plastic articles like soft drink bottles, containers etc. Thermoplastic resins are fabricated by blowing. A hot, softened thermoplastic tube called parison is placed inside a two piece hallow tube in the mould. The halves of the mould are closed and the parison is now blown by blowing compressed air through the blowing pin. The parison is inflated like a balloon and goes on expanding until it comes in intimate contact with the relatively cold interior surface of the hollow mould and assumes the shape of the hollow cavity. The mould is allowed to cool and the article is removed by opening the mould.

Biodegradable polymers and their applications:

Generallly, the polymers are discharged into land fills after their usage but most of the polymers are non-biodegradable and release toxic chemicals into the soil, environment and affects the human health.

Those polymers are easily degraded in presence of atmospheric conditions like gases, moisture, microorganisms etc., are called biodegradable polymers.

These are two types i) Natural biodegradable polymers: These are comes from nature and goes to the nature. Ex: Natural rubber, Starch, cellulose and proteins etc.

ii) Synthetic biodegradable polymers: These are prepared in laboratory from biodegradable chemicals. Starch is also added to the back bone of the polymer for quick degradation.

Ex: Poly Hydroxy Alkanoate(PHA), Poly vinyl esters, Poly vinyl alcohos etc.

Applications: i) These are used in food packing materials ii) Used in capsules iii) Used in sitches in operation iv) Used in bone fixation.

Some examples of plastic materials used in electronic gadgets:

Plastic	Electronic gadgets
1. Polythene	Cable& Wire insulation
2. PVC	Cable& Wire insulation
3. Polycarbonates	Telephones, Discs, DVD, Capacitors
4. Polyamide	Food processor bearings, Adaptors
5. Polymethy pentane	Circuit boards, Microwave grills
6. Polystyrene	Refrigerator trays/linings, TV cabinets, Radio parts

7. Urea formaldehyde	Fuse boxes, knobs, switches
8.Phenol-formaldehyde	Switches, Radio, TV parts, Handles etc.
9. Epoxy resins	Electrical components
10. Polyesters	Coffee machines, Business machine parts
11. Polyphenylene sulphide	Transformers, Hair drier grills
12. Teflon	Motors, Transformers, Cables, Wires etc.

E-plastic waste: Electronic plastic waste known as e-scrap/e-waste. The e-plastic waste consists of discarded plastic waste from the old computers, Laptops, TVs, Refrigerators, Electric cookers, Heaters, Fans, DVDs, Micro ovens, Radios, Mobile phones, Switches, Cable and electrical wires, Batteries, etc.

Most electronic waste is sent to landfills, which releases materials such as Pb, Ba, P, Ni, Co, Hg or Cd into the soil, ground water, and atmosphere, thus having a negative impact on the environment. Many materials used in computer can be recovered by recycling for use in future.

Recycling of E-plastic waste: The E-waste recycling process is highly labor intensive and goes through several steps. Below is the step-by-step process of how e-waste is recycled.

1. **Picking shed**: When the e-waste items arrive at the reclycling plants, the first step involves sorting all the items manually. Batteries are removed for quick check.
2. **Disassembly**: After sorting by hand, the second step involves a serious labor intensive process of manual dismantling. The dismantled items are then separated into various categories into parts that can be re-used.
3. **First size reduction process**: Here, items that cannot be dismantled efficiently are shredded together with the other dismantled parts to pieces less than 2 inches in diameter.
4. **Second size reduction process**: The finer E-waste particles are then evenly spread out through an automated shaking process on a conveyor belt. The well spread out E-waste pieces are then broken down further. At this stage, any dust is extracted and discarded in a way that does not degrade the environmentally.
5. **Over-band magnet**: At this step, over-band magnet is used to remove all the magnetic materials including steel and iron from the E-waste debris.
6. **Non-metallic and metallic components separation**: The sixth step is the separation of metals and non-metallic components. Copper, Al, and brass are separated from the debris to only leave behind non-metallic materials. The metals are either sold as raw materials or re-used for fresh manufacture.
7. **Water separation**: As the last step, plastic content is separated from glass by use of water. One separated all the materials retrieved can then be resold as raw materials for re-use. The products sold include plastic, glass, Cu, Fe, steel, Shredded circuit boards, and valuable material mix.

All the plastic materials retrieved are sent to recyclers who use them to manufacture items.

Fiber reinforced plastics& Conducting polymers:

Fiber reinforced plastics: Plastics are mixed with fillers inorder to increase the mechanical properties. The combination of plastic material with solid fillers is known as fiber reinforced plastics(FRP). The addition of fillers also improve i) water proof ness ii) scratch resistance iii) chemical resistane iv) heat resistance v) optical properties and vi) self-lubricating properties.

Most commonly used fillers are glass, wood-flour, clay, saw-dust, marble flour, paper pulp, carbon black, metallic oxides(like ZnO,PbO) and metal powders(like Al,Cu,Pb).

Applications: i) These are used in automobile and aircraft industry. Ii) used in making pistol iii) used in making bullet proof plastics etc.

Conducting polymers: Those polymers conduct electricity similar to metals are called conducting polymers. These are two types

i) Intrinsic conducting polymers: In these, the conductivity is due to conjugated Pi electron system in their structure.

ii) Extrinsic conducting polymers: These are obtained by adding external compounds like metal fibers to the non-conducting polymer.

Applications: i) These are used in computers, memory cards etc. ii) used in railways iii) used in scientific equipments iv) used in electronic devices etc.

Mechanical properties of polymers.

Mechanical properties:

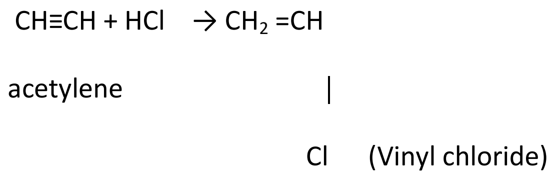
1.Toughness: The impact strength is measured as toughness. Below glass transition temperature(Tg) the polymers break with a brittle fracture and they become tougher when the temperature proceeds from room temperature to Tg. The size of the crystalline structure also determine the toughness. The small spherical crystalline masses increase toughness.

2. Strength: The strength of polymer depends on length of polymer chain, branching or cross-linking. The strength of a polymer increases with increase in molecular weight. The inter molecular forces of attraction, presence of polar groups and chain length increases the strength of the polymers. The strength of a polymer is determined by stress-strain test.

3. Elasticity: Elasticity is the property of recovering original shape after the removal of stress. Natural rubber possesses high elasticity due to the coiled helix structure of polyisoprene.

Preparation, properties and applications of some plastics:

i) Poly vinyl Chloride(**PVC**): It is prepared by polymerization of vinyl chloride using benzoyl peroxide as catalyst. Vinyl chloride is prepared by treating acetylene with HCl under the conditions of 1-1.5 atm pressure and temperature 60-80^{0}C.



$$\underset{\text{acetylene}}{CH\equiv CH} + HCl \rightarrow CH_2=\underset{\underset{Cl}{|}}{CH}\ \text{(Vinyl chloride)}$$

Properties of PVC: i) it is colourless, odourlese and non inflammable ii) it is chemically more resistant. iii) insoluble in solvents iv) resistant to light and atmospheric air.

Uses: It is used in pipes, toys, cable insulation materials and laminating materials etc.

ii) Bakelite are condensation polymerization products of phenol and formaldehyde in presence of acidic/basic catalyst.

Properties: Bakelite is hard, scratch-resistant, infusible, water-resistant, insoluble solid and insoluble in many organic solvents, but are attacked by alkalis, because of the presence of free hydroxyl group in their structure. They possess excellent electrical insulating character.

Uses: i) for making electric insulator parts like switches, plugs, switch-boards, heater handles,etc. ii) for making moulded articles like telephone parts and radio and television parts. iii) as hydrogen-exchanger resins in water softening. iv) as adhesive(e.g., binder).

iii) Poly carbonates: Polycarbonate plastic resin is produced by the reaction of bisphenol-A and diphenyl carbonate.

Properties: Polycarbonates are durable materials with high impact resistances and low scratch resistance. Polycarbonates are stronger and hold up longer extreme temperature along with high transparency to visible light. These are good electrical insulators.

Applications: 1. Being a good electrical insulator, with heat resistance and flame-retardation properties, polycarbonates are used for electrical and telecommunications hardware and also as dielectric in high-stability capacitors.

2. Polycarbonates are used in construction in industry for dome lights, flat and curved glazing and sound walls.

3. The major application is the production of compact discs, DVDs.

4. Due to low weight and high impact and cracking resistance, polycarbonates are used for making automotive head lamp lenses and bullet-proof glasses, windows in automobiles.

5. Used in laboratory safety goggles, sunglass, computer cases, name plates etc.

Elastomers: Rubbers (also known as elastomers) are high polymers, which have elastic properties in excess of 300 percent. Thus, a rubber-band can be stretched to 4-10 times its original length and as soon as the stretching force is released, it returns to its original length. The elastic deformation in an elastomer arises from the fact that in the unstressed condition, an elastomer molecule is not straight chained, but in the form of a coil and consequently, it can be stretched like a spring.

i) BUNA-S: BUNA-S is otherwise called styrene rubber or GRS (Government Rubber Styrene). BUNA-S stands for the composition of the monomers and catalyst.

BU stands for butadiene-monomer
NA stands for sodium- catalyst & S stands for styrene- monomer

BUNA-S is produced by the copolymerization of butadiene with styrene using sodium as a catalyst.

Properties: 1. It is a strong and tough polymer.
2. It posses excellent abrasion resistance.
3. It is a good electrical insulator.
4. It is resistant to chemicals.
5. It posses high load bearing capacity and resilience.

Applications: 1. Major application is in the manufacture of tyres.
2. It is used in foot wear industry for making shoe soles and foot wear components.
3.Used for making wires and cable insulations.
4. Used in chemical tank linings in industries and as an adhesive.

ii) Thiokol rubber: The copolymerization of sodium polysulphide and ethylene dichloride produces Thiokol rubber.

Properties: 1. It possess strength and impermeability to gases.
2. It possesses extremely good resistance to mineral oils, fuels, oxygen, solvents, ozone and sunlight.
3. It possesses low abrasion resistance.

Applications: 1. Fabrics coated with thiokol are used for barrage balloons, life rafts and jackets which are inflated by CO_2.
2. Used for lining hoses for conveying gasoline and oil.
3. It is used for making gaskets and seals for printing rolls.

iii) Polyurethane Rubber: Polyurethane is composed of organic units joined by carbamate(urethane) links and formed by reacting di or poly isocyanate with idol or polyol in presence of a catalyst like tertiary amines such as triethylenediamine and dimethylethanolamine.

