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I Year - I Semester (R16)

APPLIED CHEMISTRY
(EEE, ECE, CSE, IT, EIE, E. Com. E.)

Knowledge of basic concepts of Chemistry for Engineering students will help them as professional engineers later in design and material selection, as well as utilizing the available resources.

Learning Objectives:

- Plastics are nowadays used in household appliances; also they are used as composites (FRP) in aerospace industries.
- Fuels as a source of energy are a basic need of any industry, particularly industries like thermal power stations, steel industry, fertilizer industry etc., and hence they are introduced.
- The basics for the construction of galvanic cells as well as some of the sensors used in instruments are introduced. Also if corrosion is to be controlled, one has to understand the mechanism of corrosion which itself is explained by electrochemical theory.
- With the increase in demand, a wide variety of materials are coming up; some of them have excellent engineering properties and a few of these materials are introduced.
- Understanding of crystal structures will help to understand the conductivity, semiconductors and superconductors. Magnetic properties are also studied.
- With the increase in demand for power and also with depleting sources of fossil fuels, the demand for alternative sources of fuels is increasing. Some of the prospective fuel sources are introduced.

UNIT I: HIGH POLYMERS AND PLASTICS

Polymerisation : Introduction- Mechanism of polymerization - Stereo regular polymers – methods of polymerization (emulsion and suspension) -Physical and mechanical properties – Plastics as engineering materials : advantages and limitations – Thermoplastics and Thermosetting plastics – Compounding and fabrication (4/5 techniques)- Preparation, properties and applications of polyethene, PVC, Bakelite Teflon and polycarbonates Elastomers – Natural rubber- compounding and vulcanization – Synthetic rubbers : Buna S, Buna N, Thiokol and polyurethanes – Applications of elastomers.

Composite materials & Fiber reinforced plastics – Biodegradable polymers – Conducting polymers.

UNIT II: FUEL TECHNOLOGY

Fuels:- Introduction – Classification – Calorific value - HCV and LCV – Dulong's formula – Bomb calorimeter – Numerical problems – Coal — Proximate and ultimate analysis – Significance of the analyses – Liquid fuels – Petroleum- Refining – Cracking – Synthetic petrol –Petrol knocking – Diesel knocking - Octane and Cetane ratings – Anti-knock agents – Power alcohol – Bio-diesel – Gaseous fuels – Natural gas. LPG and CNG – Combustion – Calculation of air for the combustion of a fuel – Flue gas analysis – Orsat apparatus – Numerical problems on combustion.

Explosives:- Introduction, classification, examples: RDX, TNT and ammonium nitrite - rocket fuels.

UNIT III: ELECTROCHEMICAL CELLS AND CORROSION

Galvanic cells - Reversible and irreversible cells – Single electrode potential – Electro chemical series and uses of this series- Standard electrodes (Hydrogen and Calomel electrodes) - Concentration Cells – Batteries: Dry Cell - Ni-Cd cells - Ni-Metal hydride cells - Li cells - Zinc – air cells.

Corrosion:- Definition – Theories of Corrosion (electrochemical) – Formation of galvanic cells by different metals, by concentration cells, by differential aeration and waterline corrosion – Passivity of metals – Pitting corrosion - Galvanic series – Factors which

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influence the rate of corrosion - Protection from corrosion – Design and material selection – Cathodic protection - Protective coatings: – Surface preparation – Metallic (cathodic and anodic) coatings - Methods of application on metals (Galvanizing, Tinning, Electroplating, Electroless plating)

UNIT IV: CHEMISTRY OF ADVANCED MATERIALS

Nano materials:- Introduction – Sol-gel method & chemical reduction method of preparation – Characterization by BET method and TEM methods - Carbon nano tubes and fullerenes: Types, preparation, properties and applications

Liquid crystals:- Introduction – Types – Applications

Superconductors :- Type-I & Type-2, properties &applications

Green synthesis:- Principles - 3or 4 methods of synthesis with examples – R_4M_4 principles

UNIT V: SOLID STATE CHEMISTRY

Types of solids - close packing of atoms and ions - BCC , FCC, structures of rock salt - cesium chloride- spinel - normal and inverse spinels,

Non-elemental ***semiconducting Materials***:- Stoichiometric, controlled valency & Chalcogen photo/semiconductors, Preparation of Semiconductors - Semiconductor Devices:- p-n junction diode as rectifier – junction transistor.

Insulators (electrical and electronic applications)

Magnetic materials:- Ferro and ferri magnetism. Hall effect and its applications.

UNIT VI: NON CONVENTIONAL ENERGY SOURCES AND STORAGE DEVICES

Solar Energy: - Introduction, application of solar energy, conversion of solar energy (Thermal
conversion & photo conversion) – photovoltaic cell: design, working and its importance

Non-conventional energy sources:

(i) Hydropower include setup a hydropower plant (schematic diagram)

(ii) Geothermal energy: Introduction-schematic diagram of a geothermal power plant

(iii) Tidal and wave power: Introduction- Design and working-movement of tides and their effect on sea level.

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

(v) Biomass and biofuels

Fuel cells:- Introduction - cell representation, H_2-O_2 fuel cell: Design and working, advantages and limitations. Types of fuel cells: Alkaline fuel cell - methanol-oxygen - phosphoric acid fuel cells - molten carbonate fuel cells.

Outcomes: The advantages and limitations of plastic materials and their use in design would be understood. Fuels which are used commonly and their economics, advantages and limitations are discussed. Reasons for corrosion and some methods of corrosion control would be understood. The students would be now aware of materials like nano-materials and fullerenes and their uses. Similarly liquid crystals and superconductors are understood. The importance of green synthesis is well understood and how they are different from conventional methods is also explained. Conductance phenomenon is better understood. The students are exposed to some of the alternative fuels and their advantages and limitations.

Standard Books:

1. Engineering Chemistry by Jain and Jain; Dhanpat Rai Publicating Co.
2. Engineering Chemistry by Shikha Agarwal; Cambridge University Press, 2015 edition.

Reference Books:

1. Engineering Chemistry of Wiley India Pvt. Ltd., Vairam and others, 2014 edition (second).
2. Engineering Chemistry by Prasanth Rath, Cengage Learning, 2015 edition.

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3. A text book of engineering Chemistry by S. S. Dara; S. Chand & Co Ltd., Latest Edition
4. Applied Chemistry by H.D. Gesser, Springer Publishers
5. Text book of Nano-science and nanotechnology by B.S. Murthy, P. Shankar and others, University Press, IIM

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UNIT-I

HIGH POLYMERS & PLASTICS

POLYMERS

Polymers are made of two Greek words:

"poly" means many and "mers" means unit or part.

*"A polymer is a high molecular weight compound formed by joining of a large number of a small units".

*"The process is joining together of a large number of simple small molecules to form very big molecules is termed as POLYMERISATION".

*Small molecules that combine with each other to form a polymer are known as MONOMERS.

Example: polythene.

n $CH_2 = CH_2$ → $\{CH_2\text{-}CH_2\}_n$

Ethylene polythene

(monomer) (polymer)

*Homo polymer: A polymer that is obtained from only one type of monomer.

*Co polymer: A polymer that is obtained from only one type of monomers.

Eg:

Nylon6,6 (Poly hexamethylene adipate)

Its monomers;

a) Adipic acid ($HOOC\text{-}(CH_2)_4\text{-}COOH$)
b) Hexa methylenediamine($H_2N\text{-}(CH_2)_6\text{-}NH_2$)

Polymerization:

The process of joining together of a large number of simple small molecules to form very big molecules is termed as polymerization.

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TYPES OF POLYMERISATION:

In 1929 W.H. Carothers categorized the polymerization reactions in to two types.

i) Addition polymerization.
ii) Condensation polymerization.

i) Addition polymerization:

Addition polymerization is obtained by linking together the monomer molecules by achain reaction to give a polymer, whose molecular weight is exactly an integral multiple of the monomer. It is also known as 'chain growth polymerization.'

Eg: polythene.

Polythene is obtained by the polymerization of ethylene.

*A single monomer is involved in addition polymerization and hence the polymer is a homo polymer.

* Addition polymerization reaction is usually induced by light, heat or a catalyst, for opening the double bond of monomer and creating the reactive sites.

COPOLYMERISATION:

Addition polymer involving the mixture of two or more suitable monomers gives a copolymer and the process is called copolymerization.

Eg: A synthetic rubber, GR-S rubber, with elastomeric properties is obtained by copolymerization of styrene and 1, 3butadine.

Copolymers have desirable and different properties compared to the corresponding homo polymers.

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***MECHANISM OF ADDITION POLYMERIZATION:**

Addition or chain growth polymer is the linking of molecules having multiple bonds.

Addition or chain growth polymerization proceeds in three important steps:

i) Initiation step: this step involves the formation of reactive particle.
ii) Propagation step: It consists of a growing polymer chain having reactive particles.
iii) Termination step: In this step the growth of chain is finally terminated.

*polymerization of ethylene and its substituted compound (eg:CH_2=CHX) can be carried out by using any of four mechanisms.

i) Free radical polymerization mechanism.

ii) Cationic mechanism of polymerization.

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iii) Anionic mechanism of polymerization.

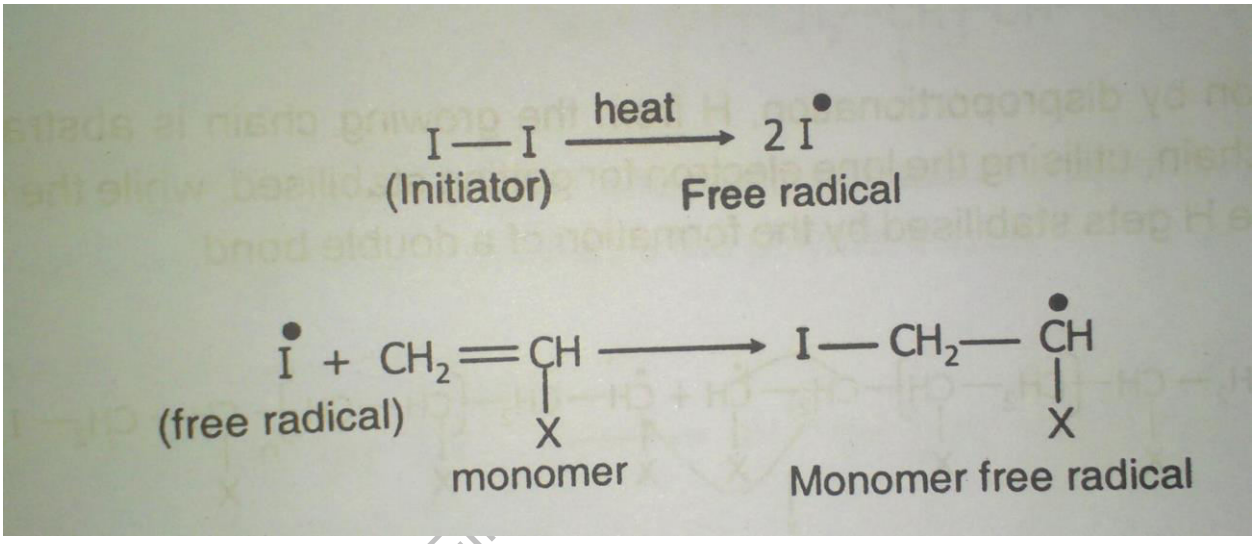
iv)Coordination polymerization or Ziegler-Natta polymerization.

i) FREE RADICALPOLYMERIZATION MECHANISM:

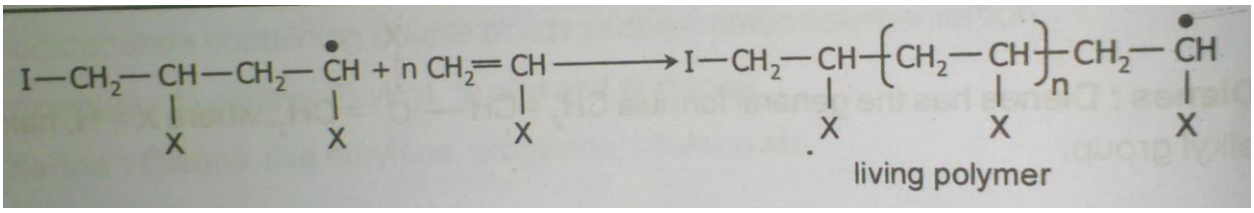
In the frère radical polymerization, monomer is activated by the action of light, heat or by adding chemicals known as initiators.

1) **Initiation step:**
   Initiators are unstable compounds and undergo homolytic fission to produce free radicals which react with π electrons of the monomer to produce monomer free radical.

Benzoyl peroxide, hydrogen peroxide are good initiators for free radical chain polymerization.



2) **progration step:**
   The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a living polymer.



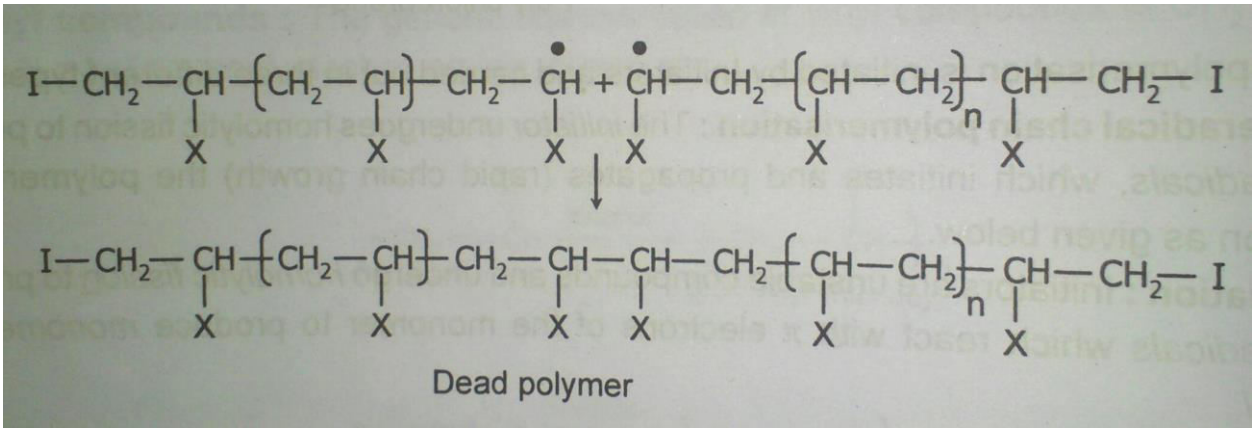
By adding fresh monomers to the living polymer with free radical site, again chain growth starts. Hence it is known as living polymer.

3) **Termination step:**Termination (to stop chain growth) of the polymer chain is carried by 'coupling' and 'disproportionation', resulting the dead polymer.

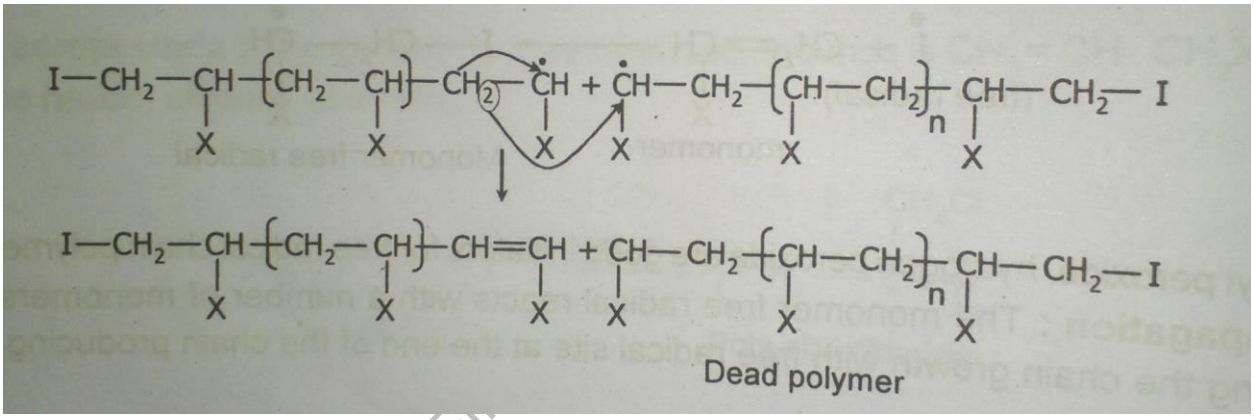
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i) **By Coupling Or Combination:** In which , the collision of the two chains at their free radical site producing a dead polymer.



ii) By Disproportionate: In which one hydrogen atom of one radical center is transformed to another radical center .This results in the formation of two polymer molecules, one saturated and one unsaturated. But this step is very rare.



ii) CATIONIC MECHANISM OF POLYMERIZATION:

In cationic polymerization ,the catalysts used are Lewis acids (electron pair acceptors), such as $Sncl_4$, $Ticl_4$,$Alcl_3$,BF_3 and $H2SO_4$.

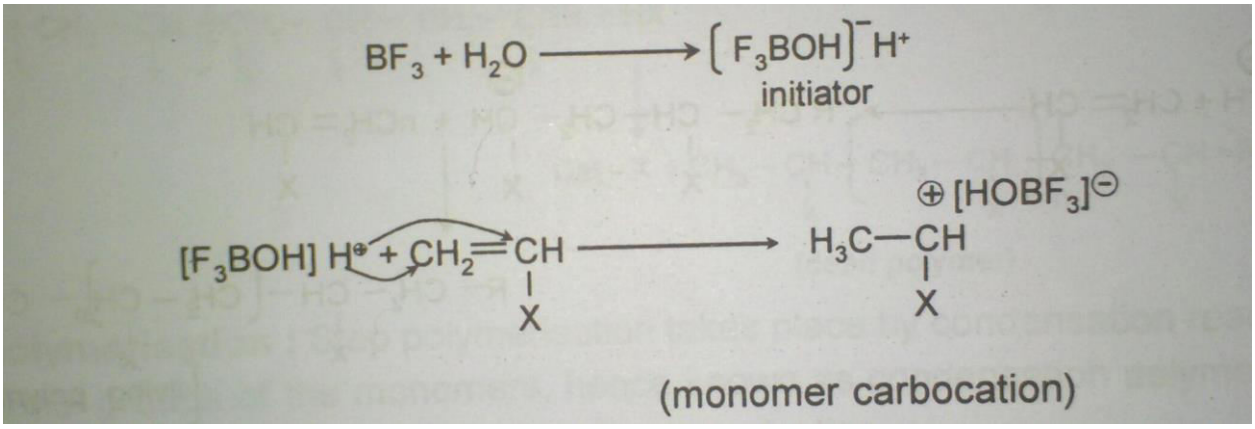
The polymerization proceeds through the formation of the carbocation and chain growth is accompanied with the transfer of the positive charge along with the polymer chains.

Its mechanism involves the following steps:

1) INITIATION STEP: In cationic chain polymerization the cation produced by the initiator attacks the π electrons of the monomer forming a monomer carbonium ion.

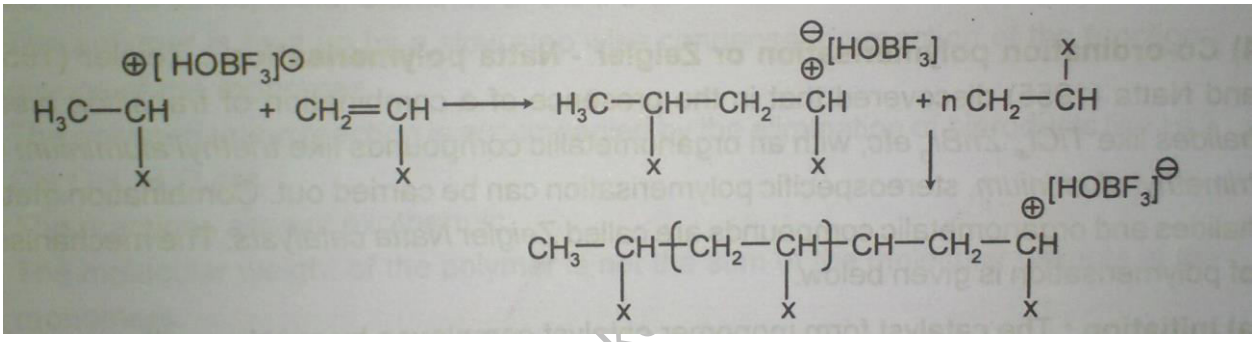
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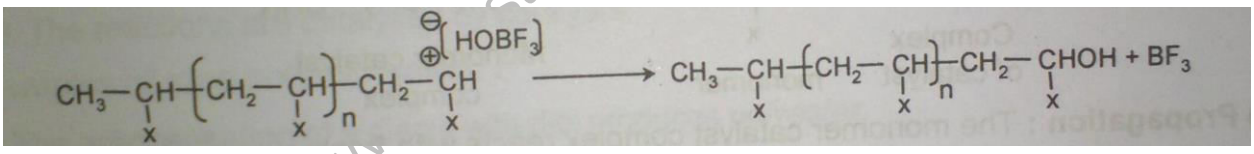


$[HOBF_3]^-$ is called counter ion, because it is always with carbonium ion of the monomer.

2) PROPOGATION STEP: The monomer carbocation attacks the π electrons of the other monomers resulting the chain growth with carbocation at the end of the chain.



3) TERMINATION STEP: Termination of cationic chain polymerization is done by coupling where the OH^- ion the counter ion terminates the polymerization.



iii) ANIONIC MECHANISM OF POLYMERIZATION:

Anionic polymerization involves the formation of carbanion. In these polymerizations, the electron donor catalysts are used.

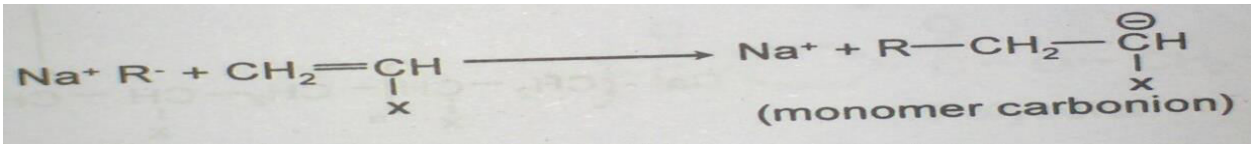
Eg: alkali metals, amides, Grignard reagents.

Its mechanism involves the following steps:

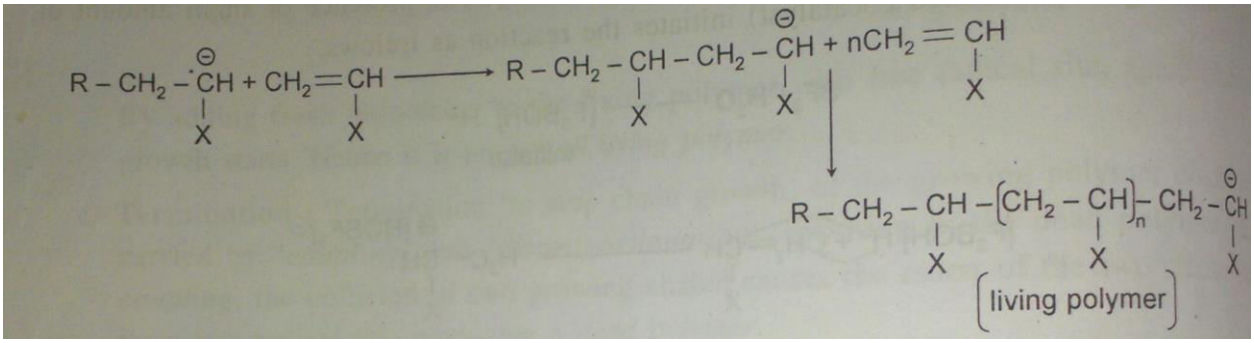
1) Initialization step: An anion produced by the initiator will react with the monomer to produce monomer carbanion.

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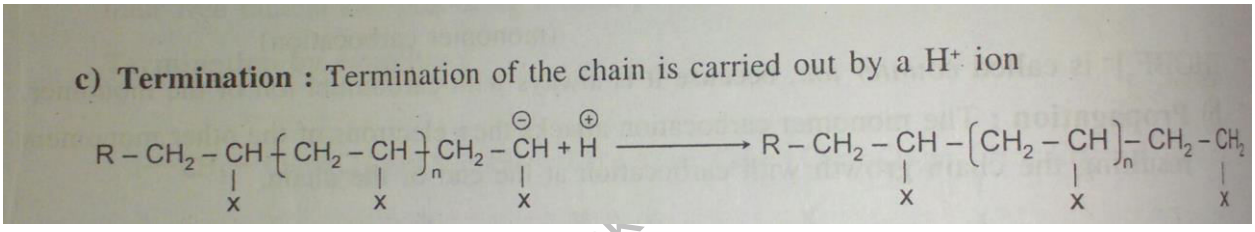
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2) **propogation step:** Attack of the monomers by monomer carbanion results in chain growth as shown below.



3) termination step: Termination of the chain is carried out by a H^+ ion.

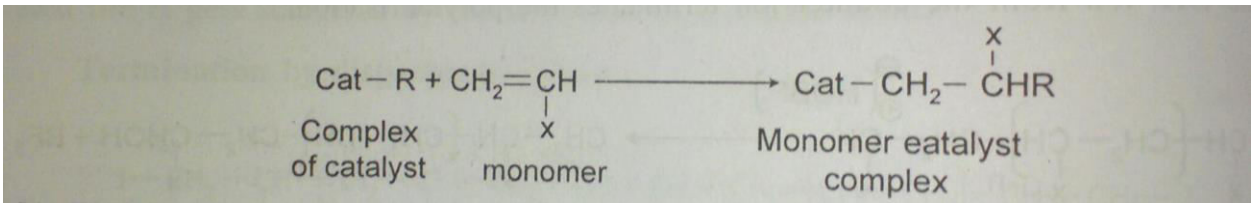


iv) COORDINATION POLYMERISATION:

Ziegler and Natta discovered that in the presence of a combination of a transition metal halide (like $Ticl_4$ or $Ticl_3$, $ZrBr_3$,$Ticl_2$,halides of v , zr ,cr ,mo and w) and an organometallic compound (like triethyl aluminium or trimethyl aluminium), stereospecific polymerization can be carried out.

Its mechanism involves the following steps:

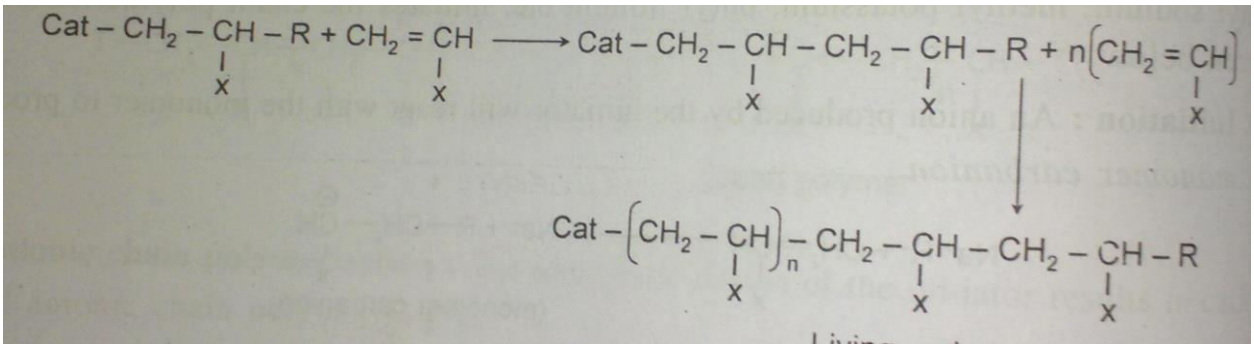
1) **Initialization step:** The catalyst form monomer catalyst complexes by reacting with monomer molecule.



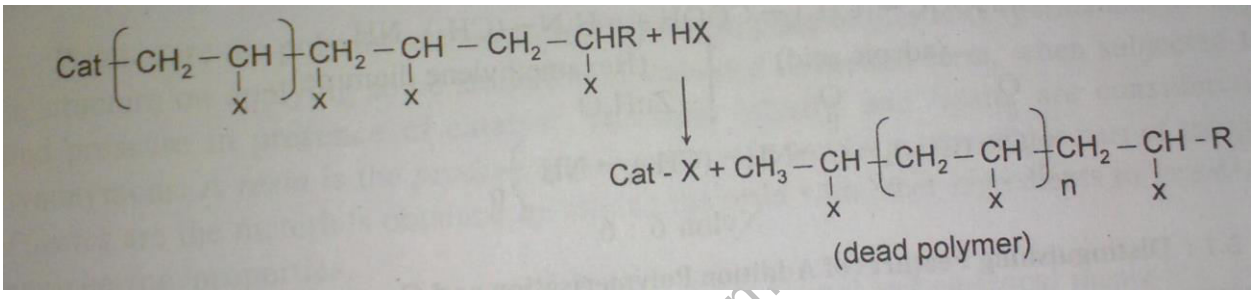
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2) **Propagation step:** The monomer catalyst complex reacts with fresh monomers resulting the chain growth as shown below.



3) Termination step: Termination is carried out with an active halogen compound.



Ziegler- natta polymerization is used to prepare polypropylene, polyethylene, polydiene etc,. the importence of this method lies in the fact that stereospecific polymers are obtained.

ii) condensation polymerization:condensation polymerization (or) step growth polymerization or is a reaction occurring between simple polar group contains monomers with the formation of polymer and elimination of small molecules like water, HCL etc.

Example:-

SYNTHESIS OF NYLON -6,6 (Poly hexamethylene adipote,

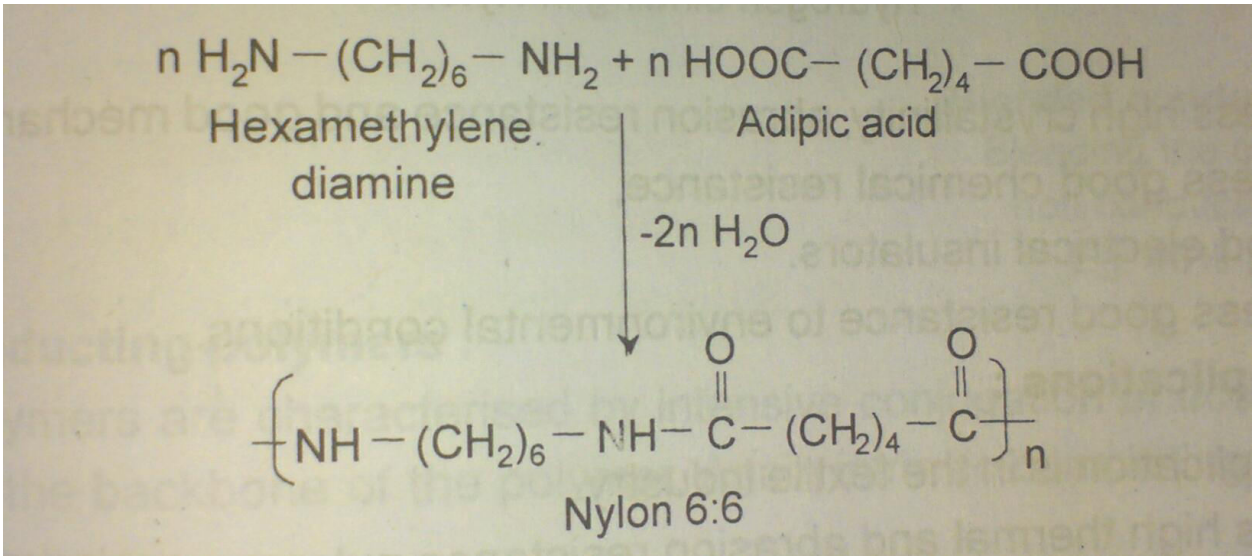
Its monomers,

(a) adipic acid (HOOC-$(CH_2)_4$-COOH)

(b) Hexamethylene diamine (H_2N-$(CH_2)_6$-NH_2)

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RESIN:- a resin is the product of polymerization. i.e., pure polymerisation product is resin.

PLASTIC:- plastics are the materials obtained by the mixing the resin with other ingredients to impart special engineering properties.

Plastics are the polymers characterized by the property of plasticity, moulded to desired form when subjected to heat and pressure in presence of catalyst

Plastics are characterized by light weight, good thermal and electrical insulation, corrosion resist chemical inertness, adhesiveness, easy workability, low fabrication cost, high abrasion resistance ,dimensional stability,strength,toughness and impermeability to water.

The term plastic and resin are considered to be resins.

*The plastic resins are broadly classified in to two categories, they are:

i) Thermo plastics resins.

ii) Thermoset resins.

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i) Thermo plastics resins:

These resins become soft on heating and rigid on cooling.

ii) Thermoset resins:

During fabrications process these resins are moulded .Once they are solidified, they cannot be softened. Plastics are formed when polymer resins are blended with certain external materials known as compounding or moulding ingredients

These ingredients provide sturdiness and other desired characteristics to polymer resins.

****DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSET RESINS****

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Thermoplastic Resins :	Thermoset Resins:
*These are prepared by addition or condensation polymerization process . *They have either linear or branched structures. *Adjacent polymer chains are held together by either vandervaal's forces or by dipole-dipole forces or by H-bonds. *They soften on heating and stiffen on cooling. * Low molecular weight thermoplastics are soluble in their suitable solvents. * They can be remoulded ,re-shaped and re-used. * During moulding ,there is no change in their chemical composition. Eg: Polyethylene, PVC	*These are prepared by condensation polymer polymerization process only. * They have three dimensional, cross linked network structure. * Adjacent polymer chains are held together by strong covalent bonds are called cross-link. *They do not soften on heating. *They are not generally soluble in any solvent. *They can't be remoulded and and hence cannot be re-used. *They undergo chemical changes such as further polymerization and cross-linking during moulding. Ex: nylons, Bakelite

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****COMPOUNDING OF PLASTICS****

Compounding or moulding constituents are:

i)resins ii)plasticizers iii) fillers iv)lubricants v)catalysts vi)accelerators vii)coloring matter.

i)RESIN:

a) The product of polymerization is called resin, and this forms the major portion of the body of plastics.

b) this acts as a binder which holds the different constituents together.

Eg: Thermoplastic and thermoset resins.

ii) PLASTISIZERS:

*Plasticizers increase plasticity and flexibility of the polymer.

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*plasticizers neutralize the intermolecular forces of attraction between polymer chains .Plasticizers decrease the strength and chemical resistance.

Eg: vegetables oils, camphor,esters, of steric acid, trycresyl phospate and trivinyl phosphate etc.,

iii) FILLERS:

*Fillers give better hardness , tensile strength, opacity, finish and workability and plastics.

*Fillers reduce the cost of the polymers.

*They reduce the shrinkage of the polymer on setting.

*Fillers reduce the brittleness of polymers.

*Some special types of fillers are added to impart special properties to polymer likebarium salts make polymers impermeable to X-rays and asbestos provides heat and corrosion resistance to polymers.

Eg:

*Wood flour, gypsum, saw dust, marble flour , paper pulp cotton fibres and metallic oxides like ZnO and PbO.

*Reinforced fillers are those which enhance the mechanical strength of the plastics.

iv) LUBRICANTS:

*Lubricants make moulding of plastic easier.

*They impart flawless, glossy, finish to the products.

*Lubricants prevent moulded article from sticking to the fabrication equipment.

Eg: waxes, oils, stearates, oleates, and soaps.

v) CATALYST OR ACCELERATORS:

They accelerate the polymerization of fusible resin during moulding operation in to cross linked infusible form for thermosetting resins.

Eg.Benzoyl peroxide, hydrogen peroxide, acetyl sulphuric acid, metals like silver ,copper & leadand metal oxide like zinc oxide.

vi) STABILIZERS:

*stabilizers improve thermal stability during polymerization.

Eg.White lead, lead chromate, red lead, stearetes, of lead, cadmium and barium.

vii) COLOURING MATERIALS:

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*The coloring agents in the form of organic dyes and opaque inorganic pigments when added to powered plastics, provide pleasing and decorative color.

Name of the pigment used	Imparted colour
Ultramarine	Blue
Carbon black	Black
Calcium carbonate	White
Chromium trioxide	Green
Ferric oxide	Red

FABRICATION OF PLASTICS:-

Depending on the type of resin, whether thermoplastic or thermo set, many methods of fabrication of plastics are used.

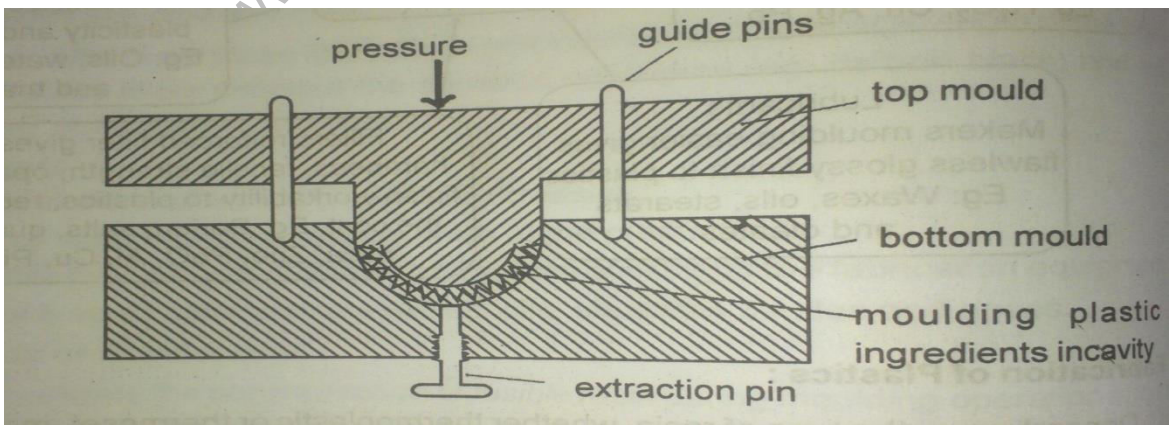
Some of them are,

1. Compression moulding
2. Injection moulding.

1. COMPRESSION MOULDING:

This method is applied to both thermo plastic and thermo setting resins. A desired quantity of compounded plastics resin is filled in the cavity present in the bottom mould, the top mould and bottom mould are capable of being moved relative to each other. When heat and pressure are applied according to specifications, the cavities get filled with fluidized plastic. The two moulds are closed tightly and curing is done either by heating in case of thermo set plastic resins or by cooling in case of thermoplastic resins. After curing the moulded article is taken out by opening the mould.

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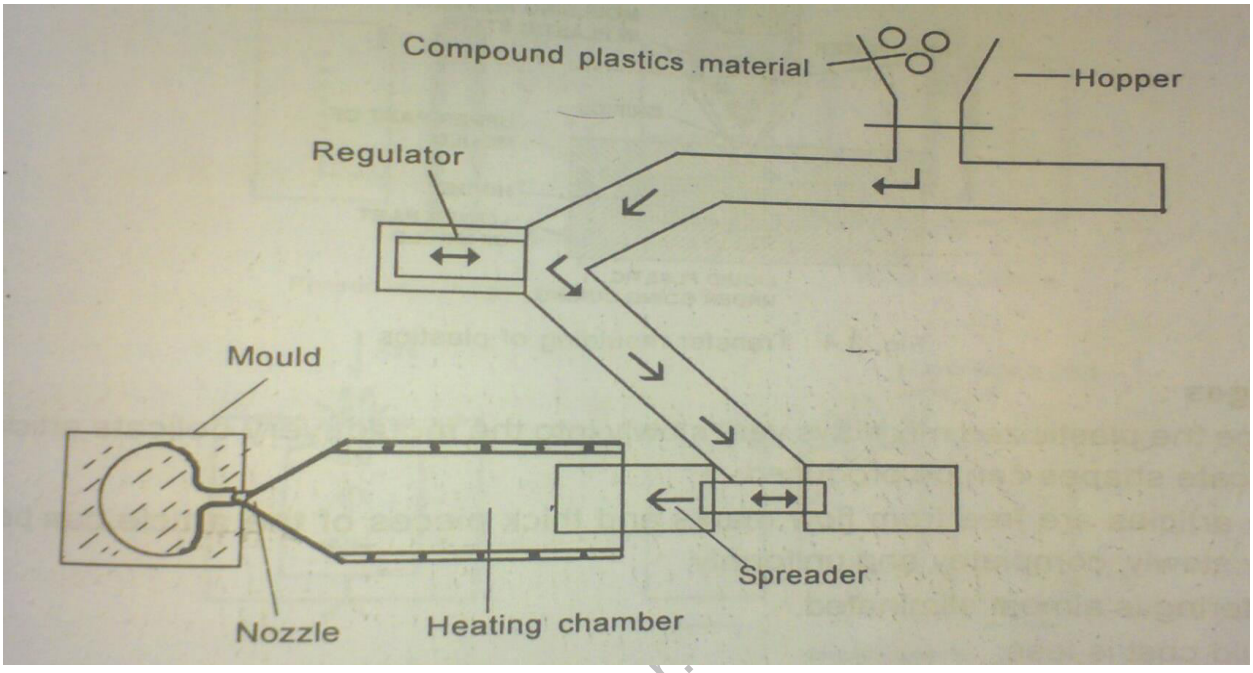
This method is used commonly for manufacture of cylinders, gears handles etc.

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2. INJECTION MOULDING:

Injection moulding is generally carried out for the fabrication of thermoplastic resins. The compounded plastic material is added from a hopper from where they move through a tube having proper dimensions for the accurate quantities to be charged to the lower cylinder as shown in the figure.



The plunger moves to and fro in the cylinder to send the plastics material into the spreader in a heating chamber where the materials are converted to viscous liquid pushed through the nozzle into cold mould maintained at room temperature. The molten thermoplastics material sets in the mould which is sometimes water cooled and proper pressure is maintained. The finished article is taken out by opening the mould.

ADVANTAGES OF INJECTION MOULDING:

1. This method is characterized by high speed production and low mould cost.
2. Loss of materials is less.

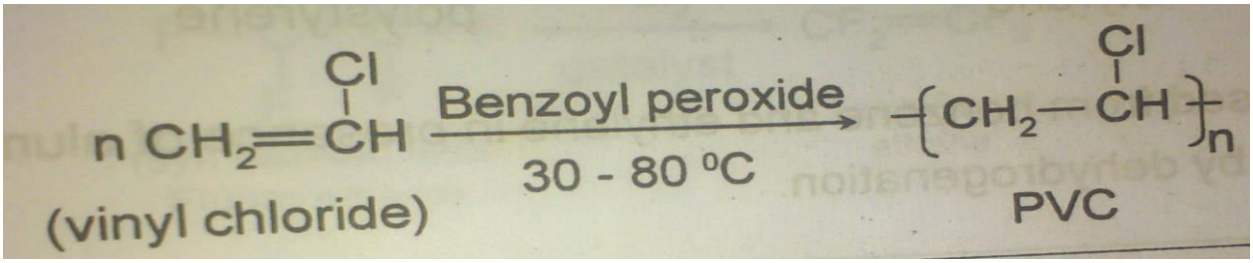
PREPARATION, PROPERTIES AND ENGINEERING APPLICATIONS OF PVC, TEFLON AND BAKELITE:

1.POLY VINYL CHLORIDE (PVC):

Poly vinyl chloride is produced by free radical chain polymerization of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide.

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PROPERTIES:

1. PVC is a colourless, non-inflammable and chemically inert powder.
2. It has specific gravity 1.33 and M.P. 148^0C.
3. Resistant to atmospheric conditions.
4. It is strong and brittle.
5. It is resistant to atmospheric conditions like O_2, CO_2 and moisture.
6. PVC is not stable to heat and U.V radiation. It undergoes degradation.

ENGINEERING APPLICATIONS:

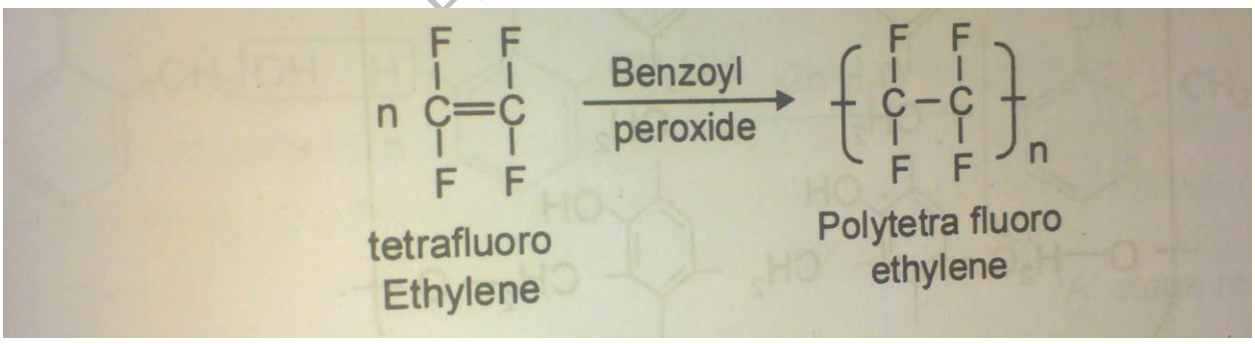
PVC treated with plasticizers is called plasticized PVC is used for electrical insulations, injection moulding articles like tool handles, radio and telephone components, chemical containers, and foams used in buildings, cameras and air crafts.

Unplasticized PVC is rigid, highly resistant to chemicals and brittle. It is used for making safety helmets, refrigerator components, tyres, cycle and motor cycle mudguards.

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2.TEFLON:

Teflon is obtained by the chain polymerization of tetrafluoroethylene in the presence of benzoyl peroxide as an initiator.



PROPERTIES:

Due to the presence of highly electronegative fluorine atoms, TEFLON has got

1. High M.P. (>350^0C)
2. Exceptionally high chemical resistance (except hot alkali metals and fluorine).
3. High density 2.1 to 2.3 gm/cc.

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4. It is very strong, hard polymer that can be machined to drilling, punching etc.
5. It is a very good electrical insulator.
6. It possess very good abrasion resistance.

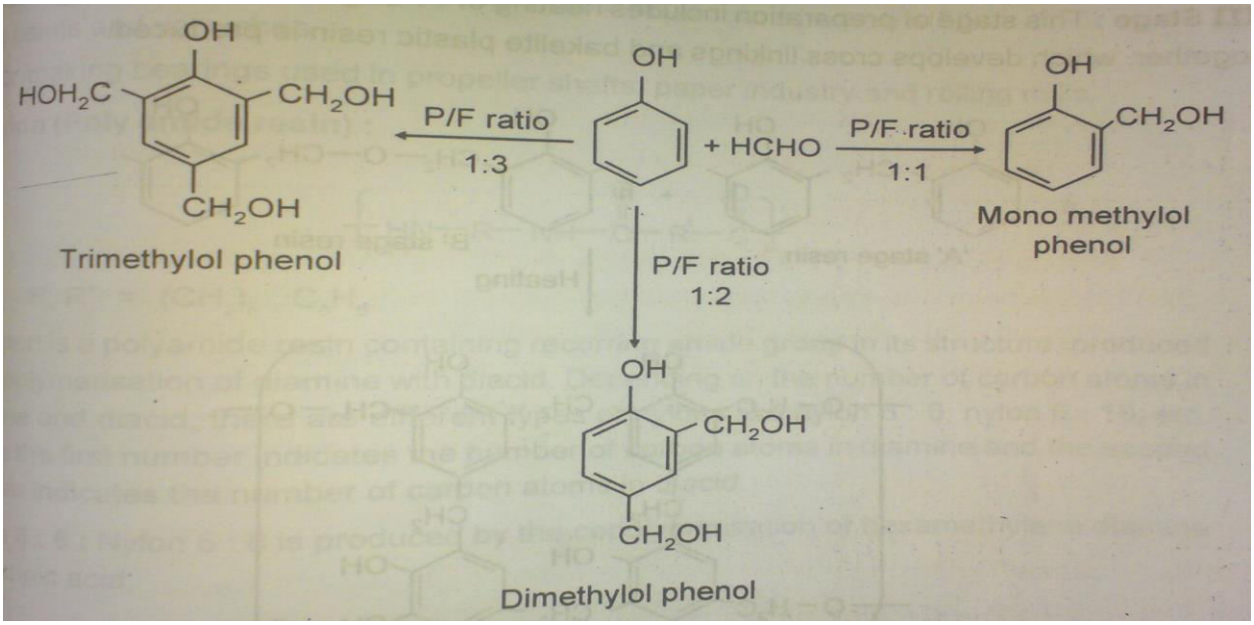
ENGINEERING APPLICATIONS:

1. It is a very good insulating material for motors, transformers, cables, wires etc.
2. It is used for making gaskets, pump parts, tank linings, tubing etc.
3. Due to its extreme chemical resistance, it is used for making chemical carry pipes.
4. Non-lubricating bearings and non-stick stop cock for burettes are made from TEFLON.

3.BAKELITE (OR) PHENOL – FORMALDEHYDE RESIN:

It is an important thermoset resin prepared by the step polymerization of phenol with formaldehyde in presence of an acid or alkali as a catalyst. This polymerization reaction takes place in 3 stages.

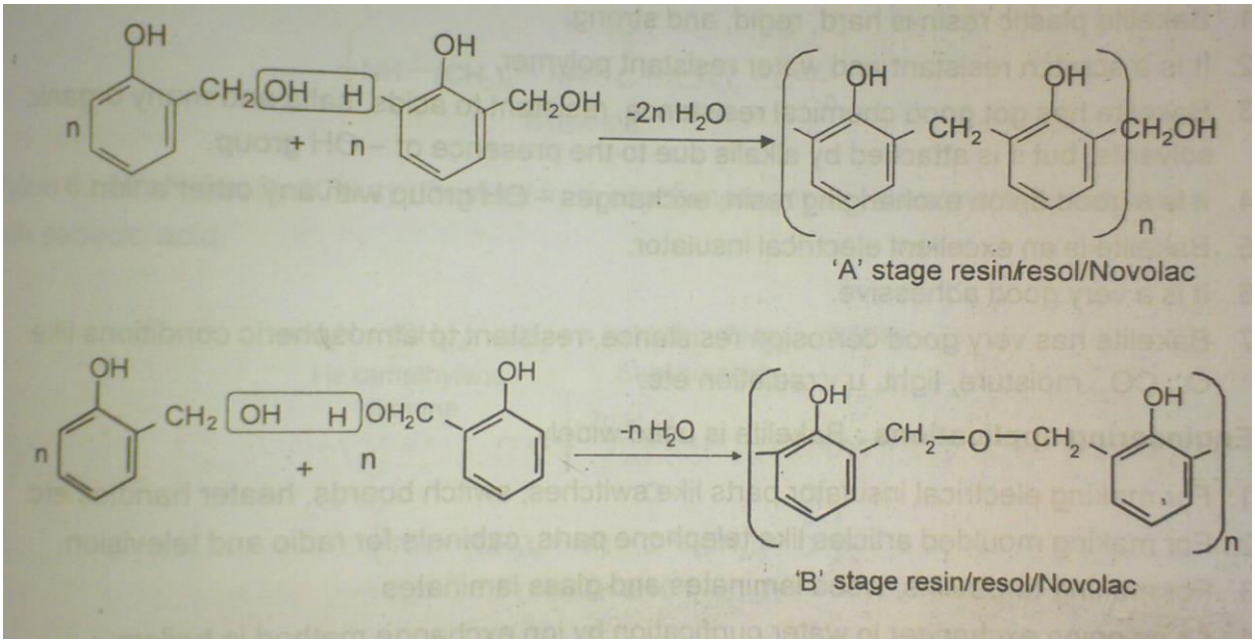
Stage 1: phenol is made to react with formaldehyde in the presence of acid / alkali to produce non-polymeric mono, di and tri methylol phenols depending on phenol – formaldehyde ratio (P/F ratio).