Properties: 1. Polyurethanes possess excellent hardness, tensile strength, abrasion and tear resistance.
2. They resist hard hard environmental factors such as heat, moisture, gases etc.
3. They are highly resistant to chemicals, oils and solvents.
4. They possess excellent electrical insulating properties.
5. They possess high flexibility and load bearing capacity.
6. Polyurethanes bond to wide range of materials like metals and wood hence an ideal material for wheels, rollers and inserts.

Applications: Polyurethanes are found everywhere in modern life, the chair you are sitting on, the bed you sleep in, car you drive plus innumerable applications. Some important applications are

1. Production of foams like flexible foams, rigid foams, surface coatings, and rubber.
2. Building insulation 3. Refrigeration and freezers 4. Furniture and bedding. 5. Foot wear
6. Automotive 7. Coatings and adhesive 8. Polyurethanes are used in purification of water and sewage for adsorption of coloring matter and heavy metals.

UNIT II: ELECTROCHEMICAL CELLS AND CORROSION

Single electrode potential: According to modern electrochemical theory, all metals have a tendency to pass into solution as ions. For example, zinc metal is dipped in a solution of zinc sulphate, zinc ions(Zn^{2+}) passed into solution leaving behind electrons on the metal. Thus metal acquires negative charge and solution acquires positive charge. But due to electrostatic force of attraction, the positive (Zn^{2+}) ions in solution are attracted towards negative charge on the metal and forms a layer around the metal and some times these may be redeposited on the metal and an equilibrium is established between metal and solution. The potential difference between positive and negative layers at equilibrium becomes a constant value, and is called electrode potential.

It is impossible to determine the absolute electrode potential of a single electrode. We can measure only difference in potential between any two electrodes. To determine the potential of an electrode, it should be connected to another electrode whose potential is known called reference electrode. Commonly used reference electrodes are calomel electrode and hydrogen electrode.

Electrochemical series: Different elements can be arranged as per the increasing or decreasing order of their potentials. The array so obtained is known as electrochemical series. The most popular representation is the arrangement of elements in the increasing order of their reduction potentials. Some common elements(in the form of reduction electrode) and their standard potentials are given as follows:

Applications: Electrochemical series provides information about i) Replacement tendency of metals ii) Relative ease of oxidation or reduction of metals iii) The relative corrosion tendencies of metals and alloys iv) spontaneity of reaction v) equilibrium constant.

Standard electrodes:

i) Calomel electrode: An electrode of this type consists of a metal(Hg), metal salt(Hg_2Cl_2) and a solution having same anion. It consists of a glass tube in the bottom of which a layer of mercury of high degree of purity is placed. The surface of mercury is covered with a paste of mercurous chloride(Hg_2Cl_2). The remaining portion of cell is filled with KCl solution. A platinum wire is dipping into the mercury layer is used for making electrical contact.

The potential of calomel electrode depends on the concentration of KCl solution at 25^0C.

For 0.1N KCl solution, E= 0.3335 volts
For 1.0N KCl solution, E= 0.2810 volts
For saturated KCl solution , E= 0.2422 volts.

ii) Hydrogen electrode: Defined as the potential that is developed between H_2 gas adsorbed on the Pt metal and H^+ of the solution. It consists of a Pt wire in a inverted glass tube. H_2 gas is passed through the tube at 1 atm. A Pt foil is attached at the end of the wire. This electrode is immersed in 1M HCl solution at 25^0C and it yields hydrogen electrode.

Applications: 1. Hydrogen electrode is used to find the PH of unknown solutions. 2. Used to determine the electrode potential of metal electrodes.

Limitations: The hydrogen electrode is readily affected by compounds of Hg, As, S and oxidizing agents like Fe^{+3} , MnO_4^-, $Cr_2O_7^{-2}$ etc, so not used in solutions containing these ions.

Glass electrode: It has glass bulb made up of thin glass membrane. Bulb is filled with HCl solution. Ag or Pt wire is dipped in HCl solution to yield glass electrode.

Applications: 1. It is used for the determination of PH of solutions, especially colored solutions containing Fe^{+3} , MnO_4^-, $Cr_2O_7^{-2}$ etc, ions.
2. Used to determine soil acidity.
3. Used to determine environmental regulations.
4. Used to analyze foods and cosmetics.

CELL (or Galvanic cell or Electrochemical cell or Voltaic cell): Cell is a device in which a redox reaction is utilized to get electrical energy (electricity). The electrode where oxidation occurs is called anode; while the electrode where reduction occurs, is called cathode.

Cells are of two types: 1.Primary cells and 2.Secondary cells.

Primary cells in which chemical reactions are not reversible i.e., once the battery is discharged, cant be recharged again.

Dry cell or laclanche cell or zinc-carbon cells:

The anode of the cell is zinc can or container containing an electrolyte consisting of the mixture of NH_4Cl, $ZnCl_2$ and MnO_2 in H_2O to which starch is added to make it thick paste like so that it is less likely to leak. A carbon rod serves as the cathode, which is immersed in the electrolyte in the centre of the cell.

The cathode reaction involves reduction of MnO_2 to Mn_2O_3 in which Mn is +3 oxidation state.

However, an acid-base reaction between OH and (from NH_4Cl) evolves $NH_3(g)$, which stops the current flow in the cell.

This is prevented by a reaction of $NH_3(g)$ with Zn^{+2} (from $ZnCl_2$) to form the complex ion $[Zn(NH_3)_2] Cl_2$.

The dry cell is a primary cell, since various reactions involved cant be reversed by passing electricity back through the cell. Dry cell is cheap to make and gives a voltage of about 1.5V.

Dry cell finds applications in flash light, torch lights, transistor radios, calculators etc.

Li ion battery is also primary cell. The cells having lithium anodes are called lithium cells, irrespective of the cathode used.
Lithium cells can be categorized into two types.
i) **Lithium cells with solid cathodes** (MnO_2): These systems may have solid or liquid electrolyte. Lithium-manganese dioxide is emerging as most widely used three volt solid cathode lithium primary battery. The cathode MnO_2 should be heated to >300^0C to remove water before incorporating it in the cathode. This is very important to improve the efficiency of the cell. The anodic and cathodic reactions are as follows.
ii) **Lithium cells with Liquid cathodes** (Lithium sulphurdioxide): Among lithium cells with liquid cathode is lithium sulphurdioxide cell. The cosolvents used are either acrylonitrile or propylene carbonate. The second type of this category is Lithium thionyl chloride cells, which consists of a high-surface area carbon cathode, a non-woven glass separator. Thionyl chloride acts as the electrolyte solvent and the active cathode. The reactions of the cell can be represented as follows.
The discharging voltage is 3.3-3.5 volts.
Electrolyte is a mixture of propylene carbonate and 1,2-dimethoxy ethane.
Applications: i) These are used in cameras, electronic devices, calculators and watches. ii) These cells are used for military and space applications iii) these are used in medical devices such as neuro-stimulators, drug delivery systems.

Zinc air cells: To meet the demands of new areas such electric vehicles etc. new electrochemical systems with high energy densities are being sought and metal-air batteries have attracted much attention because of their extremely high energy densities. The notable characteristic feature of these batteries is their open cell structure since these batteries use oxygen gas accessed from air as their cathode material. Typically metal air batteries are decided to two types according to their electrolytes. One is a cell system using an aqueous electrolyte not sensitive to moisture and other is water sensitive with aprotic solvents sensitive to moisture. Among metal air batteries Zinc-air batteries have powerful potential for use as alternative storage device, low cost, abundance, environmental benignity, flat discharge voltage and long shelf life.

Zinc-air cells are composed of three parts zinc metal as anode, an air electrode as cathode which is divided into a gas diffusion layer and a catalytic active layer and a separator. Because the solubility of oxygen very low at atmospheric pressure it is necessary to use oxygen in the gas phase not liquid. Oxygen from atmosphere diffuses into the porous carbon electrode by difference in pressure of oxygen between the outside and inside of the cell, the catalyst facilitates the reduction of oxygen to hydroxyl ions in the alkaline electrolyte by using the electrons generated by the zinc metal as anode reaction. This way we call the process a three phase reaction, catalyst(solid), electrolyte(liquid), and oxygen(gas). The hydroxyl ions migrate from the air cathode to zinc anode to complete the cell reaction which is given below.

The drawback of this battery is the working voltage of battery is much lower due to internal losses.

FUEL CELLS: Fuel cell converts the chemical energy of a fuel directly into electrical energy.

Advantages: i) it produce electric current directly from the reaction of the fuel(H_2) and oxidizer(O_2) without going through the wasteful intermediate steps.
ii) Low noise pollution and thermal pollution. iii) it takes little time to go into operation. iv) low maintenance cost. v) it produce drinking water of potable quality. And
vi) fuel cells are quite efficient and can operate on a variety of hydrocarbon fuels and produce almost no objectionable emissions.

Applications: i) The major field of applications of fuel cells is the power supply for communication systems and space craft.
ii) application to power generation in space and remote locations.
iii) fuel cell find wider use as a source of power in electric mobiles.
iv) fuel cells are widely and efficiently used for power generation, which is used for industrial and domestic purposes.

1. Phosphoric acid fuel cell: This is based upon the reactions of hydrogen and oxygen to produce electricity and water.

In this cell, hydrogen gas is diffused through a porous carbon electrode, which is coated with finely divided Pt or Pd catalyst; which acts as anode. Oxygen gas is diffused through a porous carbon electrode,which is coated with Ag or Ni, which acts as cathode. Two electrodes are separated by an electrolyte such as a concentrated phosphoric acid solution.

2. H_2-O_2 fuel cell: This is based upon the reactions of hydrogen and oxygen to produce electricity and water.

In this cell, hydrogen gas is diffused through a porous carbon electrode, which is coated with finely divided Pt or Pd catalyst; which acts as anode. Oxygen gas is diffused through a porous carbon electrode,which is coated with Ag or Ni, which acts as cathode. Two electrodes are separated by an electrolyte such as a Concentrated KOH solution.

The emf of the cell is 1.2 volts.

3. CH_3OH-O_2 fuel cell: This is based upon the reactions of methyl alcohol and oxygen to produce electricity and water.

In this cell, CH_3OH vapours are diffused through a porous nickel electrode, which acts as anode and Oxygen gas is diffused through another porous nickel electrode, which acts as cathode. Two electrodes are separated by an electrolyte such as a Concentrated KOH solution.

4. Molten carbonate fuel cell: This is based upon the reactions of hydrogen and oxygen to produce electricity and water.

In this cell, hydrogen gas is diffused through a porous nickel electrode, which acts as anode and Oxygen gas is diffused through another porous nickel electrode, which acts as cathode. Two electrodes are separated by an electrolyte alkali metal carbonate salt solution.