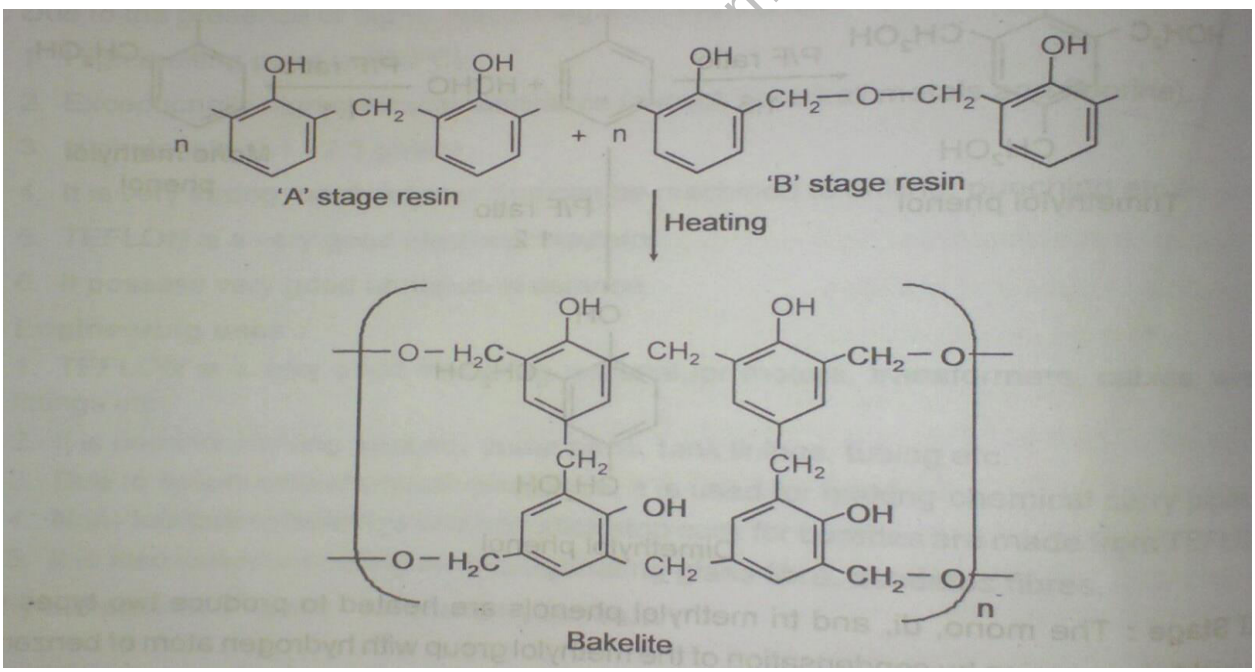
Stage 2: The mono, di and tri methylol phenols are heated to produce two types of straght chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.

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Stage 3: This stage of preparation includes heating of A stage resin and B stage resin together, which develops cross linkings and Bakelite plastic resin is produced.



PROPERTIES:

1. It is hard, rigid and strong.
2. It is a scratch resistant and water resistant polymer.
3. It has got good chemical resistance, resistant to acids, salts and many organic solvents, but it is attacked by alkalies due to the presence of - OH group.

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4. It is a good anion exchange resin.
5. It is an excellent electrical insulator.
6. It is a very good adhesive.

ENGINEERING APPLICATIONS:

Bakelite is used widely,

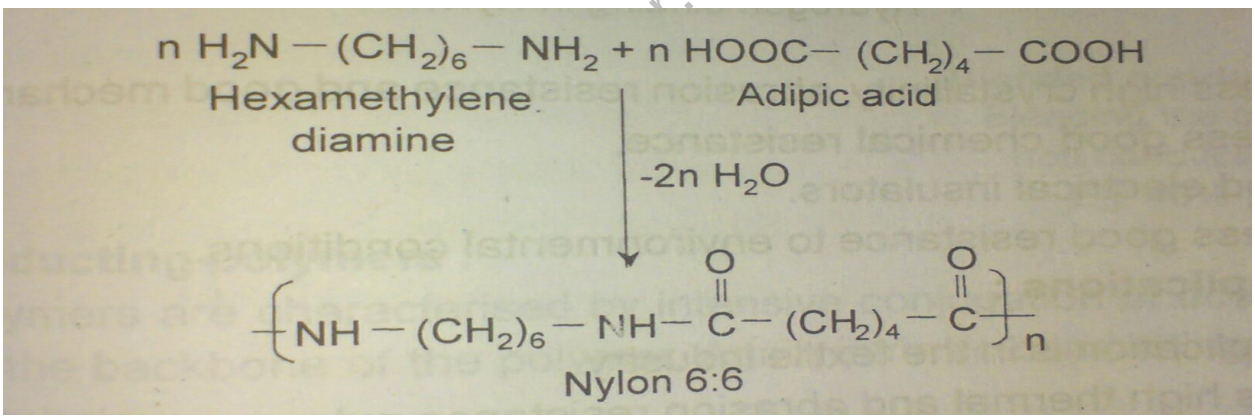
1. For making electrical insulator parts like switches, swtch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange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

FIBERS:

Those polymers which can be drawn in the form of filaments with high tensile strength, rigidity or stiffness and irreversible deformation are called fibers. These fibers possess high crystallisability and high melting points.

1.NYLON -6,6:

It is produced by the copolymerization of hexamethylene diamine with adipic acid.



PROPERTIES:

1. Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of the amide group (-NH) and oxygen of the C=O group.
2. They possess high crystallinity, abrasion resistance and good mechanical properties.
3. They possess good chemical resistance.
4. They are good electrical insulators.
5. They possess good resistance to environmental conditions.

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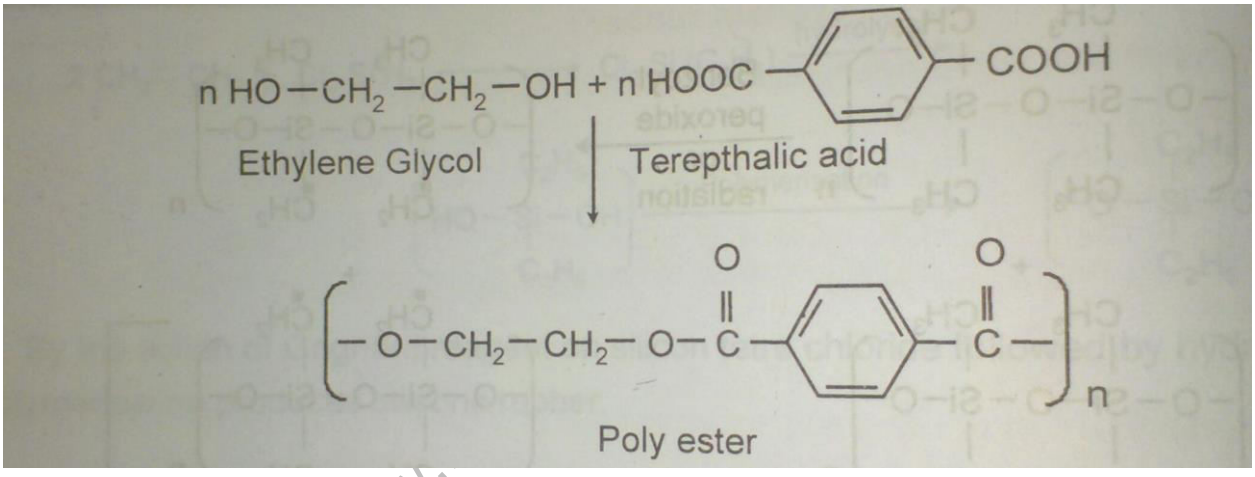
ENGINEERING APPLICATIONS:

1. The major application is in the textile industry.
2. Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.
3. Flexible tubings for convaying petrol etc are made from nylons.
4. Nylons are used as electrical insulators.
5. Nylons are used in auto mobile industry and telecommunication industry for making radiator parts and coil formers respectively.

2.DACRON:

Dacron is a saturated polyester otherwise known as terene or terylene.

The step polymerization of a diacid and dialcohol produces Dacron. The saturated polyeter is formed by the condensation polymerization of ethylene glycol with terepthalic acid.



PROPERTIES:

1. The fibers have high strtch resistance, high crease and wrinkle resistance.
2. Highly resistant to mineral acid.
3. It does not hold water.
4. It is very easy to dye.
5. It can be blended with wool, silk etc.
6. These are strong with good abrasion resistance.

APPLICATIONS:

1. It is used both as domestic fiber and industrial fiber.
2. Industrial application is to make nylon tyres.
3. It is used in the textile industry for making synthetic fibers.
4. It is blended with wool and cotton to provide better finish, wrinkle resistance enhanced life and resistance to acids and bases.

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FIBER REINFORCED PLASTICS (FRP):

Fiber reinforced plastics are produced by reinforcing a plastic matrix with a high strength fiber materials such as glass, graphite, alumina, carbon, boron, berylium and aromatic polyamide.

Natural fibers such as sisal, asbestos are also used for reinforcement.

Glass fiber is the most extensively used reinforced fiber because of durability, acid proof, water proof and fire proof nature of glass.

APPLICATIONS OF FRP:

Fibre reinforced plastics find extensive use in space crafts, aeroplance, boat hulls, acid storage tanks, motor cars, and building materials. Malamine FRP is used for insulation and making baskets.

Advantages of FRP : The fibre reinforced plastics have the following advantages.

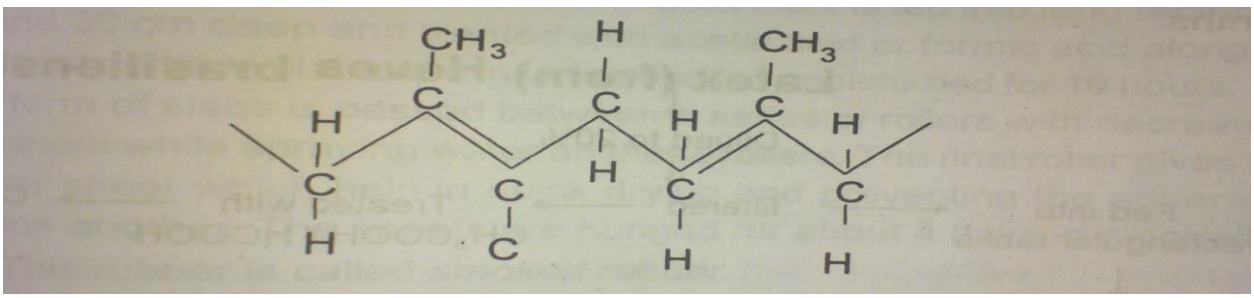
1. Low efficient of thermal expansion.
2. High demensional stability.
3. Low cost of production.
4. Good tensile strength.
5. Low dielectric constant.
6. Non inflammaaility and corrosion and chemical resistance.

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RUBBER- NATURAL RUBBER & ITS VULCANIZATION:

Those polymers which possess the property of elasticity is called rubber.

Natural rubber is processed from the cell sap (latex) of trees/ plants. The main composition of natural rubber is poly isoprene, which is in the form of long coiled chains, responsible for the elasticity of natural rubber.

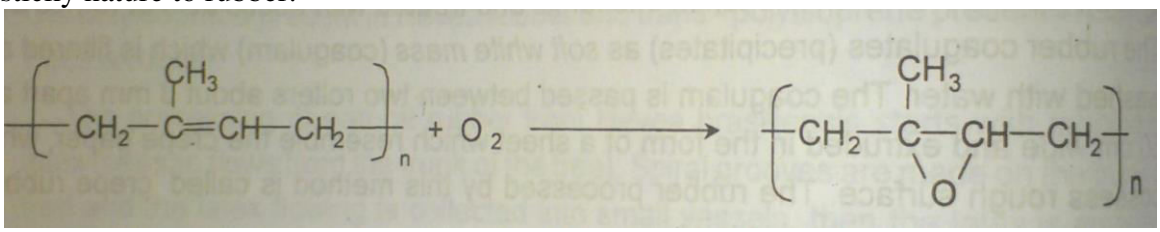


VULCANIZATION OF RUBBER:

The natural rubber extracted from the trees or plants has got some disadvantages as listed below.

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1. It is soft & plastic in nature.
2. It swells in water and easily attacked by organic solvents, acids, bases and non polar solvents like mineral oils, benzene and gasoline.
3. It posseses poor tensile strength.
4. Atmospheric oxygen attacks the rubber and produces epoxides which gives bad smell, sticky nature to rubber.



5. The rubber possess tackiness i.e., when two fresh raw rubber sheets were pressed together, they coalese to form a single sheet.
6. When stretched to a great extent, it suffers permanent deformation due to sliding or slippage of some molecular chains over each other.
7. It is attacked by atmospheric oxygen, CO_2, moisture, light, U.V radiation etc. and gets less durability.

To improve the properties of rubber, Charles Good in 1839 compounded the raw rubber with some chemicals and heated to 100^0C to 140^0C. Finally the compounded and vulcanized rubber is drawn in the form of sheet by calendering process.

Compounding & vulcanization:

The following are the materials adde to natural rubber.

1.vulcanizers:

Some chemicals like elemental sulphur, H_2S, SCl_2, benzoyl chloride and ZnO are added to both natural & synthetic rubbers.the most important vulcanizer is sulphur which combines chemically at the double bonds of the different chains producing sulphur cross linkings.

The percentage of sulphur added is in the range of 0.5 to 35%. For example the rubber used for making tyres contains 3-5% of sulphur and for making battery case the rubber contains 30% of sulphur. If the percentage of sulphur is more than 32, that rubber is called ebonite or vulcanite or hard rubber for some special purposes.

2.Plasticizers:

Plasticizers are also called as softners, which impart greater plasticity and adhesion to the rubber. The most commonly used plasticizers are vegetable oils, waxes, rosin etc.

3.Accelerators:

They catalyse the vulcanization process by reducing the time required for vulcanization. Most commonly used accelerators are litharge, magnesia and white lead. Generally 0.5 to 1% of acceleratirs are added. ZnO is also added which acts as an activator to accelerators.

4.Anti oxides:

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They retard the deterioration of rubber by light and air. Complex organic amines like phenylnaphthylamine, phenolic substances and phosphites are added as antioxides.

5.Reinforcing agents:

They give strength, rigidity, and toughness to the rubber and may form as much as 35% of rubber compound. Commonly used reinforcing agents are ZnO, $MgCO_3$, $BaSO_4$ and $CaCO_3$.

6.Colouring agents:

They impart desired color to the rubber as follows.

Lithophane, TiO_2 - white,

Lead chromate – yellow,

Carbon black – black,

Ferric oxide – red,

Chromium trioxide – green.

ADVANTAGES OF VULCANIZATION:

1. Vulcanised rubber has good tensile strength and load bearing capacity.
2. It has good elasticity depending on the extent of vulcanization.
3. It possesses low water absorption tendency.
4. Vulcanized rubber has higher resistance to oxidation and atmospheric gases like O_2, CO_2, moisture, light and UV radiation.
5. Vulcanized rubber is a good electrical insulator and ebonite is a best electrical insulator.
6. The abrasion resistance of natural rubber increases tremendously.
7. The resistance towards organic solvents and chemicals increased.
8. Vulcanized rubber possesses good impact resistance.
9. Vulcanized rubber possesses very good resilience i.e., the article made from it returns to original shape, when the deforming load is removed.

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APPLICATIONS OF NATURAL RUBBER:

1. The major application of natural rubber is in the manufacturing of tires.
2. It is used for preparing belts for power transmission and several types of materials like non-slipping, clean and shock absorbing.
3. The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.
4. To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.
5. Foamed rubber is used for making cushions, mattresses etc.
6. Toys and sports items are manufactured from natural rubber.

ELASTOMERS:

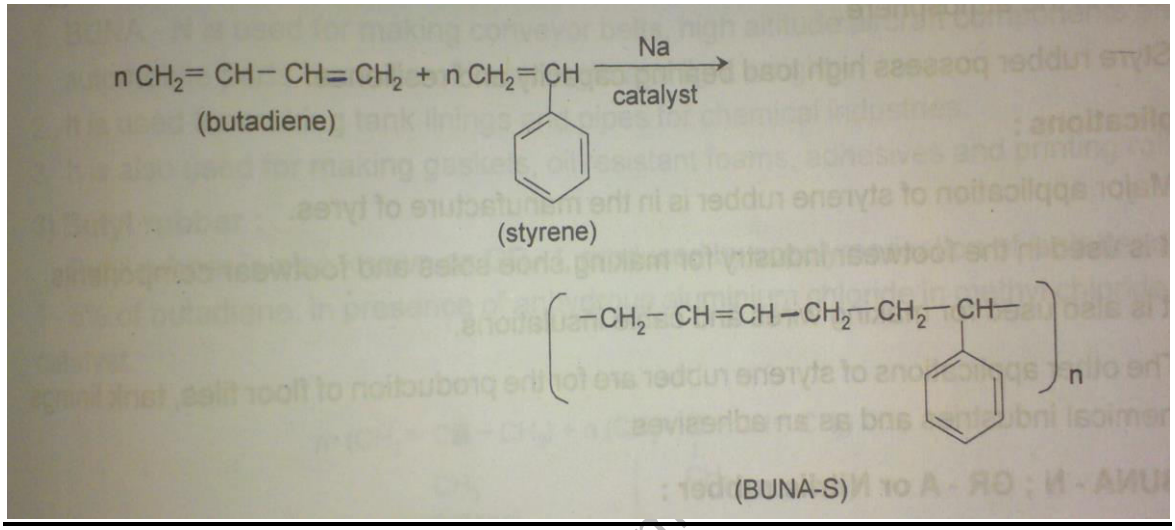
1.BUNA-S:

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BUNA-S is otherwise called *styrene rubber* or *GRS* (Government Rubber Styrene) or *Ameripol.* BUNA-S stands for the composion 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 copolymerisation of butadience with styrene using sodium as a catalyst.



PROPERTIES:

1. *Styrene rubber* is a strong and tough polymer.
2. it is vulcanised by sulphur monochloride ($S_2 CI_2$) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA – S possess excellent abrasion resistance.
5. It is resistant to chemicalls but swell in oils and attacked by even traces of ozone, present in the atmosphere.

APPLICATIONS:

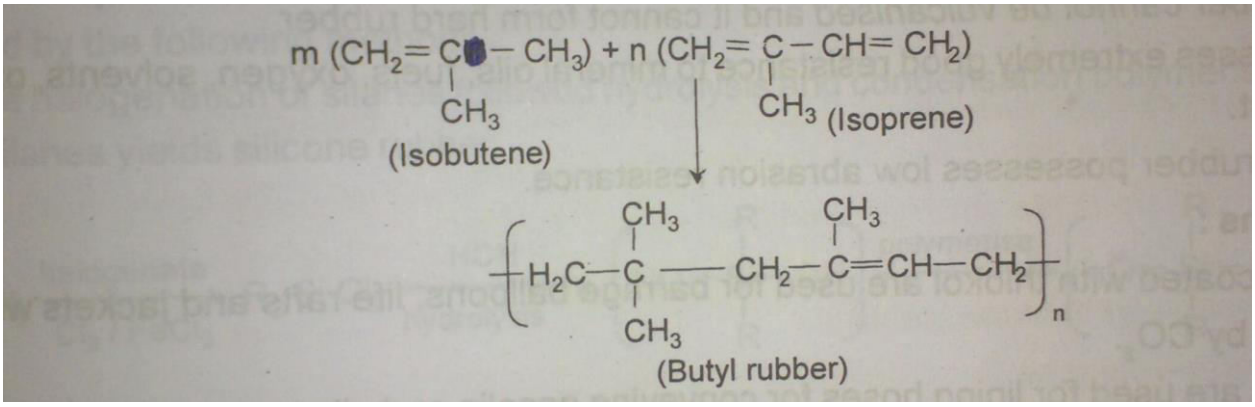
1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear componets.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor files, tank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

2. BUTYL RUBBER:

Butyl rubber is also known as GR-I, produced by copolymerization of iso butene with isoprene in presence of anhydrous aluminium chloride in methyl chloride as a catalyst.

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PROPERTIES:

1. It is a strong and tough synthetic rubber with low permeability to air and other gases.
2. It has excellent resistance to heat, abrasion, ageing and chemicals such as inorganic acids, polar solvents, but soluble in hydrocarbon solvents like benzene.
3. It possesses high abrasion resistance.
4. High resistance is to atmospheric gases and especially to ozone is possessed by butyl rubber.
5. It is a good electrical insulator.
6. It can be vulcanized with sulphur, but it possesses low hardness due to less number of double bonds.

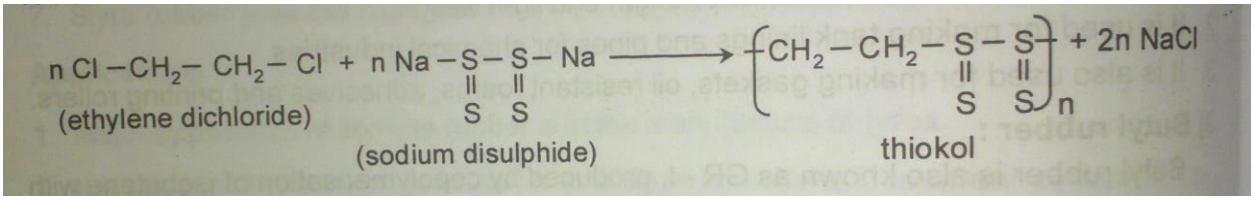
APPLICATIONS:

1. It is used for making cycle tyres and auto mobile tubes.
2. It is used for making automobile parts, and conveyer belts in food processing industry.
3. It is used as an insulator for high voltage wires and cables.
4. In chemical industries butyl rubber is used for making the linings of the tanks where chemicals are stored.

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3. THIOKOL RUBBER (OR) POLYSULPHIDE RUBBER (OR) GRP:

Thiokol rubber can be prepared by the copolymerization of sodium poly sulphide and ethylene dichloride.



PROPERTIES:

1. It possess strength and impermeability to gases.
2. It cannot be vulcanized and it cannot form hard rubber.
3. It possesses extremely good resistance to mineral oils, fuels, oxygen, solvents, ozone and sun light.

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4. Thiokol rubber possesses low abrasion resistance.

APPLICATIONS:

1. Fabrics coated with Thiokol are used for barrage balloons and jackets which are inflated by CO_2.
2. Thiokols are used for lining hoses for conveying gasoline and oil.
3. It is used for making gaskets and seals for printing rolls.

CONDUCTING POLYMERS:

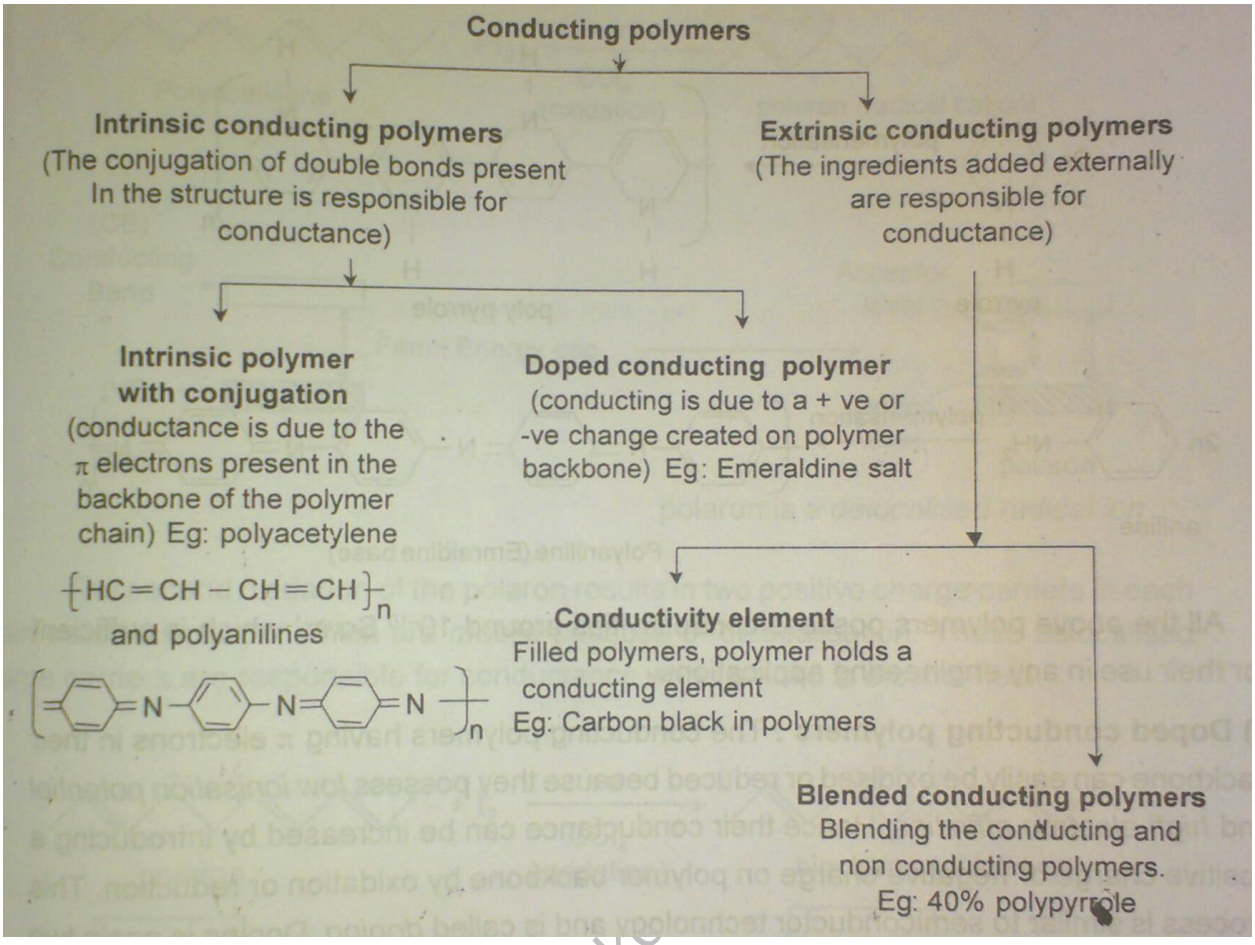
Those polymers which conduct electricity are called conducting polymers.

The conduction of polymer may be due to unsaturation or due to the presence of externally added ingrediants in them.

CLASSIFICATION OF CONDUCTING POLYMERS:

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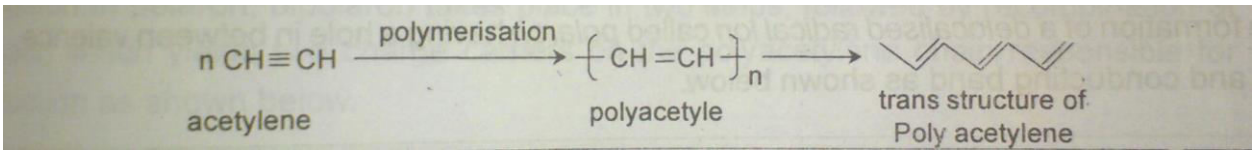
Intrinsic conducting polymers:-

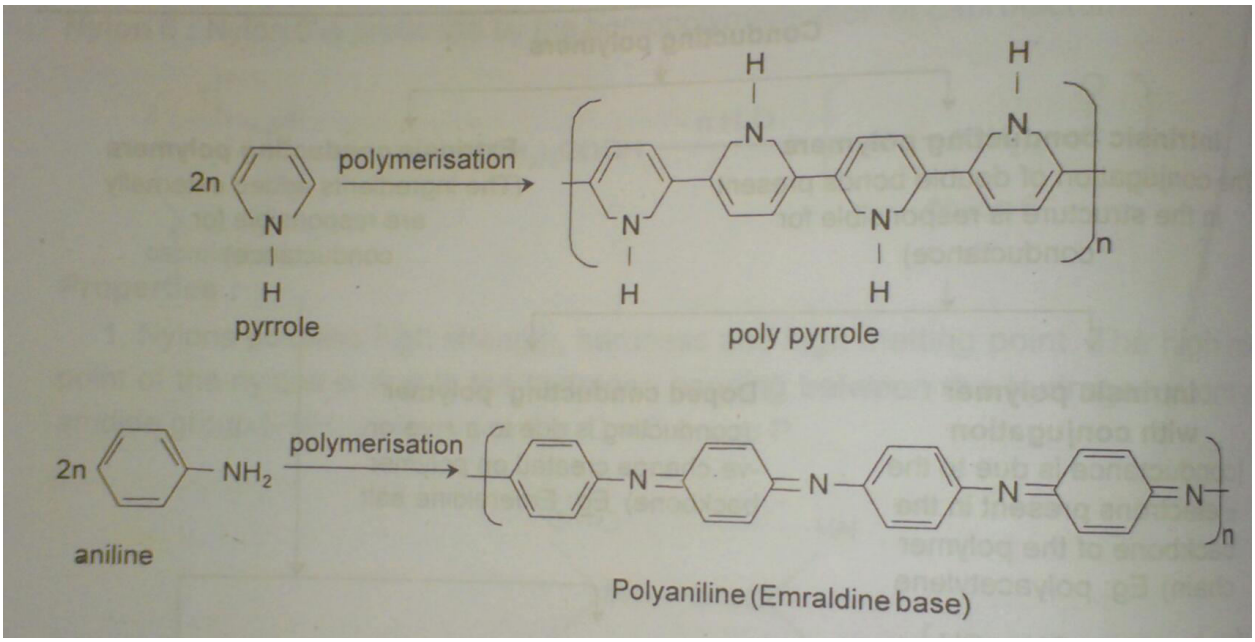
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Polymers are characterized by intensive conjugation of double bonds in their structure. Its are 2 types.

1)Conducting polymers having conjugation: Such polymers having conjugation double bonds in the backbone possess their conductivity due to π electrons. In the formation of valence bands and conducting bands which were separated by significant Fermi energy gap. The electrical conductivity takes place only after thermal or photolytic activation of the electrons, which give them sufficient energy to jump the gap and into conduction band.





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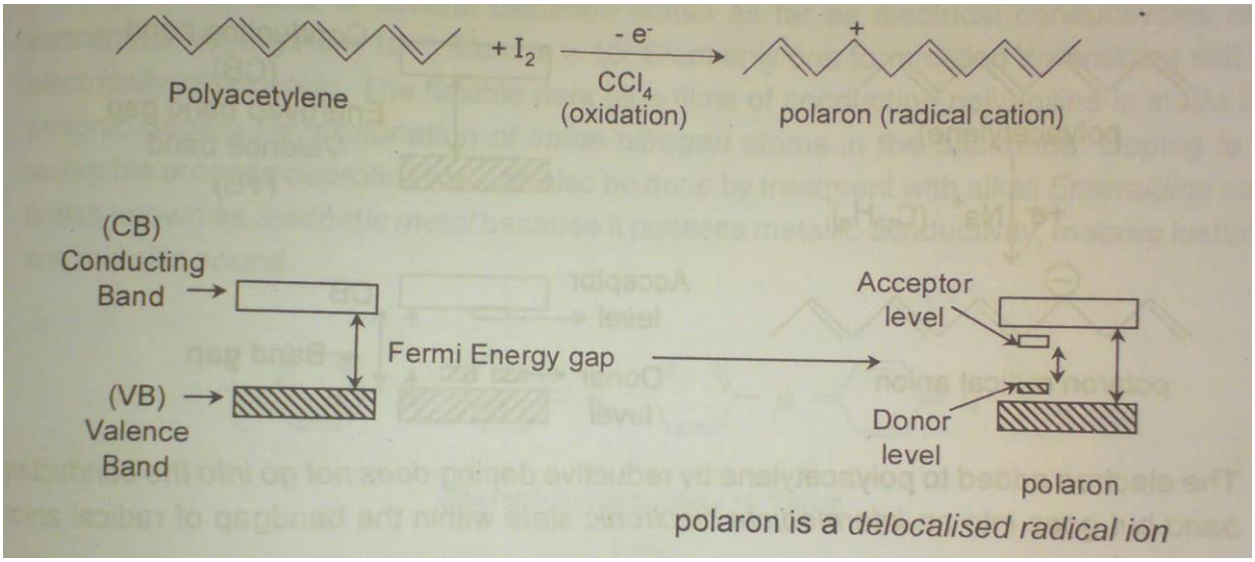
2)Doped conducting polymers : The conducting polymers having π electrons oxidized or reduced because they possess low ionization potential and high electron affinities and introducing + ve charge or –ve charge on polymer by oxidation or reduction.This processis similar to semiconductor technology and is called ***doping*** and 2 types

1. Creating a positive site on polymer backbone called p-doping .

2. Creating a negative site on polymer backbone called n-doping .

p-doping: p-doping is done by oxidation og a conducing polymer like polyacetylene with a Lewice acid or iodine vapour . This is also called oxidation doping.

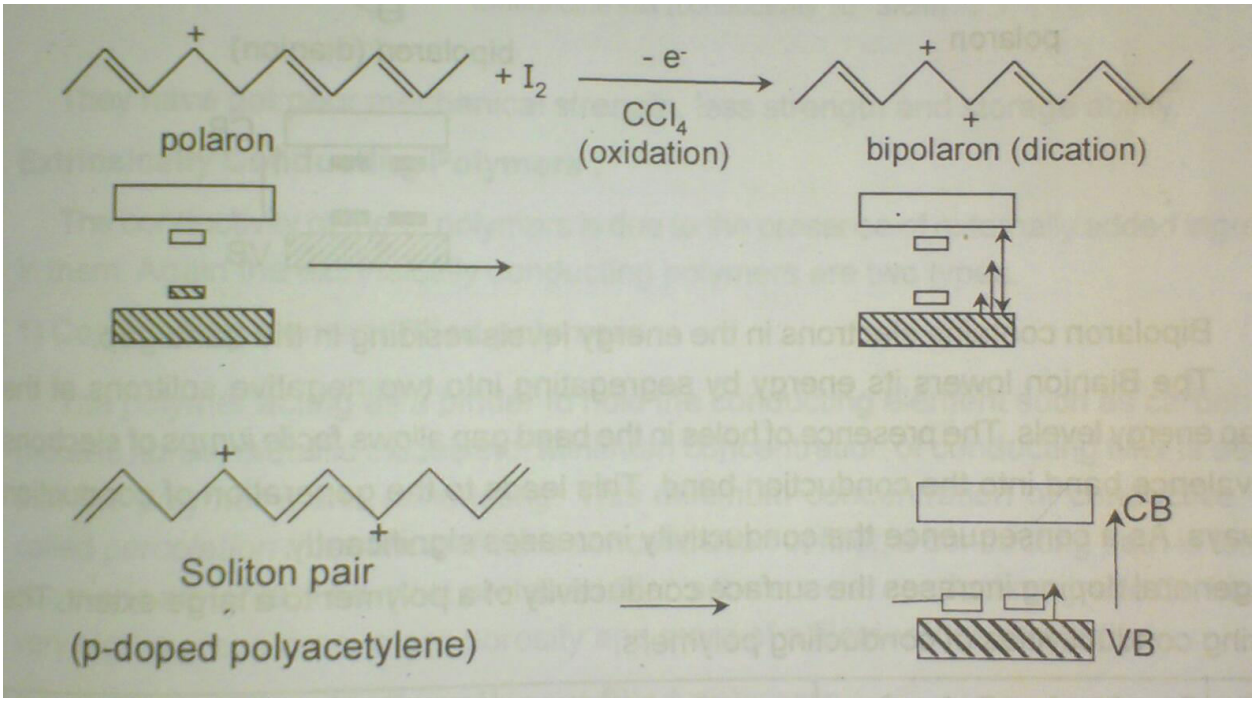
During oxidation process the removal of π electron from polymer back bone lead to the formation a delocalised radical ion called polaron having a hole in between valence band and conducting band as shown below.



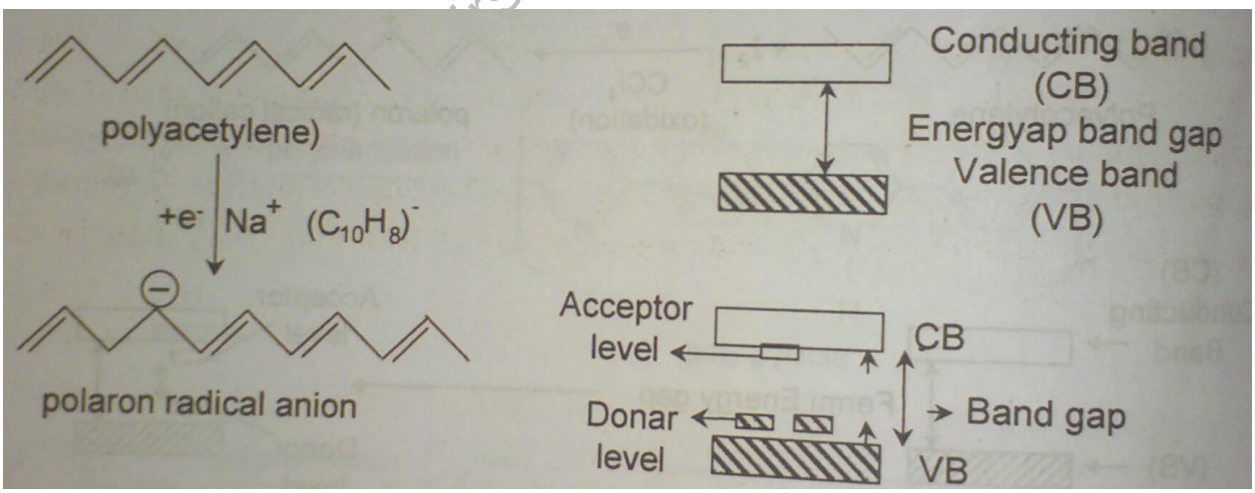
The second oxidation of the polaron results in two positive charge carriers in each chain called bipolaron, which are mobile because of delocalisation.

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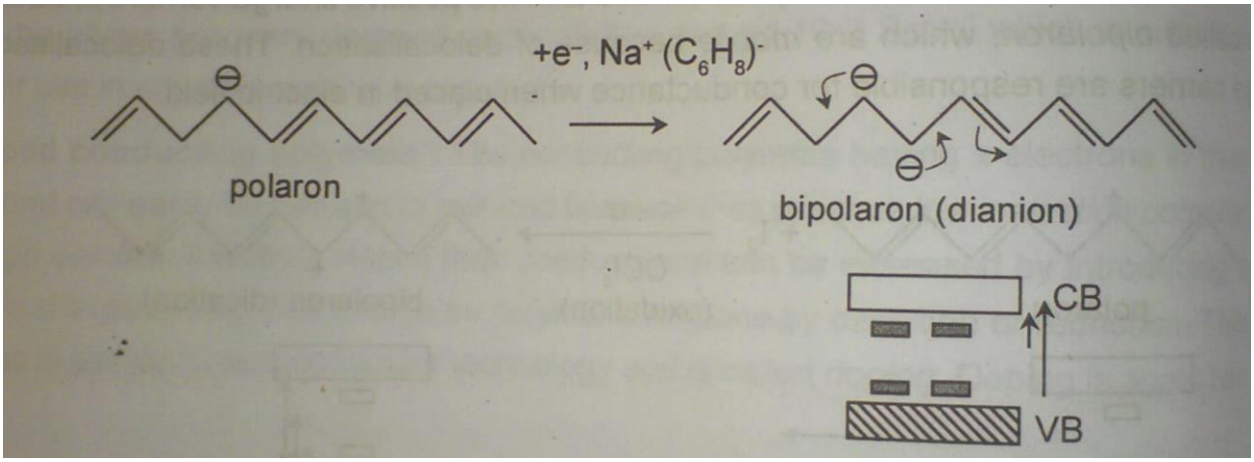
n-Doping: n-Doping is carried out by reduction process by addition of an electron to polymerbackbone by using reducing agents agents like sodium naphthalide. Formation of polaron, bipolaron takes place in two steps, followed by recombination of radicals, which yields 2 charge carriers on the polyacetylene chain responsible for conduction as shown.



The electron added to poluacetylene by reductive doping does not go into the conducting band but goes into an intermediate electronic state within the band gap of radical anion (polaron).

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The presence of holes in gap allows facile jumps of elections from valence band into conduction band . consequence the conductivity increases significantly.

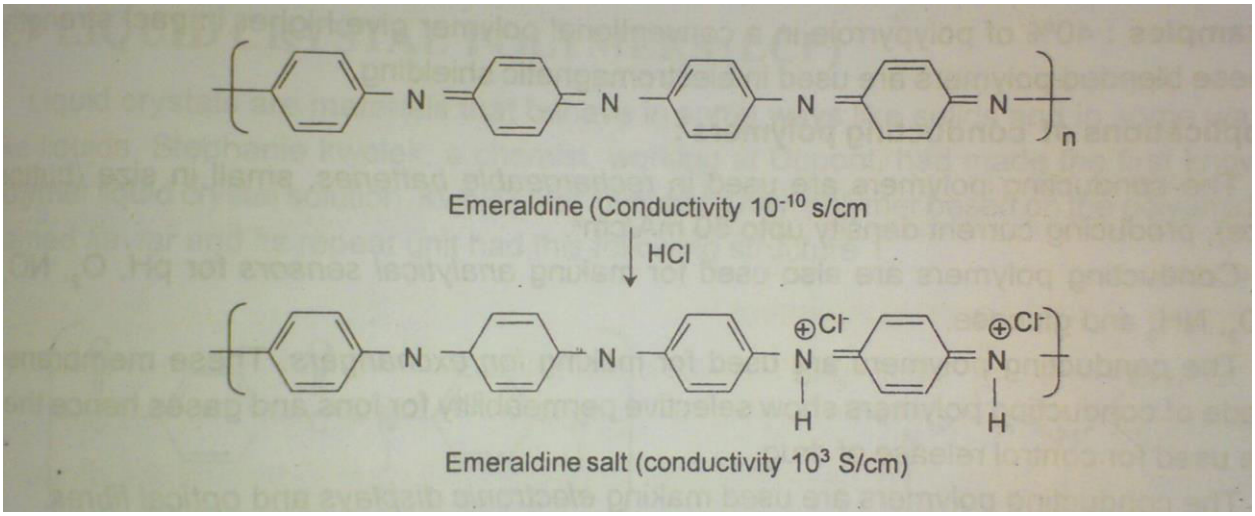
In general doping increases the surface conductivity of a polymer to a large extent. The following are the conductivities of conducting polymers.

s.No	Conducting polymer	Dopants	Conductance(Scm^{-1})
1.	Trans polyacetylene	I_2, Na ,Br_2 ,Li, ASF_5	10,000
2.	Polyaniline	HCL	1000
3.	Poly pyrrole	BF_4^+ ClO_4^+	500-7500

Polyanilines exist in several oxidation states as far as electrical conductivities are concerned varying from 10^{-11} S cm^{-1} to . 10^5 S cm^{-1} only one form called emeraldine salt is electically conducting.

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Extrinsically Conducting polymers:

The conductivity polymers presence of externally added ingredients. It is 2 types

1)Conducting element filled polymers:

The polymer acting as a binder to hold conducting element such as carbon black,metallic fibres, metallic oxidesetc .Minimum concertration of conducting filler is added Preferred filler is the special conducting grade C-black has very hidh surface area,more porosity and more of a filamentous properties

Advantages of conducting element filled polymers:

1)These polymers are low cost polymers

2)They are lidth in weight and mechanically durable.

3)These polymers are strong with good bulk conductivity .

4)They are fabricated very easily to any design.

Application of conducting elements filled polymers are used in hospitals and operation theatres.

Disavantage of conducting elements filled polymer addition 10% carbon black will drastically decrease the tensile strength, elongation strength and impact strength of polymer.

2)Blendded conducting polymers:

The conventional poluymer is blended with conducting polymer to improve physical, chemical,electrical mechanical properties along wih the processing properties.

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Application of conducting polymers:

1) conducting polymers are used in rechargeable batteries small in size producing current density upto 50 mA/cm^2

2)Conducting polymer are also used for making analytical sensors for pH, O^2, NO_x So_2 NH_3 and glucose.

3)The conducting polymer are used for making ion exchangers. These membrance made of conducting polymers show selective permeability for ions and gases hence they are for control release of drug.

4) The conducting polymer are used making electronic displays and optical fibres.

5)They are used for electron beam lithography.

6)The conducting polymers are application in photovoltaic devices.

Factors influencing the conductivity of organic polymers:

The conductivity of organic polymers is influenced by various factors, listed below.

1. Conjugation length of polymer chain: the conductivity of a polymer increase with increase in chain length or conjugation

2. Doping level: The conductivity increase with increase in doping level ,but after some time, it becomes saturated .

3. Temperature: The conductivity of conducting polymers increase with increase in temperature .At some high temperature, conductivity becomes constant.

4. Frequency of current: The conducting of these material also depend on the frequency of current, because doping is the transport mechanism of these materials.

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Advantages of intrinsic conducting polymers:

The following are the advantages of intrinsic conducting polymers

1. These polymers posses good conductivity.

2.They can store a charge.

3.Ion-exchange is possible with these polymers.

4.They absord visible light togive coloured products.

5.They are transparent to x-rays.

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6.They can be easily processed with product stability and efficient recycling.

Disadvantages of intrinsic conducting polymers:

Their conductivities are inferior to metal conductivities.

For example: The conductivity of poly acetylene is 4,00,000 S cm^{-1}.

Where as the conductivity of Cu is 6,00,000 S cm^{-1}.

BIODEGRADABLE POLYMERS:

Biodegradability is chemical transformation by enzymatic action of bacteria which are capable of further degradation.

Polymer are popular material as they attacked by environmental conditi0ons including biological attack .Biodegradation of polymers not only aimed at eliminating landfills but also compostable bags for the collection of leaf and yard waste. Those polymers which degradeby the enzymatic action of naturally occurring microorganisms and bacteria are called biodegradable polymers.

The basic requirements of the biodegradable polymer should be

(a) Production of non-toxic products
(b) Capable of maintaining good mechanical integrity until degradation
(c) Controlled rates of degradation

The factors controlling the rate of degradation include
(a) Percentage of crystallinity of polymer
(b) Molecular weight of polymer,
(c) Hydrophobicity of polymer and
(d) The environment surrounding

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The biodegradable polymers are classified as naturally occurring and synthesized polymers.

(a)Naturally occurring biodegradable polymers

There is a belief that anything that comes from nature goes back to nature. Hence it is assumed that these natural polymers are “beautiful for environment degradation”. The rate of degradation and the formation of metabolites depend very much on the structural complexity of material and the environment conditions selected for degradation. There are 4 groups of naturally occurring biodegradable polymers.

1. **Polysaccherides –Eg :Starch and Cellulose**
2. **Proteins- Eg :Gelatin ,Casein, Silk, Wool**

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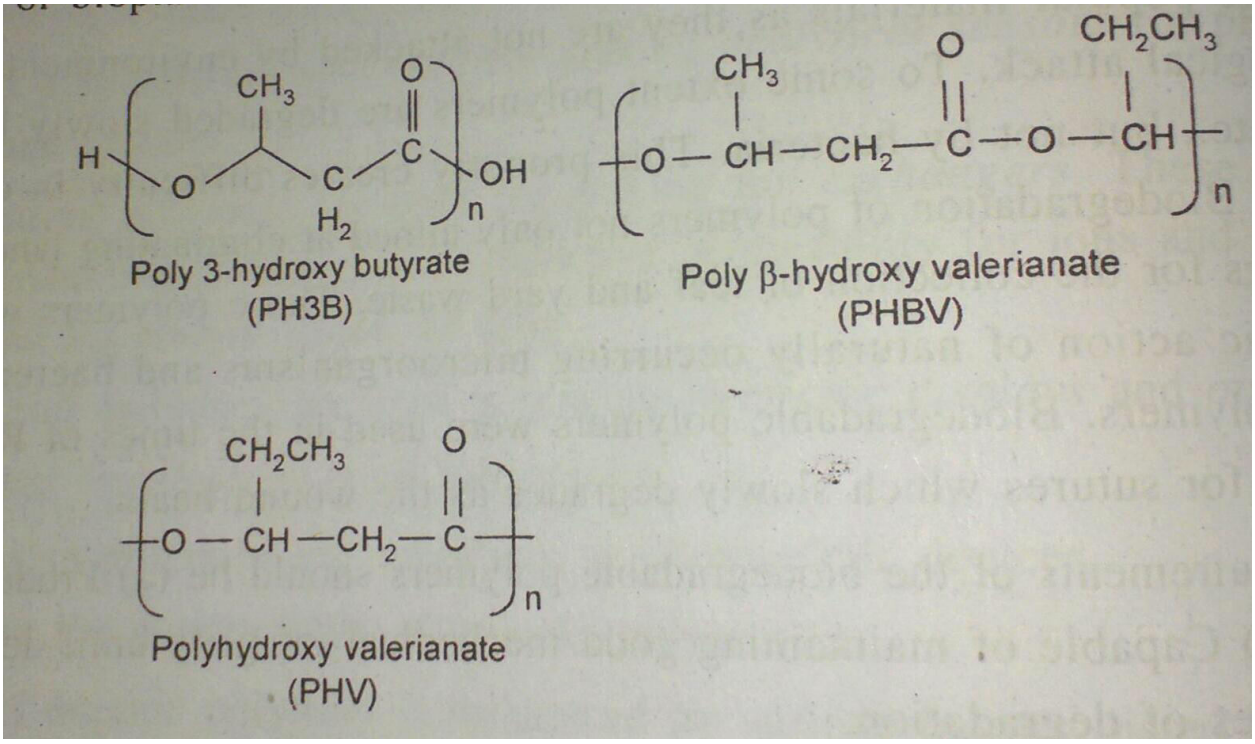
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3. **Polyesters- Eg : Polyhydroxy alkanotes**
4. **Others- Eg : Lignin, Shellac, Natural rubber etc.**

(b)Synthetic biodegradable polymers

These polymers are produced from chemicals or biologogical sources that biodegradable. The following are some types of synthetic biodegradable polymers.

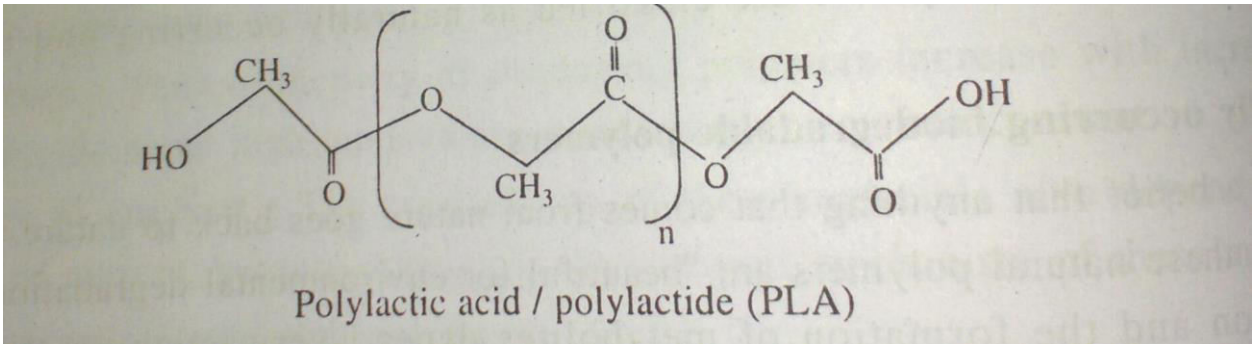
Polyhydroxy alkanoates (PHA) BOPAL: These are linear polyesters produced by bacterial fermentation of sugars or lipids and sold under the trade name biopal. These are produced by the bacteria to store carbon and energy. More than 150 monomers can be polymerized to give material with extremely different properties. These biopols are used in the production of bioplastics .The following are some biopols produced.



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1.Polylactic acid/ polylactide (PLA): This is a biodegradable thermoplastic polyester belonging to class of polyhydroxy alkanoates, derived from renewable sources such as starch, topica or sugarcane possess the following structure.



Polylactic acid / polylactide (PLA)

Biosynthesis: PHA a culture of microorganisms such as alkaligenes entrophys is placed in a suitable medium along with appropriate nutrients and changed to synthesise PHA. The yield of PHA obtained from intracellular inclusions can be as high as 80% of the organism's dry weight.

Industrially PHA is produced by microbial fermentation of sugar or glucose. PHA granules is processed mainly by injection moulding and extrusion moulding into films and hollow bodies.

Properties:

i. PHA polymers are thermoplastic.
ii. Stable to u.v.radiation.
iii. The crystallinity lie in the range of 70%.
iv. Good resistance to moisture ,aroma barrier properties are possessed by the PHA.
v. PHBV possesses good elasticity.
vi. The glass transition temperature of PLA is 60-65°C.
vii. PLA possess melting point 173-178°C
viii. PLA is a chiral compound existing as poly *l*-lactic acid (PLLA)
ix. PLA possess good biocompatibility, process ability as well as high strength and modulus.

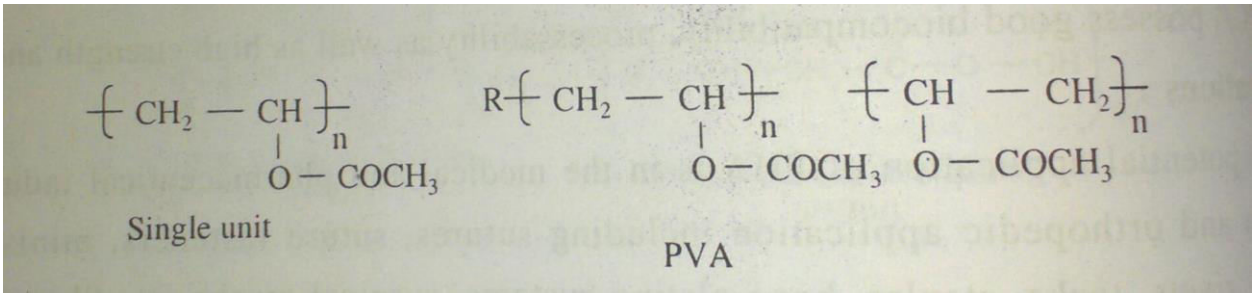
Application:

The potential application of PHA is in the medical and pharmaceutical industries, like fixation and orthopedic application including sutures ,suture fasteners, meniscus repair devices, rivets ,tacks,staples,bone plating and lemostats are produced from PHA.

Polyvinyl acetate(PVA): Polyvinyl acetate is a water soluble and biodegradable polymer, possessing excellent mechanical properties and compatibility with starch. The structure of PVA is

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PVA is another class of innovative biodegradable polymer produced from starch when is totally biodegradable in a environment as it can be hydrolysed to glucose by microorganisms or enzymes and then metabolized to CO2 and H2O. Biodegradable PVA is produced from acetic acid and acetaldehyde produced from molasses by fermentation.

Properties:

1. It belongs to the class of vinyl polymers.
2. It is water soluble
3. Posses excellent mechanical properties
4. It is compatible with starch. i.e starch mole can be introduced into the backbone for quick biodegradability.

Application:

1. Polyvinyl acetate is used in food industry as a packing material, food storage and catering, mailing compost bags.

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QUESTIONS

(1) (a) How are synthetic high polymers classified?

(b) Discuss the preparation, properties and uses of various grades of polythenes.

(2) (a) What is the difference between free-radical and ionic chain polymerization?

(b) Write a note on preparation, properties and uses of

i. bakelite

ii. PVC.

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(3) Explain the synthetic methods, properties and applications of the following elastomers:-

(a) Buna-S rubber

(b) Butyl rubber

(c) Thiokol rubber.

(4) Differentiate the following with suitable examples:-

(a) Polymer from monomer

(b) Homo polymer from co-polymer

(c) Step growth polymerization from chain polymersation.

(5) (a) Explain the terms chain and step-growth polymerizations with appropriate examples.

(b) Describe the preparation, properties and uses of

i. polythene

ii. nylon (6,6)

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(6) (a) Explain the di_erences between thermoplastics and thermoset plastics.

(b) Outline the preparation, properties and uses of polyester.

(7) (a) What is natural rubber? How is it processed?

(b) How is crude rubber obtained from latex?

(c) Write a note on preparation, properties and uses of buna-s-rubber?

OBJECTIVE QUESTIONS

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- High polymers are (c)
  a) liquids b) gasesc) solids d) colloids

- The structural units of polymers are called (b)
  a) fibres b) monomers c) fabrics d) thermo units

- Phenol formaldehyde resin is commercially known as (b)
  a) PVC b) Bakelite c) Nylon d) teflon

- Polymer commonly used in textile industry is (b)
  a) Rubber b) Nylon c) PVC d) bakelite

- Which of the following is an elastomer (d)
  a) PVC b) Nylon c) Polystyrene d) Butyle rubber

- Which one of the following is not a macromolecule (d)
  a) cellulose b) rubber c) protein d)wood

- The following polymer has ester links in its structure (d)
  a) Nylon b) Bakelite c) PVC d) Terylene

- Functionality of phenol is (c)
  a) 1 b) 2 c) 3 d) 6

- The only rubber which cannot be vulcanized is (b)
  a) butyl rubber b)Thiokol rubber c) neoprene d) nitrile

- Polyurethane rubber is also known as (d)
  a) hypanol b) Thiokol c) neoprene d) isocyanate rubber

- The common reinforcing agent to give strength and rigidity to rubber is (a)
  a) carbon b) mercaptol c) phenylnapthylamine d) wax

- Plasticizers are materials which are added to resins to increase their (d)
  a) strength b) corrosion resistance c) stability d) plasticity and flexibility

- Thermosetting resin fabricated by transfer moulding which uses the principle of (c)
  a) blowing b) extrusion moulding c) injection moulding d) compression moulding

- The least functionality of a monomer is convert to polymer is (c)
  a) 1 b) 3 c) 2 d) 6

- If the arrangement of functional groups on carbonchain is alternating,it is called (b)
  a) isotactic b) syndiotatic c) atactic d) tacticity

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UNIT-II

FUEL TECHNOLOGY

INTRODUCTION: Fuels are mainly the energy sources for industry and domestic purposes.

"A fuel is a substance which provides energy on combustion for industry and domestic purposes."

The combustion is the process of oxidation that provides heat energy with light. Every combustion is an oxidation but every oxidation is not combustion, e.g. combustion of wood, petrol and kerosene gives heat energy.

Fuel + oxidation ⟶ heat energy + light + combustion products

CLASSIFICATION OF FUELS: classification of fuels based on two factors

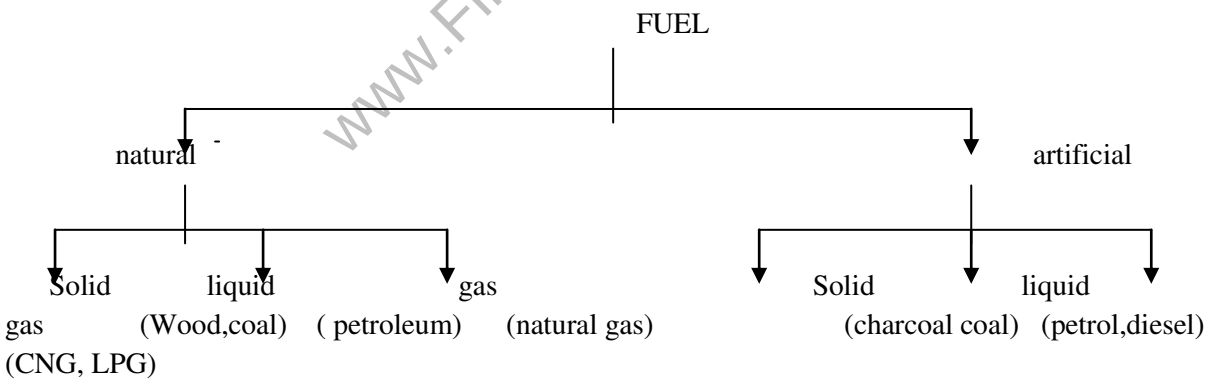
1) The way it is obtained (natural and artificial)

2) Physical state of a fuel (solid, liquid, gas)

NATURAL FUELS: Fuels which are found in nature are called natural fuels. These are also called primary fuel. e.g. wood, coal, peat, petroleum and natural gas.

ARTIFICIAL FUELS: Fuels which are prepared artificially from primary fuels are called artificial fuels. These are also called secondary fuels. E.g. kerosene, petrol, coal gas, coke etc.
On the basis of physical state of a fuel , fuels are divided into three types.

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SOLID FUELS: Because of the earth hazards trees were buried inside the earth. By the temperature, pressure and bacterial actions, they were converted into a brown-black solid named coal during thousands

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of year. Since wood contain higher carbon percentage in the form of cellulose, lignocelluloses, they are transformed in the form of coal "the process of conversion of wood into coal is called "coalification."

Wood ⟶ peat ⟶ lignite ⟶ bituminous ⟶ anthracite

TABLE:1

Fuel	% of carbon	Calorific value (k.cal/kg)	Main applications
Wood	50	4000-4500	Domestic fuel
Peat	57	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	67	6500-7100	Used for steam generation in thermal power plants for the production of producer gas
Bituminous	83	8000-8500	Used in making coal gas and metallurgical coke. Also used for steam generation in thermal plants and for using domestic heating.
anthracite	93	8650-8700	Used in households and for steam rising. Also used in metallurgical purposes, where no smoke and high local heat is desired

Analysis of Coal: The analysis of coal is helpful in its ranking. The assessment of the quality of coal is carried out by these two types of analyses: (i) Proximate analysis (ii) Ultimate analysis.

Proximate Analysis: In this analysis, the percentage of carbon is indirectly determined. This analysis includes percentage of moisture, volatile substance, ash content and carbon.

1. Moisture: A known mass of finely powdered coal is taken in a crucible. It is heated up to 110°C for an hour and cooled to room temperature in a desiccators. The moisture is removed as water vapors and the process is repeated till the constant weight is obtained.

$$\text{Percentage of moisture} = \frac{\text{Loss of weight of coal}}{Weight\ of\ Coal} \text{x}100$$

2. Volatile matter: The above sample is taken and heated at 950°C in the absence of air for 7 minutes. It is then cooled to room temperature and weighed. The loss of weight is noted as volatile matter and is removed from coal at 950°C.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal}} \text{x}100$$

3. Ash Content: Coal, free from moisture and volatile matter, is heated in a crucible at about 700°C in the presence of air, It undergoes combustion and results in the formation of ash. Crucible is cooled to room temperature and weighed. The mass of ash is then determined.

$$\text{Percentage of ash} = \frac{Mass\ of\ ash\ X100}{Mass\ of\ coal}$$

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4. Carbon: Since main component of coal is carbon, It can be determined by subtracting the sum of the percentage of moisture, Volatile substance and ash content from 100.

   Carbon % = 100 – (% of moisture + % of volatile matter + % of ash)

Significance of Proximate analysis:

Moisture: High moisture content in the fuel reduces the calorific value, increases the cost of transportation and causes wastage of heat. Hence the lesser the moisture content the better is the quality of a fuel.

Volatile matter: A coal containing high volatile matter burns with long flame, high smoke and low calorific value. Volatile matter also influences the design of the furnace since the higher the volatile matter, larger is the combustion space required.

Ash: 1. Ash reduces heating value of coal.

2. Ash content increases cost of transportation, handling, storage and disposal.

3. It determines the quality of coal. Hence, the lesser the percentage of ash, the better is the quality of coal.

Fixed carbon: The higher the fixed carbon in a coal, the greater is its calorific value.

Ultimate Analysis: This analysis includes percentages of C, H, O, S, N and ash content in coal.

1. Carbon and hydrogen determination: A known mass of carbon is taken and burnt in an apparatus. The carbon changes to CO_2 and hydrogen changes to H_2O. The vapours of CO_2 and H_2O are then passed through KOH and $CaCl_2$. The CO_2 is absorbed by KOH in the tube while H_2O is absorbed by $CaCl_2$. Because of the absorption, the weight of KOH and $CaCl_2$ increases, which is then measured.

$C_{12} + O_2 \longrightarrow CO_2$

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

$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

$CaCl_2 + 7H_2O \longrightarrow CaCl_2.\ H_2O$

Percentage of carbon = $\frac{Increase\ in\ weight\ of\ KOH}{Weight\ of\ coal} X \frac{12}{44} X 100$

Percentage of hydrogen = $\frac{\text{Increase in weight CaCl2.}}{Weight\ of\ coal} X \frac{2}{18} X\ 100$

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2. Nitrogen: The estimation of nitrogen is done by Kjeldahls method. About 1 gl of finely powdered coal sample is heated with concentrated H_2SO_4 along with K_2SO_4 catalyst in a Kjeldahls flask. Nitrogen in the coal is converted into $(NH_4)_2SO_4$.

   $2N + 3H_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$.

   $(NH_4)_2SO_4$ is heated with excess of NaOH and the liberated ammonia is distilled over and absorbed in known volume of standard acid solution. The unreacted acid in back titrated with standard NaOH. The amount of acid neutralized by liberated ammonia is determined.

   $$(NH_4)SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

   $$NH_3 + HCl \longrightarrow NH_4Cl$$

   From this the percentage of nitrogen is calculated.

   Percentage of nitrogen = $\frac{Volume\ of H2SO4\ X\ Normality}{Weight\ of\ coal} x1.4$

3. Sulphar: Sulphar is estimated gravimetrically in terms of $BaSO_4$.

   Percentage of sulphur = $\frac{Weight\ of\ BaSO4}{Weight\ of\ coal} x \frac{32}{233} x100$

4. Ash content: The coal sample is ignited and the weight of ash is measured at room temperature.

   Percentage of ash = $\frac{Weight\ of\ ash}{Weight\ of\ coal} x100$

5. Oxygen: The percentage of oxygen is determined by subtracting the sum of percentages of C, H, S and ash from 100.

Significance of Ultimate analysis:

1. Carbon and Hydrogen: The higher the percentage of carbon and hydrogen, the better is the quality of coal and higher its calorific value. Percentage of carbon helps in assessing the rank of coal.
2. Nitrogen: Nitrogen does not have any calorific value. It has no significance.
3. Sulphur: (1) Sulphur increases calorific value. (2) The products of combustion SO_2, SO_3 have corrosive effect on equipment and cause air pollution. (3) Sulphur is undesirable in the preparation of metallurgical coke and (4)Sulphur is converted into soluble sulfate by incinerating coal with 1-2 mixture of Na_2CO_3 and $MgCO_3$. Then treated with $BaCl_2$ solution so that sulfates are precipitated as $BaSO_4$. From the weight of $BaSO_4$ obtained, the sulphur present in the coal is calculated.
4. Ash Content: 1. Ash reduces heating value of coal.
   2. Ash content increases cost of transportation, handling, storage and disposal.
   3. It determines the quality of coal. Hence, the lesser the percentage of ash, the better is the quality of coal.

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5. Oxygen: High oxygen coals contain high inherent moisture and low calorific value. A good quality coal should contain low percentage of O_2.

Liquid Fuels

Crude Oil or Petroleum: Petroleum is one of the best primary liquid fuel. It is also known as crude oil. Petrol, diesel, kerosene are main liquid fuels. They are secondary liquids fuels derived from petroleum. These fuels are used for domestic works, auto vehicles and power generation. The word meaning of petroleum is 'rock oil' (petra = rock, oleum = oil). Petroleum is dark-brown viscous liquid. Petroleum is mineral found deep in earth's crest. It is mainly composed of hydrocarbons which may be solids, liquids or gases. Some optically active compounds having S and N are also present. On average the composition of petroleum is

C = 79.5 – 87.1%

H = 11.5 -14.8%

S = 0.1 -3.5%

N and O = 0.1 -0.5%

Origin of Petroleum: There are two theories to explain the origin of petroleum.

(i) Carbide theory or Mendeef's theory
(ii) Englers's theory or Organic theory

Carbide Theory: This theory is known as inorganic theory of petroleum. According to this theory the carbides which are formed from a reaction between carbon and metals at high temperature and pressure are acted upon by steam to give hydrocarbons.

$Ca + 2C \xrightarrow{\text{high temperature}} CaC_2$ (Calcium Carbide)

$4Al + 3C \longrightarrow Al_4C_3$ (aluminium carbide)

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ (acetylene)

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3\ CH_4$ (methane)

The unsaturated hydrocarbons which are produced along with the saturated hydrocarbons react with hydrogen to produce saturated hydrocarbons.

$C_2H_2 + H_2 \longrightarrow C_2H_4$
Acetylene ethylene

$C2\ H4 + H2 \longrightarrow C2\ H6$
ethane

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Englers's Theory: This theory explains the origin of petroleum to be of organic type. According to this theory petroleum is generated from aquatic animals & sea weeds under the influence of high temperature and pressure. The organic theory has been supported by the geologists because of the presence of S and N, optically active organic compounds, fossils and brine in petroleum deposits. This theory has been proved experimentally by distilling fish when a petroleum resembling liquid is obtained. This fact can be explained in terms of fish, other aquatic life and the vegetable matter like seaweeds found in the sea get covered by some eruptions from the volcanoes and in due course get converted into petroleum. This theory does not explain the availability of chlorophyll. However, no unanimously acceptable mechanism is yet available on the origin of petroleum.

The modern theory about the formation of petroleum is an admixture of the two theories discussed above. Due to some natural calamity the big forests merged into the earth's crust by tearing it by volcanoes. Due to temperature and pressure so developed and the radioactivity of various compounds, the bacteria decomposition started resulting in the formation of petroleum. The existence of chlorophyll and resins provide a proof to this theory.

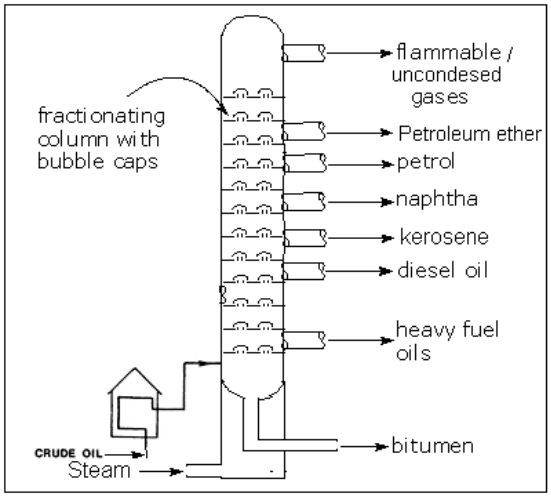
The crude oil or petroleum found deep in the earth's crust under an impervious rock can be obtained either by its automatic exist from the natural opening found in the crust of the earth or by the artificial digging of wells in the oil bearing strata and then pumping out by some suitable pumps.

Refining of Petroleum:

Crude oil obtained from the mine is not fit to be marketed. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined "as the process by which petroleum is made free of impurities, separation of petroleum into different fractions having different boiling points and their further treatment to impart specific properties". Refining of petroleum is done in different stages.

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1. **Removal of solid impurities:** The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernatant liquid is then centrifuged where in the solids get removed.
2. **Removal of water (Cottrell's process):** The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.
3. **Removal of harmful impurities:** In order to remove sulphur compounds in the crude oil, it is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and $MgCl_2$ if present will corrode the refining equipment and result in scale formation.
4. **Fractional distillation:** The crude oil is fractionally distilled in a fractionating still, which is a tower like structure having bubble tower laid inside. The crude oil or the petroleum enters through the bottom of the still by an inlet. This is made to pass through a pre-heater or it can heated with steam, inside the still to a temperature of about 400°C. As we move to the top of the fractionating still the temperature goes on decreasing.
   A number of side pipes are fitted at different heights of the column or still to collect the fractions. As petroleum enters the still, it gets vaporized the vapours move up the bubble tower. The bubble tower consists of number of horizontal trays, and each tray is provided with a number of small chimneys through which the vapours rise. The chimneys are covered with loose caps so that the vapours bubble through and get condensed, dropping back into the trays. So as the vapours go up, they become cooler and cooler and fractional condensation of the crude oil fraction takes place at different levels of the bubble tower.

S.No.	Name of the fraction	Boiling range	Approximate carbon	Applications

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			composition	
1.	Uncondensed gas	< 30^0C	C_1 - C_4	Liquefied to LPG and used as industrial, domestic and motor fuel
2.	Petroleum ether	30-70^0C	C_5 - C_7	As a solvent
3.	Gasoline or petrol or motor spirit	40-120^0C	C_5 - C_9	As a motor fuel, solvent and in dry cleaning
4.	Naphtha or solvent spirit	120-180^0C	C_9 - C_{10}	As an illuminant, jet engine fuel and also for preparing laboratory gas.
5.	Kerosene oil	180-250^0C	C_{10} - C_{16}	Diesel engine fuel.
6.	Diesel oil or gas oil or fuel oil	250-320^0C	C_{10} - C_{18}	Main utility is producing gasoline by cracking process.
7.	Heavy oil a)lubricating oil b)petroleum jelly c)grease d)paraffin wax	320-400^0C	C_{17} - C_{38}	 As a lubricant. In cosmetics, medicines and as a lubricant. As a lubricant. For preparing tropolins, wax paper, and shoe polishes and candles.
8.	Residue a)asphalt or tar b)petroleum coke	Above 400^0C	Above C_{38}	 For laying roads and water proofing of the roofs of the houses. For moulding the rods of arc lights and as a fuel.

The vapours of the liquid having the highest boiling point are the first to condense and go out and those which have the lowest boiling points go last, along with the uncondensed gases.

Secondary liquid fuels:

The following are the impotent secondary liquid fuels.

PETROL OR GASOLINE: Petrol is a highly volatile, inflammable secondary liquid fuel with great demand as it is used as a fuel in the internal combustion engines of automobiles and aero planes. Only 20% of the petrol which we are using is from petroleum fractionating column and it is called straight run petrol. 50% of the petrol utility is by a process called cracking and the remaining 30% of the petrol produced by synthesis from coal and water, which is called synthetic petrol.

Cracking: The quality and yield of petrol produced by the fractionation of petroleum is low. Hence, the middle oil and heavy oil fractions are cracked to give petrol.

Cracking is the process of conversion of bigger hydrocarbon molecules into smaller hydrocarbons of lower molecular weights.

Higher hydrocarbons (saturated) $\xrightarrow{\text{Cracking}}$ small saturated hydrocarbon +

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(paraffins) small unsaturated hydrocarbon

$$C_{12}H_{26} \longrightarrow C_7H_{16} + C_5H_{10}$$

The process of cracking is mainly two types:

(i) Thermal cracking (ii) Catalytic cracking

Thermal Cracking: This method is an old method and is now being replaced by other methods. In this the heavy oil is subjected to high temperature and pressure. When the higher hydrocarbons get converted into the lower hydrocarbons. The liquid after being cracked passes through the fractionating column and gets separated into different fractions. The yields are generally from 7 to 30%. Thermal cracking takes place by two ways. They are i) Liquid phase cracking and ii) Vapour phase cracking.

i) Liquid phase thermal cracking: The heavy oil or the gas oil stock is maintained at a temperature of 420-550° C and under high pressure ranging between 15-100 kg/cm^2, so that the reaction product is kept in the liquid state. By this method any type of the fuel, solid or liquid can be cracked. The yield obtained over here is 60-65% and the octane rating of the product is 65 to 70.

ii) Vapour phase thermal cracking: In this process, the heavy oil is first vaporized by heating to about 600°C and maintaining low pressures of 4-10 kg/cm^2, only oils of high volatility are suitable for this process and the yield is about 70%. Even though the products obtained by this process are associated with better antiknocking properties, its stability is low when compared to liquid phase cracking.

Catalytic Cracking: A better quality and yield is obtained by the process of catalytic cracking than the thermal cracking. The liquid is cracked at a temperature of 400-450°C in the presence of a catalyst. Usually aluminium silicates [$Al_2(SiO_3)_3$] or alumina [Al_2O_3] are employed as catalysts. The catalytic cracking possesses some advantages over thermal cracking.

They are

1. The yield of the gasoline is higher.
2. The quality of the gasoline produced is better.
3. No external fuel is necessary for burning. The heat required for burning is derived from the coal embedded in the catalyst, during regeneration process.
4. Requirement of low pressure for cracking.
5. The process can be easily controlled during cracking and so the desired products can be obtained.
6. The product obtained after cracking contains a very little amount of S, a major portion of which escapes out as H_2S.
7. The product of cracking contains a high amount of aromatics.
8. The gasoline produced has a higher octane rating.

There are two methods of catalytic cracking, they are

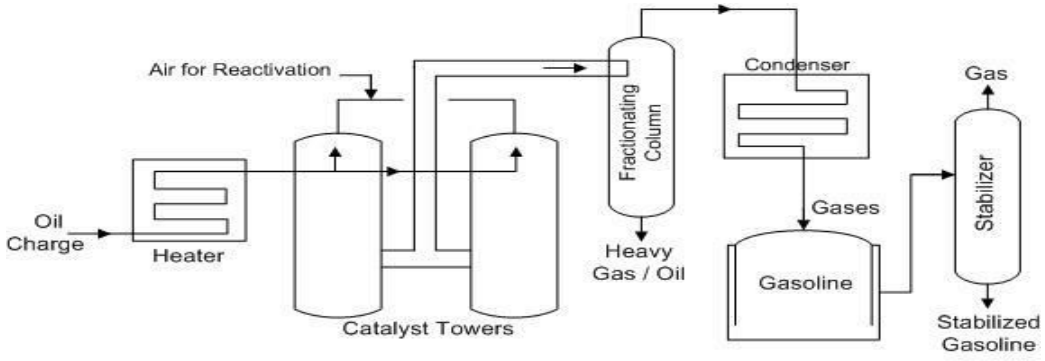
i) Fixed bed catalytic cracking

ii) Fluid bed catalytic cracking.

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Fixed bed catalytic cracking: In this method the catalyst, mixed with clay and zirconium oxide and the heavy oil charge is packed in the lower maintained at 400-450$_o$C and 1-5 kg/cm^2 pressure.



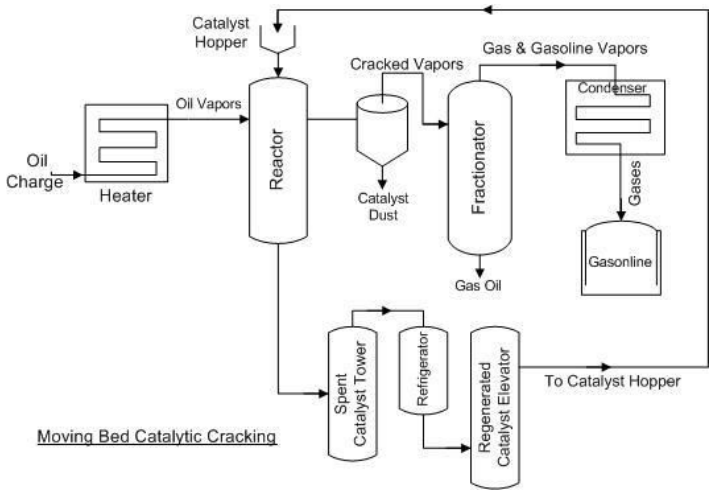
Fixed Bed Catalytic Cracking

The oil vapours get heated to the cracking temperature as they pass through the tower. Cracking takes place and the products move through the fractionating column where fractional distillation takes place. The vapours of the mixture are then led through a cooler where some gases get condensed along the with gasoline and the uncondensed gases move on. The gasoline then moves to a stabilizing tank where the dissolved gases are removes and the gasoline gets stabilized. After some time the catalyst stops functioning due to deposition of a black layer of carbon formed during cracking. A stream of hot air is passes over the catalyst when carbon gets burnt off, thereby reactivating the catalyst.

Fluid bed catalytic cracking: This process is also called as moving-bed catalytic cracking in order to carry out catalytic cracking continuously fluidized catalyst is used. The solid catalyst is very finely powdered and then circulated in the gas stream. Cracking takes place on the surface of a the turbulent catalyst bed as it circulates with the oil vapours in the reactor maintained at a temperature of 530°C and pressure 30to 5 kg/cm^2 .Here cracking of heavier molecules to lower molecules occur which move up to the top of the reactor and enter into the fractionating column and sent to cooler, where gasoline gets condensed. On passing the condensed gasoline to a stabilizer recovers pure gasoline is recovered. The ultimate product obtained contains higher proportion of aromatics and iso-paraffins, and less of gum-forming di-olefinesas those in case of thermal cracking process. The exhausted catalyst is then taken to the regenerator, where its carbon content is reduced and the catalyst can be reused. The exact details of this procedure can be followed from the figure below.

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Knocking: In an internal combustion engine a mixture of gasoline and air is used as a fuel, The combustion starts by spark in the cylinder and it produce a large quantity of hot gases which delivers a smooth thrust to the piston which in turn moves the wheel under certain circumstances the rate of oxidation is so great that the mixture detonates producing a sound in the engine, This rattling noise produced in the internal combustion engine is called "Knocking"

Knocking decreases the efficiency of engine the tendency of knocking is based on the chemical structure of hydro carbons, The knocking is maximum is open chain straight paraffins and least in aromatics there fore a fuel to be called a good fuel for the internal combustion engine should have least knocking. The efficiency of the engine depends on a factor called compression ration (CR), CR is the ration of volume of gases in the cylinder at the end of suction stroke and to the volume of gas at the end of compression stroke more the 'CR' value better will be the engine, The knocking is decreased by adding a little of tetra ethyl lead $(C_2H_5)_4$ pb, TEL is colourless, sweet and highly poisonous liquid, The efficiency of TEL decreases in the presence of sulphur and hence desulphurised gasoline is preferred, Pb & Pbo2 formed during combustion of TEL decrease the engine life and hence must be removed along with exhaust gases by adding ethylene dibromide.

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$Pb, Pbo_2 + C_2H_4Br_2 \longrightarrow PbBr2$

The lead bromide is volatile and escapes into the atomsphere and results in pollution hence now a days unleaded or low leaded gasoline is preferred.

Synthetic Petrol: Petrol is mainly obtained from crude oil from oil wells but because of the increasing demand of petrol the synthetic methods of preparation of petrol again greater importance, The synthetic process of petrol are two types.

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1) **Fisher Tropsch Process**: This method was developed by two germen scientists franz fisher and Hans Tropsch, In this process coal is converted into coke then treated with steem to obtained water gas.

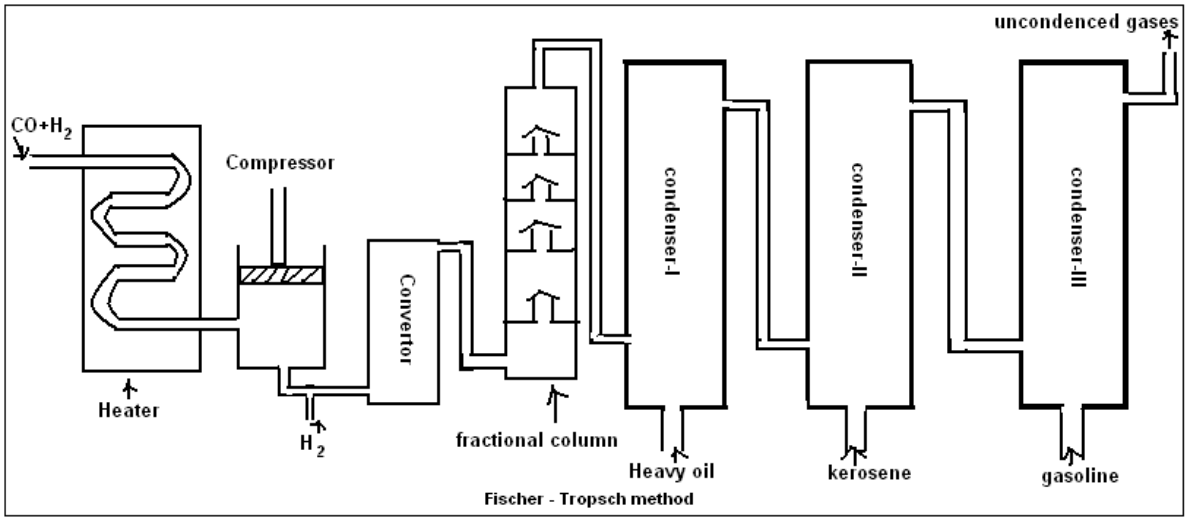
$C + H_2O \longrightarrow CO + H_2$ (Water Gas)

Water gas produced by passing steem over heated coke is treated with hydrogen in the presence of group VIII metals (Fe, CO & Ni) which gives hydeocarbons. The formation of product depends on the catalyst cobalt catalyst gives more oletins, Iron oxide with K_2Co_3 as promoter gives heavier hydrocarbons, In general the mechanism of the reactions can be represented as

$Nco + 2nH_2 \longrightarrow CnH_2\ n + nH_2O$

$Nco + (2n+1)H_2 \longrightarrow Cn\ H_2n+2+nH_2O$

In order to remove H_2S and organic sulphur compounds the gas is passed through Fe_2O_3 and then into a mixture of $Fe_2O_3 + Na_2CO_3$ pure gas is then compressed at 30 atm and led to converter containing a mixture of Fe, CO and Ni, The hot gases mixture is then cooled and fractionated and the heavy oil fraction is cracked to get gasoline.



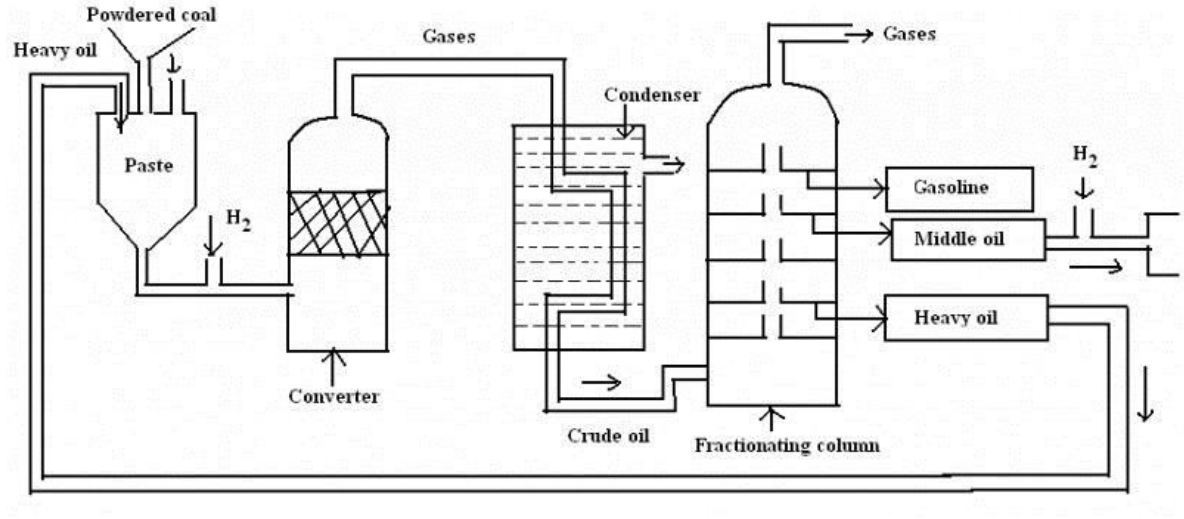
The reactions take place at 30 atm pressure and 200 – 300°C degree centigrade temperature The reaction is exothermic, The gasoline formed by this process has low anti knocking value.

2) **Bergius Process**: This method was developed by the germen scientist Bergius, In this process the low ash content coal powder is taken and mixed with heavy oil to make a paste along with a catalyst (Ni or Sn Oleate), This psate heated with hydrogen at 450° degrees centigrade and 250 atm for 1 ½ hour, The combination of the hydrogen with carbon of the coal yields various hydrocarbons from wax to gases which on cracking yeilds lower hydrocarbons, The vapours are condenced to give crude oil which is fractionated in a fractionating colomn resulting in the

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formation of gasoline middle oil and heavy oil The top fraction is condenced and synthetic gasoline is formed, The middle oil is then hydrogeneted in presence of a solid catalyst to give more gasoline and the heavy oil fraction is recycled to make a paste with fresh batch of coal powder.



Octane Number: The performance of gasoline in internal combustion engines has been rated on the basis of octane number, The higher the octane number of the fuel, The better is its performance and lower is the incidence of knock in engines, The octane number of gasoline is defined as the percentage of iso-octane and n-heptane, It has been experimently noted that the normal haptane has the lowest anti knock value where as iso-octane possesses the highest anti knocking value. The values in these cases have been taken as 0 to 100 respectively, So the octane number shows the anti knocking property of any fuel.

For example: If the octane number of any fuel is 80 it is meant that the gasoline under test will produce some knocking is done by the mixture of 80 parts of iso-octane and 20 parts of n-heptane.

To improve the anti knocking property of a fuel, certain compounds are added to gasoline which decreases the knocking such compounds are called anti knocking compounds and the process is called doping. For ex: A mixture of tetraethyl lead (TEL) along with C2H4Cl2 or C2H4Br2 are used as anti knock compounds.

Cetane Number: In diesel engines the fuel is exploded by the application of heat and pressure and not by a spark, Diesel engine fuels consists of longer chain hydrocarbons than those of internal combustion engine fuel ans as faf as possible the straight-chain ones with a minimum admixture of aromatic and side chain hydrocarbon molecules. The suitability of diesel fuel is determined by its cetane value. In other words the knocking characteristics of diesel oil is given by cetane number. Cetane is saturated hydrocarbon ($C_{16}H_{34}$) having a short ignition delay and hence its cetane number is 100.

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Cetane number of diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and α- methyl napthalene

$CH_3 – (CH_2)_{14} – CH_3$

n –hexadecane (cetane)

α- methyl naphthalene has a long ignition delay and hence its cetane number it taken to be zero. The cetane number can be improved by adding certain additives called dopes anly in small amounts i.e 2.6% eg. Ethyl nitrate isoamyl nitrate and acetone peroxide cetane number of a fuel depends on the nature and composition of its hydrocarbon. The order of cetane number for the following is given as

n-alkanes > napthalene > alkenes > brached alkanes > aromatics

Gaseous Fuels: The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. Gaseous fuels can be classified into two types

a) Primary fuels ex: Natural Gas

b) Secondary fuels ex: Coal Gas, Water Gas

Produces gas and LPG, CNG derived from natural gas and oil gas formed by cracking of kerosene oil.

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Natural Gas: The natural gas is obrained from the wells dug in the earth during mining of petroleum, It is mainly composed of methane and small quantities of ethane along with other hydrocarbons.

If the hydrocarbons present in the gas is called dry gas or lean gas but if the hydrocarbons having the heavier molecules weights are present in the gas it is known as rich gas or wet gas, Natural gas is also known as marsh gas as a major portion of it is contributed by methane, The average composition of natural gas is as follows

Methane – 88.5% Ethane – 5.5% Propene – 3.7% Butane – 1.8%

Present of H_2, CO, Co_2 and higher hydrocarbons – 0.5%

The calorific value of natural gas is 8000 – 14000 K.Cal/m3, Some times natural gas also having harmful H2S gas, It can be removed by 2-amino ethanol.

$H_2S + NH_2 – CH_2 – CH_2 – OH \longrightarrow (NH_2\,CH_2 – CH_2 - OH)_2\,H_2S$

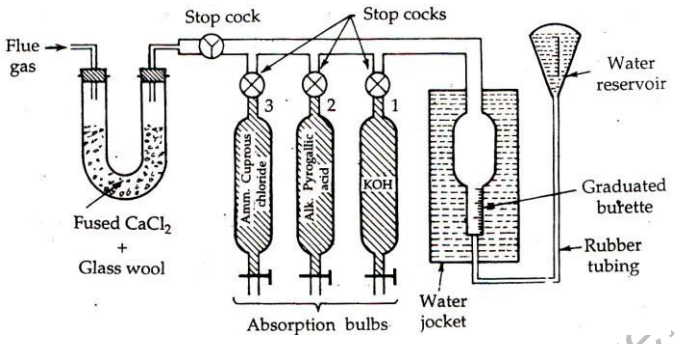
On heating H_2S gas is liberated natural gas is an excellent domestic fuel, It is also used for manufacturing no. of chemicals like carbon black, methanol, formaldehyde etc. It is also used for

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generation of electricity in fuel cells, It is also used as a source of H_2 hence ammonia can be made by reacting N_2 with H_2 obtained from natural gas.

Flue Gas Analysis: Gases coming out after combustion are flue gases (CO, CO_2, O_2), Analysis of flue gases gives an idea about complete or incomplete combustion process, In case of incomplete combustion the concentration of 'CO' will be more, It shows less supply of oxygen for combustion, If the gas analysis results in more common it means more oxygen is supplied for combustion, The analysis of flue gases is carried out with the help of orsat's apparatus.

Orsat Process: Orsat's apparatus is used for flue gas analysis. This apparatus has a measuring burette with water jacket. There are three absorption bulbs fitted with stop cocks each and connected to measuring burette. The bulbs are connected to U-tube packed with glass wool (through a three way stop cock to avoid any other impurities to come in). Water jacket maintains constant temperature in graduated burette.



Out of three bulbs, the first one has KOH solution made by 250 g KOH in 500 ml distilled water to absorb CO_2 obtained by combustion. The second one has alkaline pyro-gallic acid made by 25 g pyro-gallic acid made by 25 g pyro-gallic acid. The third bulb has ammonical cuprous chloride (375 ml water + 125 ml liquid + 100 g Ca_2Cl_2). It can absorb CO, CO_2 and O_2.

A leveling bottle containing a 25% sol of NaCl acidified with a few drops of HCl and having a few drops of methyl orange is connected to the base of burnette by rubber tubing.

After each absorption in three bulbs, the gas is sent to burette and the volume of gas is measured at room temperature. The decrease in volume after each absorption corresponds to the volume of CO_2, O_2 and CO in three bulbs. The quantitative analysis of flue gas absorbed is mage by gas chromatography.

The gas remaining in the burette after absorption of CO_2, O_2 and CO is taken as N_2, Knowing the volume of the gases absorbed and the volume of original gases, their percentages can be calculated.

Percentage of gas in the bulb $g = \frac{a/m}{V} x100$

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Where a = amount of gas in the bulb ($a=a_1, a_2, a_3$ –amount of gas in bulbs 1,2,3 respectively)

M= mass of gas in the bulb ($m=m_1, m_2, m_3$ -amount of mass in the bulbs 1,2,3 respectively)

V= Total volume of gas in the bulbs.

Calorific Value of a Fuel: The calorific value of any fuel is a very important property, It measures the heat produced by the fuel, higher the calorific value better will be the fuel,

The amount of heat produced by the combustion of unit mass or unit volume of a fuel is called calorific value of fuel, The calorific value is measured in several units of heat, They are calorie, K.Cal BTU (British Thermal Unit), CHU(Centigrade Heat Unit) relationship between above units of heat is given below.

1K.Cal = 10^3 Cal = 3.968 BTU = 2.2 CHU = 4.18 J

There are two types of calorific values of fuel.

HCV or GCV: It is defined as the amount of energy produced by the combustion of unit mass of a fuel when the combustion products are allowed to cool at room temp generally during combustion water vapour and CO_2 are formed, Water has a latent heat and the heat of vapourisation is gained on cooling at the room temp.

LCV or NCV: It is defined as the amount of heat energy produced by the combustion of unit mass of fuel when the the combustion products are allowed to escape out.

Relationship Between HCV & LCV:

If hydrogen is present in a fuel the chemical vrn is

$H_2 + ½\ O_2 \longrightarrow H_2O$

2 gr of Hydrogen will produce 18 gr of H_2O

1 gr of Hydrogen will produce 9 gr of H_2O

x gr of Hydrogen will produce 9x gr of H_2O

It release 9x XL cal/gr heat on cooling.

HCV - 9x L

HCV = LCV + 9xL

If hydrogen y%

HCV = LCV + 0.09yL

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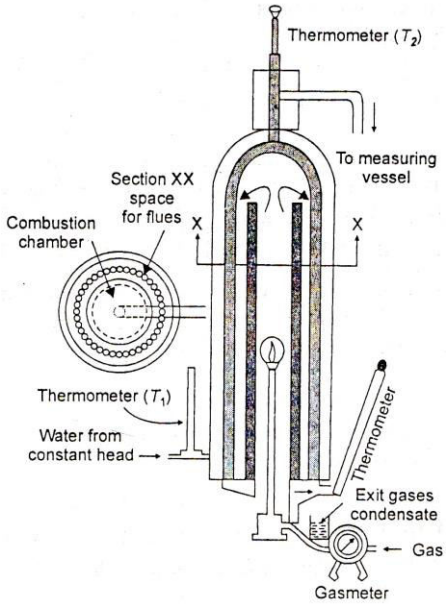
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The latent heat of steem is 587 K.Cal/ kg of water vapour formed at room temparature.

HCV = LCV+ 0.09 X y X 587

Junker's calorimeter:

Determination of calorific value of gaseous fuel by Junker's calorimeter:



Junker's gas calorimeter is used for measuring the calorific values of gaseous and liquid fuels which get vaporized easily. This calorimeter consists of a vertical cylindrical combustion chamber where the combustion of gaseous fuel is regulated with the help of a Bunsen burner clamped at the bottom. The burner can be pulled out or pushed into the combustion chamber during the process of combustion.

The supply of gaseous fuel is regulated with the help of pressure governor which controls the supply of quantity of gas at a given pressure. The volume of gas flowing in a particular time is measured with the help of gasometer. The combustion chamber is surrounded by an annular space for water and interchange coils. Radiative and convective heat loss from the calorimeter is prevented with the help of outer jacket which is chromium plated. Moreover, the outer jacket contains air which is very good heat insulator. At the appropriate places there are the openings where thermometers are placed for measuring the temperatures of the inlet and outlet water.

A known volume of gas is burned in excess of air at a constant rate in combustion chamber in such a manner that all the heat produced is absorbed in water flowing at a constant rate in annular space around the combustion chamber. The increase in the temperature of the water is measured and the heat evolved from the burning of the gas can be readily calculated. The weight of water flowing is recorded for the calculation of calorific value of gaseous fuel.

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Let, V = Volume of gas burnt in certain time 't' at S.T.P.

W = Weight of water collected in time 't'

T_1 = Temperature of incoming water

T_2 = Temperature of outgoing water

The higher calorific value (HCV) is given as

HCV = $\frac{W\,(T2-T1)}{V} k.cal/m3$

Combustion Problems: A fuel has mainly carbon, It has hydrogen oxygen, sulphur and nitrogen in very small amounts, In the combustion of the fuel following chemical reaction takes place.

$C + O_2 \longrightarrow CO_2$

$C + ½\ O_2 \longrightarrow CO$

$H_2 + ½\ O_2 \longrightarrow H_2O$

$S + O_2 \longrightarrow SO_2$

Nitrogen being less reactive, it will not be oxidised to NO_x Oxygen present already in required for combustion.

Since oxygen is supplied by air, it is necessary to know the % of oxygen in air by volume and weight.

% of oxygen in air by volume 21

% of oxygen in air by weight 23

Combustion of Carbon :

$C(12) + O_2(32) \longrightarrow CO_2(44)$

12 kg of ' C' requires 32 kg of 'O_2' for complete combustion.

The amount of oxygen required for complete combustion of 'C' kg of carbon is given as 32/12 X C kg

Combustion of hydrogen :

$2H_2\,(4) + O_2(32) \longrightarrow 2H_2O(36)$

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4 kg of hydrogen requires 32 kgs of oxygen for complete combustion. Therefore the amount of oxygen required for complete combustion of H kg of hydrogen is given as

32/4 X H kg.

If may be pointed out here that of the total amount of hydrogen, some of it is present in combined form i.e as H_2O. As this combined hydrogen is a non combustion substance, it does not take part in combustion.

Now 1 part of hydrogen combines chemically with 8 parts by mass of oxygen, the amount of hydrogen available for combustion = mass of hydrogen – Mass of $O_2/8 = (H – O/8)$

Hence the oxygen required for combustion of hydrogen = $32/4(H – O/8) = 8(H – O/8)$

Combustion of sulphur :

$S_{(s)}(32) + O_{2(g)}(32) \longrightarrow SO_{2(g)}(64)$

32 kgs of sulphur requires 32 kgs of oxygen for complete combustion.

Therefore the amount of oxygen required for complete combustion of S kg of sulphur is given as 32/32 X S kg.

On combining the above three combustion equations we get the equation for the theoretical oxygen requirement for the combustion of C, H and S as

= 32/12 C+8 (H- O/8) + S

Where C, H, S and O represent the masses of carbon, hydrogen, sulphur and oxygen respectively per kg of the fuel.

Since the percentage by weight and volume of oxygen in ain is 23 and 21, the amount of air required theoretically for combustion of 1 kg of fuel is given as

Minimum weight of air required for combustion = 100/23(32/12XC = 8(H – O/8)+ S)kg

Minimum volume of air required for combustion = 100/21(32/12XC = 8(H – O/8)+ S)kg.

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QUESTIONS

(1) Explain the following with suitable illustrations.

(a) Sweetening of petrol

(b) Bergeous method of synthesis of petrol.

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(2) What is cracking? Explain the differ types of cracking processes along with their advantages.

(3) (a) ExplainHCV and LCV of fuels and how do they di_er? What is their signifi cance?

(b) A sample of coal contains the following composition Carbon = 84%, Hydrogen = 12%, Oxygen = 2%, Sulphur = 1% and the remainder being ash. Calculate the gross and net caloric values of the fuel.