Corrosion: Corrosion may be defined as destruction or deterioration of metals by chemical or electrochemical attack by its environment. Ex: Rusting of iron.

Mechanism of corrosion or Theories of corrosion:

1. Chemical corrosion or Dry corrosion or oxidation corrosion: It is due to direct action of atmospheric gases like oxygen, halogens, H_2S, SO_2 etc on the metal surface.

When a metal is exposed to atmosphere, the atmospheric gases like oxygen reacts with metal and form an oxide film around the metal. The further corrosion of metal depends on the nature of oxide film formed around the metal surface. The oxide film is four types:

i) Unstable oxide film: In this case, the oxide film is decomposed back to give metal and oxygen. Thus , corrosion is not possible.

Ex: gold, silver, lead.

ii) Stable porous oxide film: In this case, the atmospheric gases can pass through pores into the metal and cause further corrosion of metal.

Ex: alkali and alkaline earth metals.

iii) Stable non-porous oxide film: In this case, the atmospheric gases cannot pass through pores into the metal. Thus, further corrosion of metal is not possible and non-porous oxide film acts as protective layer to the metal.

Ex: alluminium, copper.

iv) Volatile oxide film: In this case, the oxide film is volatilizes as soon as it is formed leaving behind underlying metal surface exposed for further attack. Therefore rapid and severe corrosion takes place.

Ex: molybdenum oxide (MoO_3)

According to **Pilling Bed Worth rule**, if the volume of oxide film is greater than the volume of metal then the oxide film acts as non-porous. If the volume of oxide film is less than the volume of metal then the oxide film acts as porous.

2. Wet corrosion (or) Electro-chemical corrosion: It is due to when a liquid is in contact with metal (or) two dissimilar metals which are joined together are partially immersed in a liquid.

According to electro-chemical series, the metal which is higher in series acts as anode; and the metal which is lower in series acts as cathode. i.e., wet corrosion occurs where the anodic and cathodic parts are available.

Anode involves loss of electrons and converted into positively charged ions.The conversion of metal to metal ions is said to be dissolution metal. The dissolution of metal into ions is said to be destruction or decaying or corrosion of metal. Thus, corrosion is at anode.

The electrons liberated by anode are taken up by cathode. The reactions at cathode do not affect the cathode since most metals cannot be further reduced. Reactions at cathode depends on nature of electrolyte surrounding the metal.

a) Evaluation of hydrogen gas: it occurs if the electrolyte is acidic solution.

b) Absorption of oxygen: it occurs if the electrolyte is aqueous neutral solution. The electrons liberated by anode are taken up by dissolved oxygen in the electrolyte and form OH^- ions.

The OH^- ions at cathode and Fe^{2+} ions at anode combine to form $Fe(OH)_2$.

In the presence of excess of dissolved oxygen, $Fe(OH)_2$ is further oxidized to $Fe(OH)_3$.

Rust is deposited at or near the cathode since the smaller Fe^{2+} diffuses faster than larger OH^- ions.

The presence of excess of oxygen removes more electrons from anode and more corrosion at anode. Thus, it is clear that with increase of dissolved oxygen content, the corrosion at anode increases.

Galvanic corrosion: When two dissimilar metals such as zinc and copper are electrically connected and exposed to an electrolyte. According to galvanic series, the metal which is higher in series acts as anode and undergoes corrosion. This type of corrosion is called galvanic corrosion.

The metal zinc which is higher in series and acts as anode and undergoes corrosion; while the metal copper is lower in series and acts as cathode and it is corrosion resistant. Flow of electrons takes place from anode metal to cathode metal.

The reactions at cathode depends on nature of electrolyte. If the electrolyte is acidic medium, then corrosion takes place by evolution of hydrogen gas process. If the electrolyte is neutral medium, then corrosion takes place by absorption of oxygen process.

Differential aeration (or) water line corrosion: Water is taken in a steel tank and it was observed that maximum corrosion takes place along a line just below the water meniscus, because the area below the water meniscus is poor oxygenated and acts as anode and undergoes corrosion. But the area above the water meniscus is more oxygenated and acts as cathode and it is corrosion resistant. A potential difference is established between anodic and cathodic parts, and it causes flow of electrons from anode to cathode.

Stress corrosion: Stress corrosion is the combined effect of tensile stresses and the corrosive environment on a metal(stress corrosion takes place where stressed parts are there in equipment).

Factors affecting rate of corrosion:

1. Nature of metal:

i) Position in galvanic series: When two metals are in electrical contact, in the presence of electrolyte, the metal higher in series acts as anode and suffers corrosion. The rate of corrosion of anode metal depends on difference in their positions in galvanic series. Higher the difference, greater is the corrosion of anodic metal.
ii) Areas of cathode and anode parts: When two metals are in electrical contact, in the presence of electrolyte, the metal higher in series acts as anode and suffers corrosion. The rate of corrosion of anode metal is directly proportional to the ratio of areas of cathode and anode parts.
iii) Purity of metal: When zinc metal containing impurity such as iron undergoes corrosion of zinc due to the set up of local electrochemical cell. Corrosion of metals increases with increase of impurity.

iv) <u>Nature of oxide film</u>: If the oxide film formed around the metal is porous, then further corrosion of metal takes place. If the oxide film is non-porous then further corrosion of metal doesn't takes place.

2. Nature of environment:

i) Temperature: Rate of corrosion of metals increases with increase of temperature of environment.

ii) **Influence of pH :** Acidic media($pH < 7$) are more corrosive than neutral/ alkaline($pH > 7$) media.

iii) **The presence of impurities in atmosphere:** The industrial fumes like HCl, H_2SO_4, CO_2 etc cause heavy corrosion of metals because these impurities increases the acidity of environment.

. Corrosion control/ Protection from corrosion:

To control the corrosion, the four basic principles are employed. They are 1. Proper design 2. Cathodic protection and 3.Protective coatings.

1. Design and Material selection:

i) Avoid the contact of dissimilar metals in the presence of a corroding solution**:** If this principle is not allowed, then corrosion is localized on the more active metal; while the less active metal remains protected.

ii) When two dissimilar metals are to be in contact , the anodic metal should have as large area as possiblel; where as the cathodic metal should have as much smaller area as possible.

iii) If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.

iv) Whenever the direct joining of dissimilar metals, is unavaidable, an insulating fitting may be applied in-between them to avoid direct metal-metal electrical contact.

v)Prevent the occurance of inhomogeneties in metal and in corrosive environment.

Thus, a proper design should avoid the presence of crevices(air gaps) between adjacent parts of the structure, even in the case of same metal, since crevices permit oxygen concentration differences.

Bolts and rivets are, therefore, undesirable for this reason and these should be replaced by a butt-weld.

vi) Sharp corners should be avoided, because they favour the formation of stagnant areas and accumulation of solids, etc.

vii) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.

2. Cathodic protection: The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.

Sacrificial anodic protection method: In this protection method, the metal to be protected is connected by a wire to a more active metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowlyl; while the parent structure is protected. The more active metals used are called sacrificial anodes. The commonly used sacrificial anodes are alluminium, Zinc, magnesium and their alloys.

Important applications of this method include protection of buried pipe lines, underground cables, water tanks,etc.

Impressed current cathodic protection: In this method, an impressd current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.This is accomplished by applying sufficient amount of direct current from external source like battery to an insoluble material like graphite, which is buried in the soil and connected to corroding metal. The anode is usually taken in a backfill(composed of gypsum) to maintain electrical contact with surroundings.

This type of cathodic protection has been applied to underground water pipes, water tanks, etc.

Protective coatings: Surface Preparation:

i) Solvent cleaning: is used to remove oils, greases, and fatty substances. This involves in cleaning the surfaces by the application of organic solvents like naphtha, chlorinated hydrocarbons(like carbon tetra chloride) , toluene, xylene or acetone.

ii) Alkali cleaning: is particularly well adopted for the removal of old paint coating from metal surfaces. Alkali cleaning agents are trisodium phosphate along with soaps and wetting agents like caustic soda.

iii) Mechanical cleaning: removes loose rust and other impurities from the surface. This is generally done by hand cleaning with a bristle brush plus some abrasive(like sand) and detergent(like soap).

iv) Flame cleaning: is accomplished by heating the metal surface with a hot flame to remove moisture and loosely adhering scales. This is followed by wire brushing.

After the removal of impurities, we can apply coatings on metals to prevent corrosion and for decoration.

Anodic&Cathodic coatings: In this, a layer of metal is applied on another metal to prevent corrosion.

a) **Anodic coatings**: These are produced by coating with more active metal than base metal. Ex: Coating with zinc metal on iron metal (galvanizing). If any pores, breaks, or discontinuation in metallic coating, exposing the base metal, a galvanic cell is formed between coating metal and base metal, where the coating metal dissolves anodically and the base metal is protected. Hence no corrosion occurs to the base metal until all the coating metal corrodes and disappear from vicinity of the exposed base metal spot.

b) **Cathodic coatings**: These are produced by coating with more noble or inert metal than base metal. Ex: Coating with tin metal on iron metal (tinning). Cathodic coatings provide effective protection to the base metal only when the coating is completely continuous and free from pores, breaks, and discontinuities.

When breaks, pores occurs in the cathodic coating more corrosion damage is done to the base metal. When the base metal which is anodic to the coating metal is exposed to environment, a galvanic cell is set up and an intense localized attack at the small exposed part occurs resulting severe pitting and perforation in the base metal because of a small anode and large cathode area.

Electroplating & Electroless plating:

Electroplating: In this method a layer of one metal is applied on another metal by passing direct electric current through the electrolytic solution.

Ex: Electroplating of nickel.

The metal to be protected from corrosion is taken as cathode of the electrochemical cell. The anode metal is inert material like graphite. The electrolyte solultion is the mixture of nickel chloride, nickel sulphate and boric acid. The temperature maintained is 40-70^{0}C and PH at 4.5. By passing direct current through electrolytic solution, the metal ions moved towards cathode and get coated over.

Electroless plating: In this method a layer of one metal is applied on another metal by using reducing agents without passing current through the electrolytic solution.

Ex: Electroless plating of nickel.

Electrolyte solution is nickel chloride; Reducing agent is sodium hypophosphite, temperature at 90-95^{0}C and PH at 4.5.

Metal ions + Reducing agent Metal atoms + oxidized products.

Advantages of electroless plating over electroplating: i) No electrical energy is required. ii) Better throwing power. iii) Even intricate parts (of irregular shapes) can be plated uniformly. iv) Electroless plated coatings possess unique mechanical, chemical and magnetic properties.

Paints:

Paint is a inert organic-barrier applied on metallic surfaces and other constructional materials for both corrosion protection and decoration.