(4) Distinguish between the following:

(a) Gross calorific value from net calorific value.

(b) Thermal cracking from catalytic cracking.

(c) Gaseous fuels from liquid fuels.

(5) (a) What are fuels? How are they classified? What are the advantages of gaseous fuels?

(b) Give an account of the analysis of coal by ultimate analysis and its significance.

(6) What is meant by cracking of hydrocarbons? What are its objectives? With the help of neat sketches explain the production of petrol by catalytic cracking.

(7) Classify the following fuels space by furnishing proper reasons.

(a) Coke

(b) Petroleum

(c) Benzol

(d) Biogas

(e) Lignite

(f) LPG

(g) Natural gas

(h) Anthracite.

(8) Write an account on the refining of petroleum by explaining the composition, boiling

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range and uses of deferent fractions obtained during refining.

QBJECTIVE QUESTIONS

- Which of the following fuel gasses posses highest calorific gas (d)
  a) water gas b) producer gas c) natural gas d) coal gas

- Bomb calorimeter is used for determining the calorific value of (d)
  a) solid fuels b) liquid fuels c) gaseous fuels d) solid and liquid fuels

- Ultimate analysis of a fuel is determination of percentage of (a)
  a) C, H, N, S, H_2O b) C, H_2O, ash, and volatile matter
  c) Sulphur only d) fixed carbon

- The process of splitting higher hydrocarbons into smaller hydrocarbon molecules is called (c)
  a) Pyrolysis b) decomposition c) cracking d) combusion

- Iso-octane has an octane rating of (a)
  a) 100 b) 0 c) 50 d) above 100

- Which of the following is used as a jet engine fuel (c)
  a) LPG b) power alcohol c) kerosene d) coal

- A knocking sound is produced in internal combustion engines when the fuel(c)
  a) contains some water b) contains lubricating oil
  c) burns fast d) burns slow

- Hydrocarbon content in gasoline is (b)
  a) $C_1 - C_4$ b) $C_4 - C_{12}$ c) $C_{15} - C_{23}$ d) C_{20} above

- For improving anti knock property of petrol, it is mixed with (d)
  a) lead bromide b) allyl bromide
  c) tetraethyl lead d) tetraethyl lead and ethyl bromide

- Petrol is a mixture of (a)
  a) alkanes b) alkenes c) alkynes d) aromatic hydrocarbons

- Octane number is related with the following petroleum product (b)
  a) diesel oil b) petrol c) kerosene d) lubricating oil

- Calorific value of a fuel is expressed as (c)

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a) K.cal /cm b) k.cal/cm^3 c) k.cal/m^3 d) cal/m^3

- An example of primary solid fuel is (c)
  a) Coke b) Coal Gas c) Lignite d) Charcol

- The catalyst used in moving bed catalytic cracking behaves (c)
  a) as a gas b) as a suspension c) as a fluid d) as plasma

- The presence of nitrogen in a coal sample is (b)
  a) desirable b) undesirable c) most desirable d) most undesirable

- The calorific value of fuel depends upon the percentage of (c)
  a) volatile matter b) ash c) fixed carbon d) moisture

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UNIT-III

ELECTROCHEMISTRY & CORROSION

Electron Transfer Reactions:

- Electron transfer reactions are oxidation-reduction or redox reactions.
- Results in the generation of an electric current (electricity) or be caused by imposing an electric current.
- Therefore, this field of chemistry is often called ELECTROCHEMISTRY.

Definition:

- A Branch of chemistry which deals with the transformation of electrical energy into chemical energy and vice versa.

Terms involved in Electro Chemistry:

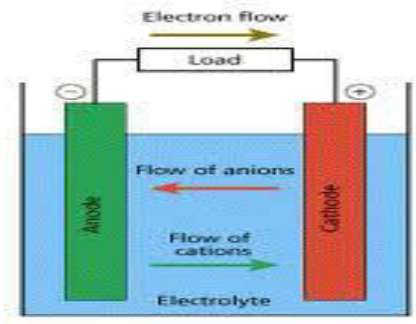
Electrolyte: A substance which in aqueous solution or in molten (fused) state liberates ions & allows electric current to pass through, there by resulting in chemical decomposition.

- **E.g.:** Acids, Bases, & Electrovalent salts.
- **Non Electrolyte:** A substance as such or its aqueous solution, if non conductor of electricity is called a non electrolyte.
- **E.g.:** alcohols, oils, starch solution, petrol etc…
- **Electrode:** Medium through which an electric current enters or leaves the electrolyte is called an electrode.
- Electrode may be a rod or a plate.
- Electrode connected to a negative terminal is cathode. It allows the current to enter the electrolyte.
- Electrode connected to a positive terminal is anode. It allows the current to leave the battery.
- Outside the electrode current flows from anode to cathode, inside the electrolyte it flows from cathode to anode.

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- **Electrolysis:** The process of decomposition of the electrolyte on passing electric current through its aqueous solution or in its molten state is called Electrolysis.
- The apparatus used for the purpose of electrolysis is called as cell.
- **cell:** A cell may be defined as a single arrangement consisting of two electrodes, electrolyte and capable of producing electricity due of chemical reaction & vice versa



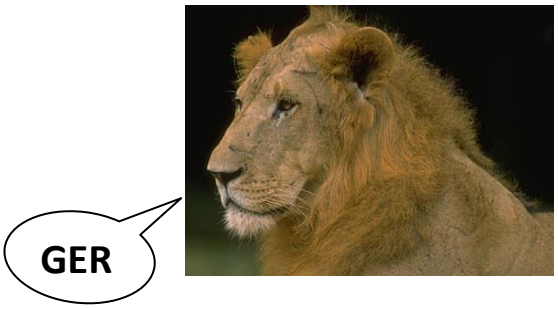
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Terminology for Redox Reactions:

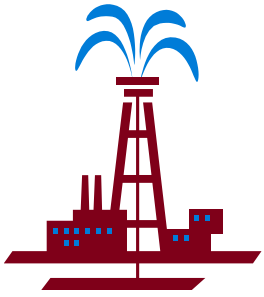
- **OXIDATION**—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- **REDUCTION**—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- **OXIDIZING AGENT:** electron acceptor; species is reduced.
- **REDUCING AGENT:** electron donor; species is oxidized.
- **You can't have one… without the other!**
- Reduction (gaining electrons) can't happen without an oxidation to provide the electrons.

- You can't have 2 oxidations or 2 reductions in the same equation. Reduction has to occur at the cost of oxidation.

LEO the lion says GER!



Another way to remember **OIL RIG**



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Concept of electro chemistry:

- The substances of the universe can fall into 4 different categories based on their capacity to flow electrons, viz,

1. Electrical conductors
2. Insulators
3. Semi conductors
4. Super conductors.

I. Electrical conductors :

- These are the substances which allow the electric current to pass through them. E.g. metals, metal sulphides, acids, bases, etc…
- These are also called as conductors.
- Based on the chemical change occurring in the substance these are divided into 2 types.

1. **Metallic conductors**: The conductors which allow electric current to pass through them without undergoing any chemical change are known as electronic or metallic conductors. E.g. metals (Cu, Fe, Pt, Ag, etc…) Non metals (graphite, certain minerals)
2. **Electrolytic conductors:** The conductors which allow electric current to pass through them & undergo chemical change are known as electrolytic conductors. E.g. acids, bases, salt solutions.

Difference between electronic & electrolytic conductors:

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Electronic conductors	Electrolytic conductors
(1) Flow of electricity take place without the decomposition of substance.	(1)Flow of electricity takes place by the decomposition of the substance.
(2) Conduction is due to the flow of electron	(2) Flow of electricity is due to the movement of ions
(3) Conduction decreases with increase in temperature	(3) Conduction increases with increase in temperature

II. Insulators: these are the substances which do not conduct electricity through them. E.g. pure water, dry wood, rubber, paper, many synthetic organic compounds (benzene, ether, etc…)

III. Semi conductors: elements which show properties intermediate between metals and non metals are known as semi conductors. E.g. elements if IV A group, especially Si, Ge.

Their conducting properties are considerably enhanced by the addition of certain impurities called doping elements.

- These semiconductors are of 2 types.

a) Donor impurities like Phosphorous give n- type semi conductors ('P' has more valance electrons than 'Si')

b) Acceptor impurities like 'B' (boron) give p- type semi conductors. (Boron has less valance electrons than Aluminum.)

IV. Super conductors: The properties of certain metals, alloys and compounds by virtue of which they conduct electricity with zero or negligible resistance is known as super conductors.

E.g. Lead is found to conduct electricity with zero resistance.

- Super conductors store infinite amount of current, because of zero resistance.

Electrical resistance & Ohm's law :

- G.S. Ohm in 1827 found that resistance (R) is related to the current passed (I) and potential difference (E) across the conductor.
- I=E/R.
- Ohm's law is defined as the current strength flowing through a conductor at uniform temperature is directly proportional to the potential difference applied across the conductor& inversely proportional to the resistance of the material.

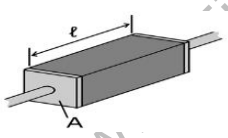
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- Ohm= Volt/Ampere.
- Thus Ohm is the resistance offered by a body when a current of 1 Ampere flows across it under the application of a potential difference of 1 Volt.
- **Resistance:** ability of a substance to resist the flow of electric current is resistance.
- Units: Ohm or Ω.
- **Conductance or conductivity of electrolyte:**
- Ability of a substance to pass electric current through it is conductance.
- A substance having lesser resistance allows more current to pass through it. i.e. conductance is more.
- The reciprocal of resistance is known as conductance.
- Conductance = 1 / Resistance.
- C = 1/R
- Units: C=1/R
- C=1/Ohm = Ohm $^{-1}$ or Ω $^{-1}$ or Mho or Siemens.

Resistivity or specific resistance:

- The resistance of a conductor is proportional to the length and inversely proportional to the area of cross section.



- Rα l/A
- R= ρl/A
- ρ (row) = specific resistance or resistivity
- *R* = the electrical resistance of a uniform specimen of the material (measured in ohms, Ω)
- l=the length of the piece of material (measured in centimeters, cm)
- *'A'* is the cross-sectional area of the specimen (measured in square centimeters, cm²).
- If l=1, a=1 cm²; R= ρ

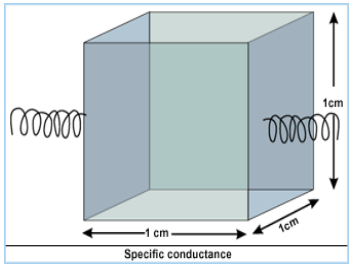
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- Specific resistance or resistivity of a conductor is the resistance between two opposite faces of a cm^3 of that substance.
- Resistance of 1 cm^3 substance or 1ml electrolyte solution is called as specific resistance. 1ml=1cm^3
- Units: R= ρ l/a
- ρ =Ra/l = Ohm X cm^2/cm = Ohm.cm

Specific conductance or conductivity (κ):

- It is the conductance of a material or solution occupying one cm^3 volume.
- Specific conductance $\kappa = \frac{1}{\rho}$
- But, ρ =Ra/l; k=l/a R



- $\kappa = \frac{l}{a}$ X conductance.
- Units: ohm^{-1}. cm^{-1} = mho. cm^{-1} (C.G.S system) or
- Siemens. m^{-1} (S.I system)
- The specific conductance depends on the nature of substance or the electrolyte.
- It increases with increase in concentration of the electrolytic solution since the number of ions per unit area increases.

Equivalent conductivity (Λ):

- The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity. It is denoted by Λ or λ.
- Let us consider the V cm^3 of solution containing one equivalent of an electrolyte. Its conductance is equal to equivalent conductance, Λ.

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- Also we know that the conductance shown by 1 cm^3 solution containing this electrolyte is called specific conductance, κ.
- i.e.,
- the conductance of V cm^3 --------- Λ
- the conductance of 1 cm^3 --------- κ
- Therefore:
- $\Lambda = \kappa.V$
- Units of Λ: = cm^2 . ohm^{-1}. $equiv^{-1}$ = cm^2 . mho. $equiv^{-1}$ or
- m^2 . Siemens. $equiv^{-1}$
- In terms of concentration $\Lambda = k.1000/c$
- C = concentration of the solution in normality or gr.eqt/lt

Molar conductivity (Λ_m or μ):

- The conductance of that volume of solution containing one mole of an electrolyte is known as molar conductivity. It is denoted by Λ_m or μ.
- It is related to specific conductance, κ as:
- $\mu = \kappa.V$
- Units of μ:= cm^2 . ohm^{-1}. mol^{-1} = cm^2 . mho. mol^{-1} or
- m^2 . Siemens. mol^{-1}
- In terms of concentration $\mu = k.1000/c$
- C = concentration of the solution in molarity or moles/lt .

The relation between equivalent conductance, Λ and molar conductance, μ:

- $\mu = \Lambda$ x equivalent factor of the electrolyte
- $\Lambda = \mu$ / charge of anion or cat ion or valence
- The equivalent factor of the electrolyte is usually the total charge on either anions or cat ions present in one formula unit of it. It may be equal to basicity in case of acids or equal to acidity in case of bases.

Cell constant (x):

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- The ratio of the distance between the electrodes, *l* to the cross sectional area, A of the electrodes is known as cell constant. It is denoted by X
- The cell constant can be determined by using following relations which can be derived easily from expressions discussed above.
- X = l/a
- l= distance between the two electrodes
- a= area of cross section of two electrodes.

Units: $X = l/a = cm/cm^2 = cm^{-1}$

Illustrative Example:

The resistance of 0.01N NaCl solution at 25^0C is 200 ohm. Cell constant of conductivity cell is unity. Calculate the equivalent conductance and molar conductance of the solution.

Solution:

- Conductance of the cell=1/resistance =1/200=0.005 S.
- Specific conductance=conductance x cell constant =0.005 x 1=0.005 S cm^{-1}

Solution Cont

Equivalent Conductance = Specific conductance x (1000/N)

= 0.005 x 1000/0.01 = 500 $ohm^{-1}cm^2eq^{-1}$

Molar Conductivity = Equivalent conductivity x n-factor = 500 x 1 = 500 $ohm^{-1}mol^{-1}cm^2$

Factors influencing the conductance of solution:

- **Temperature:** The conductance of an electrolyte solution increases with increase in the temperature due to increase in the extent of ionization.
- **Nature of electrolyte:**
- The strong electrolytes undergo complete ionization and hence show higher conductivities since they furnish more number of ions.
- Whereas weak electrolytes undergo partial ionization and hence show comparatively low conductivities in their solutions.

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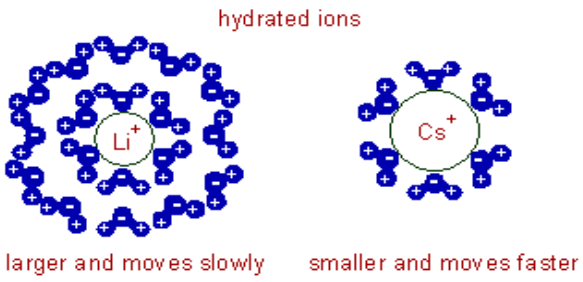
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Ionic size & mobility:

- The ionic mobility decreases with increase in its size and hence conductivity also decreases.
- E.g. In molten state, the conductivities of lithium salts are greater than those of cesium salts since the size of Li^+ ion is smaller than that of Cs^+ ion.



- However, in aqueous solutions the extent of hydration affects the mobility of the ion, which in turn affects the conductivity. Heavily hydrated ions show low conductance values due to larger size.
- E.g. In aqueous solutions Li^+ ion with high charge density is heavily hydrated than Cs^+ ion with low charge density. Hence hydrated Li^+ bigger than hydrated Cs^+. As a result, lithium salts show lower conductivities compared to those of cesium salts in water.



The nature of solvent and its viscosity:

- The ionic mobility is reduced in more viscous solvents. Hence the conductivity decreases.

Concentration:

- The specific conductance (κ) increases with increase in concentration of solution as the number of ions per unit volume increases.
- Whereas, both the equivalent conductivity and molar conductance increase with decrease in concentration (i.e. upon dilution) since the extent of ionization increases.
- Explanation: Since the concentration decreases, one can expect decrease in equivalent conductivity due to decrease in available number of ions per unit volume. However the

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increase in volume (V) factor more than compensates this effect. The volume must be increased in order to get one equivalent of electrolyte since the concentration is decreased. Hence the net effect is increase in equivalent conductivity.

Limiting equivalent conductivity (Λ_o):

- The equivalent conductivity reaches a maximum value at certain dilution and does not change upon further dilution (i.e., by adding solvent further). This concentration is also termed as infinite dilution.
- The equivalent conductivity at infinite dilution is known as the limiting equivalent conductivity *(Λ_o).* At this dilution, the ionization of even the weak electrolyte is complete.
- However at infinite dilution (i.e., when concentration approaches zero) the conductivity of the solution is so low that it cannot be measured accurately.

Conductance ratio (α) : The ratio of the equivalent conductance at given concentration, Λ_c to that at infinite dilution, Λ_o is called conductance ratio, α.

- $\alpha = \Lambda_c / \Lambda_o$
- For weak electrolytes, the 'α' is also called as degree of ionization.

Applications of conductance - Conductometric titrations:

- It is a method of volumetric analysis based on the change in conductance of the solution at the equivalent point or end point during the titrations.
- This method is based on the fact that the conductance of an aqueous solution, containing an electrolyte depends upon
    1. The number of free ions in the solution,
    2. The charge on the free ions, and
    3. The mobility of the ions.
- During the course of titration (i.e. addition of one electrolyte solution to the other) the number of free ions in the solution change, identity of the ions change.
- As a result conductance of the solution (contained in a cell) also changes.
- This technique can be readily used with
    a. Colored solutions where the selection of an indicator is difficult,
    b. Acids, bases, and their mixtures, weak acid against weak base where no indicators are available in volumetric analysis.
    c. These are useful for dilute solutions.
    d. Ions and their mixtures that are readily precipitated by the addition of titrant.

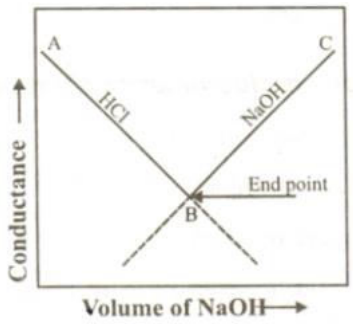
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Few examples of acid-base titrations are discussed below.

Titrations of Strong Acid Vs Strong Base:

- Strong acids dissociate completely to give H^+ ions
- These protons themselves are more conducting than all the ions & almost 2 times more conducting than OH^- ions.
  $H^+Cl^- + Na^+ + OH^- \rightarrow (Na^+ + Cl^-) + H_2O$
- Initially high conducting H^+ ions are neutralized by low conducting Na^+ ions.
- Therefore addition of alkali results in the fall of conductance (curve AB) till all the H^+ ions are neutralized.
- After neutralization if further amount of base is added, it produces high conducting OH^- ions in the solution.



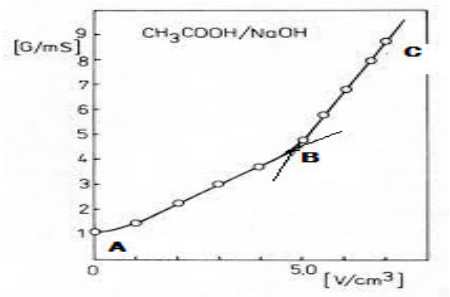
- Therefore conductance increases sharply (curve BC).
- $(Na^+ + Cl^-) + H_2O + (Na^+ + OH^-) \rightarrow$ No of Na^+ & OH^- ions increases at neutralization point.
- Observation: initial conductance decreases followed by sharp increase in conductance.

Titration of weak acid (CH_3COOH) by strong base (NaOH):

- At the beginning of the titration, a weak acid has low conductance due to incomplete ionization.
- Addition of alkali to this weak acid solution, initially results in small increase in conductance, due to replacement of H^+ ions by Na^+ ions where the $CH_3COO^-Na^+$ is formed and ionized completely.
- This indicates during neutralization ions are increased.
- Therefore conductance increases slowly (curve AB).

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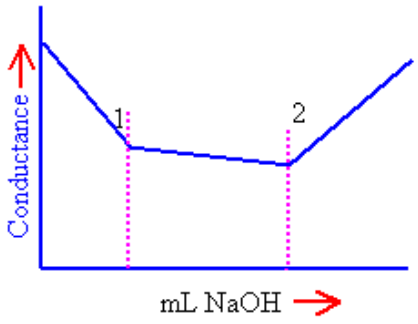


- $CH_3COOH + (Na^+ + OH^-) \rightarrow (CH_3COO^- + Na^+) + H_2O$
- After neutralization is completed, if further base is added, it produces fast conducting OH^- ions in solution.
- Therefore conductance increases rapidly (curve BC).
- $[(CH_3COO^- + Na^+) + H_2O] + (Na^+ + OH^-) \rightarrow$ No of Na^+ & OH^- ions increases at neutralization point.
- Observation: initial conductance increases slowly followed by sharp increase in conductance.

Titration of a mixture of a strong acid(HCl) & a weak acid (CH_3COOH) with a strong base (NaOH):

- Valuable feature of the conduct metric titrations is the titration of mixture of strong acid & weak acid at one titration without any indicator.
- In presence of a strong acid, the dissociation of a weak acid is completely suppressed due to common ion effect.
- Therefore first neutralization of strong acid takes place, when NaOH is added. The weak acid starts reacting only after complete neutralization of strong acid.

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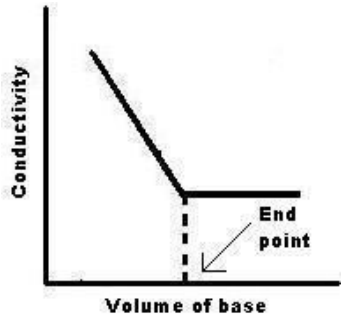
- The point 1 represents the neutralization of strong acid and the point 2 represents the neutralization of weak acid.

Strong acid (HCl) Vs Weak Base (NH_4OH):

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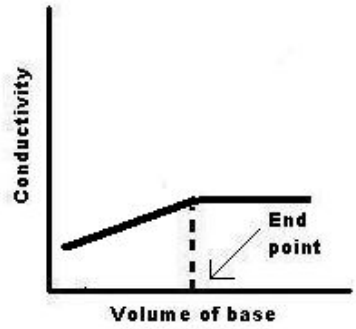
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- E.g., $[H^+ + Cl^-] + [NH4^+ + OH^-] \dashrightarrow [NH4^+ + Cl^-] + H_2$
- In this case, initially the conductance will be more because of H^+ ions. But if once the $NH_4^+ OH^-$ is added, H^+ ions will be replaced by $NH4^+$ ions and so the conductivity decreases. As NH_4OH is a weak base, it do not dissociate and so after neutralization the conductivity do not increase



Weak Acid (CH_3COOH) Vs Weak Base (NH_4OH):

- $CH_3COOH + [NH4^+ + OH^-] \rightarrow CH_3COONH_4 + H_2O$
- Weak acid with weak base does not give a sharp end point.



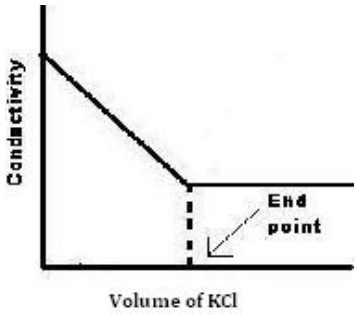
- The initial conductance of the solution is low due to the poor dissociation of the weak acid, but starts' rising as CH3COONH4 is formed.
- After the equivalence point, the conductivity remains almost constant, because the free base NH_4OH is a weak electrolyte.The end point is quite sharp in this case, by conductometric titration.

Precipitation titrations:

- During the precipitation titration, the color change of the indicator is not clear or even impossible to detect the end point by volumetric titrations.
- Addition of alcohol and using fairly dilute solutions reduces the solubility of the precipitate and prevents absorption.

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- In the titration of KCl against $AgNO_3$ the change in the conductivity on addition of $AgNO_3$ is not much, since the mobility of K^+ and Ag^+ are of the same order and the curve is nearly horizontal.
- After the end point there is sharp increase in conductance due to an increase in the number of free ions in solution.
- $K^+Cl^- + Ag^+NO_3^- \rightarrow K^+ NO_3^- + Ag^+ Cl^-$



ELECTROCHEMICAL CELL:

A cell may be defined as a single arrangement consisting of two electrodes, electrolyte and capable of producing electricity due of chemical reaction and vice versa.

Electro chemical cells are of 2 types, viz:

1. Galvanic (or) Voltaic cell
2. Electrolytic cell

Galvanic (or) Voltaic cell:

- The redox reaction in a galvanic cell is a spontaneous reaction.
- These cells use the energy released from spontaneous chemical energy to generate electricity. For this reason, galvanic cells are commonly used as batteries.
- Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow.
- A common galvanic cell is the Daniel cell.

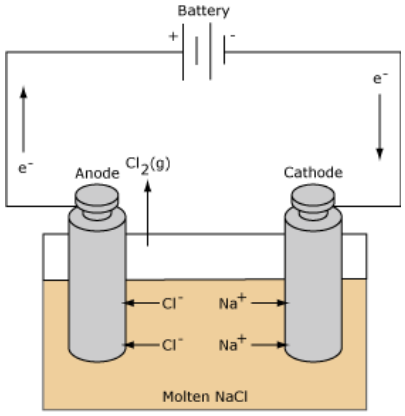
Electrolytic Cells

- The redox reaction in an electrolytic cell is nonspontaneous.

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- Electrical energy is required to induce the electrolysis reaction.
- An example of an electrolytic cell is shown below, in which molten NaCl is electrolyzed to form liquid sodium and chlorine gas.
- The sodium ions migrate toward the cathode, where they are reduced to sodium metal.
- Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas.
- This type of cell is used to produce sodium and chlorine.
- The chlorine gas can be collected surrounding the cell. The sodium metal is less dense than the molten salt and is removed as it floats to the top of the reaction container.



Electrolytic Cell

Galvanic cell:

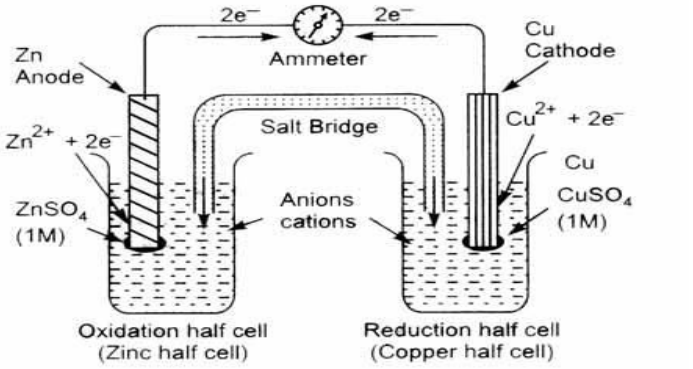
- It is a devise which converts chemical energy into electrical energy .
- When a system consists of two electrodes dipped into an electrolyte solution and electrodes connected by some metallic conductor outside the electrolyte, this produces an electric current in external circuit called a galvanic cell.
- In galvanic cell cathode has higher potential than anode.

Eg: Daniel cell

- Daniel cell is a Zinc-Copper cell that can be represented as $Zn/ZnSo_4//CuSo_4/Cu$
- Zinc rod is dipped in Zinc Sulphate solution, Cu rod is dipped in Copper Sulphate solution

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Daniell cell

- And the 2 electrodes are connected through salt bridge, Ammeter or Volt meter.
- When these connections are made current flows in external circuit.

Observation:

- The direction of deflection of ammeter indicates flow of electrons is from Zn rod to Cu rod Zn rod starts dissolving in solution to form Zn^{+2} in solutions.
- Therefore weight of Zn rod decrease. Here Zn is releasing electrons therefore Oxidation half cell reaction.

At Anode: $Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$ (OHR (Oxidation Half cell Reaction))

- Zn rod pushes the electrons into the external circuit, indicates that it is acting as a negative pole. Therefore in electrochemical cell anode is negatively charged electrode.
- The electrons released by Zn flow in external circuit and reaches Cu rod.
- Cu^{+2} ions present in solution gains electrons and reduce to Cu rod. Therefore weight of Cu rod increases.
- Cu is taking electrons hence reduction takes place.

At Cathode: $Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ (RHR (Reduction Half cell Reaction))

- Cu rod takes the electrons from external circuit indicates that it is acting as +ve pole.
- Therefore in electrochemical cell cathode is positively charged electrode.

Total cell reaction = OHR+ RHR

$$Zn_{(s)} \rightarrow Zn^{+2} + 2e^- \text{ (Anode)}$$

$$Cu^{+2} + 2e^- \rightarrow Cu_{(s)} \text{ (Cathode)}$$

$$Zn_{(s)} + Cu^{+2} \rightarrow Zn^{+2} + Cu_{(s)}$$

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- Due to reaction, potential difference between 2 electrodes of Cu, Zn is produced in the form of current in the external circuit.
- It is also known as EMF or the cell potential.

Function of salt bridge:

- ✓ It provides diffusion of ions in internal circuit.
- ✓ That is cations diffuse from anode to cathode & anions diffuses from cathode to anode through the salt bridge.
- ✓ As a result, accumulation of charge at the electrodes in the external circuit to continue the cell reactions.
- ✓ Salt bridge is made up of KCl (or) NH_4OH (or) Agar Agar.

Reduction Potential:

- ❖ In an electrochemical cell, the electrode having highest reduction potential undergoes reduction. That is it acts as cathode.
- ❖ The electrode having lowest reduction potential undergoes oxidation. That is it acts as anode.
- ❖ Zn < Fe < H_2 < Cu < Ag.
- ❖ If a cell is constructed by Fe & Cu electrodes Fe is anode & Cu is Cathode because Cu has more reduction potential.
- ❖ For any electrode it's reduction potential = -ve oxidation potential.
- ❖ R.P = -ve O.P
- ❖ E.g.: R.P of Cu = 0.43 Volts => $E_{Cu^{+2}/Cu}$ = 0.34 V, O.P of Cu = -0.34 => $E_{Cu^{+2}/Cu}$ = -0.34V.

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Electrochemical series:

- ➢ The arrangement of elements in the order of their standard electrode potential is referred to as electrochemical series.
- ➢ Generally electrode potential is expressed as reduction potential.
- ➢ Increasing order of standard reduction potential at 25^0C electrochemical series is Standard electrode potential.

Electrochemical series of few elements is as follows:

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Standard Reduction Potentials

Ox. agent strength increases

Red. agent strength increases

Reduction Half-Reaction	E°(V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$	1.23
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

EMF: ELECTROMOTIVE FORCE:

- The force that causes the flow of electrons from one electrode to the other and thus results in a flow of current is called the electromotive force. That is EMF(E_{cell}) or electromotive force.
- The potential difference between the two electrodes of a galvanic cell which causes the flow of electrons from one electrode of higher potential to the other electrode of lower potential is called electro motive force.
- UNITS: Volts

Standard EMF:

- It is defined as the EMF of a galvanic cell when the reactants and the products of a cell reaction are at unit concentration at 298°K temperature & at 1atm pressure.
- It is denoted by E^{o}

Electrode Potential or Single Electrode Potential: (E)

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- When a metal rod is dipped in its ion solution, potential difference arises between electrode and the electrolytic solution in which it is dipped.
- This potential difference is called electrode potential.
- The potential of the electrode depends on
  i. Nature of electrode
  ii. Conc. Of electrolyte solution
  iii. Temperature.
- It is not possible to determine the potential of an electrode directly. But, potential difference between electrodes can be determined.
- Therefore to determine the potential of electrode standard hydrogen electrode is taken as a reference electrode, and its electrode potential is taken as zero Volts.
- EMF of an electrochemical cell can be calculated by electrode potential of anode and cathode.

E_{Cell} = Reduction Potential of Cathode – Reduction Potential of Anode.

- $E_{Cell} = E_{Cathode} - E_{Anode}$
- $E_{Cell} = E_{Right} - E_{Left}$
- E.g.: Galvanic cell.
- $Zn_{(s)}/Zn_{(aq)}^{+2}//Cu_{(aq)}^{+2}/Cu_{(s)}$
- $E_{Cell} = E_{Cu}^{+2}{}_{/Cu} - E_{Zn/Zn+2}$
- Consider Zn –Cu cell reaction $Zn_{(s)} + Cu^{+2} \rightarrow Zn^{+2} + Cu_{(s)}$
- O.H.R -$Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$ (Anode), $E_{Zn/Zn+2} = -0.76$
- R.H.R-$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ (Cathode), $E_{Cu}^{+2}{}_{/Cu} = 0.34$
- $E_{Cell} = 0.34-(-0.76) = 1$ Volt.

Nernst Equation:

- When *Eo* is positive, the reaction is spontaneous. When *Eo* is negative, the reaction is not spontaneous. Since the change in Gibbs free energy, ΔG, is also related to spontaneity of a reaction, therefore, ΔG and *E* are related. Specifically,

$$\Delta G = -nFE$$

- This equation explains the effect of electrolyte concentration on electrode potential. Consider a general electrode reaction
- $M^{n+} + ne^- \rightarrow M_{(S)}$
- $\Delta G = \Delta Go + RTln\left[\frac{a\ product}{a\ reactant}\right]$
- Where, *n* is number of electrons transferred in the reaction, *F* is the Faraday constant (96500 C/mol) and *E* is potential difference. Under standard conditions, this equation is then

$$\Delta Go = -nFEo.$$

Since, $\Delta G = \Delta Go + RTln\left[\frac{a\ product}{a\ reactant}\right]$ **Equation (1)**

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- Substituting $\Delta G = -nFE$ and $\Delta Go = -nFEo$ into equation (1), we have:

$$-nFE = -nFEo + RTln\left[\frac{a\ product}{a\ reactant}\right]$$

- Divide both sides of the equation above by $-nF$, we have

$$E = Eo - \frac{2.303RT}{nF}\log\left[\frac{a\ product}{a\ reactant}\right] \quad \textbf{Equation (2)}$$

- Where *R, T, Q* and *F* are the gas constant (8.314 J mol^{-1} K^{-1}), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively, 'a' is activity. Thus, we have at standard temperature T = 298K, the $2.303RTF$ equals .0592 V, so equation (2) turns into

$$E = Eo - .\frac{0.0592V}{n}Log\left[\frac{a\ product}{a\ reactant}\right]$$

- In dilute solutions, activities are replaced by molar concentration terms.

$$E = Eo - .\frac{0.0592V}{n}Log\left[\frac{[M]}{[Mn+]}\right]$$

For pure solid $M_{(S)} = 1$

$$E = Eo - .\frac{0.0592V}{n}Log\left[\frac{1}{[Mn+]}\right]$$

- The above equation is the Nernst equation at 298K. at any other temperature (T)

$$E = Eo - \frac{2.303RT}{nF}\log\left[\frac{1}{[Mn+]}\right]$$

- From the above equation we can say that the electrode potential 'E' increases as $[M^{n+}]$ is increased and decreases as the temperature increases.
- Nernst equation for the cell reaction is
- a A + b B = c C + d D

$$\square E = \square E^{\circ} - \frac{2.303RT}{nF}\ log\left[\frac{[C]c\ [D]d}{[A]a\ [B]b}\right]$$

- At 298K the equation becomes

$$\square E = \square E^{\circ} - \frac{0.0592V}{n}\ log\left[\frac{[C]c\ [D]d}{[A]a\ [B]b}\right]$$

- The Nernst equation can be used to determine
  1) EMF of the cell at given concentration of reactants and products
  2) Equilibrium constant for a reaction
  3) Gibbs energy of a reaction

Types of electrodes:

- Nernst equation is applicable to the half cell reactions. Few half cell reactions & corresponding Nernst expressions for some important electrodes is discussed below.

Redox electrode:

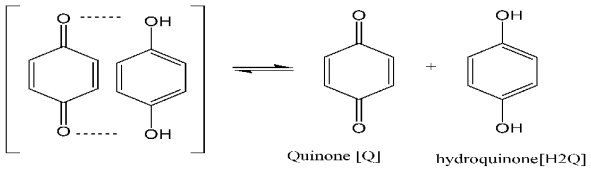
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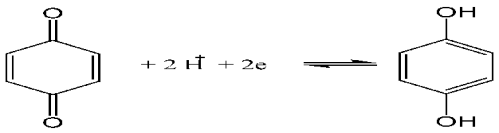
- Platinum rod dipped in a mixture of 2 different oxidation states of a metal (or) two redox states of any compound is called a redox electrode. A very good example of this kind of an electrode is Quinhydrone electrode.

Quinhydrone Electrode:

- Quinhydrone is an organic molecular compounds formed by the addition of quinone and hydro-quinone in equimolar proportion.
- It is slightly soluble in water and is partially dissociated in aqueous solution to quinone and hydroquinone



- Quinone and hydroquinone constitute a conjugate redox pair



- If an inert electrode such as platinum wire is immersed in the system potential is developed and given by Nernst equation:

$$E_{Q/H_2Q} = E^{o}_{Q/H_2Q} - \frac{0.059}{2}\log\frac{[H_2Q]}{[Q][H^+]^2}$$

$$E_{Q/H_2Q} = E^{o}_{Q/H_2Q} - \left(\frac{0.059}{2}\log\frac{[H_2Q]}{[Q]}\right) - \left(\frac{0.059}{2}\log\frac{1}{[H^+]^2}\right)$$

$$E_{Q/H_2Q} = E^{o}_{Q/H_2Q} - 0.059\,pH$$

- To measure the hydrogen ion concentration about 0.1 gm of quinhydrone is added to the solution, the quantity must be sufficient to saturate the solution and have some undissolved quinhydrone.
- After stirring for two minutes the redox potential is measured by dipping a platinum electrode and connects it with a suitable reference electrode.

❑Advantages

1. It is not affected by catalytic poisons.
2. It gives satisfactory results in presence of carbonic acid.
3. Easy to prepare and use.

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4. It comes to equilibrium rapidly.

- **Disadvantages:**

1. It cannot be used in presence of oxidizing agents which oxidize hydroquinone to quinone also reducing agents that reduce quinone to hydroquinone. This affects the ratio of $[H_2Q]/[Q]$ and makes the equation un-applicable.
2. The upper limit of the electrode use is pH 8 above which hydroquinone, which is, weak acids dissociates and affects the pH.
3. Atmospheric oxygen slowly oxidizes hydroquinone. It needs to be used freshly.

Calomel electrode (secondary reference electrode):

- It is a metal- metal insoluble salt electrode, and a secondary reference electrode for potential measurements.
- The calomel or mercury/mercurous chloride electrode is a member of a group of electrodes in which a mercurous salt is in equilibrium with a soluble anion.
- Such anions have included bromide, iodide, phosphate, iodate, acetate, and hydroxide.
- But mercury type electrodes with chloride ion as the anion in the salt are the most commonly available.
- The mercurous chloride paste is called calomel, hence the name of the electrode.

Construction:

- Calomel electrode consists of tube in the bottom of which is a layer of mercury, over which is placed a paste of $Hg+Hg_2Cl_2$.
- The remaining portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl.
- A platinum wire dipping into the mercury layer is used for making electrical contact.
- The side tube is used for electrode is formulated as; $Hg/Hg_2Cl_2/KCl$.
- The electrode can be coupled with the hydrogen electrode of unknown pH.

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Half reaction:

When it acts as anode:

$2Hg \rightarrow 2Hg^{+} + 2e^{-}$

$2Hg^{+} + 2Cl^{-} \rightarrow Hg_2Cl_2$

$2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$

When it acts as cathode:

$2Hg^{+} + 2e^{-} \rightarrow 2Hg$

$Hg_2Cl_2 \rightarrow 2Hg^{+} + 2Cl^{-}$

$Hg_2Cl_2 + 2e^{-} \rightarrow 2Hg + 2Cl^{-}$

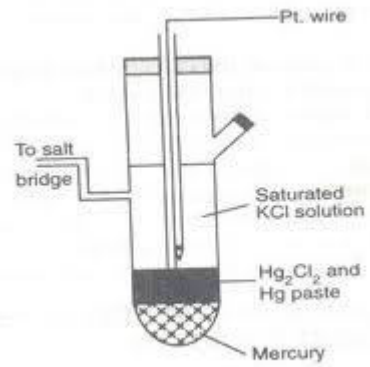


Fig. 12.15 Calomel electrode

The Nernst equation for the electrode: The potential of the electrode depends on the chloride ion concentration obtained from potassium chloride in the solution. This effect is illustrated as follows:

$$E = E^{\circ} - \frac{2.303RT}{2F} log[Cl-]^2$$

$$E = E^{\circ} - \frac{2.303RT}{F} log[Cl-]$$

At 298K $E = E^{\circ} - 0.0591\ log[Cl-]$

Calomel electrode prepared in saturated KCl, 1M KCl and 0.1M KCl has potentials of:

- However, once it is prepared in either one of these solutions it has a definite constant potential.
- When the KCl solution is saturated, 1N, 0.1N, it is called saturated calomel electrode (SCE), Normal calomel electrode (NCE), Decinormal calomel electrode (DNCE).

KCl	E volt
Saturated	0.241
1N	0.280
0.1N	0.334

Advantages:

- ✓ It is simple to construct
- ✓ Results of cell potential measurements are reproducible, stable, & do not vary with temperature.

Glass electrodes for pH-measurements:

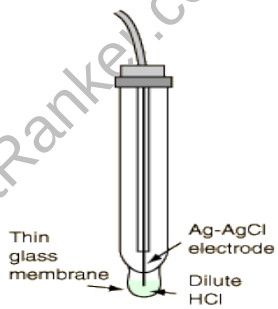
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- This is the most used one for measuring the pH. It is one of the ion selective electrodes, which is specific for hydrogen ion
- When two solutions of different PH values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane.
- The potential difference developed is proportional to the difference in pH value.
- The glass membrane acts as an ion-exchange resin, & an equilibrium is set up between the Na^+ ions of the glass[glass contains Na_2O-22%, CaO-6%, SiO_2-72%] and H^+ ions in solution.
- For a particular type of glass the potential difference varies with the H^+ ion concentration, and is given by the expression
  E_{Glass} = glass potential
  E^0_G = standard glass electrode potential
  $E_{Glass} = E^0_G + 0.0592$ V pH.
  Over a range of pH of the test solution 0-10.

Construction:

- Glass electrode consists of a thin walled glass tube or bulb containing AgCl coated Ag electrode or simply a platinum electrode in 0.1M HCl.
- Schematic representation of glass electrode is
  $Ag/AgCl_{(s)}$, HCl (0.1M)/ Glass or Pt, 0.1M HCl/ $Glass^+$



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- HCl in the bulb furnishes a constant H^+ ion concentration.
- Thus, it is a silver- silver chloride electrode reversible with respect to chloride ions.
- Glass electrode is used as "internal reference electrode" for determining the pH of solutions, especially colored solutions containing oxidizing or reducing agent.
- Usually calomel electrode is used as the second electrode.
- In order to determine the pH of the solution, the glass electrode is placed in the solution under test, and this half cell is coupled with the saturated calomel electrode& EMF of the cell is measured.
- Since resistance is very high, special electron-tube voltmeters are used to measure the EMF of the above cell.
- The EMF of the complete cell is given by
  $E_{Cell} = E_{Right} - E_{Left}$

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=0.02422V-[E^0_G + 0.0592 V pH]

pH = $\frac{0.02422V-ECell-E0G}{0.0592\ V}$

- The E^0_G value of a glass electrode can be determined by using a solution of known pH.

Advantages of glass electrode:

- It can be used in presence of oxidizing, reducing, complexing and catalytic poisonous substances. Also in reactions involving volatile constituents' noble metals….
- It is simple and can be easily used.
- Equilibrium is rapidly achieved.
- The results are accurate.

Disadvantage:

1. Delicate, it can't be used in presence of dehydrating agent e.g. conc. H_2SO_4, ethyl alcohol….
2. It can be used in the solutions with pH range 0-10.
3. Interference from Na^+ occurs above pH 12 i.e. Na^+ exchange together with H^+ above pH 12 and higher results are obtained.
4. Above pH 12 cations of the solution affect the glass interface and render the electrode useless.
5. Although glass membrane of the electrode is very thin, yet it's resistance is extremely high, which cannot be measured by ordinary potentiometers.

<u>Potentiometric titration</u>:

- ❖ Potentiometric titrations are very useful for EMF measurements.
- ❖ In this method, a cell is concentrated in which at least one of the electrode is reversible with respect to one of the ions taking part in the titration reactions.

<u>Theory</u>:

- ❖ The potential of an electrode dipped in electrolytic solution depends upon the concentration of the active ions.

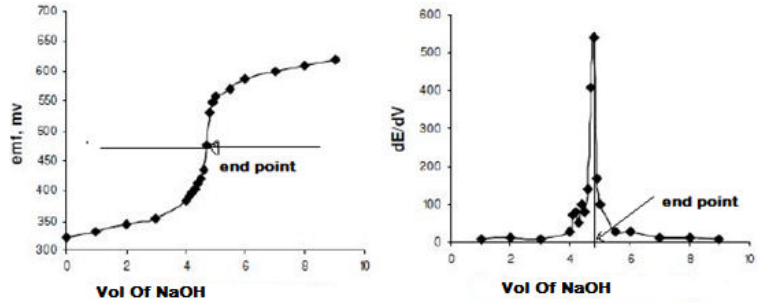
  $E = E^0 + \frac{RT}{nF} \log C$
- ❖ In titration reactions, indicator electrode potential can be measured with end point (or) equivalence point.

<u>Detection of end point</u>:

- ❖ We know that EMF of the cell changes by the addition of small lots of titrant, so, the concentration of reversible ion in contact with indicator electrode changes.
- ❖ Therefore the change of potential will be slow first, but at equivalence point it changes sharply.
- ❖ The values are then plotted against volume changes.

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- ❖ From the graphs the point where the slope of the curve is maximum is known as end point.
- ❖ Potentiometric titrations are of different types.

Acid- Base Titrations:

- In acid –base titration Quinhydrone electrode acts as a indicator electrode. & Saturated calomel electrode acts as a reference electrode.
- Consider a large beaker with definite volume of acid solution & then add a pinch of Quinhydrone & stir well, a platinum electrode is dipped in it, this electrode is connected to a calomel electrode through potentiometer.
- Now alkali solution is added from the burette, the cell EMF increases gradually, but, at the end point suddenly it will increase.
- If the plot is drawn between $^{\Delta E}/_{\Delta V}$ versus 'V' a maximum point on the curve gives the end point.
- By this method, we can titrate even strongly colored solutions, but ordinary indicator is useless.

Redox Titrations:

- Titrations involving oxidizing agents [$K_2Cr_2O_7$ (or) $KMnO_4$] and reducing agents (Ferrous salts) can be followed potentiometrically by using Pt indicator electrode.

- On addition of $K_2Cr_2O_7$ from burette, first EMF of the cell increases slowly, but, at the end point there will be sudden increase in the potential.

$$E = E^0 + \frac{RT}{F} \ln \frac{[Fe+2]}{[Fe+3]}$$

- Change in the ratio of $\frac{[Fe+2]}{[Fe+3]}$ is quite rapid at equivalence point.

Precipitation Titrations:

- Precipitation titrations followed potentiometrically by the use of active metal electrode.
- Eg: Titration of $AgNO_3$ with standard KCl solution run from the burette.
- Ag electrode is dipped in $AgNO_3$ solution is used as indicator electrode.

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- The potential of Ag/Ag^+ half cell is measured by connecting it to saturated calomel electrode through salt bridge NH_3NO_3.
- When the reaction proceeds, concentration of Ag^+ ions decreases and Ag^+ ions are precipitated as AgCl.
- $[Ag^+ NO_3^-] + [K^+Cl^-] \rightarrow AgCl + K^+NO_3^-$
- The reduction potential of indicator electrode (Ag) goes on decreasing on the addition of saturated KCl.
- At the end point, the concentration of Ag^+ change rapidly.
- If addition of KCl is continued, the Ag^+ ion concentration is not affected, except a very small decrease, due to decrease in solubility. If AgCl, on account of common ion (Cl^-) effect.
- On plotting $\Delta E/\Delta V$ versus 'V', the point of maxima gives the end point.

Concentration cells:

- Concentration cell is a galvanic cell in which electrical energy is produced by the transfer of material from a system of high concentration to a system of low concentration.
- There are two types of concentration cells.
  1. Electrode concentration cell,
  2. Electrolyte concentration cell.

1) Electrode concentration cell: In these cells emf arises as a result of two like electrodes at different concentrations dipped in the same solution of electrolyte.

- E.g.: Two Hydrogen electrodes at unequal gas pressures P_1 and P_2 immersed in the same solution of H^+ ion.
- The following cell reactions take place.
  Oxidation reaction: $H_2\ (P_1) \rightarrow 2H^+ + 2e^-$
  Reduction reaction: $2H^+ + 2e^- \rightarrow H_2(P_2)$
  Total reaction: $H_2(P_1) \rightarrow H_2(P_2)$
- It is clear that in this there is no overall chemical change and there is only transfer of H_2 gas from the electrode with pressure P_1 to the electrode with pressure P_2.
- The emf depends only on the two pressures and independent of the concentration of electrolyte solutions Hydrogen ions, in which the electrodes are dipped.

$$E = \frac{RT}{2F} \log \frac{P1}{P2}$$

- In amalgam cells two amalgams of same metal at two different concentrations are dipped in the same solution of metal ions.
- E.g.: two unequal concentrations of Zinc amalgam dipped in a solution of $ZnSO_4$.
  Zn (Hg) C_1/Zn^{2+}/Zn (Hg) C_2
  Overall reaction: Zn (Hg) $C_1 \rightarrow$ Zn (Hg) C_2

$$E = \frac{RT}{2F} \log \frac{C1}{C2}$$

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2) Electrolyte concentration cells:

- These cells consist of two identical electrodes dipped in a two electrolyte solutions of different concentrations, due to which a difference in the potential at the electrode and the electrolyte solution in which it is dipped.
- The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration.
- The emf of the concentration cell falls to zero, when the two concentrations of the electrolyte become identical.
- A concentration cell with two zinc electrodes dipped into two solutions of ZnSO4 with different concentrations C_1 & C_2 joined through a salt bridge can be represented as follows.
  $^{(+)\text{cathode}}Zn/\ Zn^{+2}\ (C_1)//\ Zn^{+2}\ (C_2)/\ Zn^{(-)\text{anode.}}$
- The concentration $C_2 > C1$, the electrode reaction on the left is oxidation.
  $Zn \rightarrow Zn^{+2}(C_2) + 2e^-$ (-) anode (oxidation)
  $Zn^{+2}\ (C_1) + 2e^- \rightarrow Zn$ (+) cathode. (Reduction)
- The emf of such cell can be calculated by the following expression based on Nernst equation.
- $E = \frac{0.0591}{n} \log \frac{C2}{C1}$
- The EMF of the cell is maximum in the beginning, slowly decreases as the reaction proceeds and becomes zero when the concentration of $C_1 = C_2$.

Applications of concentration cells:

- To determine the solubility of a sparingly soluble salt.
- To calculate the valency of cations.
- To determine the transition point.
- To calculate the extent of corrosion in metals.