Constituents and functions of paint:

Paint: Paint is a mechanical dispersion mixture of one or more pigments in vehicle. Vehicle is a liquid consisting of drying oil, thinners, driers, fillers and antiskinning agents etc.

Pigment: It is a solid substance and provide desired colour to the paint. Pigments reflect harmful uv rays and protect the paint film from sun light.

Ex: The pigments used for various colours are zinc oxide for white colour, iron oxide for red colour, chromium oxide for green colour and carbon black for black colour.

Drying oil: These are film forming constituents of paint. These are esters of high molecular weight fatty acids, generally present in animal and vegetable oils.

Ex: Soyabean oil, castor oil, fish oil, etc.

Thinners: Thinners reduce viscosity of paint and hence increases covering area.

Ex: Kerosene, Benzene.

Driers: These are added to improve drying quality of paint by absorbing oxygen from atmosphere.

Ex: Resinates, linoleates and tungstates of Co, Mn and Zn.

Fillers: These are added to give strength to paint film.

Ex: Sand, clay, quartz, mica etc.

Antiskinning agents: These are added to prevent jelling of paint.

Ex: Polyhydroxy phenols.

Special paints:

1.Luminous paints: These are made by luminophor compounds such as Zinc sulphide(ZnS), Cadmium sulphide(CdS). The luminophor compounds absorb UV light and emit radiations. Thus, the glowing/shining nature of paint is due to luminophor compounds. Such paints are used in road signs and danger signals etc.

2. Water proof paints: These are made by silicones. Silicones are prepared by hydrolysis and condensation of chlorosilanes, ethoxy silanes etc. Silicones have water repelling tendency. Thus, water proof paint doesn't absorb or react with water. Such paints are used in buses, cars, ships, etc.

3. Heat resistant paints: These are made by metallic powders like aluminium, zinc, tin, etc. These paints with stand high temperatures even upto red heat. Such paints are used in ovens, air craft combustion chambers etc.

4. Temperature indicating paints: These contain a special ingredients, which undergoes colour change at specific temperature. Such an ingredient is amine salts of Cr, Mn, Fe. Such paints can indicate any temperature of the environment in the range of 45-1450^{0}C with 10% error.

UNIT III: MATERIAL CHEMISTRY

Part-I: Non-elemental semiconducting materials:

Stoichiometric or Compound semiconductors:

The having electronic configurations similar to intrinsic semiconductor atoms like silicon or germanium. These compounds having an average of four valence electrons per atom and are covalent in character.

Compound semiconductors are prepared by combining elements of group II with those of group VI ; or group III with group V such as CdS, GaP. These compound semiconductors possess widely differing energy gaps from 0.5 to 2.3 ev. So, they can be employed at a wider range of temperature than the intrinsic semiconductor.

The energy gap in compound semiconductor is reduced by substituting one of its elements with the element of higher atomic number belonging to the same group.

Ex: GaP – 2.24 ev
GaAs – 1.35 ev
GaSb – 0.67 ev

Preparation of semi conductors:

1. Zone Refining method: For preparing semi conducting devices, the basic materials such as Si or Ge must at least 99.999% pure. Widely used method for the purification of semiconductors is Zone refining method.

Zone refining technique: Zone refining is a technique of purification which involves recrystallization. Figure shows schematically a vertical zone refiner, employed for the purification of Ge rod. A rod of Ge is clamped vertically and heated to about 1000^0C in a reducing atmosphere. The heating coil is very slowly moved from top towards bottom, when the impurities are sweft down with coil; while pure Ge rod solidifies at the upper portion. When the purification of upper portion of the rod is complete, the bottom portion of the rod(where impurities are concentrated) is separated. By using repeated zone refining, the impurity level can be reduced to 1 atom per 10^{12} atoms of Ge.

2. Czochralski crystal pulling technique: In this method, polycrystalline semiconductor material is converted into single crystalline or single crystal growth semiconductor material.

In this process, solid poly crystalline semi conducting material taken in a quartz chamber is heated, till it melts. Now, properly oriented seed crystal is attached to puller rod and this puller rod is dipped into the melt and rotate slowly. It was observed that, the melt in contact with seed crystal starts solidifying and producing the orientation identical as that of seed crystal.

3. Epitaxial growth: Single crystal growth semiconductor material cut into wafers. These wafers placed in a long cylindrical quartz tube, which then heated. For getting n-type semiconductor, PH_3 gas is passed through tube and for getting p-type semiconductor, B_2H_6 gas is passed through tube. Heating is continued till doping is takes place.

Electrical insulators: Electrical insulators are those materials through which electrical charges cannot pass. All the electrons bound to the parent molecule in an insulator, and there are no free electrons for conduction. They are non-metallic materials of high specific resistance.

Properties of electrical insulators:

1. The electrical charges cannot pass through the insulator.
2. They possess low conductivity, i.e high resistivity(10^9-10^{20} ohm-cm at room temperature)
3. A good electrical insulator should have low porosity. With increase in porosity, the moisture holding capacity increases which adversely affects the electrical properties.
4. Strong and low moisture absorption.
5.They should be resistant to chemicals, solvents, acids, alkalis, oils and organic solvents etc.
6.Non-toxic and non-inflammable.
7.The electrical properties of the materials should not altered by change in chemical composition.
8. Works in the temperature range -75^0C to +150^0C.
9. Highly resistant to abrasion.

Applications: 1.These are used in insulating electric wires, low voltage domestic cables.
2. Used in ship wiring 3.Used in air craft cables 4.Used in radios & TVs 5.Used in communication circuit cables and power submarine cables. 6. Used in telephones 7. Used for making paper for electrical insulation 8. Used in cloth tape 9. Used in capacitors and transformers 10. Used for insulation in coal mines, oil refineries etc.

Part-II

Sol-gel method for the preparation of nanomaterials:

It is bottom-up process used for the preparation of metal oxide nano materials.

Step 1: This step involves the preparation of colloidal solution by mixing starting materials (metal alkoxide) with suitable solvent like water, alcohols etc.

Step 2: The colloidal solution is stand for some time then hydrolysis and condensation reactions takes place to form viscous liquid(gel).

Step 3: The gel on further standing, poly condensation reactions takes place to form a solid mass.

Step 4: The solid mass is dried to remove excess solvent and other volatile liquids to form large single block (monolith).

Step 5: The dried solid mass is subjected to calcinations at 800^0C, to remove surface bound reactive functional groups.

Step 6: Finally, the solid mass is heated to above 800^0C to collapse pores and to remove organic impurities.

Characterization of nanomaterials:

i) **BET theory:** Brunauer, Emmet and Teller(BET) extended the Langmuir theory to the multi molecular layer adsorption and their equation is known as BET equation and is expressed by

P and P_0 are the equilibrium and the saturation pressure of adsorbates(gases) at the temperature of adsorption , v is the adsorbed gas quantity and is the monolayer adsorbed gas quantity. C is the BET constant, which is expressed by

E_1 is the heat of adsorption for the first layer, and E_L is that for the second layer and higher layers and is equal to the heat of liquefaction.

Once is determined, the total surface area S can be calculated with the following equation.

ii) TEM (Transmission Electron Microscope): TEM utilizes energetic electrons to provide internal structure of nanomaterials. TEMs are most powerful microscopes and produce high resolution, two dimensional black and white images.

Advantages: i) Images are high quality and detailed. Ii) Images provide surface features, shape, size and structure of nanomaterials

Disadvantages: i) TEMs are large and very expensive ii) Images are black and white.

Preparation and applications of CNT and Fullerenes:

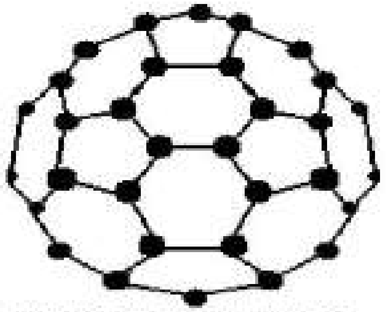
Carbon Nano Tubes(CNT): Chemical Vapour Deposition(CVD) method: It consists of a reactor containing substrates, which are made by metal catalysts. The reactor is heated to about 700^0C by using heaters. Now the mixture of carbon containing gas(CH_4) and carrier gas(N_2) is passed into the reactor. At 700^0C carbon containing gas(CH_4) decomposed and deposit carbon as Nanotubes on substrates.

Applications: i) Because of its strength, used in bullet proof jackets and in concrete instead of steel. ii) used in electrical cables, wires, transistors, capacitors, conducting polymers, memory cards , solar cells, in medical fields etc.

Advantages: This process is cheap and produce large length of nanotubes and rate of formation is very high.

Disadvantages: It is difficult to seperate nanotubes from metal substrates.

Fullerenes: Fullerenes are prepared by passing high current between two graphite rods.



The C_{60} molecule used in smart materials

Applications: i) used in medicine ii) used in solar cells iii) used in fuel cells iv) used as catalyst in hydrogenation.

Liquid Crystals: Some crystalline solids doesn’t melt directly into liquid state, but passes through an intermediate states known as mesomorphic or polycrystalline states. These intermediate states are called liquid crystals. Thus liquid crystals are treated as intermediate states of matter between solid and clear liquid.

In solids, the molecules are highly ordered but have little transitional freedom. In liquid crystals, the molecules are not ordered as solids but have high transitional freedom. The irregular arrangement of molecules in liquid crystals is the property of anisotropy.

The intermolecular forces in liquid crystals is strong enough to hold the molecules together but not so strong to restrict the movement too much. The intermolecular forces are delicate and sensitive to external conditions like pressure, temperature, electric or magnetic fields.

Classification of liquid crystals: Liquid crystals are classified into three types: 1.**Nematic liquid crystals:** In these, the orientation of all the molecules is same but not arranged in regular manner.

2. Smectic liquid crystals: In these, the orientation of all the molecules is same and also arranged in regular manner.

3. Cholestric liquid crystals: These are similar to nematic liquid crystals, but these are optically active i.e., they rotate linearly polarized light.

Applications of liquid crystals:

1. These are used in digital watches, pocket calculators etc.
2. Most widely used in LCD’s (liquid crystal display).
3. These are used as solvents in spectroscopy.
4. These are used in gas-liquid chromatography.
5. These are also used in pressure sensors.
6. These are used in thermography for identification of tumors in our body.

Super conductivity: It is a phenomenon in which a metals or alloys exhibit zero resistance to the flow of electricity.

The electrical resistance of metals depends upon temperature. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute temperature(0K). Materials in this state are said to possess super conductivity.

The phenomenon was first discovered by kammerlingh ones in 1913, he found that mercury becomes super conducting at 4K. The temperature at which a substance starts behaving as super conductor is called transition temperature, which lies between 2 to5 K in most of the metals exhibiting this phenomenon.