Batteries:

Battery is an electrochemical cell or often, several electrochemical cells are connected in series that can be used as a source of direct electric current at a constant voltage.

Principle: A battery is a device which converts chemical energy into electrical energy, it is

- ✓ An electrochemical cell
- ✓ A source of direct electric current at constant voltage.
- ✓ Operating on the basis of the principle of galvanic cell.

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Batteries are of three types.

1. **Primary battery or A Primary cell:**

- In this type of batteries cell reaction is not reversible.
- In these electrical energy can be obtained by at the expence of chemical energy, only as long as the active materials are present.
- Thus, when all the reactants are converted into products, no more electricity is produced and the battery becomes dead.
- These are non rechargeable and are meant for a single usage and are meant to be discarded after use.
- These cells are used in ordinary gadgets like torch light, watches & toys.
- Eg: dry cell.

2. **Secondary battery or A Secondary cell:**

- It is one in which the cell reaction can be reversed by passing direct electric current in opposite direction.
- Once used, a secondary battery can be recharged.
- The redox reaction gets reversed during recharge. They are also known as storage cells.
- These are rechargeable and are meant for multy cycle use.

3. **Flow battery or fuel cells:**

- These are ones in which materials pass through the battery this is simply an electrochemical cell.

Primary cells:

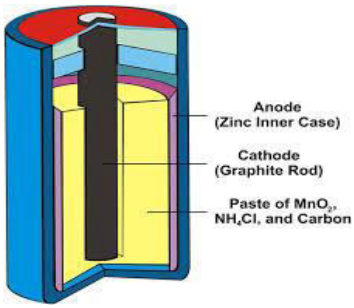
Dry cell (Leclanche cell):

Anode: cylindrical Zinc container.
Cathode: Graphite rod placed in the centre (but not touching the base).
Electrolyte: paste of NH_4Cl and $ZnCl_2$

- Graphite rod is surrounded by powdered MnO_2 and carbon.
- The cell is called dry cell because of the absence of any liquid phase.
  The electrolyte consists of NH_4Cl and $ZnCl_2$ and MnO_2 Mixed with starch to make a paste to prevent leakage.
- The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pitch.
- The dry cell (Zn-MnO_2) is represented as Zn/Zn^{+2}, $NH_4^+/MnO_2/C$
- EMF is 1.5 V.
  At anode: $Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$ (Oxidation)
  At cathode: $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$
  The net cell reaction is: $Zn_{(s)} + 2MnO_2 + H_2O \rightarrow Zn^{+2} + Mn_2O_3 + 2OH^-$

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- The resulting OH^- ions react with NH_4Cl to produce NH_3 which is not liberated as gas but immediately combines with the Zn^{+2} and Cl^- ions to form a complex salt $[Zn(NH_3)_2Cl_2]$ Diammine dichloro Zinc.
  $2\ NH_4Cl + 2\ OH^- \rightarrow 2\ NH_3 + 2Cl^- + 2H_2O$
  $Zn^{+2} + 2\ NH_3 + 2Cl^- \rightarrow [Zn\ (NH_3)_2Cl_2]$

Advantages:

- These cells have voltage ranging from 1.25 V -1.50 V
- Primary cells are used in torches, radios, transistors, hearing aids, pacemakers, watches, etc…
- Price is low.

Disadvantages:

- These cells do not have a long life, because the acidic NH_4Cl corrodes the container even when the cell is not in use.

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Lithium cells:

- These are primary cells.
- Lithium is used as anode, cathode may differ.
- Lithium is used as anode because of it's light weight, high standard oxidation potential (>3V) and good conductivity.
- As the reactivity of lithium in aqueous solution is more, lithium cells use nonaqueous solvent as electrolyte. Lithium cells are classified into two categories.
  a. Lithium cells with solid cathodes.
  b. Lithium cells with liquid cathodes.

a) Lithium cells with solid cathode:

Anode: Lithium metal

Cathode: MnO_2 as an active metal.

Electrolyte: $LiBF_4$ salt in a solution of propylene carbonate and dimethoxy ethane.

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- $MnO_2$is heated to 300^0C to remove water from it so as to work efficiently before keeping it in the cathode.
- Cell potential is 3V.

Reactions: At anode: $Li \rightarrow Li^+ + e^-$

At cathode: $MnO_2 + e^- \rightarrow MnO_2^-$

Net reaction: $Li + MnO_2 \rightarrow LiMnO_2$

Applications:

- Coin type cells are used in watches and calculators.
- Cylindrical cells are used in fully automatic cameras.

Lithium cells with liquid cathode:

Li-$SOCl_2$ cells are example for this.

Anode: Li metal

Cathode: $SOCl_2$ adsorbed on to high surface area carbon cathode.

Electrolyte: $SOCl_2$

Cell reactions: At anode: $4Li \rightarrow 4Li^+ + 4e^-$

At cathode: $4Li+4e^-+2SOCl_2 \rightarrow 4LiCl + SO_2 + S$

Net reaction: $4Li+2SOCl_2 \rightarrow 4LiCl + SO_2 + S$

In this cell discharging voltage is 3.3V – 3.5V.

Uses:

- They are used for military and space applications.
- In medicinal devices such as neuro stimulators, drug delivery systems.
- Electrical circuit boards for supplying fixed voltage for memory protection and stand by functions.

Solid electrolyte lithium cells:

Anode: Li metal

Cathode: poly-2-vinyl pyridine (P_2VP)

Electrolyte: solid lithium iodide (LiI)

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At anode: $2Li \rightarrow 2Li^+ + 2e^-$

At cathode: $2Li^+ + 2e^- + P_2VP.nI_2 \rightarrow P_2VP.(n-1)I_2 + 2LiI$

Net reaction: $2Li + P_2VP.nI_2 \rightarrow P_2VP.(n-1)I_2 + 2LiI$

Uses:

- Because of low current applications and long shelf life

Lithium ion cells – Secondary battery:

Anode: Carbon compound, Graphite.

Cathode: Lithium oxide.

- Cathode consists of a layered crystal (graphite) into which the lithium is intercalated.
- Experimental cells have also used lithiated metal oxides such as $LiCoO_2$, $NiNi_{0.3}Co_{0.7}O_2$, $LiNiO_2$, LiV_2O_5, LiV_6O_{13}, $LiMnO_9$, $LiMn_2O_4$, $LiNiO_{0.2}CoO_2$.

Electrolyte: usually $LiPF_4$, although this has a problem with aluminum corrosion, and so $LiBF_4$ is also used.

- Lithium metal batteries have safety disadvantages. These are overcome in lithium ion batteries.
- In these batteries, membranes are necessary to separate the electrons from the ions. Currently the batteries in wide use have micro porous poly ethylene membranes.
- Intercalation in the cathode keeps the small ions (such as Li^+, Na^+ & the other alkali metals) into the interstitial spaces in a graphite crystal.
- This makes the graphite conductive, dilutes the Li for safety, reasonably cheap. & does not allow dendrites or other unwanted crystal structures of Li to form.

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Lead Acid Storage Battery:

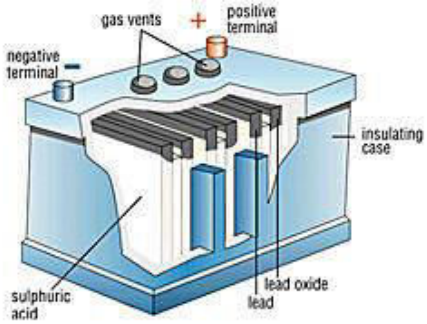
The electrodes are lead grids.

Anode grid: filled with spongy lead.

Cathode grid: lead dioxide (PbO_2)

- A number of electrode pairs with inert porous partitions in between, are dipped in approximately 20% H_2SO_4.
- The battery is encased in a plastic container.

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Electrode reactions for discharging reaction:

- At anode: $Pb \rightarrow Pb^{+2} + 2e^-$

$$Pb^{+2} + SO_4^- \rightarrow PbSO4$$

$$Pb + SO_4^- \rightarrow PbSO4 + 2e^-$$

- At cathode: $PbO2(s) + 4H^+ + 2e^- \rightarrow Pb^{+2} + 2H_2O$

$$Pb^{+2} + SO_4^- \rightarrow PbSO4$$

$$PbO2(s) + 4H^+ + 2e^- + SO_4^- \rightarrow PbSO4 + 2H_2O$$

- Net reaction : $Pb(s) + PbO2(s) + 2H2SO4(aq) \rightarrow 2PbSO4(s) + 2H2O(l) + Energy$
- The potential of lead storage cell depends on the concentration of H_2SO_4
- When the density of H_2SO_4 falls below 1.2 gm/cc the battery needs charging.

Charging: during charging / recharging of the battery an external emf greater than 2V is passed, so that the cell reactions are reversed as shown below.

Electrode reactions for charging reaction:

- At cathode: $PbSO4(s) + 2e^- \rightarrow Pb(s) + SO4^{-2}(aq)$
- At anode: $PbSO4(s) + 2H2O(l) + 2e^- \rightarrow PbO2(s)$
- Net reaction: $2\ PbSO4(s) + 2H2O(l) + Energy \rightarrow Pb(s) + PbO2(s) + 2H2SO4(aq)$

Applications:

- They are extensively used in automobiles, electric supply in telephone exchanges, railway trains, and hospitals.

Advantages:

- The lead storage battery is both a voltaic cell and a electrolytic cell. During discharge process it acts as voltaic cell, during charging process it acts as electrolytic cell.
- It has relatively constant voltage of 12V.
- It is portable and inexpensive.

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Nickel- Cadmium Cells:

Anode: Cadmium

Cathode: $NiO(OH)_{(S)}$

Cell reactions:

At anode: $Cd_{(s)} + 2OH^- \rightarrow Cd(OH)_{2(S)} + 2e^-$

At cathode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_{2(S)} + 2\ OH^-_{(aq)}$

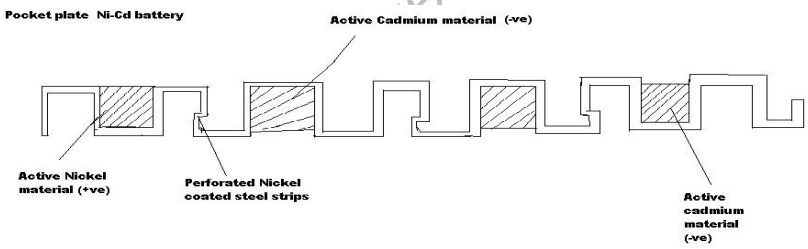
Net reaction: $2NiO(OH) + 2H_2O + Cd_{(s)} \rightarrow Cd(OH)_{2(S)} + 2Ni(OH)_{2(S)}$.

Recharging Ni-Cd Battery:

- The reaction can be easily reversed because the reaction products $2Ni(OH)_{2(S)}$ & $Cd(OH)_{2(S)}$ adhere to the electrode surface.
- Ni-Cd cell gives a1.4V and they can be connected in series to give Ni-Cd storage battery.
- There are two types of Ni-Cd batteries.

A. Pocket plate Ni-Cd Battery:

- Two perforated Nickel coated steel strips acts as pocket plates here.
- Anodic and cathodic materials are filled in these pocket plates, and connected in series as shown below.



- These cells have long shelf life >20 years with capacities between 10 – 1000 ampere and maintain voltage of 1.4 – 1.45 V.

B. Sintered – plate Ni –Cd battery:

Anode: fine Ni sintered in a mold around a Nickel screen impregnated with Nickel Nitrate and processed to produce Nickel hydrate in the pores.

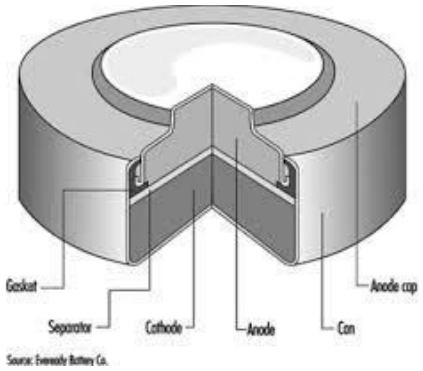
Cathode: the molds are impregnated with Cadmium salt processed to get hydrated oxides inside the pores.

Electrolyte: KOH solution with specific gravity 1.24 -1.3.

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- Anode And cathode are assembled with suitably placed separators such as porous polymer membrane.
- The oxygen liberated during electrolysis, liberated through the porous membrane to Cd cathode to produce Cd $(OH)_2$, which helps in charging.



- The sealed cells are made in three different designs – plates, button cells, & spirally wound cylindrical cells.

Advantages:

- The potential of Cd anode is below the Hydrogen potential. Hence, the Cd electrode is comparatively inert to electrolyte. It requires no float current to keep charged. The water consumption and float charge currents are extremely low.
- These are suitable to very high rate discharge and low temperature operations.
- They have long shelf life without any maintenance.

Applications:

- The Ni –Cd batteries are used for aircraft and diesel engine starting, lighting of trains, emergency power supply and for many military applications.

Fuel cells:

Definition: It is an electrochemical cell, which converts chemical energy contained in readily available fuel oxidant system into electrical energy.

Principle: The basic principle of the fuel cell is same as that of an electrochemical cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel & the oxidant are supplied continuously and separately to electrodes at which they undergo redox reactions.

Fuel cells are capable of supplying current as long as reactants are replenished.

Fuel + oxidant → oxidation products + electricity.

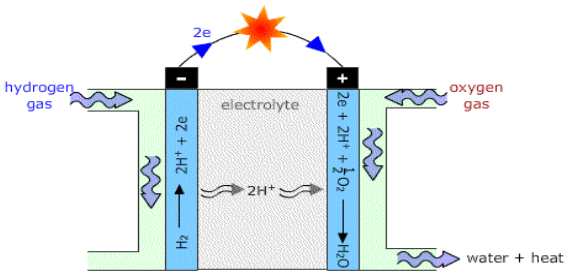
Eg: $H_2 – O_2$ fuel cells, methanol – O_2 fuel cells.

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Hydrogen – Oxygen Fuel Cells:

- This is similar to a galvanic cell.
- Both the half cells have porous graphite electrode with a catalyst (Pt, Ag, or a Metal oxide.)
- The electrodes are placed in the aqueous solution of NaOH or KOH, which acts as an electrolyte.



- Hydrogen and Oxygen are supplied at anode & cathode respectively, at about 50 atm pressure.
- The gases diffuse at respective electrodes.
  Cell reactions:
  At anode: $2H_{2(g)} \rightarrow 4H^+ + 4e^-$

$$4H^+ + 4OH^- \rightarrow 4H_2O$$

$$2H2 + 4OH^- \rightarrow 4H2O + 4e-$$

  At cathode: $O_2 + 2\,H2O + 4e- \rightarrow 4OH^-$

  Net reaction: $2H2 + O2 \longrightarrow 2H2O$

- EMF of the cell is 1V.
- In place of NaOH or KOH phosphoric acid is also used as electrolyte.
- The fuel cells are used at temperatures above 100^0C.

Uses:

- They are used as auxiliary source of energy in space vehicles, submarines etc…
- Because of light weight, these are used in apace crafts.

Advantages:

- Product water is used as drinking water source for astronauts.
- The energy conversion is very high (75 – 82%)
- Noise and thermal pollution are low.
- Fuel cells offer excellent method for use of fossil fuels.
- Maintenance cost is low.

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Disadvantages:

- Life time of a fuel cell is not accurately known.
- Initial cost is high.
- Pure Hydrogen is also costly; liquefaction of hydrogen requires 30% of storage energy.

Methyl Alcohol – Oxygen Fuel Cell:

Anode: Porous Nickel electrode impregnated with Pt/Pd catalyst.

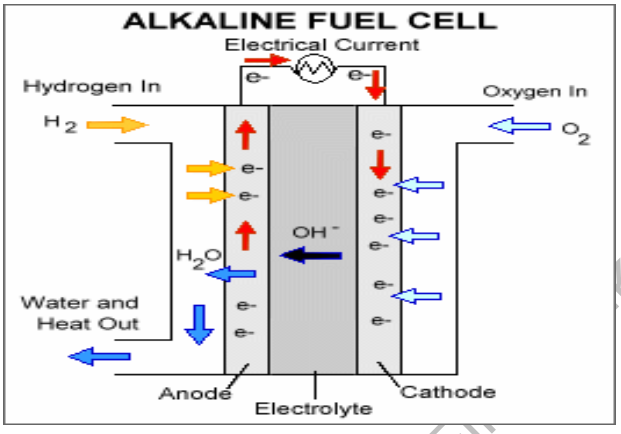
Cathode: Porous Nickel electrode coated with silver catalyst

Electrolyte: KOH

Fuel: Methanol

Oxidant: Oxygen.

CH_3OH, O_2 are sent continuously into their respective electrodes.



Cell reactions:

At anode: $CH_3OH + 6OH^- \rightarrow CO_2 + 5H2O + 6e^-$

At cathode: $3/2\ O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$

Overall reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H2O$

Advantages:

- Methanol fuel cells are reasonably stable at all environmental conditions.
- Easy to transport.
- Do not require complex steam forming operations.
- These are targeted to portable applications.
- Because of high Hydrogen concentration in methanol it is an excellent fuel.

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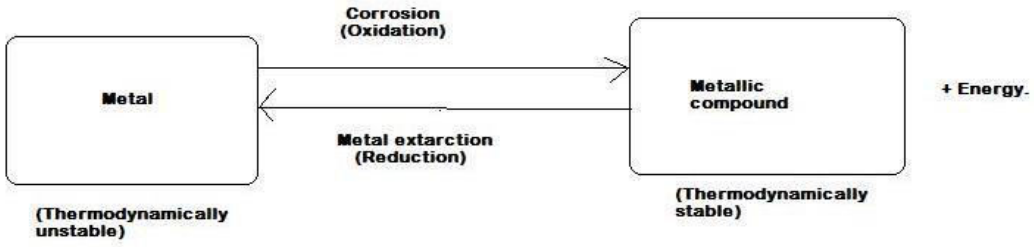
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- Methanol possesses less risk to aquatic plants, animals and human beings than gasoline.
- Methanol has lower inflammability limit than gasoline. Hence, possess fewer fire risks than gasoline.
- There is zero emission by the cells hence are eco friendly.

Applications: These cells are fuel for fuel cell motor vehicles like NECAR – 5 in Japan, USA etc…

CORROSION AND ITS CORROSION CONTROL

- Most metals (except nobel metals like Au, pt etc) exist in nature in combined forms as their Oxides, Carbonates, Sulphides, Chlorides and Silicates.
- These are generally known as metallic ores.
- During their extraction processes metallic ores are converted to pure metals.
- The pure metals are unstable due to their higher energy state than the corresponding ores.
- They have the natural tendency to reverting back to combined state, i.e; lower energy state.



- Extraction of a metal from the metallic ore is a endothermic process.

Definition: Corrosion is defined as destruction or disintegration of a metal or alloy by chemical or electrochemical reaction with its environment.

- But, physical or mechanical wearing away of a metal is not called corrosion, but, it is called erosion.
- If corrosion and erosion takes place together, the destruction of the metal takes place very much faster.

Causes:

- All metals and alloys are susceptible to corrosion.
- Corrosion is a spontaneous process which always results in decrease of free energy.
- Eg: corrosion of Iron is known as rusting. During corrosion metal is converted to its compounds.
- Therefore the process of corrosion the metal passes from a thermodynamically less stable state to more stable state, releasing energy. This is the basic trigger for corrosion.

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- Eg: Gold (Au) has excellent resistance to corrosion under atmospheric conditions but get readily corroded by mercury at ambient temperature.
- Therefore the secret of effective engineering lies in controlling rather than preventing corrosion, because it is impracticable to eliminate corrosion.

CONSEQUENCES OR EFFECTS OF CORROSION:

- Plant shutdown due to failure
- Replacement of corroded equipment
- Preventive maintenance (such as painting)
- Necessity for over design to allow for corrosion.
- Loss of efficiency
- Contamination or loss of the product (e.g. from a corroded container)
- Safety (e.g. from a fire hazard or explosion or release of a toxic product or a collapse of construction because of a sudden failure)
- Health (e.g. from pollution due to a corrosion product or due to an escaping chemical from a corroded equipment.

THEORIES OF CORROSION:

Two theories were proposed to explain the mechanism of corrosion.

a. Chemical corrosion (or) Dry corrosion.
b. Electrochemical (or) Wet corrosion.

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CHEMICAL CORROSION:

- Direct chemical attack by gases such as Oxygen, Halogen, Hydrogen Sulphide, Sulphur dioxide, Nitrogen, or anhydrous inorganic liquid with metal surfaces in immediate proximity at atmospheric temperature results in corrosion.
- Chemical corrosion is of 3 types.
  a. Oxidation corrosion
  b. Corrosion by other gases
  c. Liquid metal corrosion

A. OXIDATION CORROSION:

- In dry conditions or in the absence of moisture attack of oxygen on the metal surface at low or high temperatures results in this type of corrosion.
- Generally metals are oxidised to a smalledr extent.
- But, alkali metals (Li, Na, K, Rb etc…) and alkaline earth metals (Be, Ca, Sr, etc…) are rapidly oxidised at low temperatures.

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- Except Au, Ag, and Pt all metals are oxidised at high temperatures.

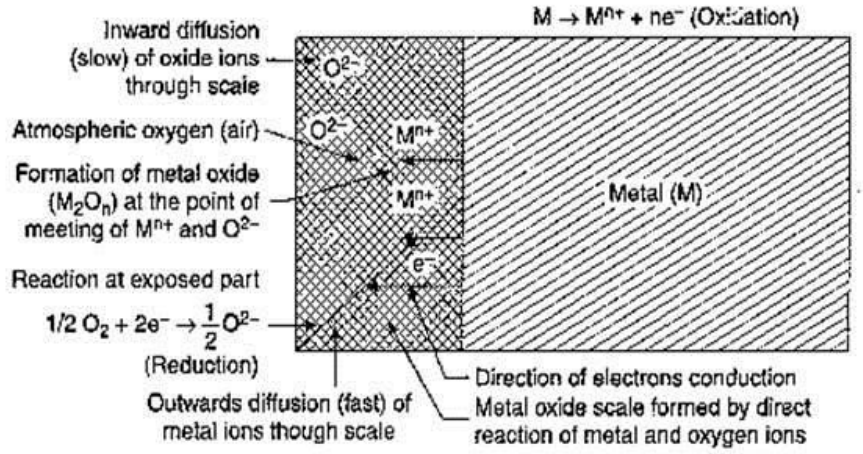
$2M \rightarrow 2M^{+} + 2e^{-}$ (Oxidation by loss of electron)

$O_2 + 2e^{-} \rightarrow 2O^{-2}$ (Reduction by gain of electrons)

Total reaction: $2M + O_2 \rightarrow 2M^{+} + 2O^{-2} \rightarrow 2MO$

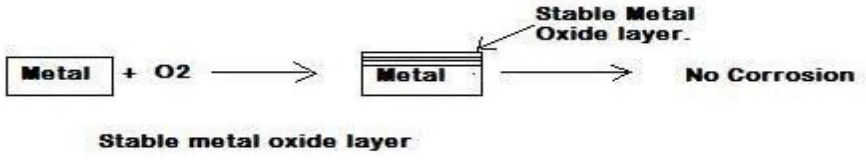
Mechanism of Oxidation corrosion:

- The oxidation of the metal occurs at the surface first, there the metal oxide scale is formed, which restricts further oxidation.
- After the formation of the metal oxide scale, further corrosion may occur in two ways
  a. Metal diffusion out of the scale.
  b. Oxygen diffusion through the scale to the underlying metal.
- Of the two types of diffusion metal diffusion takes place rapidly, because the size of the metal ion is smaller thatn the size of the oxygen ion, hence higher mobility to metal ion.



Nature of the metal oxide formed plays an important role in oxidation.

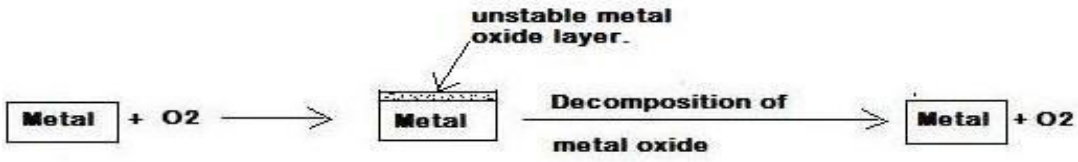
1. If stable metal oxide layer is formed, it protects the underlying metal from further oxidation. Stable metal oxide film is with fine grained structure, adheres tightly to the metal surface and impermeable to the attacking oxygen. E.g. the oxide film on Al, Sn, Pb, Cu, Cr, W etc… Iron corrodes faster than aluminium because Al forms non-porous, tightly adhering protective Al_2O_3 film on the Al metal surface.



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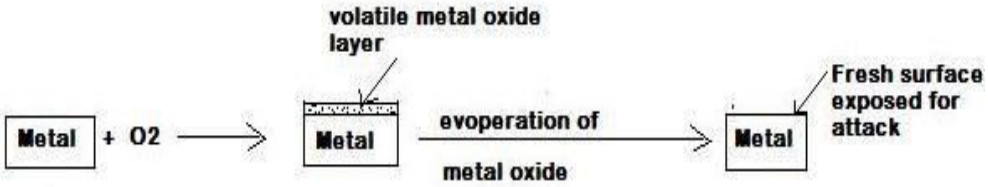
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2. If unstable metal oxide film is formed it decomposes back to the metaland oxygen. In such cases oxidation corrosion is not possible. E.g. Ag, Au, Pt do not undergo oxidation orrosion.



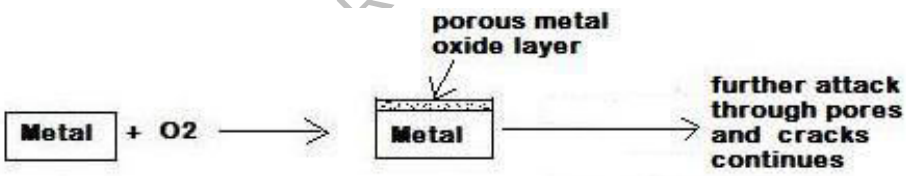
unstable metal oxide layer

3. If a volatile oxide layer is formed it evaporates as soon as it is formed and the metal surface is exposed for further attack. In such cases rapid and continuous corrosion occurs. E.g. molybdenum oxide (MoO_3) is volatile.



volatile metal oxide layer

4. If porous metal oxide layer is formed, it contains pores & cracks in it, through which oxygen can diffuse thereby causing underlying metal to corrode till entire metal gets converted into its metal oxide. E.g. alkali & alkaline earth metals form such type of oxide film.



porous metal oxide layer

Pilling Bedworth rule:

- This rule was postulated to express the extent of protection given by metal oxide to the underlying metal.
- It states that, the smaller the specific volume ratio (volume of metal oxide/ volume of metal), the greater is oxidation corrosion.
  i. If the volume of the metal oxide layer is at least as greater as the volume of the metal from which it is formed is non-porous and becomes protective layer by tightly adhering to the base metal from which it is formed. No corrosion occurs as the oxidation of the metal reaches to zero. For example, the specific volume ratio of W,

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Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in tungsten (W).

ii. If the volume of the metal oxide is less than the volume of the metal, the oxide layer is porous, non continuous, non protective and faces strains. Hence, cracks and pores are developed in the layer, creating access to the atmospheric oxygen to reach the underlying metal. In this case corrosion is continuous and rapidly increases. For example Li, Na, and K.

B. CORROSION BY OTHER GASES:

- The gases like SO_2. Cl_2, CO_2, H_2S and F_2 also cause chemical corrosion.
- The extent of corrosion depends on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of the metal compound films.
- If the film is protective in nature the degree of attack decreases. E.g. Cl_2 on Ag forms AgCl. This film protects the film from further attack.
- If the film formed is not protective in nature, the surface of the complete metal is gradually destroyed. E.g. $Cl_2 + Sn \rightarrow SnCl_2$. This film is volatile, as soon as it is formed it gets evaporated and the metal surface is exposed. Hence, lead to rapid corrosion of the metal.

C. LIQUID METAL CORROSION:

- This is due to chemical action of the flowing liquid at high temperature on solid metal or alloy.
- E.g. corrosion in devices used for nuclear power generation.
- This corrosion reaction involves
  i. Dissolution of solid metal by liquid metal
  ii. Internal penetration of the liquid metal into the solid metal.

ELECTROCHEMICAL CORROSION (OR) WET CORROSION:

- Electrochemical corrosion takes place in wet or moist conditions.
- Wet corrosion is more common than dry corrosion.
- Electrochemical cell is developed during this type of corrosion, hence name electrochemical corrosion.

Essential requirements for the formation of the electrochemical corrosion are:

1. Cathodic and anodic areas separated by conducting medium.
2. At anode oxidation takes place and electrons are liberated. $M \rightarrow M^{n+} + ne^-$
3. Electrons liberated at anodic area are transported to cathodic area through the metal.
4. During the cathodic reaction H_2O and either H^+ or O_2 are consumes electrons and generates non metallic ions like OH^- or O^{-2} either by evolution of H_2 gas or absorption of O_2.

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5. Through the conducting medium metal ions and non metallic ions (OH^- or O^{-2}) diffuses towards each other, and formation of metallic product takes place in between the anodic and cathodic areas. Without conducting medium no corrosion takes place.
6. Mechanism of Electrochemical corrosion can be explained by taking corrosion Iron as an example.

CORROSION (or) RUSTING OF IRON:

- In Iron wet corrosion takes place.
- Whenever Iron is in contact with water and if any damage occurs to the metal, electrochemical cell formation takes place.
- Anodic area and cathodic area are formed, water acts as an electrolyte (conducting medium).
- In the process of rusting iron has higher oxidation state, Iron is converted to hydrated ferric oxide.
- Rusting is considered as an oxidative process.

At anode: Anode reactions:

- The metal atoms lose electrons to the environment and pass into the solution (water) as ferrous ions.
- At anode oxidation takes place.
- $Fe \rightarrow Fe^{+2} + 2e^-$
- Above reaction takes place in Iron in the presence of moisture.
- If metal ions and electrons are not removed from the environment the forward reaction will stop and corrosion will not proceed.
- When corrosion is taking place, the ferrous ions move away and react with hydroxyl ions of the solution and form less soluble ferrous hydroxide.
- $Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$
- In an oxidizing environment ferrous hydroxide oxidizes to ferric hydroxide, which is insoluble & appears as oxides of iron found in Iron rust.
- $4\ Fe(OH)_2 + O_2 + 2\ H_2O \rightarrow 2Fe_2O_3.3\ H_2O$
- Rust formula is $Fe_2O_3.3\ H_2O$

At cathode: Cathodic reactions:

- The electrons released at anode are conducted to the cathode.
- At cathode two types of reactions takes place. Hydrogen evolution type reactions and Oxygen absorption type reactions.

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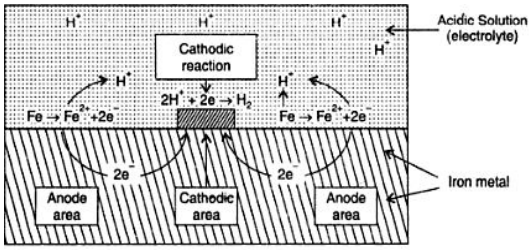
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Evolution of Hydrogen:

Evolution of hydrogen takes place in the absence of Oxygen.

a) In Acidic media:
- In acidic media protons are available. Hence, hydrogen ions acquire electrons and generate H_2 gas.
- $2H^+ + 2e^- \rightarrow H_2 \uparrow$

b) In neutral and alkaline media:
- In neutral media and alkaline media H_2O is available; hence water takes up electrons' and liberates hydrogen gas.
- $2\ H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$



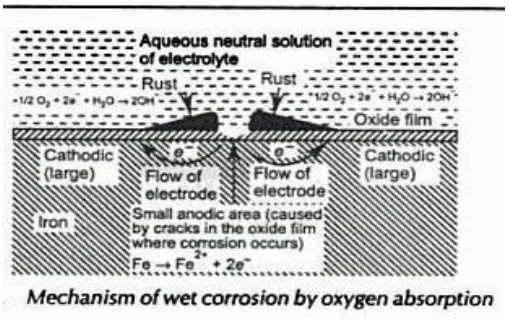
Diagrammatic representation of the mechanism of wet corrosion by hydrogen evolution.

Absorption of Oxygen:

Absorption of oxygen type of reactions take place in the presence of dissolved oxygen, either in acidic media or in neutral or alkaline media.

a) In acidic medium:
- Protons from acidic media takes up electrons react with oxygen to generate water molecules.
- $4\ H^+ + 4e^- + O_2 \rightarrow 2\ H_2O$

b) In neutral and alkaline medium:
- H_2O in the neutral and alkaline media acquires electrons and react with oxygen to give hydroxyl ions.
- $2\ H_2O + 4e^- + O_2 \rightarrow 4OH^-$

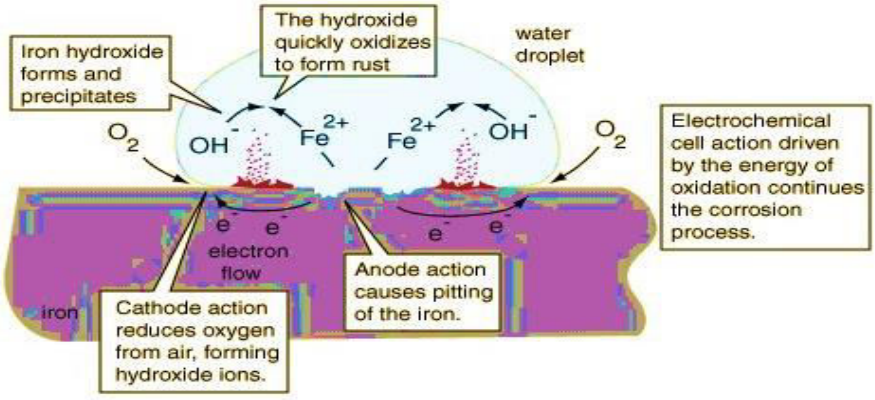


Mechanism of wet corrosion by oxygen absorption

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- Corrosion occurs at anode, rust formation takes place in between the cathodic and anodic areas as the metal ions and OH^- ions move towards opposite electrodes from where they are formed.
- $4\ Fe(OH)_2 + O_2 + 2\ H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2Fe_2O_3.3\ H_2O$



COMPARISON OF CHEMICAL CORROSION WITH ELECTROCHEMICAL CORROSION:

S.No	Dry or Chemical Corrosion	Wet or Electrochemical Corrosion
1.	It occurs in dry conditions.	It occurs in wet conditions in presence of electrolyte medium.
2.	Corrosion is uniform	Corrosion is not uniform if the anodic area is small, pitting is more frequent.
3.	It is a slow process	It is a rapid process.
4.	It involves direct chemical attack of the metal by environment.	It involves the formation of large number of electrochemical cells.
5.	It is explained by absorption mechanism.	It is explained by mechanism of electrochemical reactions.
6.	It occurs both on homogeneous and heterogeneous solutions.	It takes place only on heterogeneous process.
7.	Corrosion products are produced at the place of corrosion	Corrosion occurs at anode & corrosion product occurs in between anodic and cathodic areas.

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Basic requirements of rusting of Iron:

- Oxygen and water are essential for rusting. Iron will not undergo rusting in dry conditions or water that is completely free from oxygen.
- Rusting of Iron is accelerated by
  i. Rust itself
  ii. Presence of acids and electrolytes
  iii. Contact with less corrosion active metals like Cu, Ag etc…

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- Production of anodic and cathodic areas on the metal surface.

Types of corrosion:

Several types of corrosion are often distinguished as follows.

(1) Galvanic Corrosion :

- Galvanic corrosion may take place when two different metals contact (or) (connected by an electricalconductor) are exposed to an electrolytic solution.
- The difference in electrical potential between the two metals provides the driving force to pass current through the corrodent and results in corrosion of the anodic metal.
- The larger the potential difference between the two metals,the greater may be the galvanic corrosion.The relative areas of the cathodic and anodic metals are also important.
- A much larger area of the more noble metal compared to the active metal, accelerates the attack.
- E.g. when Zn, Cu are connected and provided electrical environment following reactions take place.
- At Anode: $Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$ (oxidation)
- Cathode: $Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ (reduction)

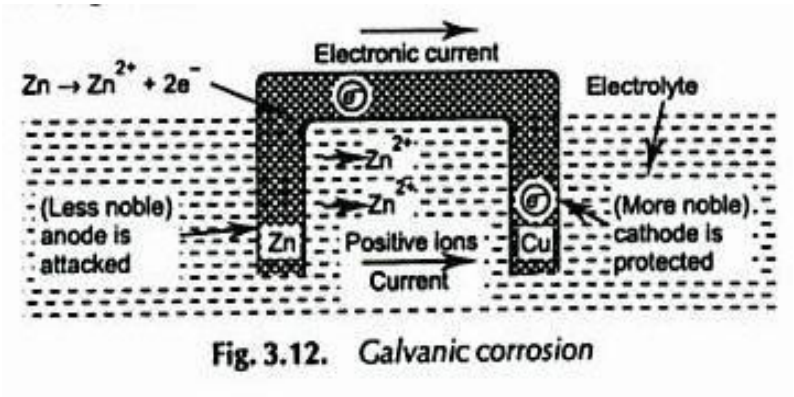


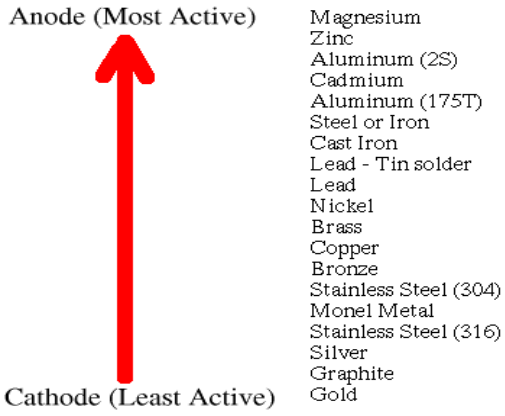
Fig. 3.12. Galvanic corrosion

Galvanic series:

- Electrochemical series may not provide sufficient information about the metal which undergoes corrosion when two different metals are in contact with each other.
- This is because several side reactions taking place may influence the corrosion reactions.
- Hence, oxidation potentials of several metals and alloys are measured using standard calomel electrode as the reference electrode and immersing the metals and alloys in sea water.
- Decreasing order of activity of the oxidation potentials of metals and alloys is known as galvanic series.
- Galvanic series gives more practical information about the corrosive tendency of metals and alloys.

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- And corrosion takes place always at the metal which acts as anodic part, and cathodic part is protected.

Examples of galvanic corrosion:

1. A steel screw is a brass marine hardware.
2. Lead antimony solder around copper wire (lead, antimony solder becomes anodic).
3. A steel propeller shaft in bronze bearing (steel becomes anodic).
4. Steel pipe connected to bronze plumbing (steel becomes anodic).

Difference between Galvanic and Electrochemical series:

S.No	Galvanic series	Electrochemical series
1.	It predicts the corrosive tendencies of metals and alloys.	It predicts the relative displacement tendencies.
2.	Calomel electrode is used as the reference electrode.	Standard hydrogen electrode is used as reference electrode.
3.	Position of a metal or alloy may change.	Position of a metal is fixed, it cannot be changed.
4.	The metals and alloys are immersed in the sea water for study.	The electrolyte contained particular concentration of salts of the same metal that was being used.
5.	Electrode potentials are measured for both metals and alloys.	Electrode potentials are measured only for metals and non-metals.

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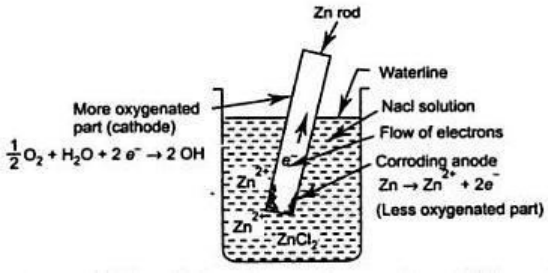
2) Water line corrosion:

- It is a type of concentration cell corrosion.
- Concentration cell corrosion may arise due to
  i. Difference in the concentration of the metal ions or
  ii. Difference in the exposure to air/Oxygen (differential aeration corrosion) or
  iii. Difference in temperature or
  iv. Inadequate agitation or
  v. Different diffusions of metal.

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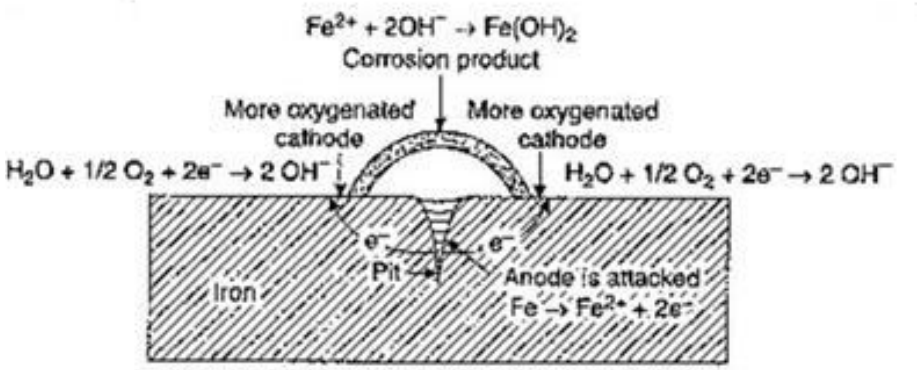
- Waterline corrosion is a best example for differential aeration corrosion.
- It is when a metal is exposed to different air concentrations or concentration of salts etc…
- It has been found that the poorly oxygenated metallic part becomes anodic and well oxygenated part becomes cathodic.
- Difference of potential is created, which causes the flow of electrons between the two differently aerated parts of the same metal.



- E.g. Zn rod immersed deep in NaCl: - anodic solution; Zn rod above NaCl solution: - cathodic part.
- The flow of electrons takes place from anodic part to cathodic part through the metal.
- Migration of ions takes place through the electrolyte.
- The Zn starts corroding in the anodic area immersed in sodium chloride solution.
- Other examples are ship hulls, storage tanks, iron pole immersed in water etc

3) <u>Pitting corrosion:</u>

- A cavity, pinholes, pits, and cracking of the protective film developed on the metal surface creates the formation of small anodic areas in the less oxygenated parts and large cathodic areas in well oxygenated parts.
- The flow of electrons takes place from anodic part to cathodic part through the metal.



- Migration of ions takes place through the medium (atmospheric moisture).
- The corrosion product is formed between anodic and cathodic areas.
- Damage of the protective film may be due to
  i. Surface roughness or non uniform stresses
  ii. Scratches or cut edges
  iii. Local strain of metal
  iv. Alternating stress

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v. Sliding under load
vi. Impingement attack
vii. Chemical attack

a) **Carry over in boiler causing corrosion to turbine plates**:

- The boiler water concentrated with dissolved salts, is carried along the steam or in the form of droplets of water and deposits on the turbine plates.
- The metal under the drop becomes anodic due to high concentration of dissolved salts and starts corroding while the remaining large area of the turbine plates becomes cathodic.
- The flow of electrons takes place through the metal and ions through the medium.
- The electrochemical corrosion due to concentration cell occurs to the metal.

b) **Corrosion due to Caustic embrittlement**:

- Boiler water contains certain amount of sodium carbonate which decomposes to sodium hydroxide under the high pressure of the boiler, which deposits in the hair cracks, pits, etc... of the boiler plate creating a concentration cell.
- The metal deposited with NaOH becomes anodic while the metal surround the drop becomes cathodic.
- $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$
- The concentrated alkali in the anodic areas dissolves the metal as sodium ferrite (Na_2FeO_2), which decomposes a short distance away from the point of formation as magnetite and sodium hydroxide thereby enhancing corrosion.
- $6\ Na_2FeO_2 + H_2O + O_2 \rightarrow 12\ NaOH + 2Fe_3O_4$.
- The concentration cell formed can be represented as
  [Iron (-) anodic/ Concentrated NaOH/Dilute NaOH/Iron (+) (Cathodic)].

4) Intergranular corrosion:

This corrosion occurs along the grain boundaries. The main reason for the corrosion of grain boundaries is

- Grain boundaries where the metal is sensitive to corrosive attack
- The corrosive attacking liquid/reagent possesses the character of only attacking at the grain boundary.

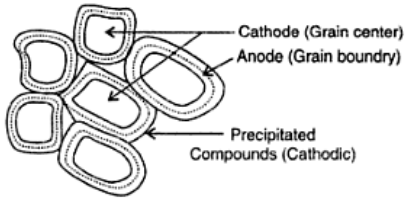


FIGURE 9.17 **Intergranular corrosion.**

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- ⇨ The grain boundary contain a material which shows electrode potential more anodic at the grain boundary and
- ⇨ The precipitation of certain compounds at grain boundary producing a solid solution depleted in one constituent, making the grain boundary anodic.

- ❖ Grain boundary behaves as anodic and centre of the body behaves cathodic.
- ❖ Electrons flow from anode to cathode through metal.
- ❖ Corrosion product is formed in between anodic and cathodic areas.
- ❖ E.g. welding of stainless steel is done by deposition of chromium carbide at the grain boundaries which makes the grain boundaries anodic and corrosion occurs.

FACTORS INFLUENCING CORROSION:

The rate of extent of corrosion depends on the following factors.

A. Nature of metal
B. Nature of corroding environment.

NATURE OF THE METAL:

1. **Position in the galvanic series**:
   - ❖ When two metals or alloys are in electrical contact in presence of an elctrolyte, the metal with higher oxidation potential suffers corrosion.
   - ❖ The rate and severity of corrosion depends upon the difference in their positions in electrochemical series and greter is the difference, the faster is the corrosion of the anodic metal.
2. **Over voltage**:
   - ❖ If a pure Zn is placed in 1N H_2SO_4, it undergoes corrosion, forms a film with liberation of H_2 gas on the immersed metal surface, initial rate of reaction is very slow due to high voltage i.e. 0.70V.
   - ❖ But corrosion of zinc can be accelerated by adding a drop of $CuSO_4$ or a drop of platonic chloride.
   - ❖ Because, some copper gets deposited on the Zn, forming minute cathodes where hydrogen over voltage reduces to 0.33. Thus accelerates corrosion.
3. **Relative areas of the anodic and cathodic parts**:
   - ❖ When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the areas of the cathodic and anodic parts.
   - ❖ E.g. corrosion is more rapid, severe and highly localized if the anodic area is small.
   - ❖ E.g. a small pipe made of steel fitted in a large copper tank.
   - ❖ Due to smaller anodic areas the current density at a smaller anodic area is much greater.
   - ❖ The large cathodic area demands more electrons, which should be met by smaller anodic areas only by undergoing corrosion rapidly.
4. **Purity of the metal**:

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- ❖ As the extent of exposure and impurity increases, the extent of corrosion increases with the increasing exposure and impurities.
- ❖ E.g. Zn metal containing impurity such as Pb or Fe undergoes corrosion due to formation of local electrochemical cells.
- ❖ When impurities are present heterogeneity is produced which forms tiny electrochemical cells.

5. **Nature of surface film:**
   - ❖ if the "specific volume ratio" is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.
   - ❖ E.g. the specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in tungsten (W) even at elevated temperatures.
6. **Physical state of metal:**
   - ❖ The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion.
   - ❖ The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility.
   - ❖ The areas under stress become anodic and corrosion takes place in these areas.
7. **Passive character of the metal:**
   - ❖ Metals like Ti, Al, Cr, Mg, Ni, & Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series.
   - ❖ This is because the metals form very thin, highly protective corrosion film, by reacting with atmospheric oxygen.
   - ❖ If the film is broken, it compensates the film by re-exposure to oxidizing conditions.
   - ❖ Thus they produce "self healing film".
   - ❖ This property is called passive character of the metal.
   - ❖ E.g. corrosion resistance of "stainless steel" is due to passivating character of chromium present in it.
8. **Volatility of corrosion product:**
   - ❖ If a volatile oxide layer is formed it evaporates as soon as it is formed and the metal surface is exposed for further attack. In such cases rapid and continuous corrosion occurs. E.g. molybdenum oxide (MoO_3) is volatile.
9. **Solubility of corrosion product:**
   - ❖ The corrosion product acts as a physical barrier between the metal and environment.
   - ❖ If the oxide film formed as corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate.
   - ❖ E.g. $PbSO_4$ film formed by Pb on sulphuric acid medium.

NATURE OF THE CORRODING ENVIRONMENT:

1. **Temperature:**

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- ❖ The rate of corrosion reaction and diffusion rate increases with increases in temperature, causing the increase in rate of corrosion.

2. **Humidity of air**:
   - ❖ The humidity of air is a deciding factor for rate of corrosion.
   - ❖ The relative humidity above which, the rate of corrosion increases sharply is called "critical humidity".
   - ❖ The value of critical humidity depends on the physical characteristics of the metal and the nature of corroding atmosphere.
   - ❖ The moisture or vapor present in atmosphere furnishes water to the electrolyte, essential for setting up an electrochemical cell.
   - ❖ The oxide film formed has the tendency to absorb moisture, which creates other electrochemical cell corrosion.
   - ❖ The rain water not only supplies necessary moisture for electrochemical attack but also wash away a good amount of oxide film from the metal surface, leading to enhanced atmospheric attack, unless the oxide film is exceptionally adherent.

3. **Presence of impurities in atmosphere**:
   - ❖ Gases like CO_2, SO_2, H_2S, etc., and fumes of H_2SO_4, HCl etc, suspended particles of chemical activity/inactive by nature like NaCl, $(NH_4)_2SO_4$ and charcoal are present in atmosphere.
   - ❖ The gases and acidity of the atmosphere increases the electrical conductivity, thereby increases corrosion.
   - ❖ In marine atmosphere the presence of sodium and other chlorides lead to increased conductivity there by increased corrosion.
   - ❖ The suspended particles absorb moisture and act as strong electrolytes increasing the rate of corrosion.
   - ❖ These suspended impurities also absorb both gases and moisture and slowly enhance the rate of corrosion.

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4. **Nature of ions present in the medium:**
   - ❖ The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which inhibit further corrosion.
   - ❖ On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal, there by exposing the metal surface for fresh corrosion attack.
   - ❖ Presence of traces of copper in marine waters enhances the corrosion of the Iron pipes or steel body of the ships.
5. **Conductance of the corroding medium:**
   - ❖ For the conductance of underground or submerged structures of the corroding medium place an important role.

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- ❖ The conductance of dry sandy soil is lower than the conductance of clayey and mineralized soils.
- ❖ Hence the rate of corrosion is more in clayey and mineralized soils, causing severe damage to metallic structures buried.

6. **Amount of oxygen in atmosphere:**
   - ❖ As the % of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell.
   - ❖ The decay of the metal occurs at the anodic part and the cathodic part of the metal is protected.
   - ❖ Anodic reaction for iron: $Fe \rightarrow Fe^{+2} + 2e^-$
   - ❖ Cathodic reactions: $2H_2O + O_2 + 2e^- \rightarrow 4OH^-$
   - ❖ Corrosion product: $2\ Fe^{+2} + 4OH^- \rightarrow 2Fe(OH)_2$
   - ❖ $2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 \rightarrow 2Fe(OH)_3 \rightarrow Fe_2O_3.3\ H_2O$
7. **Velocity of ions which flow in the medium:**
   - ❖ As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

8. **P^H value of the medium:**
   - ❖ It has greater effect on corrosion. When the P^H value is lowered, the corrosion is increased.

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CORROSION CONTROL METHODS:

Corrosion of a metal leads to many practical problems. Hence, it is necessary to control corrosion. There are different types of corrosion control methods.

CATHODIC PROTECTION:

The principle involved in this method is "to force a metal to behave as a cathode". If metal behaves as a cathode it is uneffected. There are two types of cathodic protection

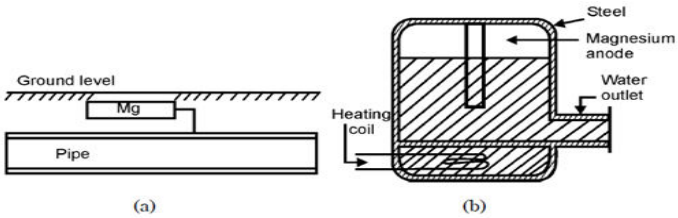
i. Sacrificial anodic protection
ii. Impressed current cathodic protection.

A. Sacrificial anodic protection:

- In this method the metal to be protected is called "base metal "converted into cathode by connecting it to more active metal(less noble)
- The active metal acts as auxiliary anode, Zn, Mg, Al, are commonly used anodes.
- These metals being more active acts as anode, and undergo preferential corrosion, protecting the base metal.

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- Since the anodic metals are sacrificed to protect the base metal, it is known as sacrificial anodic protection.
- Exhausted anode metals are replaced by new ones as and when required.
- E.g. a Mg block connected to a buried oil storage tank. Mg bars are fixed to the sides of ocean going ships; Mg blocks are connected to buried pipelines.



Advantages:

- Method is simple
- Low installation cost
- Does not require power supply

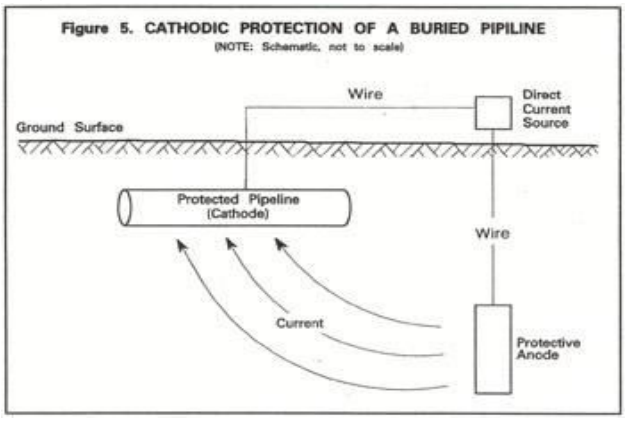
Disadvantages:

- Recurring expenditure for replacement of consumed anode.

B. Impressed current cathode protection:

- It is carried out by applying direct current little more than corrosion current in opposite direction to nullify the corrosion current producing a reverse cell reaction.
- The impressed current source may be a battery or rectified A.C. line.
- The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- In this case base metal behaves as cathode hence does not undergo corrosion.
- E.g. water tanks, open water box coolers, buried water or oil pipelines, condensers, transmission line towers, marine pipes.

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Advantages:

- One installation can protect large area of metal
- Low maintenance cost

Disadvantages:

- Expensive, it needs high current
- If impressed current is not uniform, localized corrosion takes place.
- May suffer hydrogen embrittlement.

Disadvantages of cathodic protection:

1. The cathodic protection may be efficient in protecting a pipeline but it may increase the corrosion of the adjacent pipelines or metal structure because of stray current.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e. the use of much higher potential than the open circuit voltage for the metal/ metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H_2 or formation of OH^- will take place.

METALLIC COATINGS:

- Metallic coatings are produced by coating one metal on the surface of another metal.
- The metal which is protected is called "base metal".
- The metal which is coated on the surface of the base metal is called "coating metal".
- Metallic coatings are broadly divided into two types:
    1. Anodic coatings
    2. Cathodic coatings

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Anodic coatings:

- ⇨ These types of coatings are produced by coating metals whose reduction potentials are lower than that of base metal.
- ⇨ E.g. Zn, Al, and Cd are coated over Iron.
- ⇨ If any pores, breaks, or discontinuation in metallic coating, & the base metal is exposed, there develops a galvanic cell.
- ⇨ The coated metal acts as anode and gets corroded, base metal acts as cathode and protected till all the coated metal is consumed.

Cathodic coatings:

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- ⇨ These types of coatings are produced by coating metals whose reduction potentials are higher (noble metal) than that of base metal.
- ⇨ Coated metal protects the base metal due to their higher corrosion resistance than the base metal.
- ⇨ But, in these type of coatings if any pores , breaks or discontinuation occurs to the coated metal corrosion occurs severely and the base metal is damaged.
- ⇨ This is because when damage occurs to the coated metal, base metal exposes to the environment and a galvanic cell is developed, base metal acts as anode and coated metal acts as cathode.
- ⇨ E.g. coating of tin over Iron.

Comparison of anodic and cathodic coatings:

S.No	Anodic coatings	Cathodic coatings
1.	These coatings involve coating of anodic metal on the surface of base metal.	These coatings involve coating of noble metal on the surface of base metal.
2.	Protects the underlying base metal "sacrificially"	Protects the underlying base metal by their noble character and higher corrosion resistivity.
3.	Reduction potential of the coating metal is lower than that of base metal.	Reduction potential of the coating metal is higher than that of base metal.
4.	Even If any damage occurs to the coating metal, base metal is protected.	If any damage occurs to the coating metal, base metal is corroded.
5.	e.g. galvanization.	e.g. tinning.

Objectives of coating:

- ⇨ To prevent corrosion
- ⇨ To enhance wear and scratch resistance
- ⇨ To increase hardness
- ⇨ To insulate electrically, thermally
- ⇨ To impart decorative color.

METHODS OF APPLICATION OF METALLIC COATINGS:

Following are the methods for application of metallic coatings.

1. Hot dipping, 2. Metal cladding, 3. Electroplating, 4. Electroless plating, 5. Cementation

1. **Hot dipping**:
   - ➢ Coating a low melting metal such as Zn, Sn, Pb, Al on the surface of high melting metal such as Iron, steel etc.. is hot dipping.

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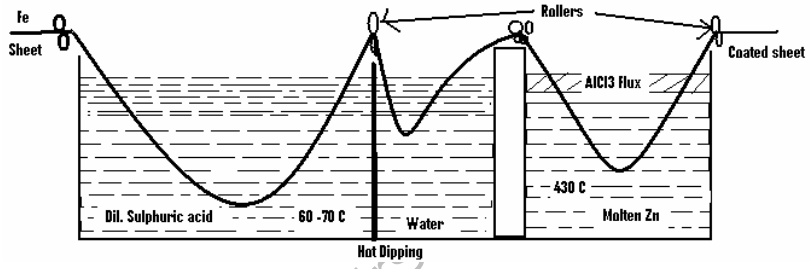
- The metal to be coated is dipped in the molten bath of the coating metal for efficient time and then removed along with the adhering film.
- Two widely used hot dipping methods are:
  A. Galvanization
  B. Tinning.

A. <u>Galvanization</u>:

- It is a process of coating Iron or steel with a thin coat of Zinc to prevent Iron from rusting.

<u>Process</u>:

- The base metal Iron or Steel is cleaned with H_2SO_4 by acid pickling method at 60-90℃ for 15-20 minutes.
- The steel is then washed and dried.
- It is dipped in molten Zn bath maintained at 425-430℃.
- The surface of the bath is covered with aluminum chloride flux to prevent oxide formation.
- The sheet is taken out and excess Zn is removed by passing it between a pair of hot rollers.
- Then the sheet is subjected to annealing process at 650℃ and cooled slowly.
- An alloy of Zn and Iron are formed at the junction of the base metal coating.



<u>Applications</u>:

- It is mostly used to protect the iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes.

<u>Limitations</u>:

- Galvanized utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because Zn dissolves to form highly toxic or poisonous compounds.

B. <u>Tinning:</u>

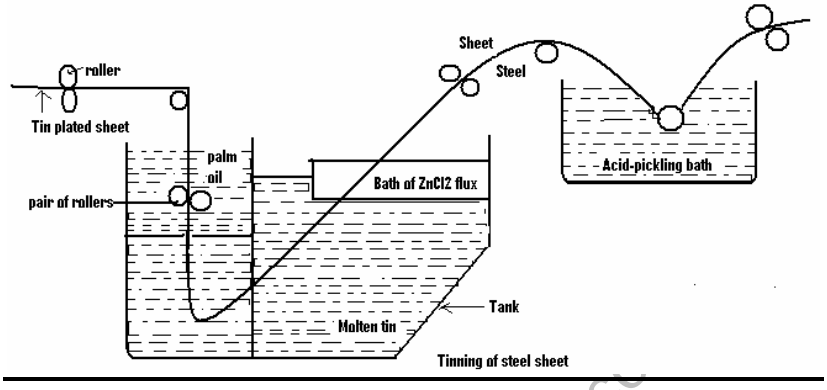
- It is the process of coating tin over Iron or Steel.
- Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack.

<u>Process:</u>

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- Iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film if present.
- A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil.
- Tinning of mild steel plates is done mostly for the requirements of the foodstuff industry. Tin is a nobler metal than iron, therefore, it is more resistant to chemical attack.
- if the coating formed does not cover the surface completely during use and leaves iron exposed, more rapid corrosion of iron will take place.
- A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.



Applications:

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

Comparison of galvanization and tinning:

S.No	Galvanization	Tinning
1.	A process of covering iron with a thin coat of 'Zinc' to prevent it from rusting.	A process of covering iron with a thin coat of 'tin' to prevent it from Corrosion.
2.	Zinc protects the iron sacrificially.(Zinc undergocorrosion)	Tin protects the base metal without undergo any corrosion (nonsacrificially)
3.	Zinc continuously protects the base metal even if broken at some places.	A break in coating causes rapid corrosion of base metal.

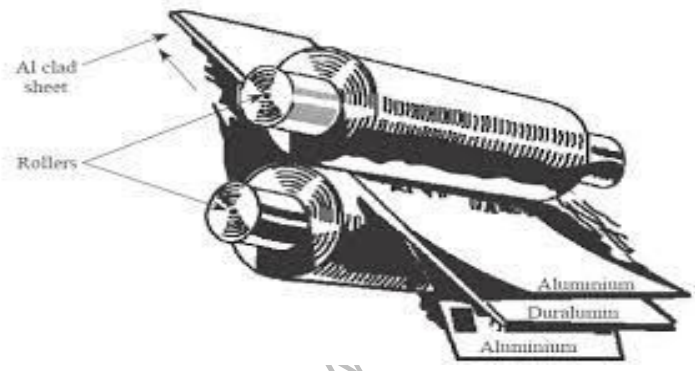
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4.	Galvanized containers cannot be used for strong acidic food stuffs as Zinc becomes toxic inacidic medium.	Tin is non-toxic in nature of any medium.
5.	After galvanization process the sheet is subjected to annealing process.	No annealing process.
6.	Galvanized articles are good engineering materials.	Tinned articles are used majorly in food processing industries.

2. Metal cladding:

- ⇨ Coating of a thin homogeneous layer of a coating metal on a base metal an fused so that it strongly binds permanently either on one side or on both sides and passed through rollers under heat and pressure is called metal cladding.
- ⇨ The metal cladded is called cladding metal.
- ⇨ Only plain surfaces can be cladded.
- ⇨ The process of metal cladding is a kind of "metal sandwiching".
- ⇨ The surface to be protected is sandwiched between two thin layers of coat metal and pressed between rollers.



- ⇨ The finished product may be welded at the edges or riveted at some points.
- ⇨ The coat metal has to be anodic to the base metal.
- ⇨ This method is used for coating Al, Cr, Ni, Duralumin, etc.
- ⇨ All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt, and alloys like steel nickel alloys can be used as cladding materials.
- ⇨ Base metals on which cladding is done are mild steel, aluminium, copper, nickel and other alloys.
- ⇨ E.g. A 99.5% pure Al is subjected to cladding to protect duraluminium to produce 'alclad', which is widely used in air craft industry.

Applications:

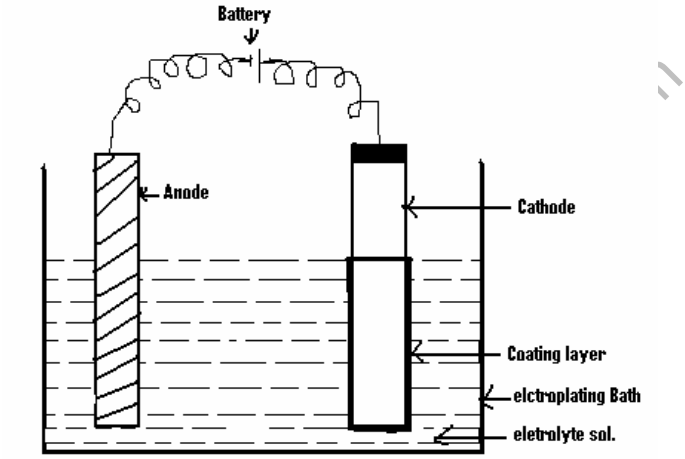
- ⇨ This method is widely adopted in aircraft industry and automobile industry.

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3. Electroplating or Electrodeposition:

- ✓ The process of deposition of coating metal over base metal/non metal by electrolysis is called electroplating.
- ✓ Base metal is anodic to coating metal.
- ✓ The article to be electroplated is cleaned with trichloroethylene to remove oil, grease etc...
- ✓ Then it is subjected to acid pickling with dil. HCl or H_2SO_4 to remove scales, oxide films.
- ✓ The base metal is made cathodic and coating metal is made anodic with graphite, and the electrodes are dipped in the electrolytic solution containing metal ions of coating metal which becomes an electrolytic cell.
- ✓ The electrolytic salt is added continuously to maintain the proper concentration in the electrolytic bath.
- ✓ D.C (direct current) is passed through the electrolyte.
- ✓ The coating metal ions migrate to the cathode and deposit on the surface of the base metal article as a thin layer.
- ✓ For brighter and smooth deposits, conditions like low temperatures, medium current density, and low metal ion concentrations are used.



- ✓ E.g. electroplating of copper on iron article, the following are maintained
  - Electrolyte: Copper sulphate.
  - Temperature: 40-70℃
  - Current density: 20-30mA /cm^2.
  - Anode: 99% pure copper pellets taken in a titanium mesh basket or graphite.
  - Cathode: base metal article.

Applications:

1. Plating for protection from corrosion and chemical attack, hardness, wear resistance.
2. Plating for decoration.
3. Plating for special for special surface and engineering effects.

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4. Electroforming
5. Plating on non-metallic materials.

Therefore, this process is widely used in automobiles, aircrafts, refrigerators, jewelry, radios, cameras, type-writers, umbrellas, watch etc.

4. <u>Electroless plating:</u>

- The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called Electroless plating.
- This process is also called chemical plating or autocatalytic plating.
- The metal ions (M^+) are reduced to the metal with the help of reducing agents(R^-).
- When the metal (M) is formed, it gets plated over a catalytic surface.
- $M^+ + R^- \rightarrow M + R$
- The metal surface to be subjected to electroplating is prepared by
  - Etching (acid treatment)
  - For non conducting surfaces like plastics or printed circuit boards, treatment with stannous chloride and palladium chloride alternatively used.
  - To get an active surface, electroplating followed heat treatment is adopted.
  - For Ni surface treatment of organic solvents followed by acid treatment is used.

The following are the requirements for Electroless plating:

- Soluble electro active metal in the form of metal chlorides or sulphate.
- The reducing agents like formaldehyde, hypophosphite.
- Complexing agents like citrate, tartarate and succinate.
- Exaltants like succinates, glycinates, and fluorides to improve the rate of plating.
- Stabilizers which prevent decomposition of bath. E.g. Pb^{+2}, Ca^{+2}, Th^{+2} ions and thio urea.
- To control p^H of the bath buffer solution was added.

<u>Electroless plating of Nickel</u>:

- The base object, plastic materials like acrylonitrile-butadiene styrene (ABS) can be coated with Nickel.
- Preparation of base metal surface is by stannous chloride followed by palladium chloride, to get the layer of Pd and the surface is dried.
- The base metal is dipped in the following solutions
  - Metal ions solution : Nickel chloride
  - Reducing agent: sodium hyposulphite
  - Buffer: sodium acetate
  - Complexing agent and exalt: sodium succinate
  - pH : 4.5
  - Temperature: 93℃
- The following reactions take place and Ni is plated electrolessly on the surface of base object.
- $Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3 + 2H^+$

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Properties:

- ❖ Electroless plated Ni objects has better corrosion resistance, deposits are pore free, hard and wear resistant.

Applications:

- ❖ Electroless Ni plating is extensively used in electronic application providing a non magnetic underlay in magnetic components.
- ❖ ABS plastics coated objects are used for decorative applications automotive, electronic, domestics of industry like knobs in hi-fi equipment, tops on perfume bottles costume jewelry and car decorative.
- ❖ They are also used in digital and electronic instruments for electromagnetic interference shielding.

5. Cementation of diffusion coatings:

- ➢ This type of coating is obtained by heating the base metal in a revolving drum containing powdered coating metal.
- ➢ Diffusion of the coating metal into the base metal takes place, resulting in the formation of layers of alloy of varying composition.
- ➢ The layer adjacent to the base metal is solid solution and the outer layers are richer in coating metal.
- ➢ There are different types of cementation

  - Sherardizing
  - Colorizing
  - Chromising
  - siliconizing

i. Sherardizing:

- ✓ It was developed by Sherad Cowpercoles in 1890.
- ✓ Coating metal is Zinc power.
- ✓ Base metal is Iron.
- ✓ The Iron article to be coated is cleaned by acid pickling method and rotated for 2-3 hours in the drum containing Zn dust is maintained at 350-370℃.
- ✓ Zn diffuses into Iron.
- ✓ Fe-Zn alloy is formed at the junction of base metal and coating metal.
- ✓ Thin layer of Zn is deposited over Iron.
- ✓ This method is used for coating small articles like nails, nuts, bolts, screws, threaded parts, washers, valves and gauge tools.
- ✓ Advantage of this metal is coating is uniform and there is no change in the dimention of the article.

ii. Colorizing:

- ✓ It is coating Aluminium over Iron.

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- ✓ The base metal article is cleaned by sandblasting and heated in a drum tightly packed with a mixture of aluminium powder and aluminium oxide together with trace of aluminium chloride as flux in a reducing atmosphere of hydrogen.
- ✓ The layer formed has the approximate composition of Al_2Fe_3 containing about 25% by weight of aluminium.
- ✓ This method is used for the protection of furnace parts.

iii. Chromising:

- ✓ The base metal is heated with a mixture of 55% Cr, and 45% alumina powder to 1300-1400℃ for 3-4 hours.
- ✓ A mixture of volatile chromous chloride and hydrogen with steel parts produced the protective layer of chromium diffused into Iron surface.
- ✓ This method is fairly used for the protection of turbine blades.

iv. Siliconizing:

- ✓ Coating silicon on the surface of molybdenum is called siliconizing.
- ✓ Silicon tetrachloride is used as coating metal.

ORGANIC COATINGS – PAINTS:

PAINTS: Paint may be defined as the mechanical dispersion mixture of pigments and fillers which are in a liquid medium and later becomes film forming oil. The volatile liquids such as thinners are again added to these liquids.

Requisties of a good paint :

CONSTITUENTS OF PAINT:

a. Pigment
b. Vehicle or drying oil
c. Thinners d. Driers
d. Fillers or extenders
e. Plasticizers
f.. Anti-skinning agents

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a) Pigment:

It is solid constituent present in paint which provides a decorative color effect to protect it from ultraviolet rays. Pigment is one of the essential constituents of paint.

The essential functions of pigments are-

- To provide desired color, opacity and strength to the paint.
- To give aesthetical appeal to the paint film,
- To give protection the paint film by reflecting harmful ultraviolet light,
- To provide resistance to paint film to moisture and
- To increase the weather-resistance of the film.

The following are the common pigments used:

S.No	Common pigment	Color imparted by the pigment

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1.	White lead, Zinc oxide, Lithophone etc…	White
2.	Red lead, ferric oxide, chrome red etc…	Red
3.	Chromium oxide	Green
4.	Prussian blue	Blue
5.	Carbon black	Black
6.	Umbre brown	Brown

Characteristics of a good pigment:

- ✓ A good pigment must be opaque, chemically inert, non toxic, freely mixable and cheap.

b) **Vehicle (or) drying oil :**

It is a film forming constituent of the point. These are glyceryl esters of high molecular – weight fatty acids generally, present in animal and vegetable oils. The most widely used drying oil, are linseed oil, soyabean oil, and dehydrated caster oil.

CH2COOR
|
CHCOOR
|
CH2COOR glyceryl ester.

The important functions of vehicle oil are:

- They hold the pigment on the metal surface
- They form the protective film,
- They impart water-repellency, durability and toughness to the film, and
- They give better adhesion to the metal surface.

c) Thinners:

- Viscosity (or consistency) of the paints are reduced by the addition of thinners. So paints easily applied on the metal surface.

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The important functions of thinners are:

- Thinners reduce the viscosity of the paint to suitable consistency, so that it can be easily handled and applied to the metal surface.
- They dissolve the film-forming material and also the other desirable additives in the vehicle.
- They evaporate rapidly and help the drying of the paint film.
- They suspend the pigments in the paint film.
- They increase the elasticity of the paint film,
- They also increase the penetration power of the vehicle.

d) Driers:

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- The drying of the oil is accelerated or catalyzed by driers. They do this by oxidation, polymerization and condensation. In fact, driers are oxygen carrier catalysts. The important functions of the driers are-Linoleates, borates, naphthalene's, resonates and tungstates of heavy metals like Pb, Zn, Co and Mn.
  - Surface driers: Cobalt substances,
  - Bottom- driers: Lead substances,
  - Through driers: Manganese substances.

e) <u>Fillers or extenders</u>:

- Fillers are inert materials which are used to improve the properties and reduce the cost of the paint.

The important functions of fillers are:

- They reducing the cost of the paint.(Expensive pigments which have excellent hiding power
  (Like TiO_2 and $ZnSO_4$) are used in a admixture with cheap extenders for reducing the costwithout reducing the efficiency),
- They serve to fill the voids in the film,
- They increase random arrangement of the primary pigment particles, and act as carriers for the pigment color,
- They improve the durability of the film by reducing the cracking of the paints after drying.

f) <u>Plasticizers</u>:

- Plasticizers are added to the paint film to give elasticity to the paint film and to prevent cracking of the film, to increase the elasticity to the film.

Ex: Tri cresyl phosphate, triphenyl phosphate, dibutyl tartarate, and tributyl phthalate.

g) <u>Antiskinning agents</u>:

- Antiskinning agents prevent the gelling and skinning of the paint film. E.g.Polyhydroxy phenols

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<u>Requirements of a Paint</u>:

1. The adhesion capacity of the paint should be high to the material on which it is to be used.
2. The paint should spread easily over the surface to be protected.
3. On drying, the paint film should not be cracked.
4. The paint film should have high corrosion resistance property so as to protect the painted surface from the corrosion environment.
5. The paint film should be stable.
6. The paint film should be prepared such a way as to be applicable easily by spraying or brushing.
7. The paint film should yield a smooth and uniform surface.

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8. The paint film obtained on the surface should be tough, uniform and adherent.
9. The color of the film should be stable and should not get affected by the environment conditions.
10. The covering power of the paint should be high.

QUESTIONS:-

(1) (a)What are concentration cells? How can the EMF of a concentration cell be evaluated?

(b) Write short notes on single electrode potential and its significance.

(2) (a) What do you understand by electrochemical series? How is this series useful in the determination of corrosion of metals.

(b) The resistance of a 0.1N solution of an electrolyte of 40 ohms. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm2. Calculate equivalent conductivity.

(3) (a) Give reasons for the following statements:-

i. When a zinc rod is dipped in a solution of aq. copper sulphate, copper is precipitated out.

ii. Nernst equation is applicable for the determination of emf of a concentration cell.

(b) State and explain the Kohlrauschs law and its applications.

(4) (a) Define the terms specific, equivalent and molar conductivities. How do they vary . . with dilution.

(b) Calculate the cell constant of a cell having a solution of concentration N/30 gm equiv/litre of an electrolyte which showed the equivalent conductance of 120 Mhoscm2 gm equivalent:

(5) (a) Write a short note an electro chemical series?

(b) Explain the functioning of a Galvanic cell?

(6) (a) Distinguish Electrochemical cells from Electrolytic cells with suitable illustrations.

(b) What is electrode potential? How is it determined by using Calomel Standard Electrode?

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(7) (a) What is cell constant? How is it determined?

(b) Describe a method for the determination of pH of a solution using Standard Calomel electrode.

OBJECTIVE QUESTIONS:-

- Which of the following does not conduct electricity (c)
  a) Molten NaCl b) Solution of NaCl
  c) NaCl crystal d) none of the above
- The specific conductance of a solution increases with (a)
  a) Increase in concentration b) decrease in concentration
  c) Decrease in temperature d) none of the above
- The ionization of a strong electrolyte increases when the solution is diluted and the relation is given by (c)
  a) Nernst equation b) Ostwald's law
  c) Arrhenius equation d) law of mass action
- Acetic acid is a weak electrolyte because (b)
  a) Its molecular weight is high b) it is weakly ionized
  c) It is a covalent compound d) it is highly unstable
- Pure water does not conduct electricity because it is (b)
  a) Acidic b) low boiling
  c) Almost not ionize d) decomposed easily
- The potential of standard Hydrogen electrode dipped in a solution of 1M concentration and Hydrogen gas is passed at 1atm pressure (c)
  a) 1volt b) 10 volt
  c) 0 volt d) 100 volts
- Calomel electrode is reversible with respect to (b)
  a) Mercury ion b) chloride ion
  c) Both ions d) none of the above
- The electrode potential is the tendency of a metal (c)
  a) To gain electrons b) to lose electrons

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c) Either to lose or gain electrons d) none of these

- Calomel is (c)
  a) Mercuric sulphate b) mercurous sulphate
  c) Mercurous chloride d) mercuric chloride
- The cathode of a Ni-Cd battery is composed of (c)
  a) Cadmium b) nickel
  c) Paste of NiO(OH) d) paste of Cd(OH)2
- Fuel cell converts (a)
  a) Chemical energy to electricity b) chemical energy to heat
  c) Chemical energy to pressure d) none of these
- When Hydrogen is used as fuel in Hydrogen – Oxygen fuel cell, the electrode are made of (a)
  a) Alloy of Pd and Ag b) Al
  c) Fe d) none of the above
- When storage cell is operating as voltaic cell it is said to be (b)
  a) Charging b) discharging
  c) Neutral d) none of the above
- In lead – acid storage cell during discharging operation the concentration of H_2SO_4 (a)
  a) Decreases b) increases
  c) Constant d) none of the above

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QUESTIONS:-

(1) (a) What are the factors that lead to caustic embrittlement in boilers? How can this be prevented?

(b) Distinguish between Zeolite process and Ion-Exchange process.

(2) (a) Discuss the influence of following factors on corrosion:-

i. Over voltage

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ii. Nature of the metal

iii. Nature of environment.

(b) Explain the nature and role of constituents of organic paints

(3) (a) Explain the electrochemical theory of corrosion of metals with special reference to rusting of iron.

(b) Write a note on galvanizing and metal cladding.

(4) (a) How are metals protected by impressed current method?

(b) Explain the galvanization and tinning processes of metals.

(5) (a) Outline the electrochemical theory of corrosion and explain the mechanism of rust formation in acidic and neutral medium.

(b) Write a brief account of cathodic protection.

(6) (a) Explain sacrificial anodic protection method of controlling corrosion.

(b) Write a note on anodic protection and the nature of corrosion product.

(7) Write notes on the following:-

(a) Hot dipping

(b) Galvanizing

(c) Tinning

(d) Electroplating.

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OBJECTIVE QUESTIONS

- The rusting of iron is catalyzed by (d)
  a) Fe b) O2
  c) Zn d) Hydrogen ion
- Corrosion is an example of (a)
  a) Oxidation b) reduction
  c) electrolysis d) erosion

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- The metal at the top of electrochemical series is (d)
  a) most stable b) best protective
  c) most noble d) most active
- During galvanic corrosion the more noble metal acts as (b)
  a) anode b) cathode
  c) anode as well as cathode d) corroding metal
- The process of cementation with Zn powder is known as (c)
  a) galvanizing b) zincing
  c) sheradizing d) tinning
- Anodic coating protects the underlined metal due to (b)
  a) noble character b) sacrificial
  c) higher electrode potential d) none of the above
- Drying oil supply to paint film (d)
  a) main film forming constituent b) medium or vehicle
  c) water proof ness d) all of these
- The process of covering steel with tine to prevent it from corrosion is called (b)
  a) galvanizing b) tinning
  c) metal cladding d) electroplating
- Sand blasting is used for removing the following from the metal surface (a)
  a) oxide scale b) oils
  c) greases d) old paint
- The following reagents are used for solvent cleaning of the metal surface(a)
  a) naphtha b) acid
  c) alkali d) Na2CO3
- The oxygen carriers of the paint is called (a)
  a) drier b) pigment
  c) thinner d) drying oil
- Opacity and desired color to paint is provided by (a)
  a) pigments b) extenders

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c) driers d)thinners

- The following metal is used for the cladding of Aluminum (a)
  a) 99.5% pure Al b) 100% pure Al
  c) 98.5 % pure Al d) 99% pure Al
- The metal at the top of the electrochemical is (d)
  a) most stable b) most noble
  c) least active d) more active
- The deciding factor on atmosphere corrosion is (a)
  a) presence of O2 b) presence of SO2
  c) humidity of air d) frequency of rainfall

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Chemistry of Advanced materials

* Nano materials :-

→ The materials like metals, Ceramics, polymeric materials (or) Composite materials with dimensions and tolarences in the range of 1nm to 100nm are called "nano materials"

→ One nanometre (nm) = One billianth (10^{-9}) of a meter

i.e., $1nm = (1/10^9)\,m$ (or) $10^{-9}\,m$

→ 1m = 39 inches = 3 feet

→ Centi = 10^{-2}

→ milli = 10^{-3}

→ micro = 10^{-6}

→ Nano = 10^{-9}

* Nanometer is used to measure the objects which are very small in size.

Ex:- Size of hydrogen atom = 0.1nm

→ water molecule < 1nm

→ RBC = 5000nm

→ Human hair = 50000nm

→ limit of human eye's visibility = 10000nm

→ Diameter of a carbon nanotube = 1.3nm

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* At this level, Nanomaterials exhibit unique properties (different from those observed in bulk materials) like melting point, reactivity, reaction rates, electrical conductivity, colours, transparency etc.

* Nanomaterials may be biological, inorganic (or) Organic by their Origin.

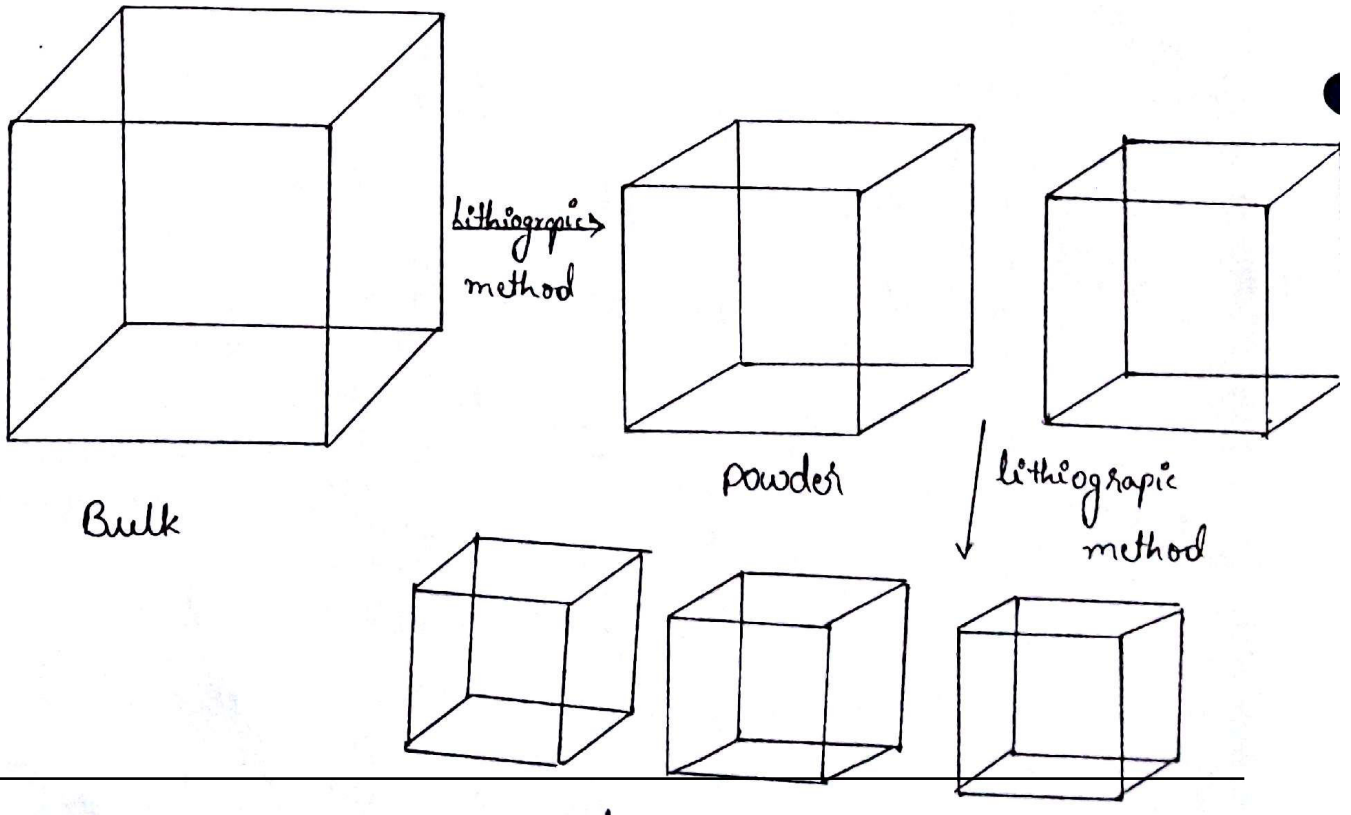
* A nanoparticle is defined as a small object that behaves as a whole unit in terms of its transport and properties and exhibits a number of special properties (both) relative to bulk materials.

* Methods of preparation of Nanomaterials :-

1. Top down approach :-

→ In this method bulk materials are converted to powder and then to nanoparticles by making use of lithographic methods

→ This method is used in the microelectronic industry



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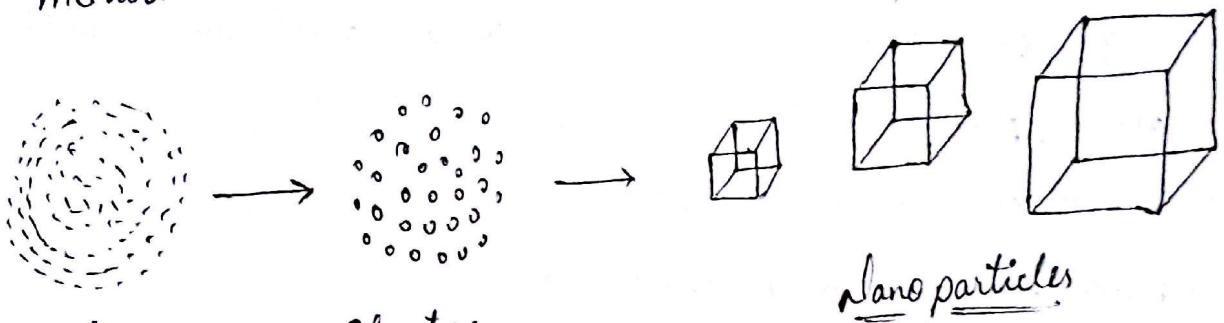
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Bottom up approach :-

→ In this method very small particles like individual molecules (or) atoms are assembled to get clusters which in turn are aggrigated etc to get nanoparticles

→ This method is used to prepare a new class of nanomaterials

Ex :- Fullerenes and polymer nano composites are prepared by this method



* Sol- Gel method :-

→ Sol-gel method is bottom up approach for the synthesis of nano materials

→ A sol is a colloidal (or) molecular suspension of solid particles of ions in a solvent

→ A gel is a semi rigid mass that forms when the solvent from sol begins to evaporate and particles (or) ions left behind begin to join together in a continuous net work.

→ Sol-gel processing is wet chemical technic that uses a sol to produce an integrated network i.e., gel

→ Metal Oxides (or) metal chlorides undergo hydrolysis and polycondensation reactions to form a colloid which is a

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term composed of nanoparticles dispersed in a solvent

→ The solvent evolves towards the formation of an inorganic continuous network containing a liquid phase (gel).

→ Formation of metle oxide involves connecting the ~~metle~~ metal centres with Oxo (M-O-M) (or) hydroxo (M-OH-M) bridges generating metal-oxo (or) metal-hydroxo polymers in the solution.

→ After a drying process the liquid phase is removed from the gel and calcination is performed in order to enhance the mechanicle properties.

→ Alcohol is used as solvent.

* Advantages of Sol-gel method :

→ Able to get uniform and small size powder

→ Can get new microstructure and composition at low temprature

→ Can produce uniform multicomponent systems

→ Better control over the reactions

* Chemicle reduction method :-

→ Chemical reduction method is also belongs to bottom up approach

→ Metal nanoparticles particularly silver nanoparticles are prepared by this method.

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* Preparation of Silver Nano particles :-

→ For the preparation of Silver nanoparticles silver nitrate solution (From 1 ppm to 6 ppm) and 8% w/w sodium dodecyl Sulphate (SDS) are used as metal salt (process) precursor and metal stabilizing agent respectively.

→ Hydrazine hydrate (2-12 ppm) and citrate solution (1ppm) are used as reducing agents

→ The transparent colourless solution will be converted to pale yellow and red colour which indicates the formation of Silver nano particles

→ To remove the excess silver ions the solution is washed with deionised water under nitrogen stream for three times

→ The nano particles are characterised by UV and X-ray crystallography

→ General preparation is carried out by mixing the metal slts salts with transfer agents and reducing agents.

→ Different types of phase transfer agents are ~~coated~~ used for the preparation of different mette nano particles.

→ Metal salt solution + metal salt ~~precursor~~ precusor + Stabilizer + reducing agent → stand for sometime → Nanoparticles separate → purification → Centrifugation → Freze drying → metal nano particles.

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Applications :-

→ Nano particles like silver, gold, platinum, etc are prepared by this method

* Brunaer - Emmett - Teller (Bet) method :-

→ Nano crystalline particles of $Co_xFe_{(3-x)}O_4$ are synthesized by combustion reaction method using iron nitrate, cobalt nitrate and urea with Asa's fuel without template and subsequent heat treatment

→ The process is simple and inexpensive since it does not involve intermediate decomposition (&) calcination steps

→ The maximum reaction temprature range 850 - 1010°c and combustion lasts for 30 seconds for all systems

→ The materials are washed with deionized water and the byproducts are rinsed off producing pure nano particles.

* Transmission electron microscopic (TEM) method :-

→ This is a method for synthesis of colloidal platinum nano particles which is potentially important in the field of catalysis.

→ Catalytic reactivity depends on site and shape of the particle.

→ A solution of potassium platinum chloride (0.00001M) is prepared in water and treated with 0.2 ml of 0.1 M Sodium poly acrylate.

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→ The resulting solution is boiled with stirring for 20 minutes

→ The platinum ions are reduced by bubbling H_2 gas for 5 minutes

→ The reaction vessel is sealed and overnight

→ The solution turns light golden and nanoparticles are purified and separated

* Properties of nanomaterials :-

Nanoparticles are specific in their nature behaviour because the physical behaviour of the particles change with decreasing size of the particle

1. Properties based on size of particles :-

(a) Magnetic properties :-

Magnetic properties increase with decrease in the size of the materials due to increased orderly electronic spins

(b) Melting point :-

Melting point of the nanomaterials increases, when compared with other materials depending on the size of the particles.

(c) Solubility :-

Solubility of nanomaterials is more than other material due to the decreased size.

(d) Colour :- The physical propuly colour is again size dependant. As the size of the particle decreases the colour of the material changes.

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Ex:- Bulk gold looks yellow, whereas nanosized gold particles looks red, due to the decreased size of the particle and intern different scattering of light

(e) Transparency :-

Transparency of nanomaterials is more than the other materials due to decreased size of the particles and increased transmission of light.

(f) Catalytic behaviour :-

Due to increased surface area, the catalytic activity of the nanomaterials is more than other materials.

2. Properties based on composition of nanomaterials :-

(a) Collidal properties :-

→ The collidal nanoparticles are called "Coercing colloids."

→ The collidal properties of coercing colloids is more than the colloidal solutions, like optical properties, electrical, magnetic and gel properties.

(b) Chemical reactivity :-

Nanomaterials posses high chemical reactivity than other materials

(c) Reaction rates :-

High reaction rates were observed with nanomaterials when compared with other materials.

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3. Properties due to surface of Nanomaterials :-

(a) Dispersibility :-

The nanomaterials exhibit good dispersibility

(b) Conductivity :-

The nanomaterials can be used as good conducting, semiconducting and insulating depending on the structure of Nanomaterials.

(c) Catalytic behaviour :-

→ The nanomaterials posses very good catalytic activity due to increased surface area of contact than other materials.

→ In crystalline particles, the place where two faces of crystal are in contact is called "edge" and the place where two (or) more faces come together are called a 'point'.

→ These edges and points are the seat of pronounced catalytic activity. Because the crystalline nano particles contain enormous number of edges and points, their catalytic activity is maximum

* Engineering applications of Nanomaterials :-

1. Electronics :-

(a) Commertial digital switching devices, integrated in 10^{12} devices on a single chip are fabricated

(b) High sensitivity and high selectivity environmentle sensors to sense gaseous chemicals like CO, NO, NO_2 and O_3 in high traffic environments are fabricated

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(c) In making light emitting electroluminiscence devices which find application in flat panel display technologies like T.V, computer monitor, colour changing fabrics etc

2. Magnetic applications :-

Magnetic nanoparticles from iron and palladium have been found to self arrange automatically and these materials are extensively used in the manufacture of magnetic storage devices producing terrabyte storage capabilities

3. Biomedical applications :-

(a) Drug delivary of bio medical drugs which are bounded to magnetic nano crystals to the region of body where the drug is required is carried out

ex :- Rare tumour causing cells can be targetted by nano crystals, the captured and removed from blood stream.

(b) Medical dignostics is a field which extensively use (nO) nanocrystals silica coated iron Oxide nanocrystals with embedded magnetic colloidal particles are sent into blood stream where the antibody reacts and binds with the target harmone and move rapidly which can be separated and ~~move rapidly~~ detected from blood sample.

→ DNA detection through calorimetric technique by using oligonucleotide functionalised gold nanocrystals is developed.

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* Structural and mechanical material applications:

(i) Coating nanocrystals of metals with ceramics is carried nanostructuring by getting the benifits of ceramics (corrosion resistant, hard and ware resistant) and metals (ambient ductility). These coatings are superior coatings.

(ii) Fabrication of ceramic components is easier through nano structuring.

→ By nanoscale distribution of tungsten carbide improves the life and performance of cutting tool material.

* Industrial catalysts should contain high surface area and capacity to make any material attach to their surface

→ Cerium oxide, platinum, gold, molybdenum, nickel, nano particles are extensively used as catalysts.

* Because of high tensile strength, light weight and flexible nature some nanomaterials like CNT are extensively used in aircraft industry

* Nanomaterials like fullerences are used extensively in making consumer goods, cleaning products and fabrics etc

* Agriculture is another field where nanomaterials find their use in delivary of genes and drugs to animals for health and genetic improvement and in delivary the biodegradable chemical for plant nourishment is adopted.

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Fullerenes :-

→ Fullerene is defined as a molecule composed entirely of carbon, in the form of hollow sphere, ellipsoid (&) tube

→ Spherical fullerenes are also called ~~(buckes)~~ bucky balls as they resemble the balls used in foot ball (Soccer) ~~as they resemble the balls used in~~

→ Fullerenes are similar in structure to graphite which is composed of graphene sheets of linked hexagonal rings, may also contain pentagonal (&) heptagonal

→ The first ~~the~~ fullerene molecule was prepared in 1985 Richard Smally and H. kroto at Rice university, USA, called carbon-60 (C_{60}). They named that as "Buckminister fullerence" after the name of an architect Buckminister fuller, well known for building geodesic domes.

→ They were awarded Nobb prize in 1996 ~~in~~ for their work

* Types of fullerenes :-

Due to structural variations fullerenes exist in the following different types

(a) Buckyball clusters
(b) Carbon nano tubes
(c) Mega tubes
(d) polymers
(e) Nano 'onions'
(f) linked ball and chain dimers.

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Buckminster Fullerene:

→ In 1985, it was discovered by R. Smalley and H. kroto at Rice university, USA.

→ They named it as Buckminster fullerene after the name of an architect Buckminster fullerene, who is well known for building geodesic domes.

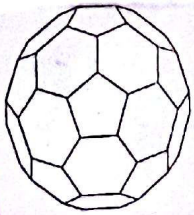
→ It is the smallest fullerene molecule containing pentagonal and hexagonal rings

→ It is naturally occuring fullerene found in soot.

→ The structure C_{60} is called turncated icosahedron, which resembles foot ball containing 20 hexagons and 12 pentagons

→ The vandercwall's diameter of C_{60} is 1.1nm and its average bond length is 1.4 A°

→ The smallest fullerene is dodecahedral (C_{20})



BUCKMINSTER FULLERENE (C_{60})

→ Now several number of fullerenes are present such as C_{70}, C_{76}, C_{84}, C_{240}, and C_{540}

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→ Fullerenes are a class of closed cage carbon molecule, C_n, characterically containing 12 pentagons and a variable number of hexagons.

$$\text{Number of hexagons} = \frac{(\text{Carbon atoms}, n) - 20}{2}$$

* Preparation of Fullerenes :-

→ A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere.

→ The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.

→ The fullerenes are extracted from soot using multi step procedure.

* Properties of Fullerenes :-

→ Fullerenes are stable with sp^2 (hybridisation) hybridised carbon atoms.

→ The reactivity of fullerenes is increased by attaching active groups in their surfaces

* Solubility :- Fullerens are sparingly soluble in many solvents. Common solvents are toulene, CS_2.

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* Quantum mechanics :-

wave particle duality is exhibited by fullerenes as a result several sculptures symbolizing wave particle duality are created

* Hydrogenation :-

C_{60} exhibits a small degree of aromatic character, undergoes addition with hydrogen to polyhydro fullerenes.

* Halogenation :-

Addition of F, Cl and Br occur for C_{60} under various conditions, produce a vast number of halogenated derivatives.

Ex:- $C_{60}Br_8$ & $C_{60}Br_{24}$

* Addition of Oxygen :-

C_{60} can be oxygenated to epoxide $C_{60}O$ and Ozonisation of C_{60} in orthoxylene at 257 k gives Ozonide $C_{60}O_3$ which can be decomposed into 2 forms of $C_{60}O$ and the same decomposition (of) at 296 k gives epoxide.

→ C_{60} is the most symmetric molecule.

→ physically, bucky balls are extreamely strong molecule, able to resist great preassure. They will bounce back to their digonal shape after being subjected to over 3000 atm.

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* Applications of fullerenes :-

→ Fullerenes can be added to polymer structure to create new copolymers with specific physical and mechanical properties

→ Fullerens have potential ability to transfer hydrogen. Therefore, they are used as catalysts for hydrogenation.

* In Medicine :-

Buckminster fullerene inhabit the HIV virus. C_{60} inhabits a key entyme in human immunodeficiency virus known as HIV-1 protease which could inhabit the reproduction of HIV virus in (~~immune~~) immune cells. when impregnated with He, C_{60} buckyballs can be used as chemical tracers in human body

* In solar cells :-

The optical absorption properties of C_{60} match solar spectrum, hence finds its application in solar cells

* Carbon Nanotubes (CNT) :-

→ Carbon Nanotubes are sheets of graphite about 0.4nm in diameter rolled up to make a tube of few nm in diameter.

→ Carbon nanotubes are called buckey tubes

→ CNT ~~discovered~~ in was observed in 1991 in carbon soot of graphite electrodes during arc discharge.

→ First production of CNT was 1992 by arc discharge at the fundamental research laboratory, U.S.A

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* Preparation of CNT :-

1 Arc discharge method :-

→ By arc discharge of graphite electrode in presence of ionised gas to reach high temperatures and by using a current of 100 amps CNT was produced.

→ During this process, the carbon contained in the negative electrode sublimates because of high-discharge temperature.

→ This method has been widely used method of CNT synthesis.

→ The yield is 30% and produces both single and multi-walled nanotube with lengths of upto 50 micrometers with few structural defects

2. Chemical vapour deposition (CVD) method :-

→ The method was developed in 2007 (in) at university of Cincinnati, USA

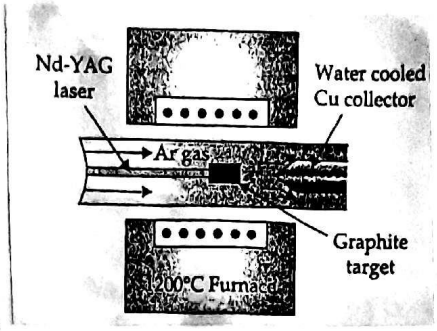
→ ~~(Using)~~ During CVD process a substate was prepared with layer of metal catalyst nanoparticles (Ni (s) Co)

→ The substrate is heated to 700°c and a mixture of nitrogen and carbon containing acetylene (g) ethylene (g) ethanol (g) methane was passed

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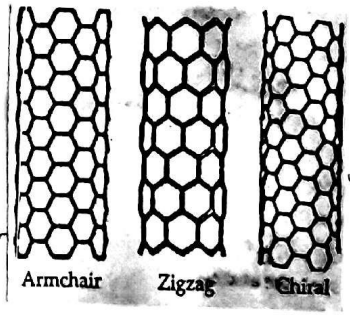
→ The CNT grows at the surface of the catalyst particle where the carbon containing gas is broken and carbon is transported to the edges of the particle where it forms CNT



→ CVD method is most promisable for industrial production of CNT because of its low cost and direct growth on the catalyst surface.

* Types of CNT :-

1) Single-walled carbon nanotubes (SWCNT) :-



→ These are different types depending on the manner in which the graphene sheets are rolled

→ The basic varieties being zig-zag, arm chair and chiral.