Applications of super conductors: The phenomenon of super conductivity has many practical applications such as: 1. super conductors are used as memory or storage elements in computers. 2. They are used in scientific and research equipments. 3. they are used in medical field as diagnostic tool.

Based on their magnetization behavior in external magnetic field, super conductors are classified into Type-1 & Type-2 super conductors.

Type-1 super conductor	**Type-2 super conductor**
1. It looses magnetization suddenly	1. It looses magnetization gradually.
2. It exhibit complete meissner effect	2. It doesnot exhibit complete meissner effect.
3. No mixed state is present.	3. Mixed states are present.
4. It contains one critical magnetic field(Hc)	4. It contains two critical magnetic fields(Hc1 & Hc2)
5. The transition from super conducting state to normal state is sharp& well defined.	5. The transition is not sharp and well defined.
6. These are also called soft super conductors.	6. These are called hard super conductors.
Ex: Pure metals	Ex: Alloys

UNIT-IV SPECTROSCOPIC TECHNIQUES & NON-CONVENTIONAL ENERGY SOURCES

PART-A SPECTROSCOPIC TECHNIQUE:

Electromagnetic spectrum: The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is known as complete electromagnetic spectrum.

Laws of absorption: There are two laws which govern the absorption of light by the molecules. These are: i) Lamberts law and ii) Beers law

i) Lamberts law: It states that, when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

Mathematically, the law is expressed as $-dI/dx = k I$

Where I = intensity of radiation after passing through a thickness x, of the medium.

d I = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium.

- dI/dx = rate of decrease of intensity of radiation with thickness of the absorbing medium.

K = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let I_0 be the intensity of radiation before entering the absorbing medium(x=0).
Then I, the intensity of radiation after passing through any thickness, say x of the medium can be calculated as.

ii**) Beers law**: It states that, when a beam of monochromatic radiation is passeed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of the incident radiation as well as the concentration of the solution.

Mathematically, the law is expressed as $-dI/dx = k\,Ic$

Where c= conc. Of the solution in moles/litre

k = molar absorption coffecient and its value depends upon the nature of the absorbing substance.

Suppose I_0 be the intensity of the radiation before entering the absorbing solution.(when x=a) , then the intensity of the radiation, I after passing through the thickness x, of the medium can be calculated as.

UV INSTRUMENTATION: A spectrophotometer is a device which detects the percentage of transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light.

The modern ultra-violet-visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are: Tungsten Filament lamp and hydrogen-deuterium discharge lamp which cover the whole of the UV-visible region.

The various wavelengths of a light are separated with a prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording purposes. The selected beam is monochromatic which is then divided into two beams of equal intensity.

One of the beams of selected monochromatic light is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent. The solvent as well as the solution of the sample may be contained in cells made of a material which is transparent throughout the region under study. Glass cannot be used since it absorbs strongly in the Ultra-Violet region. Silica cells or quartz cells can be used. This type of spectrometer is called double beam spectrophotometer.After the beams pass through the sample cell as well as the reference cell , the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument.

Theory of electronic spectroscopy: When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the ground state to the higher energy state. In the ground state, the spins of the electrons in each molecular orbital are essentially paired. In the higher energy state, if the spins of the electrons are paired, then it is called an excited singlet state. On the other hand, if the spins of the electrons in the excited state are parallel, It is called an excited triplet state. The triplet state is always lower in energy than the corresponding excited singlet state. Therefore, triplet state is more stable as compared to the excited singlet state. In the triple excited state, electrons are farther apart in space and thus, electron-electron repulsion is minimized. Normally the absorption of ultraviolet or visible light results in singlet ground state to excited singlet state transition, i.e., excitation proceeds with the retention of spins. An excited singlet state is converted to excited triplet state with the emission of energy as light. The transition from singlet ground state to excited triplet state is symmetry forbidden. The energy states are designated as high energy molecular orbitals and also called antibonding orbitals. In most of the cases, several transitions occur resulting in the formation of several bands.

Chromophores and Auxochromes:

Chromophores: A chromophore was considered any system which is responsible for imparting colour to the compound. Nitro-compounds are generally yellow in colour. Clearly, nitro group is the chromophore which imparts yellow colour. Similarly, aryl conjugated azo group is a chromophore for providing colour to azo dyes.

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region.

Some of the important chromophores are ethylenic, acetylenic, carbonyls, acids, esters, nitrile group etc. A carbonyl group is an important chromophore, although, the absorption of light by an isolated group does not produce any colour in the ultraviolet spectroscopy.

Auxochromes: An auxochrome can be defined as any group-which does not ifself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum(longer wave length). The absorption at longer wavelength is due to the combination of a chromophore and an auxochrome to give rise to another chromophore. An auxochromic group is called colour enhancing group. Some common auxochromic groups are –OH, -OR, -NH_2, -SH etc. The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons. For example, benzene shows an absorption maximum at 255mµ where as aniline absorbs at 280mµ. Hence, amino(-NH_2) group is an auxochrome.

Intensity Shifts:

a) Bathochromic effect: It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome or by the change of solvent. Such an absorption shift towards longer wavelength is called Red shift or bathochromic shift.

b) Hypsochromic shift: It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength. The absorption shifted towards shorter wavelength is called Blue shift or hypsochromic shift. It may be caused by the removal of conjugation and also by changing the polarity of the solvent. In the case of aniline, absorption maximum occurs at 280mμ because the pair of electrons on nitrogen atom is in conjugation with the pi bond system of the benzene ring. In its acidic solutions, a blue shift is caused and absorption occurs at shorter wavelength (203mμ) because the electron pair is no longer present and hence conjugation is removed.

c) Hyperchromic effect: It is an effect due to which the intensity of absorption maximum increases. For example, absorption maximum for pyridine is 257mμ is shifted to 262mμ for 2-methyl pyridine. The introduction of an auxochrome usually increases intensity of absorption.

d) Hypochromic effect: It is defined as an effect due to which the intensity of absorption maximum decreases. The introduction of group which distorts the geometry of the molecule causes hypochromic effect. For example, biphenyl absorbs at 250mμ where as 2-methyl biphenyl absorbs at 237mμ. It is due to distortion caused by the methyl group in 2-methyl biphenyl.

Applications of UV-spectroscopy:

Ultra-violet spectroscopy has been mainly applied for the detection of functional groups(chromophore), the extent of conjugation, detection of polynuclear compounds by comparison etc. Some important applications of ultraviolet spectroscopy are as follows:

a) Detection of functional groups: The technique is applied to detect the presence or absence of the chromophore. The absence of a band at a particular wave length may be regarded as an evidence for the absence of a particular group in the compound. A little information can be drawn from the UV spectrum if the molecule is very complicated.

b) Extent of conjugation: The extent of conjugation in polyenes can be estimated. Addition in unsaturation with the increase in the number of double bonds shifts the absorption to longer wavelength.

c) Distinction in conjugated and non-conjugated compounds: It also distinguishes between a conjugated and a non-conjugated compound. The following isomers can be readily distinguished since one is conjugated and the other is not.

d) Identification of an unknown compound: An unknown compound can be identified by comparing its spectrum with the known spectra. If the two spectra coincide, the two compounds must be identical. If the two spectra do not coincide, then the expected structure is different from the known compound.

e) Examination of polynuclear hydrocarbons: Benzene and polynuclear hydrocarbons have characteristic spectra in the ultra-violet and visible-region. Thus, the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds.

f) Determination of configurations of Geometrical isomers: The results of absorption show that cis-alkenes absorb at different wavelengths as compared to their corresponding trans isomers. The distinction becomes possible when one of the isomers is forced to be non-coplanar by steric hindrance. Thus, cis-forms suffer distortion and absorption occurs at lower wavelength.

g) Distinguishes between equatorial and axial conformations: This technique also distinguishes between equatorial and axial conformations.

FT-IR INSTRUMENTATION: The most important source of Infra-red light for scanning the spectrum of an organic compound is Nernst glower which consists of a rod of the sintered mixture of the oxides of Zirconium, Ytterium and Erbium. The rod is electrically heated to 1500^0C to produce Infra-red radiations. A rod of silicon carbide(globar) can also be electrically heated to produce Infra-red radiations.

To obtain monochromatic light , optical prisms or gratings can be used. For prism material, glasss or quartz cannot be used since they absorb strongly through most of the Infra-red region. Sodium chloride or certain alkali metal halides are commonly used as cell containers or for prism materials as these are transparent to most of the Infra-red region under consideration.

Light from the source is split into two beams. One of the beams is passed through the sample under examination and is called the sample beam. The beam is called the reference beam. When the beam passes through the sample, it becomes less intense due to the absorption of certain frequencies. Now, there will be a difference in the intensities of the two beams. Let I_0 be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively.

The absorbance of the sample at a particular frequency can be calculated as: $A= \log(I_0/I)$

Also transmittance, $T= I/I_0$

Or $A= \log(1/T)$

Intensities of the bands can be recorded as a linear function T against the corresponding wave-number. Intensities of the two beams are converted into and measured as electrical energies with the help of detector thermopile. It is then amplified with the help of amplifier(A). Due to the difference in intensities of the two beams, altering currents start flowing from the detector thermopile to the amplifier. The amplifier is coupled to a small motor which drives an optical wedge. The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on the calibrated chart. The movement of the wedge continues till the detector receives light of equal intensity from the sample and the reference beams.

MRI(Magnetic Resonance Imaging) scan: MRI uses a strong magnetic field and radio waves to create detailed images of the organs and tissues within the body. An MRI scanner contains two powerful magnets. These are the most important parts of the equipment.

The human body is largely made of water molecules, which are comprised of hydrogen and oxygen atoms. At the centre of each atom lies an even smaller particle called a proton, which serves as a magnet and is sensitive to any magnetic field.

Normally, the water molecules in the body are randomly arranged, but on entering an MRI scanner, the first magnet causes the water molecules to align in one direction, either north or south.

The second magnetic field is then turned on and off in a series of quick pulses, causing each hydrogen atom to change its alignment when switched on and then quickly switch back to its original relaxed state when switched off.

Passing electricity through gradient coils, which also cause the coils to vibrate, creates the magnetic field, causing a knocking sound inside the scanner. Although the patient cannot feel these changes, the scanner can detect them and, in conjunction with a computer, can create a detailed cross-sectional image for the radiologist.

Uses: The development of the MRI scan represents a huge milestone for the medical field. Doctors are now able to examine the inside of the human body in high detail using a non-invasive tool.

The following are the examples in which an MRI scanner would be used:

a. Anomalies of the brain and spinal cord.
b. tumors, cysts, and other anomalies in various parts of the body.
c. breast cancer screening for women who face a high risk of breast cancer.
d. injurious or abnormalities of the joints, such as the back and knee.
e. certain types of heart problems.
f. diseases of the liver and other abdominal organs.
g. the evaluation of pelvic pain in women
h. suspected uterine anomalies in women undergoing evaluation for infertility.
i. infections, swellings, blood vessel issues.

The test normally takes 30-60 minutes.

CT(Computed Tomography) scan: A computed tomography scan allows doctors to see inside your body. It uses a combination of X-rays and a computer to create pictures of your organs, bones, and other tissues. It shows more detail than a regular X-ray.

CT scanner use a narrow X-ray beam that circles around one part of your body. This provides a series of images from many different angles. A computer use this information to create a cross-sectional picture. This process is repeated to produce a number of slices. The computer stacks these scans one on top of the other to create a detailed image of your organs, bones, or blood vessels.

Uses: a. they can help to locate a tumor, blood clot, excess fluid, or infection.
b. they show internal injuries and bleeding, such as those caused by a car accident.
c. CT scans can detect bone and joint problems, like complex bone fractures and tumors.
d. pinpoint the location of masses and tumors(including cancer).
e. cancer and heart disease.
f. diagnose dangerous diseases they can cause stroke, kidney failure, and death.
g. diagnose spinal problems and skeletal injuries.

PET scans and CT scans use ionizing radiation, which can damage DNA and cause cancer. Two other imaging technologies, MRI and Ulltral sound, do not use radiation.

CT scan risks: a. skin redding and tissue injury.
b. hair loss   c. cataracts   d. birth defects if used during pregnancy
e. increased life time risk of cancer.

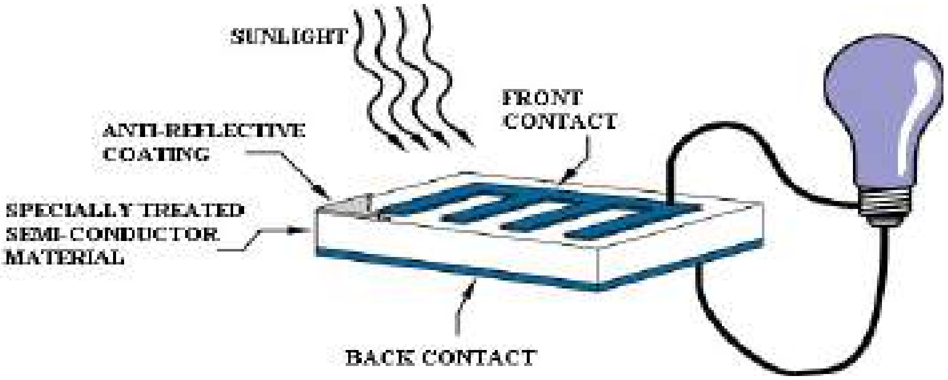
PART-B NON-CONVENTIONAL ENERGY SOURCES

Non conventional energy sources are those energy sources which are renewable and ecologically safe such as solar energy, wind energy, ocean energy(tidal energy, wave energy, ocean thermal energy), geothermal energy, nuclear energy etc.

Solar cells/Photo-voltaic cells: Solar cells were developed in 1950 for producing power supply for space satellites.

A typical solar cell consists of two very thin layers of materials. The lower layer has atoms with single electrons in the outer orbital which are easily lost. The upper layer has atoms lacking one electron in the outer orbital and hence can readily gain electrons.

The kinetic energy of light striking this sandwitch dislodges electrons from the lower layer, which are trapped into the upper layer. This creating an electric potential between two layers. This potential provides the electric current through the circuit. Thus, solar cells convert light energy directly into electrical power.

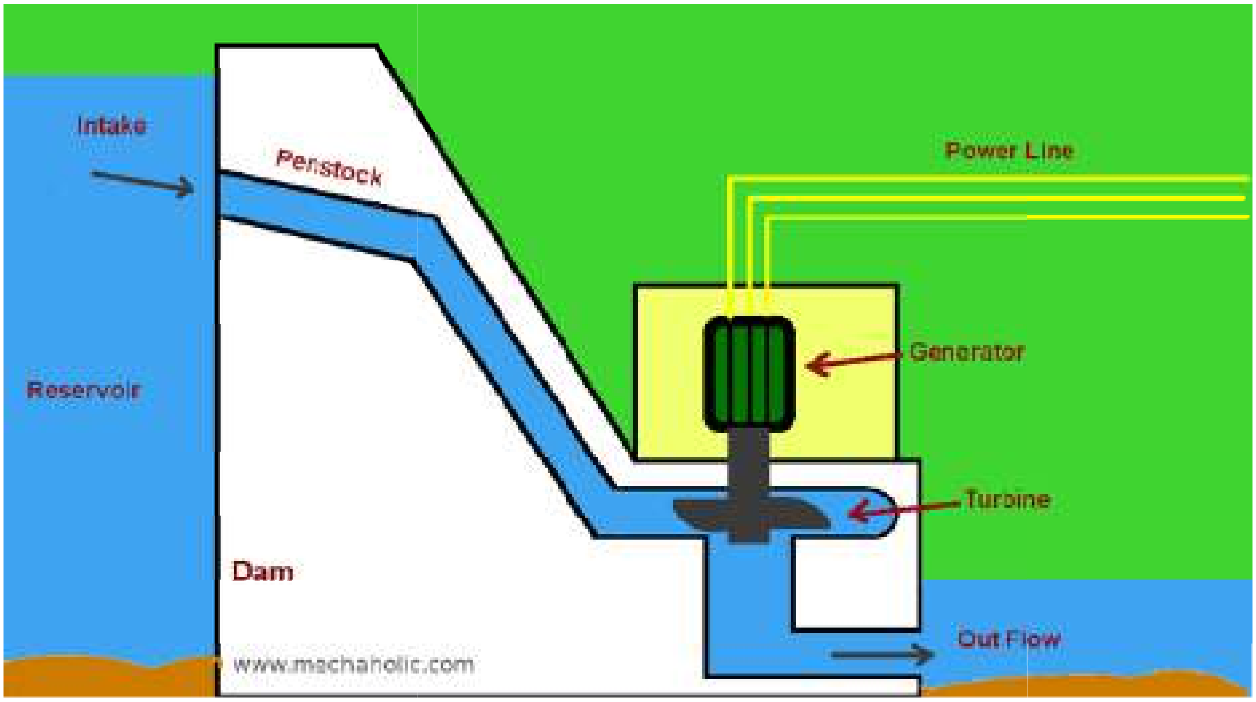


Applications of solar energy: 1.For providing electricity on artificial satellites.
2. For producing electricity for street lights, running radio, T.V sets in remote areas.
3. For operating electronic watches, calculators and other small instruments.

Hydropower: Flowing water creates energy that can be captured and turned into electricity. The power available in a river or stream depends on the rate at which the water is flowing and the height which it falls down.

The core of a hydro scheme is the turbine, which is rotated by the moving water. Different types of turbines are used depending on the head and flow at the site. For Ex: Pelton turbines are used for low flow of water, Francis turbines are used for higher flow of water and also cross-flow, Propeller turbines are used for large flow of water.

The most common type of hydro electric power plant uses a dam on a river to store water in a reservoir. Water released from the reservoir flows through turbine, spinning it, which inturn activates a generator to produce electricity.



Construction and working of hydropower plant: In hydropower plant we use gravitational force of water to run the turbine which is coupled with generator to produce electricity. Power plant plays an important role to protect our fossil fuels.

Fundamental parts of hydro power plant are area, dam, reservoir, turbines and generator.

For construction of hydropower plant first we choose the area where the water is sufficient to reserve.

The main function of dam is to stop the flow of water and reserve the water in reservoir. The reservoir holds lots of water which is employed to generate power by means of turbines.

A small dam in the river bed directs the water to a settling tank, which allows the silt to settle out of the water and the clean water flow into a canal or a pipe to a settling tank called forebay has a screen to trap slit and floating debris. Water flows out into a pipe called penstock, which is made as steep as possible to transfer water to the turbine. Water leaving the turbine is led into the stream through the outlet pipe or tail race.

Advantages:

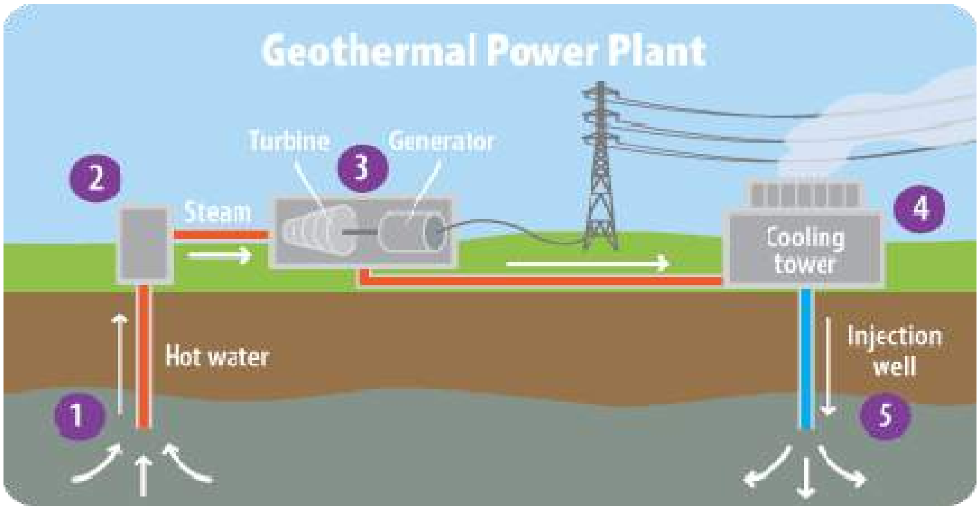
1. it is eco-friendly energy source.
2. it has low operational cost compared to fossil fuels.
3. dam made for generation of electricity also help in irrigation project.

Disadvantages: 1. Building a dam effects the environment and adjacent livings.

2. building of dam causes a lot of pollution.
3. dams are expensive to build.
4. it can be generated only in areas with heavy rain fall and sufficient supply of water.

Geothermal energy: Geo means earth and thermal means heat. Geo thermal energy is the heat energy from the earth. It is clean and sustainable. The first geothermal electricity was produced in Italy in 1904.

To produce geothermal generated electricity, wells sometimes 1.6 kms deep or more are drilled into the under ground reservoirs to tap steam and very hot water that drive turbine and turbines drive electricity generators.



There are three types of geothermal power plants.