→ Identification of a particular variety can be made by following pattern across the diameter of the tube and analysing their cross sectional structure.

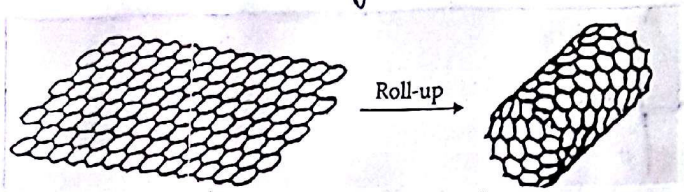
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2) Multi-walled carbon nanotubes (MWCNT)

→ It consist of several concentric SWCNT with different diameters.

→ The forms are more complex (have) here as each SWCNT can have different structures resulting in a variety of sequential arrangements



* Properties of CNT :-

1. Strength :- CNTS are strongest and stiffest materials due to covalent sp^2 bonds between the individual carbon (bonds) atoms. CNT possess strength upto 100 gigapascals (GPa)

2. Hardness :-

Standard single walled CNT with stands a pressure upto 25 Gpa without deformation.

3. Electrical properties :-

Because of symmetry and unique electronic structure of graphene, CNT is semi conducting with a very small band gap between valance band and conducting band. Because the electrons propagate only along the tube axis and involve quantum effects, CNT is referred as one-dimensional conductor.

4. Thermal properties :-

CNT are very good thermal conductor and exhibit a property called ballistic conduction

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→ Single walled CNT at room temperature has thermal conductivity 3500 $WM^{-1}K^{-1}$ which is more than Cu metal (385 $WM^{-1}K^{-1}$)

→ The temperature stability of CNT is 2800°C in vaccum and 750°C in air.

5. Toxicity :-

→ CNT possess toxicity

→ Under certain conditions CNT can ~~possess~~ cross the membrane barriers and reach organs which induces harmful effects inflammatory, fibrotic (toxicological changes in lungs) reaction and can cause cell death.

* Applications of CNT :-

→ Because of the superior mechanical properties CNTs are used to make bullet proof clothing

→ used for producing CNT field effect transistors.

→ Because of their high conductivity CNTs are used for making nano-tube polymers composites which are used for making electrical cables and wires.

→ CNT can store hydrogen to be used as a fuel source.

→ Because of their strong UV/vis-NIR absorption characteristic it is used in solar panals

→ Used in cancer treatment

→ CNT can make waterproof and tear-resistant fabrics.

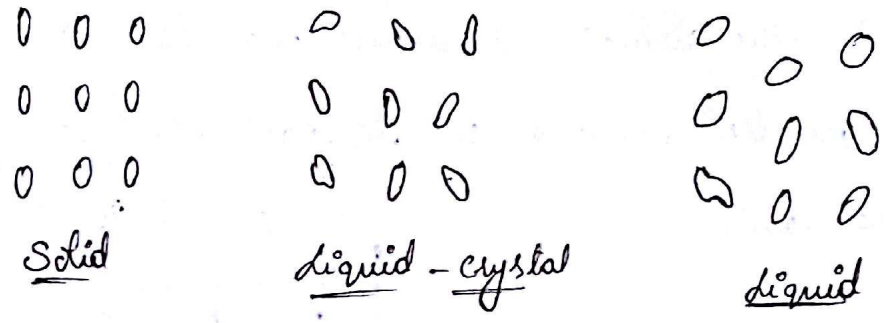
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* Liquid crystals :-

→ Liquid crystals (LCs) are highly anisotropic fluids that exists between boundaries of the solid and isotropic liquid phase.

→ Liquid crystals have the fluidity of a liquid and can exhibit the optical properties of a solid



→ In liquid crystals the molecules are able to move, but not as much as they can move in liquid phase.

→ All the molecules in liquid phase tend to align along a common axis called director. This property is called anisotropy.

→ In liquid crystals, the orderly arrangement is sufficient to impart some solid like properties and at the same time the force of attraction between the molecules are not strong enough to prevent the flow

* Classification of liquid crystals :-

There are two types of liquid crystals

1. Thermotropic liquid crystals
2. lyotropic liquid crystals.

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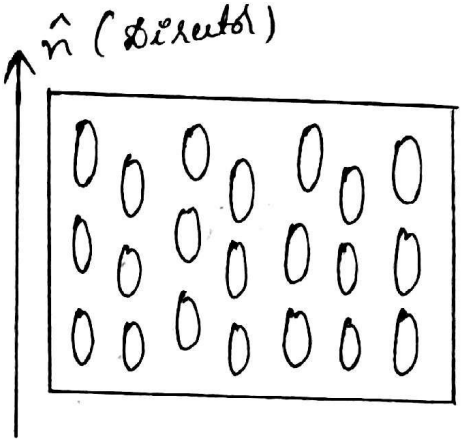
* 1. Thermotropic liquid crystals :-

→ These are formed only by the adjustment of the temperature

→ Thermotropic liquid crystals are further classified into (i) Nematic (ii) Cholesteric (iii) Smectic liquid crystals.

(i) Nematic liquid crystals :-

→ The molecules in the nematic structure maintain a parallel (or) nearly parallel arrangement to each other along the long molecular axis.



→ It is a one dimensional structure in which the molecule are mobile in three directions and rotate about one axis.

→ whenever the nematic structure is heated, it is generally transformed into the liquid

→ Even a dust particle can distort the nematic structure to liquid structure

(ii) Cholesteric liquid crystals :-

→ These liquid crystals are formed by mesogenic molecules containing a chiral centre, which produces (their inter molecular forces.

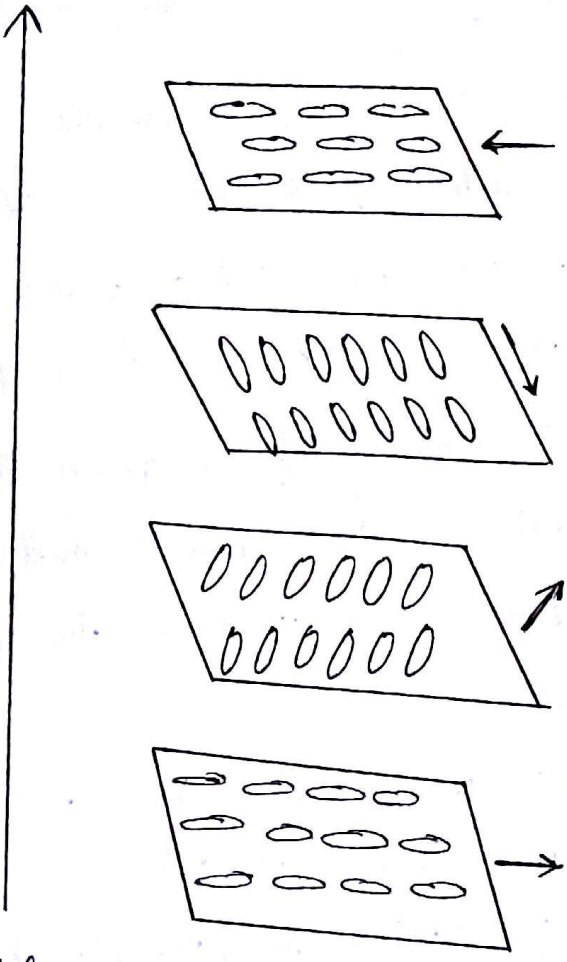
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→ These inter molecular forces are responsible for alignment between molecules at a slight angle.

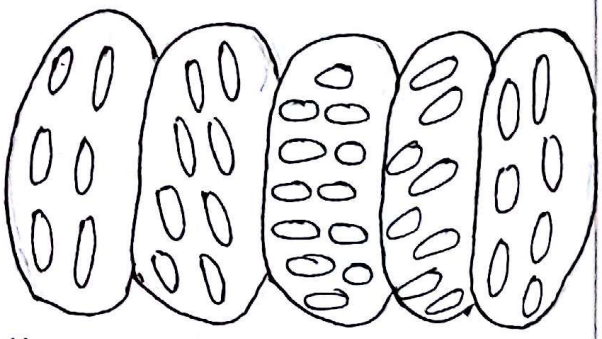
→ This structure appears as a stack of very thin nematic like layer in which the director is twisted with respect to above and below layers

→ As many compounds that forms this mesophase are derivatives of cholesterol, hence this structure is named as cholesterol liquid crystal phase.



* Pitch :- The pitch (P) is defined as the distance it takes for the directors to rotate one full turn in the helical structure.

→ When the pitch length is equal to corresponding wave length of light in visible spectrum, then the liquid crystal reflects light of wavelength equal to pitch length.



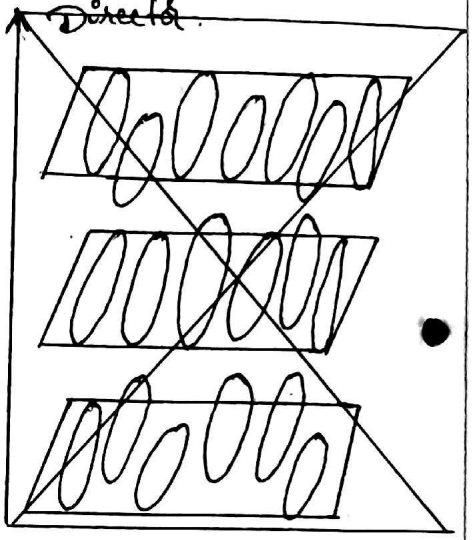
→ Increase in the temperature of the molecule decreases the pitch length and vice-versa. Thus by identifying the reflected colour, we can determine the temp of a liquid crystal

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(iii) Sematic (or) Smectic (Structure) liquid crystals :-

→ It is also another distinct mesophase of liquid crystal substances in which the molecule maintain the general orientational order of nematics, but also tend to align themselves in layers (or) planes

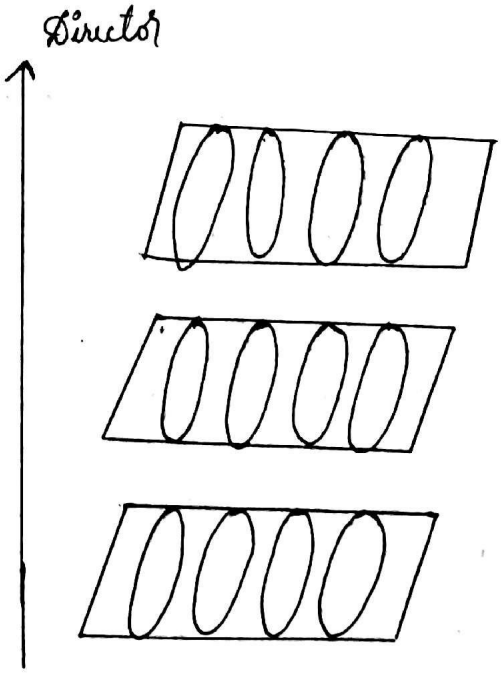


→ Motion of molecules is restricted within these planes and separate planes are observed to flow past each other

→ The Smectic state is more solid like (form) than nematic.

Ex: Thick slippery substance often found at the bottom of soap dish.

→ There are several types of Smectic structure labelled by the alphabet letters A to H. Some of them are



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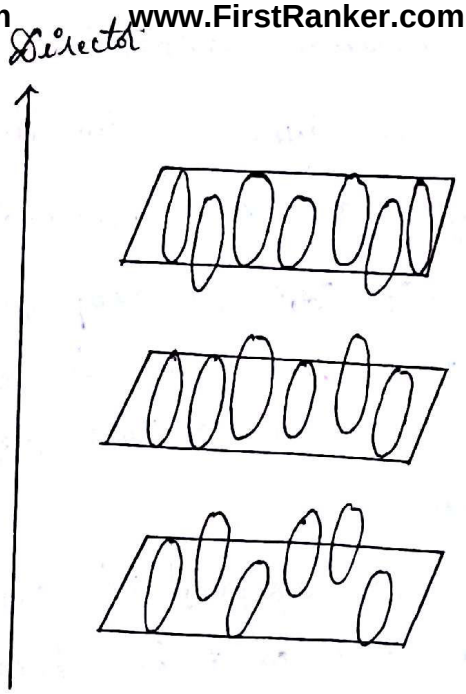
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* Smectic - A :-

→ It is the least ordered phase of all the smectic structures.

→ The molecules in this phase are arranged in equally spaced layers with a definite repeated distance

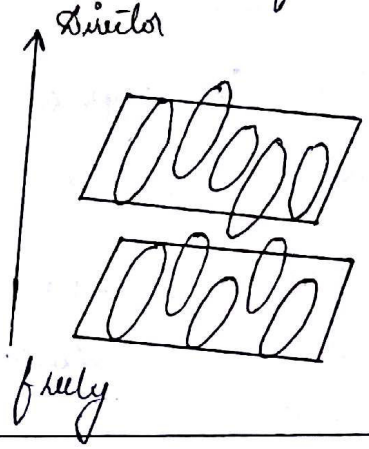
→ In this phase, long axes of the molecule is generally perpendicular to the layer plane



* Smectic - C :-

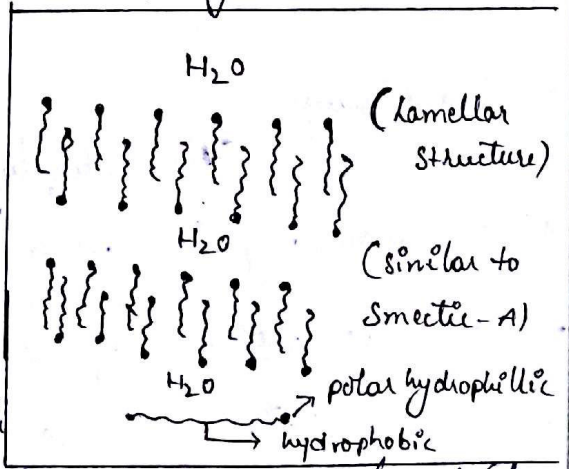
→ It is similar to that of section - A, except that the molecule in the layers are tilted at a uniform angle with respect to the normal structure.

→ In this phase, the molecules are disorganised positionally and move about freely



* 2. Lyotropic liquid crystals :-

→ Some compounds are transformed to a liquid crystal phase, when mixed with solvent (or) when the concentration of one component is increased. Such component which exhibit liquid crystallinity on mixing with a solvent (or) changing its concentration are called lyotropic liquid crystals.



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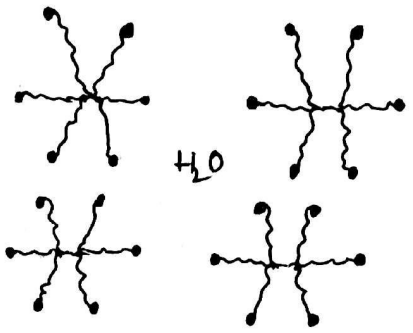
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Ex: Sodium laurate in water

→ This type of liquid crystle phases are imptant in soaps, gels and colloids.

→ Consider a soap film. The amphiphillic soap molecules arrange themselves in a bilayer in water so that there is minimum contact between paraffic tails and the water molecules

→ The amphiphilic molecules can also exist in hexagonal phase, cubic phase etc



* Applications of liquid crystals :-

→ Liquid crystal technology is widely used in many areas of science and technology.

→ They have been used in temprature sensors, display for watches and calculators, high definition TV's and industrial products

→ Indisplays :-

The display of these material runs with low power consumption and with a better charity.

→ As the colour of cholesteric liquid crystals changes with temprature, these can be used in the measurment of temprature. The cholesteric liquid crystal always

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www.FirstRanker.com exhibit the same colour at a temperature. This precise colour is very sensitive to changes in temperature using liquid crystle sensors, temperature variations of less than 0.01°c can be easily distinguished.

→ Nematic liquid crystals are useful in the application of NMR (Nuclear Magnetic Resonance). Samples that are dissolved in nematic liquid crystle solvents gives high resolution spectrum that can be used to identify the structure of sample.

→ Liquid crystal layers are used for stable monochromatic emmission.

→ Medical applications of liquid crystals are for studying circulatory system, detection of tumours, skin and breast to breast cancers.

→ Liquid crystals are also used in finding the efficiency of heat engines and testing of radiations.

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* Superconductors :-

A solid which offers no resistance to the passage of electricity through it, is called superconductor. The phenomenon was discovered by Dutch physicist kammerlingh onnes in 1911, when he was measuring the resistivity of mercury below 4.2°k. The niobium alloys were the earlist superconductors to be studied elaborately. Superconductivity can be understood with the help of quantum physics.

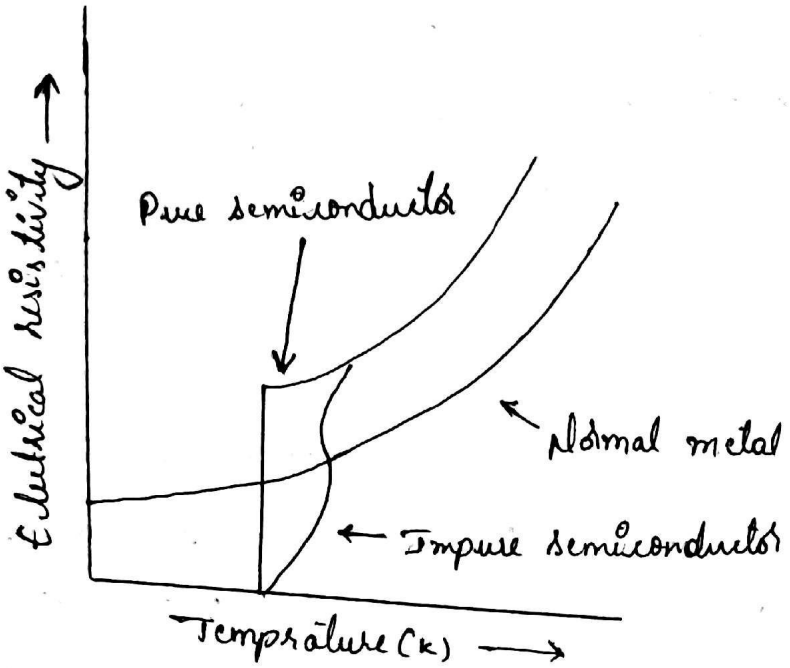
Charged particles in solids can travel only in fixed direction & levels. The electrons in a normal metallic conductor can collide with the metal atoms and shift themselves from one level to another, but the electrons in a superconductor are prevented from such shifts by a unique quantum effect. These electrons are confined to their signal level and therefore cannot collide with the atoms, and consequently must travel endlessly along fixed directions. Under such a circumstances, they head in one direction and continue to carry current endlessly

Superconductivity is exhibited by several metals, but only at low temperatures. The temperature at which the normal metal passes into superconducting state is called

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the superconducting transition temperature (or) critical temperature denoted by T_c. The resistivity temperature behaviours for the superconductive and nonsuperconductive materials are differentiated below in the figure.



Types of superconductors :-

Superconductors are dived into two types based on their magnetic response.

(a) Type I (or) ideal superconductors

(b) Type II (or) Hard superconductors

Type-I superconductors are those which become completely diamagnetic in the superconducting state. These materials exhibit 'meissner effect' i.e., the expulsion of magnetic flux from the interior of a piece of superconducting (phase).

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material as the material undergoes the transition to the super-conducting phase.

Type-II superconductors are those in which the ideal behaviour is seen upto a lower critical (temperature) magnetic field beyond which the magnitization gradually changes and attains zero at an upper critical magnetic field.

* Yttrium barium cuprate ($YBa_2Cu_3O_{7-x}$ where x is small)

This functions as a superconductor at a critical temperature (T_c) of 90°K. The constituents of this material i.e., yttrium, barium and copper are in 1:2:3 molar stoichiometric ratio and hence are called as 1:2:3 superconductors

* Synthesis of 1:2:3 superconductors by ceramic method

$YBa_2Cu_3O_{7-x}$ can be synthesised by solid state ceramic technique. This involves the following steps

(a) Preparation of a homogeneous mixture of three oxides (Y_2O_3, $BaCO_3$ and CuO) in their molar ratioes

(b) Heating them to obtain oxygen deficient superconductor in a muffle furnance

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(c) Annealing the above compound (b) to room temperature to retain its composition, structure and superconducting properties

* Classes of superconductors :-

Superconductors belong to different classes like

1) elements ⟶ Ex :- Hg, Nb, La
2) alloys ⟶ Ex :- La_3In, Nb_3Ge
3) Simple compounds → Ex :- NbN
4) molecular crystals → Ex :- $C_{60}K_x$
5) Non stachiometric crystals having defects → Ex :- TiO, NbO, $BaBi_{0.25}Pb_{0.75}O_3$
6) Ceramic ⟶ Ex :- mixed metal oxides
7) Inorganic polymers ⟶ Ex :- $(SN)_x$
8) Organic compounds ⟶ Ex :- charge-transfer compounds between electron donors and electron acceptors. (like tetracyanoquinodimethane)

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* Properties of superconductors :-

1) Superconducting materials are generally brittle in nature. This property limits their ability to be fabricated into useful forms such as wires.

2) At room temperature, the resistivity of superconducting material is greater than other elements

3) A superconductor exhibits perfect diamagnetism. Because of diamagnetic nature, superconducting materials strongly repeal external magnets which leads to a levitation effects.

4) Thermoelectric effects of materials disappear in the superconducting state.

5) If the sufficiency of strong magnetic field is applied below T_c (superconducting transition temperature), its super-conducting property is destroyed.

6) when current is passed through the superconducting materials, the heating loss I^2R is zero

[$\because$ Resistivity $\rho = 0$ at $T = T_c$;

$\therefore R = \rho l/A = 0$; $\therefore I^2R = 0$]

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* Applications of Superconductors :-

1) Superconductors can be used to perform logic and storage functions in computers. Superchips made of superconductors for computers can function 1000 times faster than currently used silicon chips

2) Power can be transmitted through superconducting cables without loss as there is no I^2R loss in a superconductor.

3) A zero resistance combined with high current densities make superconductors useful for strong electromagnets. They can be used for producing very strong magnetic field of about 50 tesla; which is much larger than the field obtainable from an electromagnet

4) Superconducting magnets capable of generating high field with low power consumption are currently employed in scientific and research equipment. They are used for magnetic resonance imaging (MRI) in the medical field as a diagnostic tool

5) Superconductors serve as gas sensors because their electrical resistivity sharply changes on contact with certain gases. For example $La_{2-x}Sr_xCuO_4$ is a good sensor for alcohol vapours.

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6) Some superconductors function as excellent catalysts for industrial chemical processes. For example $YBa_2Cu_3O_{7-x}$ and the related cuprates act as catalysts in oxidation & dehydrogenation reactions

7) More powerful magnets can be made with the help of superconductors, which are likely to enhance the probability of laboratory nuclear fusion reactions

8) Superconducting magnets are employed for operating frictionless, high-speed levitating trains

9) Superconductors have very promising application as electronic filters. One possible use for these superconducting electronic filters would be in cellular telephone systems, where it would allow more remote cables to be accessed

10) Superconducting material may be used in the manufacture of electrical generators and transformers in exceptionally small sizes having efficiency of 99.99%

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UNIT-V

Solid State chemistry

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* Types of crystalline solids:-

There are four types crystalline solids based on the nature of forces binding.

1. Ionic solids
2. Covalent solids
3. Molecular solids
4. Mettalic solids

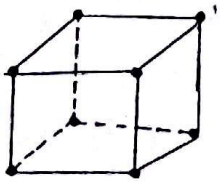
→ Ionic solids:-

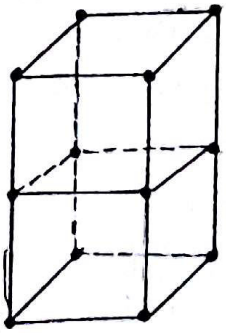
These solids are constituted by positive and negetive ions arranged in a characteristics pattern by electro-valent (ions) bond between opposite charged ions. A stable and electrically neutral ionic crystal structure contained an ion surrounded by a shell of as Many oppositely charged ions as possible.

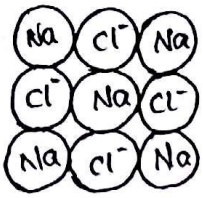
Characteristics of ionic solids:-

1. Ionic crystal possess has high Lattic energy, Hardness high Melting point and boiling points and brittleness due to their strong electrostatic attraction.
2. Ionic solids are soluble in polar solvents like water, alcohol etc...
3. Due to Large binding energies ionic solid possess small Vapour pressure.
4. Because all the charged-ions occupy well-defined positions, and also due to strong electrostatic forces, the ionic solids are insulators. However in Molten state they are good conductors due to disorderly arranged ions.

Examples:- NaCl, LiF, CaO, etc...







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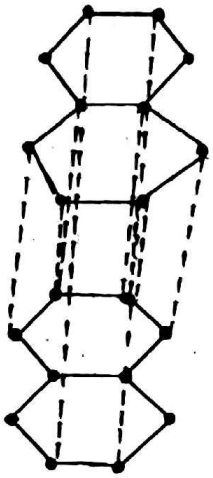
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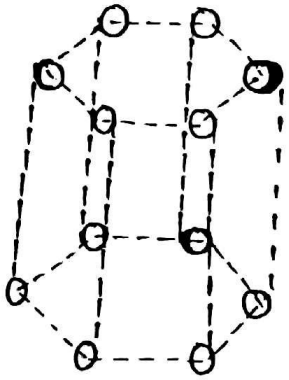
→ Covalent solids:- covalent crystals are formed by an array of atoms linked together by a continuous system of strong covalent bonds, extended in a fixed direction. The unit cells of covalent solids are atoms of either same element (or) different elements. For example diamond & graphite are constituted by same atoms i.e., carbon atoms only and silcon carbide is constituted by Si & C only.

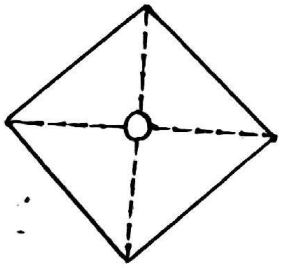
Characterstics of covalent solids:-

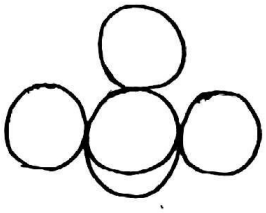
1. It possess high Melting point & hardness due to strong and directional covalent bonds.
2. All covalent solids are insulators except graphite.
3. These solids possess high hardness & brittleness.

Eg:- Diamond, graphite, silicon carbide, zinc sulphide etc...









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→ Molecular solids:- A Molecular crystal is constituted by symmetrical aggregates of discrete Molecules bounded by weak Vander Wall-forces of attraction. Eg: I_2, CO_2, Napthalene etc...

Characterstics of Molecular solids:-

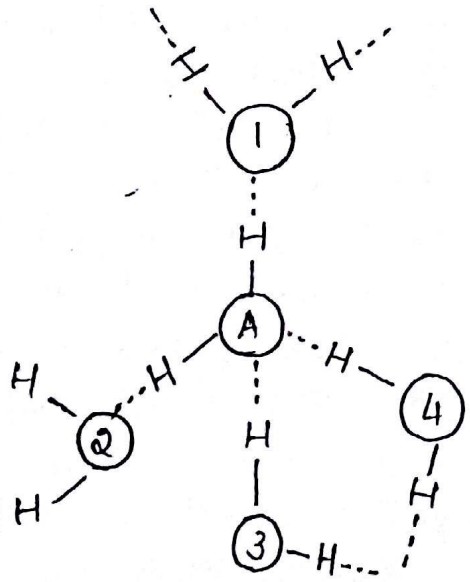
1, Because Molecular solids are constituted by weak Vander Wall-forces of short range they are relatively soft and volatile

2, Molecular solids possess low Melting and boiling points hence they Liquify (or) solidify at Low temperatures

3, Molecular solids are electrically neutral because of the Localized electrons

4, Molecular solids are good insulators.

5, Some Molecular solid crystals are held together by hydrogen bonding between atoms of different electronegativities Eg:- ice crystal.



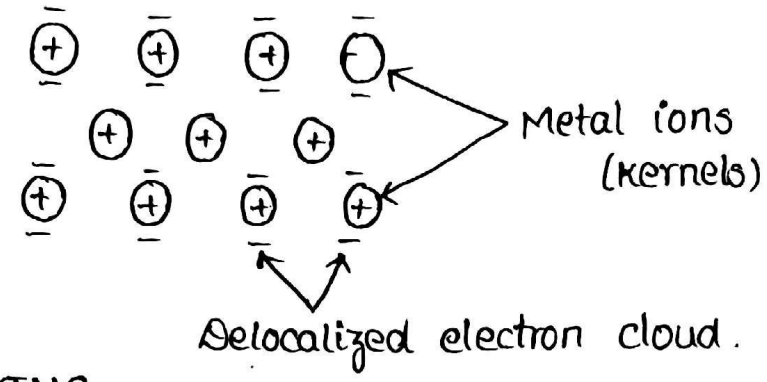
→ Metallic solids:-

Due to high electropositive nature of Metal atoms, all metal atoms loose their Valence electrons and form metal ions called "Kernels." and the electrons released becomes "delocalized electron cloud". The binding force of the Metallic solids is the attraction between positive ions of the metal and the delocalized electron cloud. The delocalized electrons are mobile and move freely within

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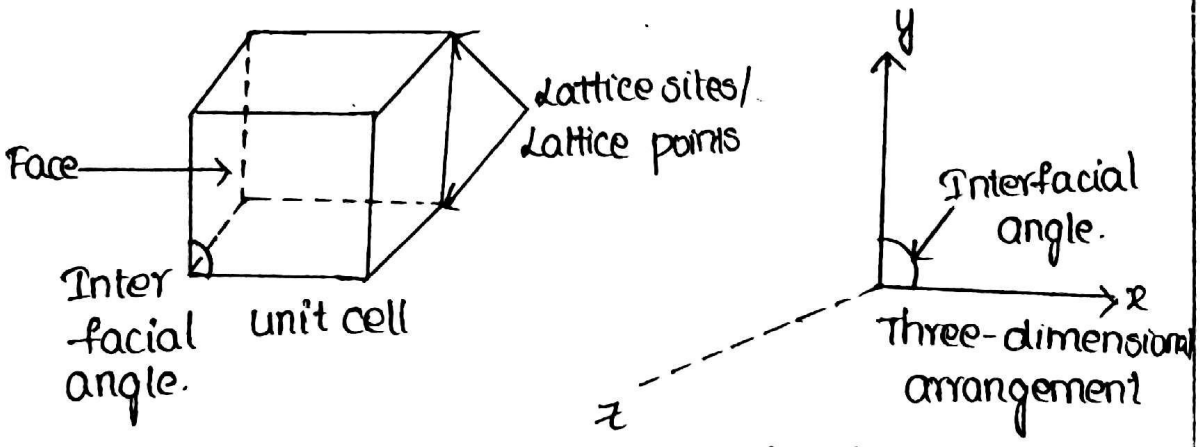
the crystal from one lattice to another quite similar to that of Molecular gas Eg:- Sodium, Lithium, Copper etc...



* CLOSE PACKING OF ATOMS AND IONS

Crystallinity is a condition of Matter resulting from an orderly cohesive, three dimensional arrangement of its component particles in space. this three dimensional arrangement of particles is called a crystal lattice or space Lattice.

The position occupied by the particle in crystal lattice are called Lattice sites (or) Lattice points. the Lattices are bound by planar surfaces, known as faces of the crystal. The smallest geometrical portion of the crystal which can be used as repitative unit to build up the whose crystal is called a unit cell. Thus the unit cell is the simple unit of the space Lattice which when extended in three dimensions reproduces perpendiculars to the two intersecting faces is termed as the interfacial angle.



It may clearly be understood that is possible to have Lattice sites other than the corners of the

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Geometrical pattern.

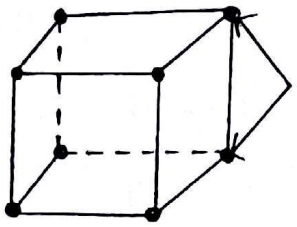
In fact for the simplest Lattice system, i.e the cube there may be three posibilities as given below

1. Simple cube.
2. Body centered cubic
3. Face centered cubic
4. Hexagonal close packing.

The Lattice sites being disposed in space in a manner that a particle situated at any of these is surrounded in identical manner by other particle of Lattice

Simple cubic:-

The figure shown below the particles are occupying the corners of the cube.



→ No. of faces = 6
→ No. of Lattice sites = 8
→ No. of particles accommodated in unit cell = $1\left(\frac{1}{8} \times 8\right)$
→ Co-ordination Number = 6
→ Interfacial angle = 90°
% of Volume utilized in the Crystall lattice = 56

The no. of Lattice sites are 8. In order to count the no. of particles in a unitcell, it must be observed that each corner particle of the unit cell is equally shared by eight other unit cells of the space lattice.

Hence $\frac{1}{8}$ of the corner particle belongs to the unit cell. there are 8 Lattice sites and the no. of particles accomoded in simple cubic system is equal to $\frac{1}{8} \times 8 = 1$ particle There is another interesting point about cubic Lattices, The coordination number (or) Legency. It is the no. of particles immediately adjacent to each other in the crystal lattice. For example in simple cubic Lattice each particle is adjacent to six other particles, hence coordination number is 6. The axial characteristic is a=b=c

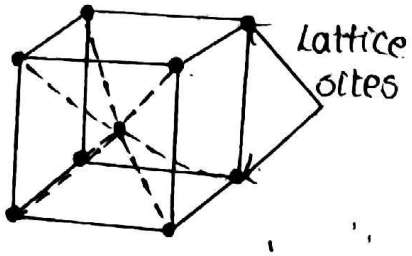
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Examples of simple cubic crystals. NaCl, CsCl, KCl etc

BODY CENTERED CUBIC LATTICE SYSTEM (BCC) :-

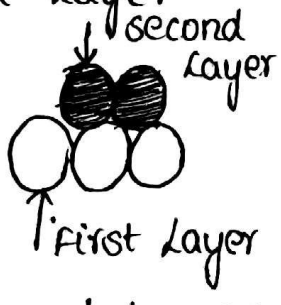
The body centered cubic lattice is a simple cubic system with one particle at the centre of the cube in addition to all occupied corners (8)

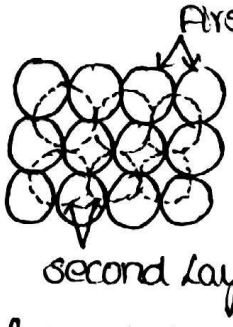


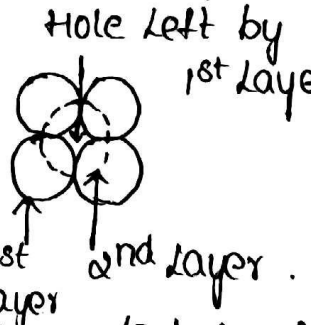
No. of faces = 6
No. of lattice sites = 9(8+1)
No. of particles accomodated = 2$(\frac{1}{8}\times 8+1)$
Coordination number = 8
% of volume utilized in the crystal Lattice = 68%

The no. of particles in the unit cell. is counted as follows There are eight particles in the corner sites which is shared by eight other unit cells of the space lattice system contributing one particle $(\frac{1}{8}\times 8 = 1)$ and the body centered particle belongs to the entire unit cell and thus body centered cubic lattice has two particles. The coordination of BCC crystal system is 8.

The percentage of space utilized in the crystal lattice is 68%. The b.c.c system is produced by close packing of atoms one Layer over the other Fig shows such two Layers. The 1st Layer of atoms are closely packed and holes voids Left by the 1st Layer become the centre for the 2nd Layer of atoms. Thus the second layer of closely packed. sphere caps the holes voids Left in the close packing of the first Layer.







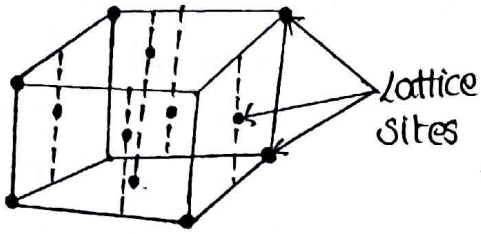
As these holes are formed by four spheres (3 belonging to 1st Layer & 1 to 2nd Layer) they are called tetrahedral holes. A few metals have tetrahedral structure for ex:- Sg. Indium and Iron at room temparature exhibit Bcc. structure. alkali metals etc...

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Face centered cubic structure :- (FCC)

Face centered cubic lattice is also cubic system with one particle in the centre of each phase



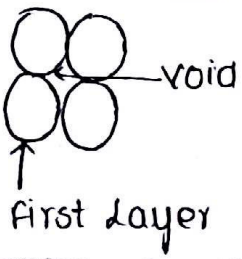
no. of faces = 6
no. of lattice sites = 12 = (8+6)
no. of particles accomodated.
$(1/8 \times 8) + (1/2 \times 6) = 4$.
% space utilized = 74
coordination number = 12.

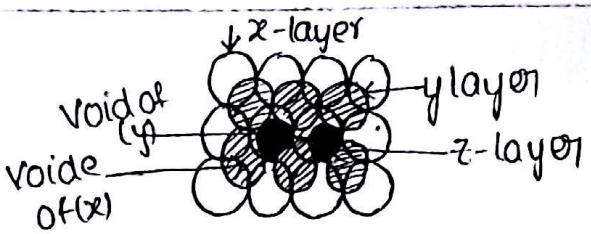
There are 8 lattice sites in all the corners of cubic system, which are shared by eight other unit cells. The particle present in the centre of face is shared by two unit cells. The number of particles accomodated are one particle from corner lattice sites as each corner particle is shared by 8 other unit cells $(\frac{1}{8} \times 8 = 1)$. The facial particle is shared by 2 unit cells. There are six faces contributing 3 particles $(\frac{1}{2} \times 6 = 3)$ as $\frac{1}{2}$ particle belongs to each face. The to number particles accomodated are 4. $\left[\frac{1}{8} \times 8 = 1 + \frac{1}{2} \times 6 = 3\right]$ The percentage of space utilized by the particle is 74.

The coordination no. of fcc system is 12. The packing of atoms in f.c.c system takes place in the following manner. The close packing of first layer takes place & the voids left by the first layer becomes centre for the second layer. The second layer of atoms caps the hole left by the 1st layer. Now the third layer of atoms are placed covering the voids left by the second layer. created a 3rd layer units which is different from the other two layers and the pattern of repeating units are written as xyz, xyz xyz ... In f.c.c ~~pto~~ close packing. each sphere is surrounded by twelve other spheres & coordination number is 12. Face centered cubic lattices are know to be present in Cu, Ag, Au, Pb, Al etc

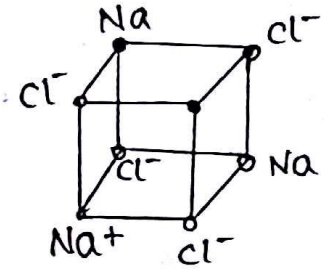
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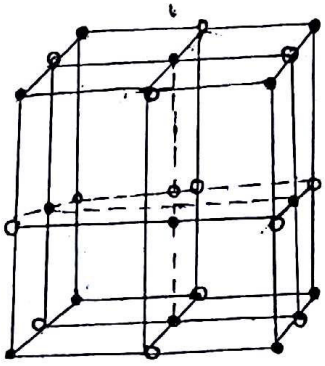
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* **STRUCTURE OF ROCK SALT:-** Rocksalt also known as Nacl is an ionic compound and occurs naturally as white simple cubic crystals. The structure is formed by repeating unit cell with a ratio of Na:Cl as 1:1 as shown below

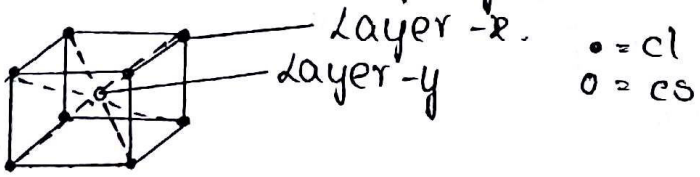




It is clear from the structure that each sodium ion and each chloride ion is clustured by six sodium ions in the lattice structure. Number faces for unit cell are 6 and no of lattice sites are 8 coordination number is 6. and percentage of space utilized is 52. Interfacial angle is 90°.

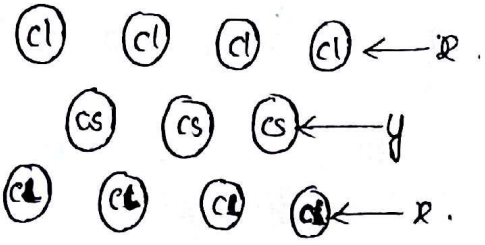
* **STRUCTURE OF CESIUM CHLORIDE:-**

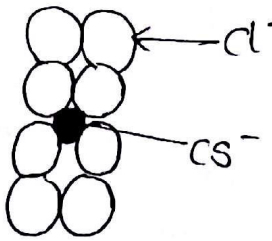
It adopts by b.c.c lattice where the chloride atoms lie upon the lattice points at the edges of cube. where as cesium atom lies in the centre of the cube. Each cesium ion is surrounded by eight chloride ions. The coordination number is 8:8 and 68% of volume is ultilized by atoms. The packing of layers in two layers as shown below. The second layer of atoms are placed in the voids left by the first layer. Thus each chloride ion is surrounded by eight cesium ions



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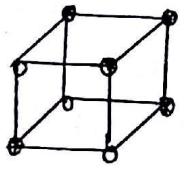


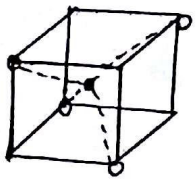


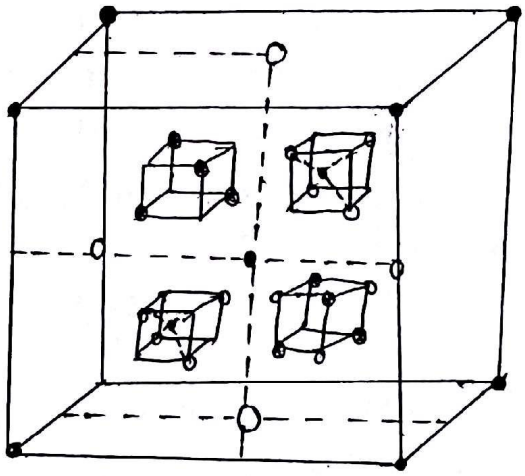
* STRUCTURE OF SPINEL :-

Spinel is the Magnesium aluminium oxide and it has the formula $MgAl_2O_4$ and the general formula is AB_2X_4 where A = divalent cation like Mg, Cr, Mn, B = tri-valent cation like Al, Ga, In etc and X = O, S, Se etc. A normal spinel is represented as $(A^{II})^{tet}(B^{III})^{oct}O_4$ Eg: $MgAl_2O_4$

Inverse spinels $(B(AB)O_4)$ The A^{II} ions occupy octahedral voids, where as B^{III} ions occupy tetrahedral voids. It can be represented as $(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$. Eg: $CoFe_2O_4$, $NiFe_2O_4$







* NON- ELEMENTAL SEMICONDUCTORS :-

These semiconductors are formed by the combination of elements of group III-V or group II-VI and certain other compounds which have valencies in non-stiochimetric compositions

→ Stiochimetric semi-conductors :-

The crystal and band structure similar to that of Si & Ge. are developed by the combination of group III and group V elements and group II & group VI elements named as. stiochemetric semiconductors. For example Ga-As semiconductor. The $4s^2, 4p^1$ level of Ga and $4s^2, 4p^3$ level of

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As overlap to give rise to hybrid band containing 4N electrons per N atom of Ga and As with ferry energy gap 2.24(eV) The following is the list of some stiochemetric semiconductors and their fermi energy gaps

Group III & V combination		Group II & VI combination	
Semiconductor	Fermi energy gap	Semiconductor	Fermi energy gap
Gap	2.24.		
GaAs	1.35	CdS	2.42
GaSb	0.67	CdSe	1.74
InAs	0.36	PbS	0.37

Characterstics :-

1. They have wide energy gap, which leads to broad exhaustion zone with high conductivities, Hence they can be used at wider range of temperatures.
2. It is possible to alter the energy gap (E_F) of these semiconductors by substituting elements in its composition by an element of lower atomic number belonging to the same group for ex:- In GaP, If P is replaced by As the energy gap reduces from 2.24 to 1.35 (eV)
3. They can be doped to n or p-type semiconductors

→ Controlled valency semiconductors :-

$Ni^{2+}_{0.7}\ Ni^{3+}_{0.2}\ O$ is a hopping semiconductor producing hopping semiconductivity by hopping of electrons from Ni^{2+} to Ni^{3+} ions the concentration and conductivity of Ni^{3+} is controlled by the addition of small amount of Li^{+} ions.

$$LiO + NiO + O_2 \longrightarrow Li_x Ni^{2+}_{1-2x} Ni^{3+}_{x} O$$

The semiconductors show conductivities depending on temperatures and find applications as thermistors these semiconductors can be used over a wide range of tempurature at 200°c The compound containing the compo-

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sition $Li^{+}_{0.05}\ Ni^{2+}_{0.9}\ Ni^{3+}_{0.05}\ O$ is electroneutral semiconductor which is shown as below

Positive charge	Negitive charge
$Li^{+}_{0.05} = 0.05 \times 1 = 0.05$	$O^{2} = 2$
$Ni^{2+}_{0.9} = 0.9 \times 2 = 1.8$	
$Ni^{3+}_{0.05} = 0.05 \times 3 = 0.15$	
2.0	2

Thus $Li^{+}_{0.05}, Ni^{2+}_{0.9}, Ni^{3+}_{0.05} O$ is neutral semiconductor.

- Chalcogen photo semiconductors:-

Oxygen (O), sulphur (S), selenium (Se) and Tellurium (Te) are collectively called chalcogens or ore forming elements because a large no. of metal ores are oxides (or) Sulphides

Characterstics:-

1. They behave as semiconductors or photoconductors either alone or by combining with other elements
2. they rapidly form glass on cooling and viscous Liquid on melting.
3. chalcogen based glasses have conductivities in the range of $10^{-3} - 10^{-13}$ mho/cm
4. The conductivities of pure chalcogens increase with increase in atomic mass.
5. Selenium is an excellent photo conductor. Its conductivity increases enormously on exposing to light. Hence it is used in photo copying process (xerox)

* preparation of semiconductors:-

The semiconducting elements used for the application of semiconductor devices must be 99.99% pure i.e., one atom of impurity for every 10^{8} atoms of Si or Ge To prepare such ultra pure Materials the following steps were involved

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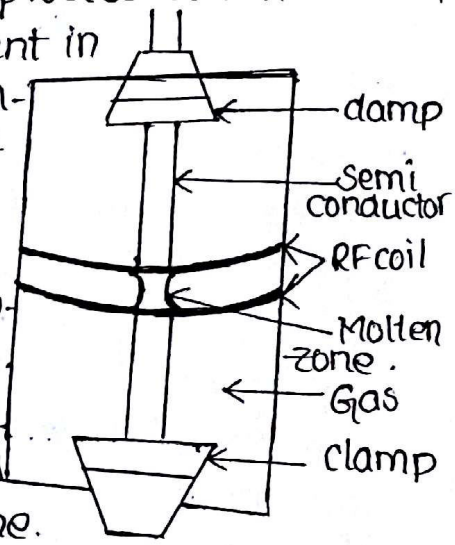
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1. Preparation of ultra pure Si or Ge:-

(Gecly) Germanium tetrachloride is used as a starting material, which contains arsenic (As) impurity which is removed as $AsCl_3$ and seperated by distillation

a) Distillation:- It is a process where seperation is carried out by taking the difference in boiling points as advantage. Ge is taken in a series of stills with a layer of HCl over it and heated it, while passing chlorine through it. the vapour produced were collected and passed into a fractionality column. the distilled vapours are collected into a recieved placed in ice bath. pure Gecly thus obtained is treated with water to get GeO which is reduced in as atmosph-ere of N_2 to elemental germanium, which is further subject purifaction by zone refining.

b) Zone-refining:- It is Metallurgical process which is based on principle that the impurities present in a Metal are mote soluble in molten m-etal than in solid metal. For the purif ication of Ge Vertical zone refiner is used. A rod of Ge to be purified is clamped and heated by RF coil is mo-ed down, the impurities Move with the Molten part of the Material. pure Ge rod solidies at the upper portion. the proces is repeated several times to reduce the. impurity level & Lower end of rod is removed after getting the desired purity because it is concentrated with impuri ties. By zone refining process the impurity level 1 atom in 10^{12} atoms of Ge is obtained



c) preparation of ultra pure silicon:- It is prepared by follow-ing Method

Chemical Method:- Trichlorosaline is first distilled to get pure trichlorosaline than it is reduced to elemental silicon by heating in an atmosphere of hydrogen by bubbling hydrogen through trichlorosaline which vapourizes

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The vapours are fed into a tubular furnace fitted with a highly pure silicon rod and heated to 950°c. At this temperature, the vapours of trichlorosilane decompose leaving behind pure silicon on the surface of the highly pure silicon rod. The thickness of silicon rod increases from 2.5 to 10cm.

Hcl vapour produced in the reaction are removed through a vent. It cannot be adopted for the preparation of ultrapure silicon, because boron impurity has same solubility in molten and solid silicon and a high temperature is required to melt silicon.

→ Preparation of single crystals of Si or Ge:-

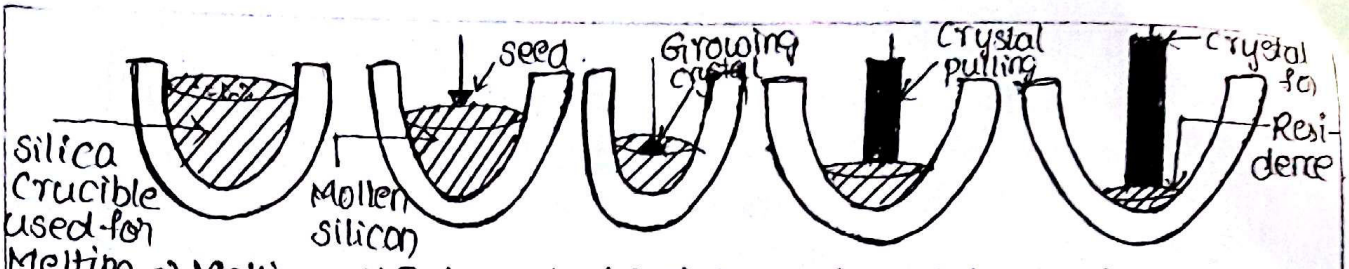
The base requirement for the fabrication of a semiconductor used must be a single crystal. The preparation of Si and Ge produces polycrystalline products i.e., crystals of various size. Hence single crystal of Si and Ge are produced by Czohralski crystal pulling technique.

Czochralski crystal pulling technique:- This process was named after the polist scientist Jan Czochralski who invented the Method in 1916 by accident while studying crystallization Method.