1. Dry steam: Dry steam geothermal generator takes steam out of fractures in the ground and uses it directly to drive turbine.
2. Flash: Flash geothermal plants pull deep, high pressure hot water into cooler, low pressure water. The steam that is produced is used to drive the turbine.
3. Binary: Binary geothermal plants, the hot water is passed by a secondary fluid with much lower boiling point than water, producing vapours of the secondary fluid, which can drive a turbine. Most geothermal plants in future will be binary plants.

Geothermal plants have advantages over other thermal plants, that no fossil fuel is burned, no emission of CO_2 and other gases.

Advantages: 1.Maintenance cost of plant is very low.

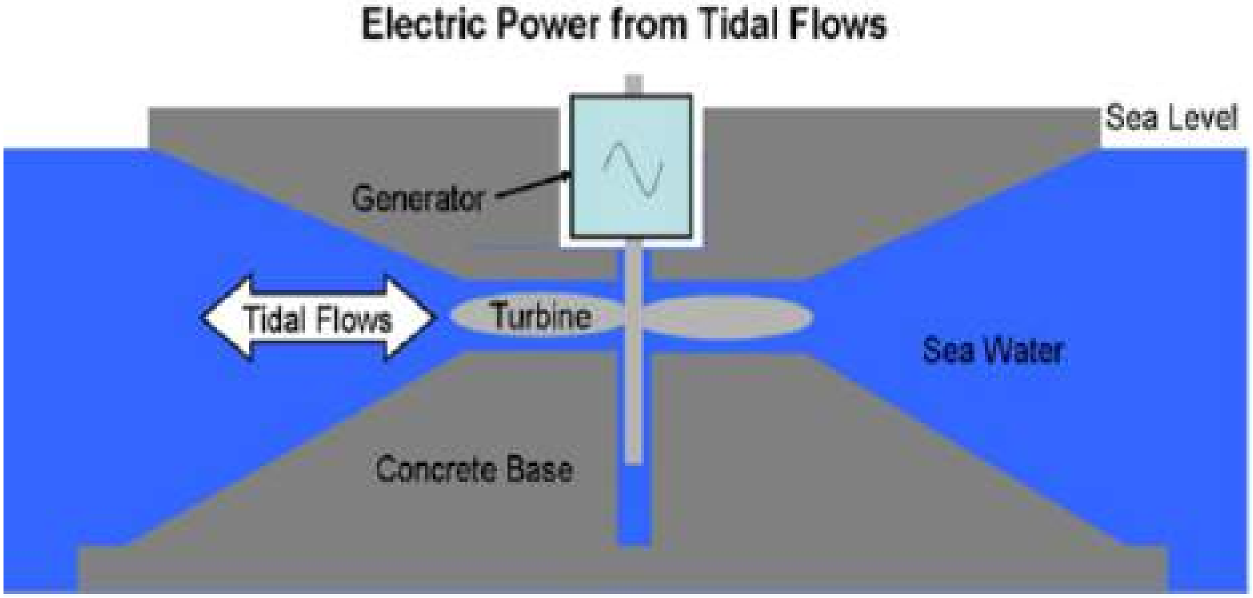
2. Unlike solar energy it is not depend on weather conditions.

Disadvantages: 1. Only few sites have the potential of geothermal energy.

2. The installation cost of power plant is very high.

Tidal and wave power: Tidal power is also called tidal energy is a form of hydro power that converts the energy obtained from tides into useful forms of power mainly electricity. Tidal energy has potential for future electricity generation. Tides are more predictable than wind energy and solar energy, but tidal energy is more costly and limited availability of sites. The worlds first large-scale power plant is the Rance tidal power plant in France.

The oceanic tides on the earth are ultimately due to gravitational interaction with the moon and sun and the earths rotation. Tidal power is practically inexhaustible. Movement of tides causes a loss of mechanical energy in the earth moon system due to the pumping of water through natural restrictions around coast lines and consequent viscous dissipation at the sea bed and turbulence. This loss of energy has caused the rotation of the earth to slow in the 4.5 billion years, since its formation. During the last 620 million years, the period of rotation of the earth is slower than the rotation of earth since its formation. Tidal power is taken from earths oceanic tides. The rise is called high tide and fall is called low tide. This building up powerful movement of water, it causes even sinking of ships. These tides rotates the turbines and produce electricity.



Tidal power is generated in four methods:

1. Tidal steam generator(TSG): This method make use of the kinetic energy of moving water to power turbines in a similar way as wind power turbines. Tidal generators can be built into the structure of the existing bridges, land constructions such as straights or inlets. These turbines can be horizontal, vertical, open placed near the bottom of the water column.

2. Tidal barrage method: Tidal barrages make use of the potential energy difference of high and low tides. Potential energy is converted into mechanical energy to produce electric power through the use of generators.

3.Dynamic tidal power method(DTP): This is a promising technology that exploits. The interaction between potential and kinetic energies in tidal flows. Long dams are built into the ocean without enclosing an area, leading to a significant water level difference producing low and high tides from which power is generated.

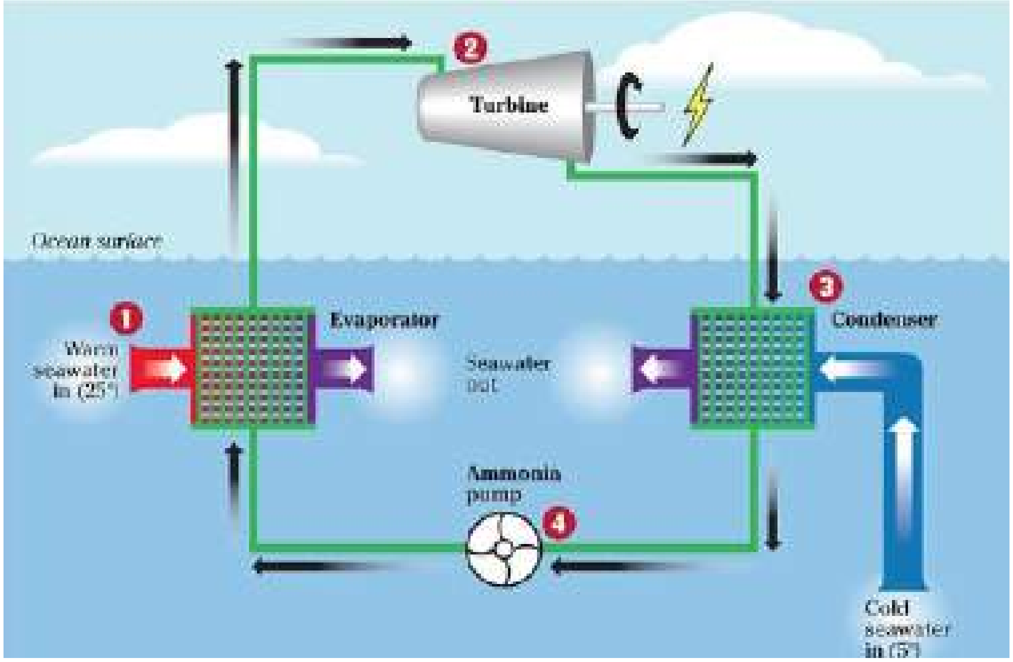
4. Tidal lagoon: A newer tidal energy design is to construct circular retaining walls embedded with the turbines that can capture the potential energy of tides. The reservoirs similar to tidal barrages are created called lagoon which can be in double format without pumping and with pumping that will flatten out the power output.

The above said four turbines are placed in areas with high tidal movements and capture kinetic energy of the ocean waves to produce power.

Advantages: 1. It is inexhaustible source of energy.

2. it is eco-friendly and doesnot produce green house gases.
3. the life of tidal energy power plant is very long.
Disadvantages: 1. The cost of construction of power plant is high.
2. Influences the aquatic life badly.

Ocean thermal energy conversion: Ocean thermal energy conversion is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water. OTEC plant pump large quantities of deep cold sea water and surface sea water to run a power cycle and produce electricity.
There are three types of OTEC systems
1. Closed cycle system: These systems use fluid with a low boiling point such as ammonia(-33^{0}C) to power a turbine to generate electricity. 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.



2. Open cycle OTEC: Open cycle OTEC uses warm surface water directly to make electricity. The warm sea water is first pumped into a low pressure container, which causes it to boil. In some processes, the expanding steam drives low pressure turbine attached to an electrical generator. The steam leaves its salt and 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.

3.Hybrid OTEC: A hybrid cycle combines the features of closed and open cycle systems. In a hybrid warm sea water enters a vaccum chamber and flash evaporated, similar to open cycle evaporation process. The steam vaporizes the ammonia working fluid of close cycle loop on the other side of an ammonia vaporize. The vaporized fluid then drives a turbine to produce electricity. The steam condenses within the heat exchanger and provides desalinated water.

UNIT-V ADVANCED CONCEPTS/ TOPICS IN CHEMISTRY

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. It is widely used in the design of new drugs and materials.

Computational chemistry methods range from very approximate to highly accurate; the latter are usually feasible for small systems only.

Molecular motors and machines:

Molecular motors, also called **molecular machines**, are either natural or synthetic **molecules** that convert chemical energy into mechanical forces and motion. An example of a biological **motor** is the protein kinesin, which uses the hydrolysis of adenosine triphosphate to move along microtubule filaments.

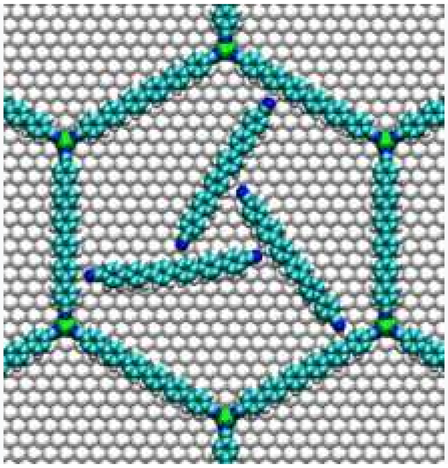
Molecular motors are natural (biological) or artificial molecular machines that are the essential agents of movement in living organisms. In general terms, a motor is a device that consumes energy in one form and converts it into motion or mechanical work; for example, many protein-based molecular motors harness the chemical free energy released by the hydrolysis of ATP in order to perform mechanical work. In terms of energetic efficiency, this type of motor can be superior to currently available man-made motors. One important difference between molecular motors and macroscopic motors is that molecular motors operate in the thermal bath, an environment in which the fluctuations due to thermal noise are significant.

Some examples of biologically important molecular motors-

i. Cytoskeletal motors : Myosins are responsible for muscle contraction, intracellular cargo transport, and producing cellular tension.

ii. Polymerisation motors: Actin polymerization generates forces and can be used for propulsion. ATP is used. Dynamin is responsible for the separation of clathrin buds from the plasma membrane. GTP is used.

iii. Rotary motors: The bacterial flagellum responsible for the swimming and tumbling of *E. coli* and other bacteria acts as a rigid propeller that is powered by a rotary motor. This motor is driven by the flow of protons across a membrane, possibly using a similar mechanism to that found in the F_o motor in ATP synthase.

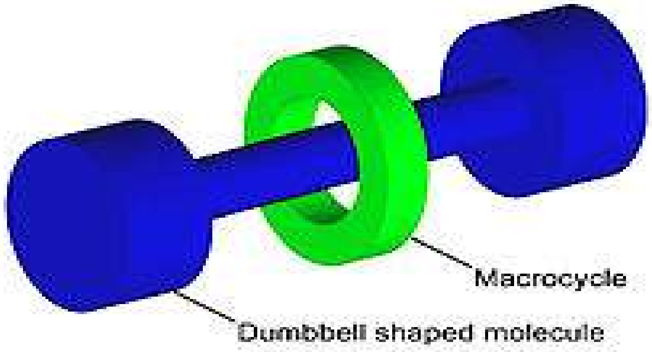


iv. Nucleic acid motors: RNA polymerase transcribes RNA from a DNA template. DNA polymerase turns single-stranded DNA into double-stranded DNA.

v. Enzymatic motors: Catalase, Urease, Aldolase, Hexokinase, Phosphoglucose isomerase, Glucose Oxidase

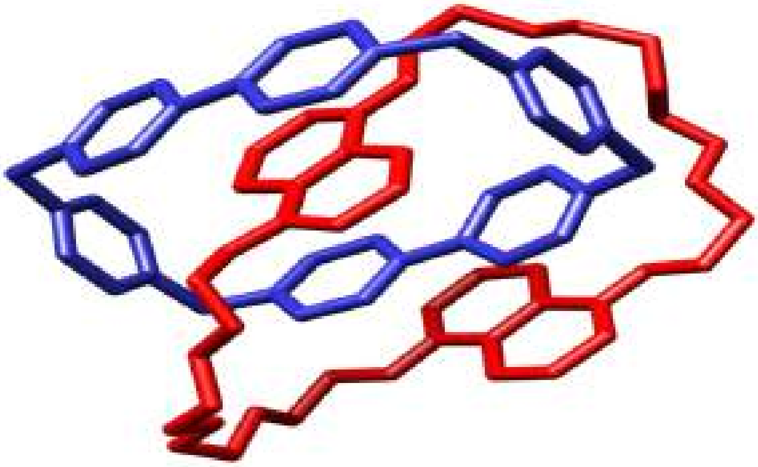
Rotaxanes: A **rotaxane** is a mechanically interlocked molecular architecture consisting of a "dumbbell shaped molecule" which is threaded through a "macrocycle". The name is derived from the Latin for wheel (rota) and axle (axis). The two components of a rotaxane are kinetically trapped since the ends of the dumbbell (often called stoppers) are larger than the internal diameter of the ring and prevent dissociation (unthreading) of the components since this would require significant distortion of the covalent bonds.

Much of the research concerning rotaxanes and other mechanically interlocked molecular architectures, such as catenanes, has been focused on their efficient synthesis or their utilization as artificial molecular machines. However, examples of rotaxane substructure have been found in naturally occurring peptides, including: cystine , cyclotides or lasso-peptides such as microcin



Catenanes:

A **catenane** is a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles, i.e. a molecule containing two or more intertwined rings. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles. Catenane is derived from the Latin *catena* meaning "chain". They are conceptually related to other mechanically interlocked molecular architectures, such as rotaxanes, Recently the terminology "mechanical bond" has been coined that describes the connection between the macrocycles of a catenane.



Prototypes:

A **prototype** is an early sample, model, or release of a product built to test a concept or process. It is a term used in a variety of contexts, including electronics, and software programming. A prototype is generally used to evaluate a new design to enhance precision by system analysts and users. Prototyping serves to provide specifications for a real, working system rather than a theoretical one. In some design workflow models, creating a prototype (a process sometimes called **materialization**) is the step between the formalization and the evaluation of an idea.

Basic prototype categories

Prototypes explore different aspects of an intended design:

- A **Proof-of-Principle Prototype** serves to verify some key functional aspects of the intended design, but usually does not have all the functionality of the final product.
- A **Working Prototype** represents all or nearly all of the functionality of the final product.
- A **Visual Prototype** represents the size and appearance, but not the functionality, of the intended design. A **Form Study Prototype** is a preliminary type of visual prototype in which the geometric features of a design are emphasized, with less concern for color, texture, or other aspects of the final appearance.
- A **User Experience Prototype** represents enough of the appearance and function of the product that it can be used for user research.
- A **Functional Prototype** captures both function and appearance of the intended design, though it may be created with different techniques and even different scale from final design.
- A **Paper Prototype** is a printed or hand-drawn representation of the user interface of a software product. Such prototypes are commonly used for early testing of a software design, and can be part of a software walkthrough to confirm design decisions before more costly levels of design effort are expended.
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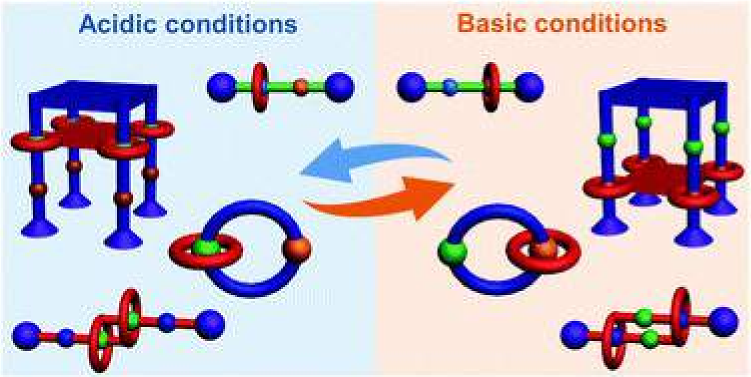
Acid-base controlled molecular shuttle:

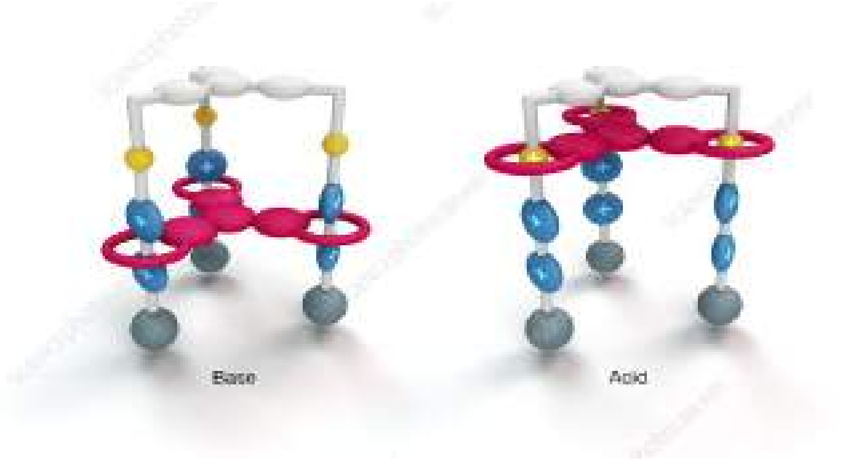
Mechanically interlocked molecules (MIMs), especially rotaxanes and catenanes, allow large-amplitude movement at the molecular level, making them the perfect prototypes for artificial molecular switches and machines. By applying external stimuli, the noncovalent interactions between their subcomponents can be interrupted and formed reversibly, leading to mechanical motions. Among various stimuli, pH stimulation is one of the most powerful and commonly used means of controlling motions by acids and bases. In this review, we summarize the pH-controlled mechanical motions including translocation in rotaxanes, circumrotation in catenanes and other kinds of motion in more sophisticated mechanomolecules, and discuss their operating mechanisms. In addition, we present several more recent developments of alternative stimuli for pH responsive motions.

The system consists of a bistable rotaxane that behaves as an **acid**–**base controlled molecular shuttle**, whose ring component bears a tether ending with a nitrile group. The latter can be coordinated to a ruthenium complex that acts as the load, and dissociated upon irradiation with visible light.



Molecular elevator:

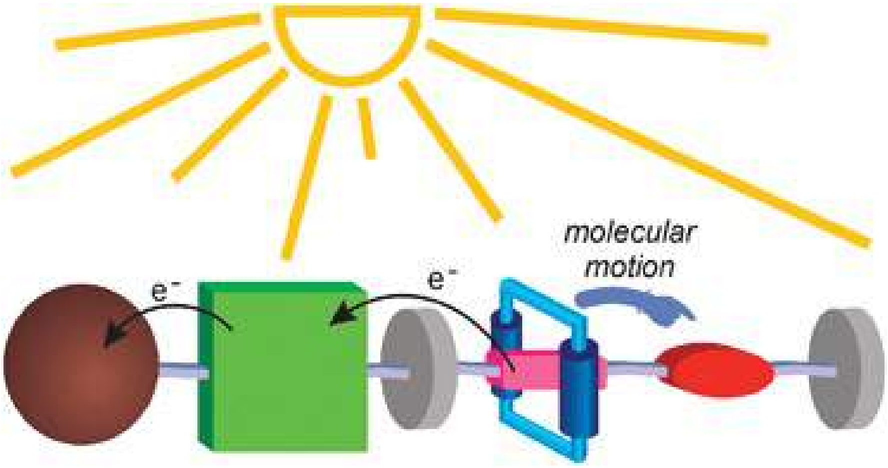
A molecular elevator: The operation of this device, which is made of a platform like component interlocked with a trifurcated ring like component and is only 3.5 nanometers by 2.5 nanometers in size, relies on the integration of several structural and functional molecular subunits. This molecular elevator is considerably more complex and better organized than previously reported artificial molecular machines. It exhibits a clear-cut on-off reversible behavior.



Autonomous light-powered molecular motor:

Able to operate without external intervention (in other words, in a constant environment) as long as the energy source is available. Hence, **autonomous molecular motors** are free-running devices that do not require controlled and repeated addition of chemicals or other environmental changes.

The bottom-up construction and operation of mechanical machines of molecular size is a topic of high interest for nanoscience, and a fascinating challenge of nanotechnology. Like their macroscopic counterparts, nanoscale machines need energy to operate. Although most molecular motors of the biological world are fueled by chemical reactions, light is a very good choice to power artificial molecular machines because it can also be used to monitor the state of the machine, and makes it possible to obtain systems that show autonomous operation and do not generate waste products. By adopting an incrementally staged design strategy, photoinduced processes can be engineered within multicomponent (supramolecular) species with the purpose of obtaining light-powered molecular machines.



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