In this Method single crystals are grown in such a way that during crystal growth atoms reproduce the same atomic arrangement as that of the seed crystal. The process begins when the chamber which contains a crucible with silicon is heated to approximately 1500°c. when silicon is fully Melt, a small sp seed crystal Mounted on the end of rotating shaft is slowly lowered until it just dips below the surface of Molten silicon. The shaft rotates in anticlockwise & the crucible in clockwise direction The rotating rod is then drawn upwards very slowly about 25mm per hour when making a crystal of silicon allowing in the form of boule to be formed. The boule can be form one to two meters, depending on the amount of silicon in the crucible

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a) Melting of poly silicon b) Introduction of seed crystal c) Begining the crystal growth d) crystal pulling e) formed crystal with a residence of silicon

when silicon is grown in silica crucible O_2 from crucible is introduced as an impurity at a concentration of 10^{18} cm^3. Careful an annealing process condition were adopted to remove oxygen. The above process is adopted even for the crystal pulling of germanium

→ **Doping:-** Introducing an impurity into the semiconducting crystal is called doping. Doping is carried out by an expitaxy diffusion implantation techniques. Doping is carried out in the crystal pulling state. calculated amount of dopants are added to the Melt before crystal pulling.

a) **Epitaxy:-** It is a process of deposition of a crystalline over layer on a crystalline subtrate the overlayer can be called as an Expitaxial film. the term epitaxy comes from Greek - epi means 'over' and taxy Means "Ordered Manner' Epitaxy refers to deposition of crystalline over layer on a Crystalline substrate. which acts as seed crystal. The following are some of techniques molecular beam epitaxy. A source of Material is heated to produce an evoparated beam of particles. which ~~treate~~ travel through high vaccum to the substrate where they condense MBE has lower throughout than other forms of epitaxy. This is widely used for growing group III, IV & V semiconductor crystals

b) **Diffusion:-** An epitaxial layer can be doped during deposition by adding impurities to source gas such as Arsine, phosphine. The concentration of impurity in the gas phase. determines the concentration in deposited film. the impurities change the deposition rate. At high temperature the chemical vapour deposition May allow dopants to diffuse into the.

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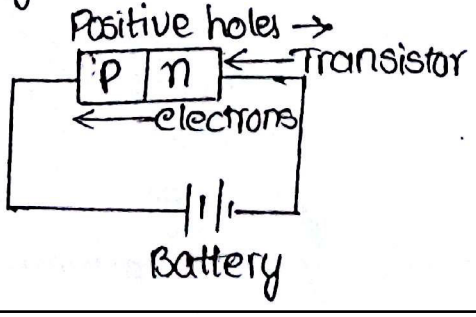
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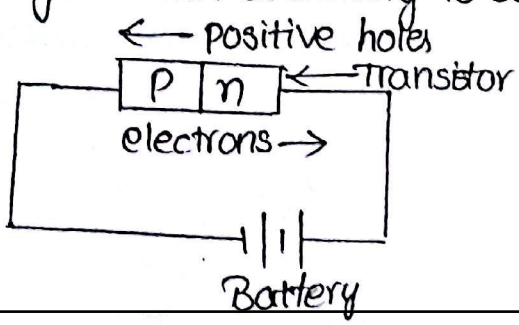
growing layer from layer to other in water. p-type Ge water is heated just below the Melting point in an atmosphere of n-type dopant such as P or Sb causing diffusion of impurity into the material and produces pn-type semiconducting Material.

c) Ion implantation technique:- In this a semi-conductor Material is bombarded with an electrically controlled beam having higher energy of 10 kev containing impurity ions like boron or phosphorous. This results in the implantation of some dopants into semiconducting crystals Ion implantation method is extensively used in the fabri-cation of high frequency devices.

✳ P-n JUNCTION AS A RECTIFIER :-

Current from an Outside source is allowed to flow through a rectifier only in one direction. and this is very useful because it helps in converting alternate current to direct current. The function of p-n junction as rectifier is discussed below. A transistor with two zones, One p-type and other n-type with p,n- junction in between is known diode If p-type semiconductor region is conne-cted to the positive terminal of battery and n-type region is connected to the negative terminal of the same battery. From n-type region electrons with migrate towards p,n- junction. where as holes will migrate towards the p-n junction At the p-n junction of diode, The Migration electrons from the n-type region move into the vacant holes in valancy band of p-type region. This Migration of electrons and holes can continue and current flows as long as the external voltage than a battery is suppli ed.



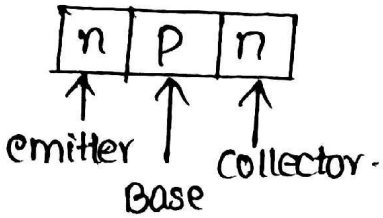


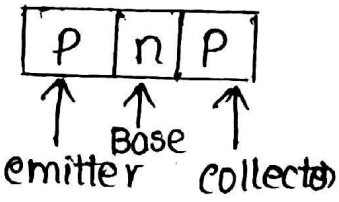
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when the connection is reversed. i.e., p-type region is connecting to the negetive terminal of the battery & n-type region is connecting to the positve terminal of battery the positive holes move away from p-n junction in p-type region and the electrons migrate away from p-n junction in the n-type region The current doesn't flow at junction as there are no electrons or positive Holes

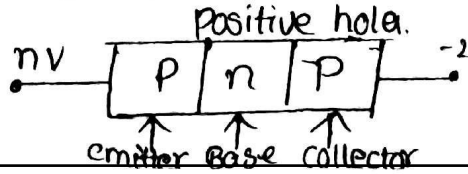
* JUNCTION TRANSISTORS:- They are single crystals of Silicon which have been doped to give three zones, either p-n-p or n-p-n as shown below.

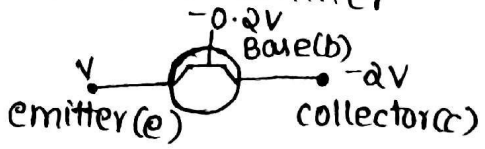




Different voltages Must be applied to the three regions of transistor to Make it work w.r.t emitter the base is typically -0.2V & the collector is typically -2volts.

In p-n-p the charge carriers in the emitter are +ve holes, which migrate from emitter at 0 V to base -0.2V. The +ve holes cross the emitter/base p-n junction In n-type base region some holes combine with electrons & are destroyed electrons flow in the reverse direction from base to emitter. There is thus a small base current. Since the collector has Much greater Negative voltage & base is Very thin, Most of positive holes pass through the base to collector, where they combine with electrons from positive holes Typically if the emitter current is 1mA, The base current is 0.02mA and the collector current is 0.98mA The n-p-n transistor work in a similar way, except the polarity of the base voltage is reversed. Thus the collector and base are positive w.r.t emitter





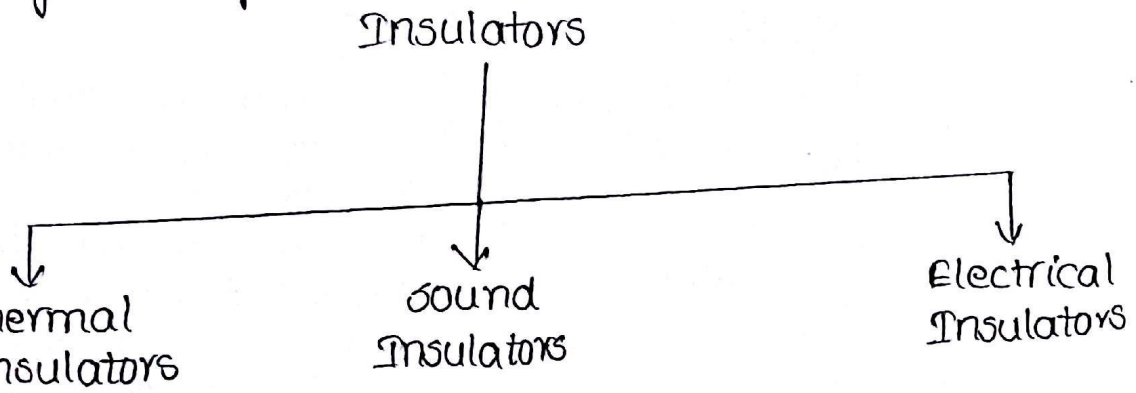
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Application of Transistor:- They are Most widely as i) amplifiers and oscillators in radio, T.V, Computers & hi-fi circuits, phototransistors, solar cells, detectors for ionizing radiations, thermisters and tunnel diodes

* Insulators:- The substance which are capable of retarding (or) prohibiting the flow of heat or electricity (or) sound through them are known as Insulators

They are 3 types:-



→ Classification of Insulators:-

According to American Institute of electrical engineers all insulating materials are divided into three classes according to their constitution They are.

a) Gaseous Insulators
b) Liquid Insulating Materials &
c) Solid Insulators.

→ a) Gaseous:-

Dielectric gases are used on both as insulants and heat transfer medium. The major problem associated with them are abnormalities in dielectric behaviour at high pressures, temparature instability. and fire hazards Taking into consideration the dielectric strength, dielectric loss, chemical stability, corrosion resistance etc.. They May be classified as follows

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Insulator	Properties	engg. Applications
1. Simple gases i) Air	Most important of all dielectric gases. It acts as a relible insulating material when voltages are not very high. However Oxygen in air causes Oxidation, which reduces the life of an electrical equipment	It provides insulation between overhead transmission lines without any cost.
b) Nitrogen	It is chemically inert dielectric.	used in transformers to replace harmful. oxidising atmosphere Nitrogen under high pressure is used as dielectric in certain types of electrical capacitors
c) hydrogen	It is of special interest due to its lightness & coolant property. Organic insulators in contact with hydrogen are less susceptible to ageing because. there is no oxidising effect.	used as coolant in. electrical Machines like Large & turbo generators, synochronous condensers etc...
d) Carbondioxide	The dielectric strength of CO_2 is comparable with that of air.	CO_2 is used as an insulant in certain types of fixed capacitors and is also used as preimpregnant for oil-filled high voltage. apparatus such as cables and transformers.

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2. Electronegative gases like SF_6 & CCl_4	They have high di electric strength as compared to N_2 & air for eg: The dielectric strength of SF_6 is 235 times & of carbon tetra chloride is 6.33 times that of the air. These gases are also non-inflammable & non-explosive SF_6 is not toxic, stable when heated upto 800°c. However presence of sulphur in SF_6 Molecule yield corrosion effect under some condition.	SF_6 is used in electrical devices like capacitors, Cables etc.

2. Liquid Insulating Material:- Insulating Liquids are used for purely dielectric purposes in order to eliminate air or other gases, or as an insulating & Heat transfer medium. usually Liquid insulants are used in conjunction with solid Insulants. These can be broadly classified into

Insulator	Properties.	Application.
1. Mineral Oils	These are obtained from crude petroleum. these electrical Properties & resistance to thermal oxidation are greatly influenced by presence of non hydro carbon compound O_2, sulphur, N_2 etc. These are used in the temperature range of -50°c to 110°c.	They find extensive application as insulating oils in cables, capacitors transformers swith gares etc..
ii) Askarels	These are synthetic insulating Liquids which are non inflammable and which under the influence of electric	Askarels are used as transformer fluids. In practice, the askarels are

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	arc does not decompose to produce inflammable gases. These are also used in the temparature range of -50°c to 110°c. Most widely used askarels are chlorinated hydrocarbons i.e chlorinated diphenyl, penta chloride diphenyl, trichloro diphenyl, hexa chloro diphenyl, trichloro benzene. Further askarels possess excellent fire resistance, high dielectric strength, dielectric constant of the order of 4 to 6 tolerable dielectric loss at normal temparatures & power-frequencies, adequate thermal; chemical and electrical stability.	usually used to impregnate cellulosic insulating material such as paper or press board etc.
(iii) Silicone fluids	These are used in the temparature range of -90°c to 200°c. Silicone fluids are organic compounds of silicone with a structure of alternate atoms of silicone and oxygen. They are clear water like white liquids with an only consistency and are available with a wide range of viscosity. They have stability at high temparatures, non-corrosive to metals upto 200°c. Silicone fluids have a tendency to breakdown in the presence of electric arc to give considerationer) considerable amount of gases and residue consisting of c, sic & SiO_2.	They are used as coolants for radar. Pulse, aircrafts & radio transformers. However they are too costly to be used as coolants for large power transformers they are also not recommended as switch gear oils
iv) Flourinated fluids:-	These are used in the temperature range of -50°c of 200°c they have a very high chemical stability	They are used in small size electric & radio devices electronic

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These are flourine substituted organic compounds	non-inflammable and their vapours are non-explosive. They ensure much better heat transfer from the windings & Magnetic circuit than mineral oils or silicone fluids. However flourinated liquids are degraded in their electrical properties. under the influence of moisture. Moreover they possess high voltality	transformers etc..
v) Synthetic Hydrocarbon Liquids:- eg:- polybutene & polypropylene	used in temparature range of -50°to 110°c. They have similar ~~dielectric strength, stability and oxidation thermo~~ dielectric strength thermal stability and oxidation suspectibilty as that of Mineral oils	They are used in high pressure gas-filled. power cables & DC voltage capacitors, Viscous synthetic Hydrocarbon liquids are also used as thickners of Mineral oils used for the impregnation of solid power cables.
vi) Organic ester liquids:-	These operate in temperature range of -50° to 110°c. they possess low dielectric losses and high dielectric constant	They are well suited for certain high frequency capacitor applications
vii) Vegetable oils:- These include drying oils like linseed oil, non drying oils like castor, coconut, palm, olive, peanut oils	used in the temparature range -8°to 100°C	Drying oils are used in formulation of Insulating Varnishes, which are used in treatment of transformers and. Motor coils etc. Non drying oils are used as plasticzers in insulating resin compositions which are applied as structural & insulating Materials & coating. Composition in electrical equipments

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c) Solid insulating Materials:- They are classified according to the temparature upto which they can be used, because insulating material retain their insulating property as long as certain temparature is not exceeded.

Insulator	Properties	Engg. Applications
i) paper & press boards are made from wood cellulose $(C_6H_{10}O_5)_n$ where n is very large number. paper is also made from rags, cotton linen and various types of humps	Paper and card boards made from alkaline wood cellulose Mechanically stronger and more heat resistant	Paper and Press-boards are used for windings and cable coil insulation transformer insulation etc. Mineral oil impregnated Papers & boards are advantages in bushings and cables. while diphenyl & Vegetable oil impregnated papers are Preferred for capacitors.
ii) Fibrous insulator like cotton, silk, wool, jute, rayon, nylon, terylene, teflon, fibre-glass etc..	They have high mechanical strength, durability, cheapness, flexibility & easy processing. Their drawbacks include hygroscopicity and low dielectric strength.	They are used in conductor insulation, backing for mica insulation, manufactor of vanished cloth which finds wide application in electrical Machine & Cables
Inorganic fibrous Materials like. asbestos, glass fibre possess greater heat resistance than organic fibrous Material	They operate at high temperatures (180°C) They possess elasticity., poor flexibility as compared to organic fibrous Materials	

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iii) Impregnating, Coating, and bonding materials are synthetic high molecular weight organic & organo metallic compounds they are classified as.		
a) waxes, which are complex organic compound of Natural and synthetic origin.	They are soft and Mechanically weak.	Natural waxes have limited applications as insulants, but synthetic waxes are used as impregnants
b) Insulating Varnishes are solutions of substance like bitumen, drying oil, resin etc.	coating varnishes from tough smooth, water proof films on the surface of objects. Hard solid films have low Hygroscopicity and they adhere well to surface	The Main application of insulating varnishes are impregnation coatings & adhesion impregnation for porous hard and fibrous insulant like paper, fibre yarn etc.
c) Bonding Material adhesives:- These are the solutions of Modified phenolic resins in alcohol	They are available in the form of films, tapes etc..	They are used in electric apparatus & low capacity electrical machines. They are used to seal separated insulated parts. Adhesive tapes are extensively used in stationary.
iv) Resins are Natural or artificially made organic substance of high m.wt		
a) Natural resin are copal, rosin shellac and amber.	shellac obtained from tropical trees possess high adhesive property	Rosin obtained from pine trees is used in the Manufacture of insulating varnishes

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		Amber is used to make electrical insulating components in measuring instruments.
b) synthetic resins:- i) polythene is obtained by polymerization of ethylene.	It is available in pellet powder, sheet, film rod, tube & foam forms	It is used as high frequency insulator in radio, television & communication circuit cables and also in power cables, submarine cables etc...
ii) polystyrene is produced by polymerization of styrene. High polymeric styrene is hard rigid transparent solid.	It possess excellent dielectric properties. It is available in the form of transparent film rod, tube and foam forms.	It is used as dielectric in DC & high frequency capacitors, electrical bushings, telephones, flourescent ligh accessories etc.
iii) PVC is obtained by polymerisation of Vinyl chloride.	It is chemically inert mechanically strong, has extremely low moisture absorption property, has high dielectric constant.	used in flexible wire coverings, cable sheathings, insulating electric wires, and low voltage cables.
iv) teflon obtained by polymerization of tetraflourro ethylene.	It is available in rods, sheets, tapes, it is thermally & chemically stable & can be used as insulant upto 327°C.	used as capacitor dielectric & insulating Material for almost all kinds of windings
v) Epoxy resins:-	These resins posess excellent electrical & Mechanical properties.	Mostly used in Making insulators, bushings etc.. for high voltages. Also used for Making laminates & insulating Varnishes.
vi) polyester resins:-	They possess good dielectric properties. and highly resistant to most acids, bases, salts & solvents.	Used in making paper, cloth mat for electrical insulation. Its films are used for wire and cable insulations & in motors, transformers & capacitors

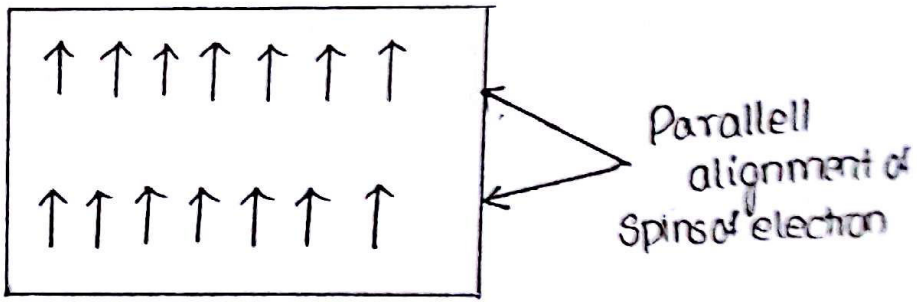
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d. Rigid insulators

Glass:-	They possess low temperature coefficient, high dielectric constant & dielectric strength.	Used for wire coating line insulations, glass to metal seals & other electrical engineering applications

* Ferro Magnetism:- The atomic moments in these materials are very strong interactions, which are produced by electron exchange forces and results in parallel alignment of atomic moments. The electron exchange force is due to the relative operations of spins of two electrons.
  The distinctive characterstics are spontaneous magnetization and magnet ordering temperature
  Ex: Fe, Ni and Co
* Ferri Magnetism:- As a result of crystalline structure of ionic compounds such as oxides, more complex Magnetic ordering occurs and one type. Magnetic Ordering is called Ferri Magnetism.



* HALL EFFECT AND ITS APPLICATIONS:-
  It is the production of a voltage difference across the electrical conductor, transverse to an electric current in the conductor and a magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.
  When a current carrying semiconductor is kept in a magnetic field, the charge carriers of the semiconductor experience a force in a direction perpendicular to both Magnetic field & current. At equilibrium a voltage

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appears at semiconductor edges. The simple formula for the Hall coefficient given above becomes more complex in semiconductors, where there carriers are generally both electrons & holes which may be present in different concentration & have different mobilities. For Moderate Magnetic fields the Hall coefficient is $R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2}$

or equivalently.

$$R_H = \frac{(p - nb^2)}{e(p + nb)^2}$$

with $b = \frac{\mu_e}{\mu_h}$.

where n is electron concentration, p = the hole concentration

μ_e = the electron mobility

μ_h = the hole mobility &

e = elementary change

For large applied fields the simple expression analogous to that for a single carrier type holds.

Applications;

1. It is used as magnetometers to measure magnetic field
2. Hall effect devices suitable for Labaratory instruments.
3. Hall effect sensors have mass application & analog-to-digital convertors
4. A hall effect thurster is used in space craft application
5. Industrially Hall effect joysticks are used to control. hydraulic valves, scissor lifts, cranes, mining trucks etc..

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Non-Conventional Energy Sources and Storage Devices

Introduction:

Solar energy is a renewable ecofriendly energy. As the conventional sources of other electrical devices are going to extinct, much attention is paid to solar energy. A solar cell is an electrical device that converts the energy of light directly into electricity by photovoltaic effect. Solar cell is a form of photoelectric cell, which when exposed to light, can generate and support an electric current without being attached to any external voltage source.

Applications of solar energy:

1. The main application of solar cells is to generate large scale or small scale electricity from sun light.
2. Solar photovoltaic cells are often electrically connected and encapsuled as a module which are connected in series to create additive voltage and to yield high current.
3. To make use of solar generated energy, the current is fed into electricity grid using inverters in stand alone systems and batteries to store energy.

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4. Solar panels can be used for making power or recharge the portable devices and heating water etc.
5. Solar panels can be used for solar street lighting, home lighting systems and lanterns.
6. Solar cells are majorly used in electronic industry for calculators, components, solar flash light etc.
7. Solar power not only helps preserving the environment but also a good economic renewable energy source.

* Photovoltaic Cells

The term photovoltaic comes from greek word 'phos' meaning light and volt is the unit of emf which was named after inventer of the battery, an Italian physicist Alessandro Volta. This term photo-voltaic is in use since 1849.

Photovoltaic is a field related to practical application of photovoltaic cells, producing electricity from light and it is often used specifically to refer to the generation of electricity from sun light, lamp light or artificial light. When the source of light is not sunlight it is used as a photodetector (Ex: Infrared detectors) and also to detect electromagnetic radiation near the visible range and measuring light intensity.

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Working of Photovoltaic cell

A solar photovoltaic cell works on the following steps:

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

When the photon hits the semiconducting material,

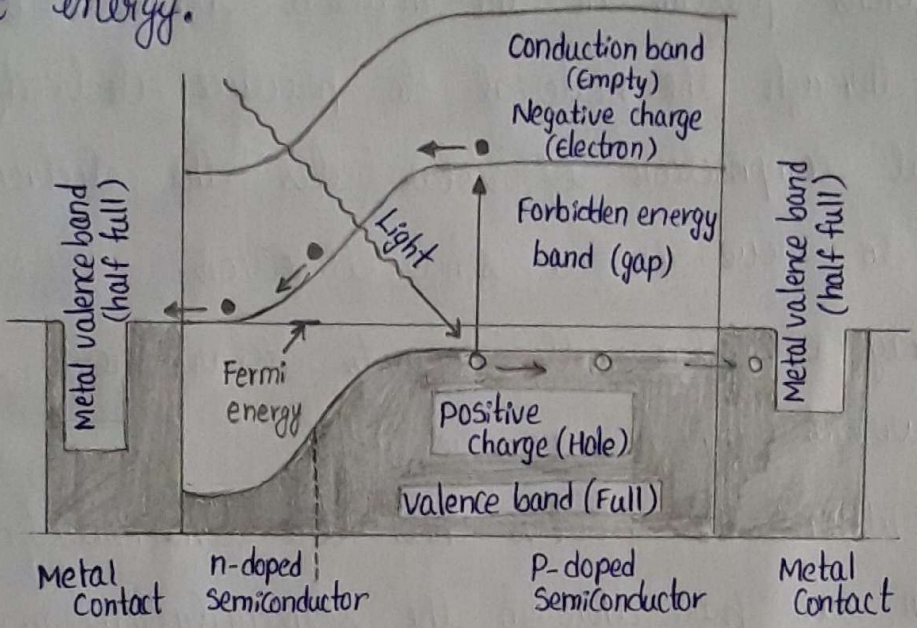
a) photon can pass through the semiconducting material.
b) photon can be reflected.
c) photon can be absorbed by the material.

When a photon is absorbed its energy is given to an electron in the crystal lattice in the valence band and the electron gets excited and jumps to conduction band. Where it is free to move around in the semiconductor as there are no covalent bonds which tightly bound with neighbouring atoms thus creating a hole. Later this hole is filled by another neighbouring electron, creating another a hole there, which results in movement of hole through the lattice. A photon should possess more energy than

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fermi energy of the band gap. Usually the photon coming from sun possess more energy than the fermi energy gap and the difference of energy is given out in the form of heat via lattice vibrations inturn the unusable electric energy.



Band diagram of silicon solar cell under short circuit cohditions.

Charge carrier separation is carried out mainly by two ways : 1. Drift of carriers - driven by an electric field established across the device.

2. Diffusion of carriers is due to their random thermal motion until they are captured by electric fields existing at the edge of the active region.

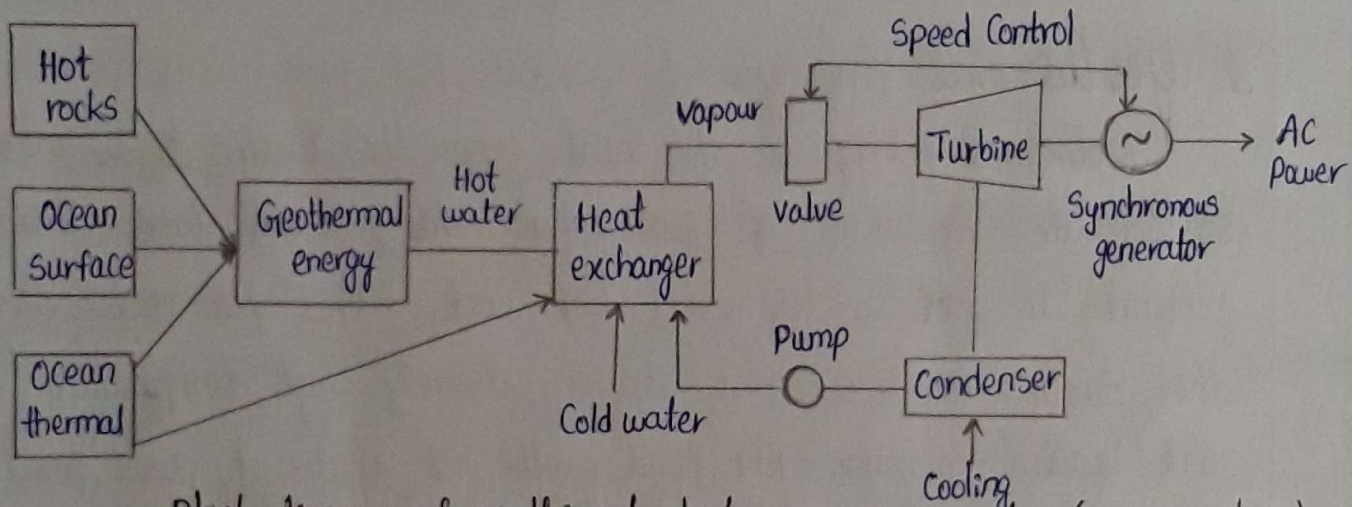
The most commonly known solar cell is constituted by a P-n junction made from silicon, which is a layer of n-type silicon in direct contact with P-type silicon. The P-n junction of solar cells are made by diffusing n-type dopant into

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3. 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 and conversion.



Block diagram of geothermal electric power generation (Binary system)

3. 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 poten-tial for future electricity generation. Tides are more predictable than wind energy and solar power, but tidal energy is more costly and limited availability of sites. The world's first large-scale power plant is the Rance tidal power plant in France.

The oceanic tides on the earth are ultimately due to

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water and the clean water flow in to a canal or a pipe to a settling tank called forebay which is sited above the power house. The canal or pipe can be fairly long. The outlet from the forebay has a screen to trap silt and floating debris. Water flows out into a pipe called penstock, which is made as steep as possible to transfer water to the turbine. Water leaving the turbine is led into the stream through the outlet pipe or tail race.

2. Geothermal Energy:

Geothermal energy is the heat from the Earth. It is clean and sustainable. Resources of geothermal energy range from shallow ground to hot water and hot rock found few miles beneath the Earth's surfaces and deeper extremely high temperature molten rock called magma. The first geothermal electricity was produced in Italy in 1904.

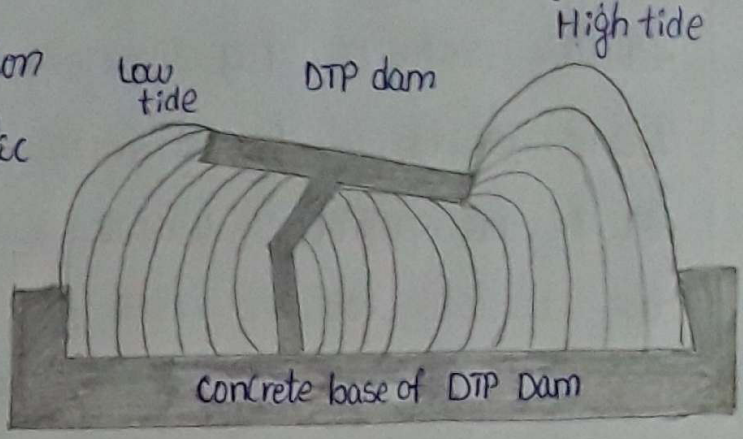
To produce geothermal generated electricity, wells sometimes 1.6 kms deep or more are drilled into the under ground reservoirs to tap steam and very hot water that drive turbine and turbines drive electricity generators. There are three types of geothermal power plants. 1. Dry steam 2. Flash 3. Binary.

1. Dry steam geothermal generator takes steam out of fractures in the ground and uses it directly to drive turbine.
2. 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.

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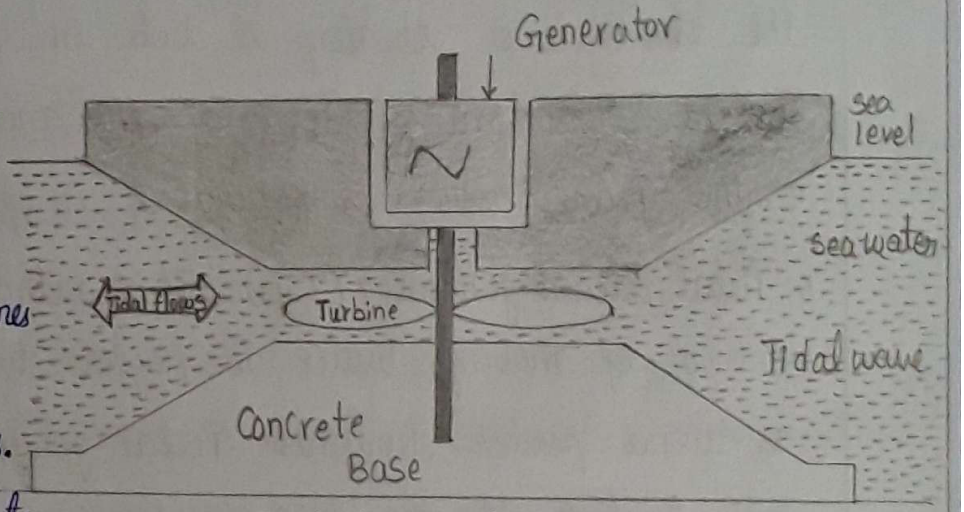
3 Dynamic tidal power method (DTP): This is a promising technology that exploits the interaction between potential and kinetic energies in tidal flows. Long dams are built into the oceans without enclosing an area, leading to a significant water level difference producing low and high tides from which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



Top down view of a DTP dam

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. Solar energy or wind energy is used for pumping.



Production of tidal wave power

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

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gravitational interaction with the moon and sun and the earth's rotation. Tidal power is practically inexhaustible. Tidal power is taken from earth's oceanic tides. The tidal forces are periodic variations in gravitational attraction exerted by celestial bodies. These forces create corresponding motions or currents in the world oceans. Due to strong attraction to the oceans, a bulge in the water level is created, causing temporary increase in sea level when sea level is raised, water from the middle of the ocean is forced to move towards the shore lines creating a tide in an unfailing manner, due to the consistant pattern of the moon's orbit around the earth. 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 or ducted and placed near the bottom of water column.
2. Tidal barrage method: Tidal barrages make use of the potential energy difference of high and low tides. The potential energy of the tides is seized through strategic placement of specia-lized dams. The temporary increase in the level of the tide is channeled into a large base behind the dam and the potential energy of the tide is converted in mechanical energy to produce electric power through the use of generators.

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4. Biomass and Biofuels

The term biomass most often refers to organic matter such as timber and crops grown specially to be burnt to generate heat and power. Biomass is defined as living or recently dead organis-ms and any by-products of those organism plant or animal. Biomass can be used to produce renewable electricity, thermal energy or transportation fuels. The energy stored in biomass can be released to produce renewable electricity or heat.

The most common biomass feed stocks are:

1. Grains and starch crops like sugar cane, iron, wheat, sugar beels and instrial sweet potatoes.
2. Agricultural residues like corn stover, wheat straw, orchad prunings etc.
3. Food waste such as waste produce and food processing waste.
4. Forestry materials like logging residues, forest thinnings.
5. Animal by-products which include tallow, fish, oil, manure etc.
6. Energy crops like switch grass, miscanthus, hybrid poplar, willow algae etc.
7. Urban and suburban wastes like municipal solid wastes, laun wastes, sludge of waste water treatment, urban wood wastes, disaster debris, trap grease, waste cooking oil etc.

Biofuels

The term biofuels refers to fuels derived from biomass, i.e., from agricultural and domestic waste and by anerobic digestion of sewage such as

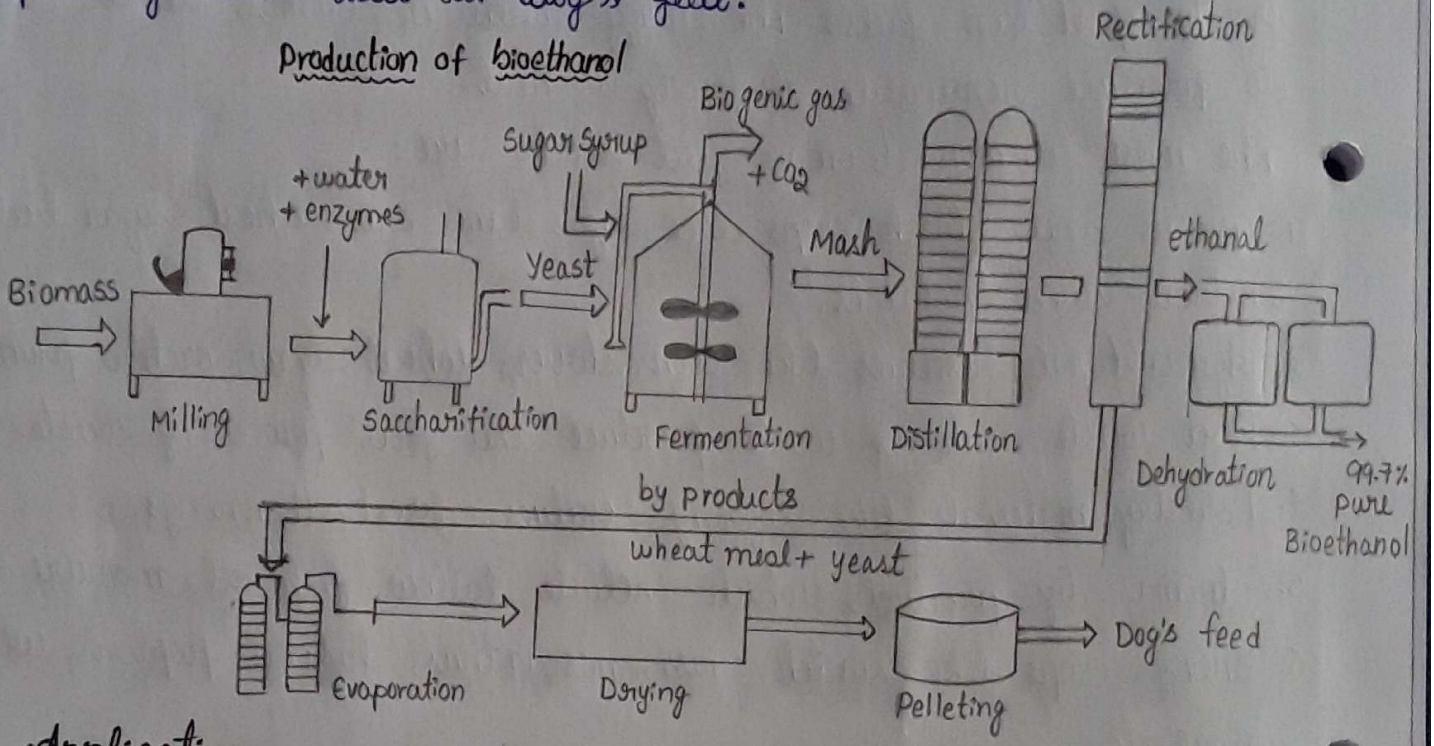
a) Bioethanol (C_2H_5OH): It is a denatured alcohol also called methylated spirits, made by fermentation of sugar and starch components of plant products. The biomass was first subjected

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to milling and mixed with water and enzymes. Then sugar syrup and yeast were added and subjected to fermentation follo -wed distillation. Then the bioethanol is subjected to rectification to remove impurities. Finally the alcohol is subjected to dehydration and 99.7% pure bioethanol is produced. The by-products obtained during rectification are evaporated, dried and made in the form of pelleting and used as dog's feed.

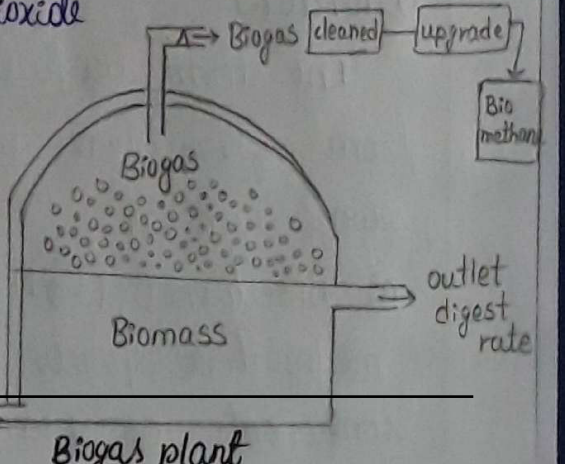
Production of bioethanol



Application:

1. Bioethanol is blended with petrol to make a transport fuel.
2. It is used in cosmetics and other manufacturing process.

b) Biomethane : It is otherwise called biogas which is the mixture of methane (CH_4) 47 - 70%, carbondioxide (CO_2) 32-43%, and small amounts of nitrogen < 1% (H_2S), produced by anaerobic oxidation of biomass. Biogas can be compressed in the same way as natural gas (CNG).



Biogas is produced as land

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3 Ocean Thermal Energy Conversion (OTEC)

It is a process that can produce electricity by using the temperature difference between cold ocean water and warm tropical surface water. OTEC plant pump large quantities of deep cold sea water and surface sea water to run a power cycle and produce electricity. OTEC is a base loaded electricity generation. OTEC theory was developed in 1880 and constructed in 1926.

An amount of large quantity of cold water is a by-product that can be used for air conditioning and refrigeration. There are 3 types of OTEC system.

1. closed cycle 2. Open cycle 3. Hybrid.

To operate the cold sea water was brought to the surface. Primary processes are pumping and desalination.

1. **Closed cycle systems:** These systems use fluid with a low boiling point such as ammonia (B.P = -33°C) to power a turbine to generate electricity. Warm surface sea water is pumped through a heat exchanger to vaporise 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.

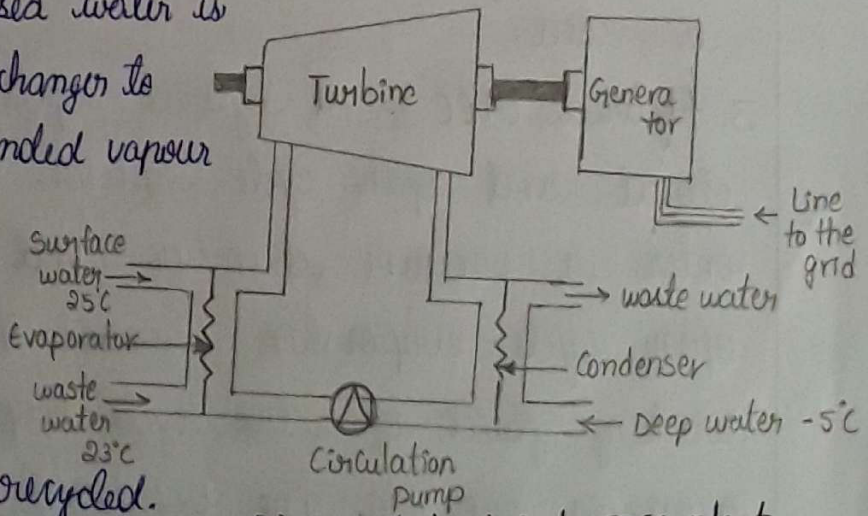


Diagram of closed cycle OTEC plant

2. **Open cycle OTEC:**

Open cycle OTEC uses warm surface water directly to make electrici ~~ty. The warm sea water is first pumped into a low pressure~~

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container, which causes it to boil. In some processes, the expan-ding steam drives low pressure turbine attached to an electric generator. The steam leaves its salt and contamin-ants in the low pressure container to give pure fresh water. It is cond-ensed to a liquid by exposure to cold temperatures from deep-ocean water. This method produces desalinated fresh water, suitable for drinking, irrigation and agriculture.

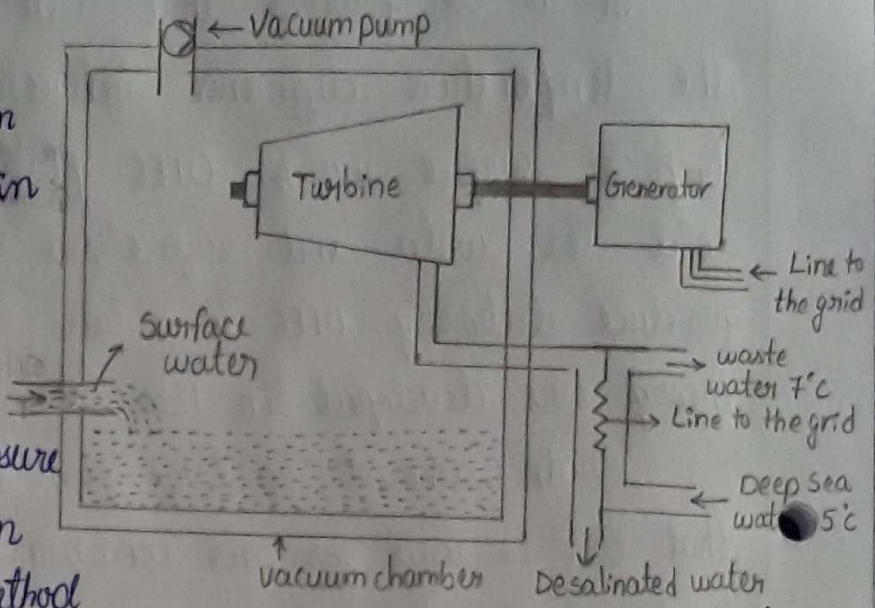


Diagram of an open cycle OTEC plant.

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

3. Hybrid OTEC : A hybrid cycle combines the features of closed and open cycle systems. In a hybrid warm sea water enters a vacuum 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 with in the heat exchanger and provides desalinated water.

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fill gas (LFG) by break down of biodegradable waste inside land fill due to chemical reactions and microbes by anaerobic oxidation. The plants make use of feed stock maize silage, sewage sludge and food waste. During the process the micro organisms transform biomass waste to biogas (mainly methane and CO_2) and digestate which is used as manure.

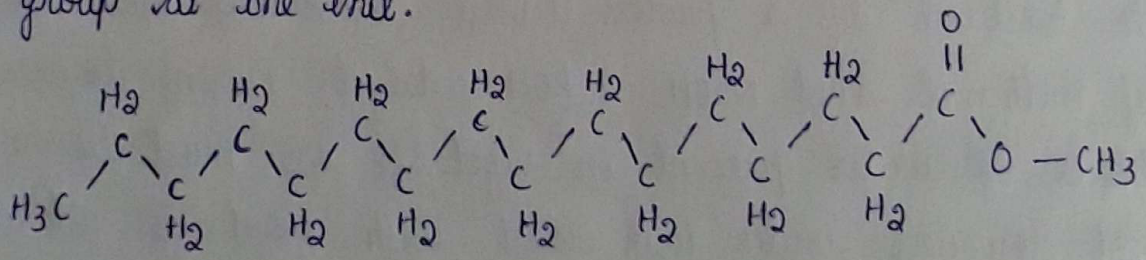
Biogas in India is traditionally based on dairy manure as feed stock and called gobar gas.

Applications :

1. Biogas is compressed and used as motor fuel.
2. It is used as domestic fuel.
3. Biomethane is used by gas turbines to produce electricity and heat.
4. The digestrate is used as agricultural fertilizer.

c) Biodiesel :

It is chemically very similar to diesel and is produced by transesterification of vegetable oil. A typical biodiesel molecule is shown below, which is a long chain carbon atoms containing an ester group at one end.

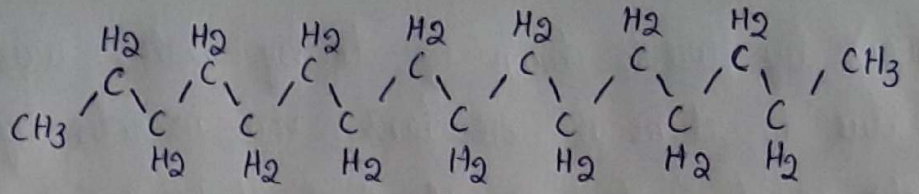


Biodiesel molecule

The regular diesel also has a long chain of carbon atoms which does not have ester group as shown below.

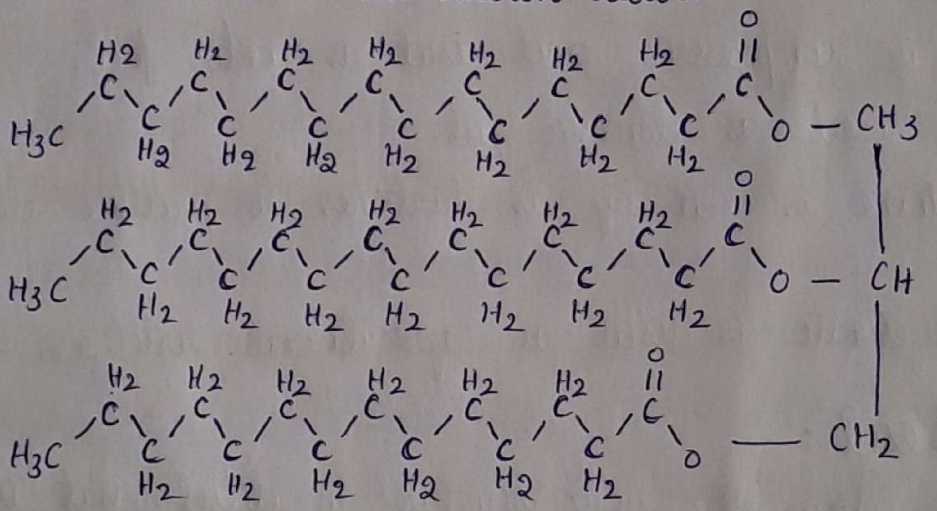
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Regular diesel molecule

Diesel engines can burn biodiesel fuel with no modifications (except for replace some rubber tuling that may soften with biodiesel) because of the chemical similarity to regular diesel. Coming to the history the first diesel engines did not run on diesel fuel but on vegetable oil, whose molecule is three times larger than normal diesel molecule as shown below.



Vegetable oil molecule

The large size of vegetable oil causes gels in cold weather. This gel formation is prevented by converting the vegetable oil to biodiesel by a process called transesterification in presence of methanol and NaOH or KOH catalyst. During transesterification traces of water present in vegetable oil must be removed, if not removed water will react with vegetable oil and produces soap.

Production of biodiesel: Biodiesels are produced transesterification of vegetable oils in presence of methanol and KOH in several steps. The first step is to remove any traces of water in

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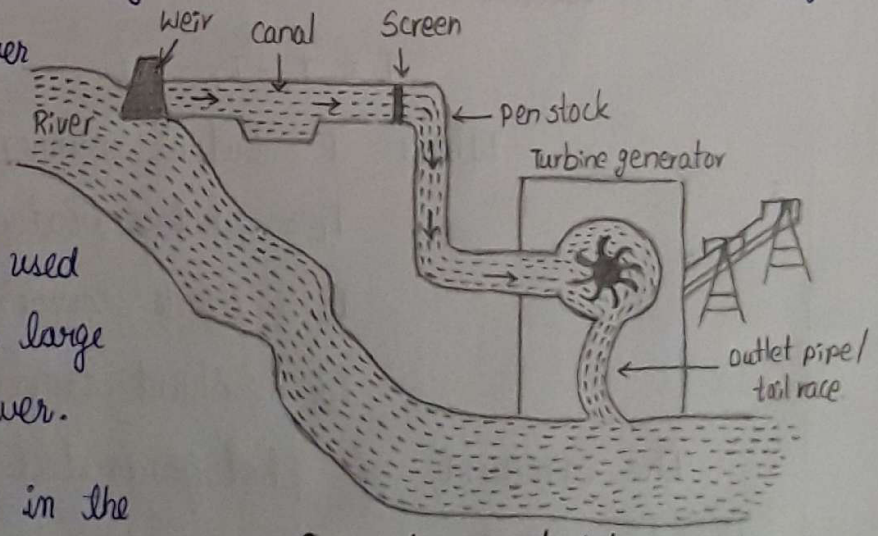
* NON-CONVENTIONAL ENERGY SOURCES :

1. Hydro Power

Flowing water creates energy that can be captured and turned into electricity. The power available in a river or stream depends on the rate at which the water is flowing and the height which it falls down. The hydro schemes are classified into four group but the basic principles of opuration are the same for all.

1. Large scale : Power output is about 3mW and above
2. Mini scale : power output is, 100kW - 2kW
3. Micro scale : power output is 5kW - 100kW
4. Pico scale : power output is less than 5kW

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. River current turbines are like a wind turbines immersed in water and used to extract power from a large flow of water in a river.



Generation of hydal power

A small dam in the river lied directs the water to a settling tank (weir), which allows the silt to settle out of the

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one side of the P-type wafer or vice-versa. If a piece of P-type silicon is placed in intimate contact with a piece of n-type silicon, the diffusion of electrons occurs from the region of high electron concentration to the region of low electron concentration. As the electron diffuse across the P-n junction they recombine with holes on the P-type side. The charge build up on either side of the junction create an electric field, which creates a diode that promotes charge flow known as drift current which eventually, balance the diffusion of electrons and holes. The region where electrons and holes diffused across the junction is called depletion region and also as space charge region.

The current produced by a solar cell is equal to the current produced by the source, minus the current flows through the diode minus current flows through the shunt resistor.

$$I = I_L - I_D - I_{sh}$$

Where I = Output current in amperes

I_L = photogenerated current in amperes

I_D = Diode current in amperes

I_{sh} = shunt current in amperes.

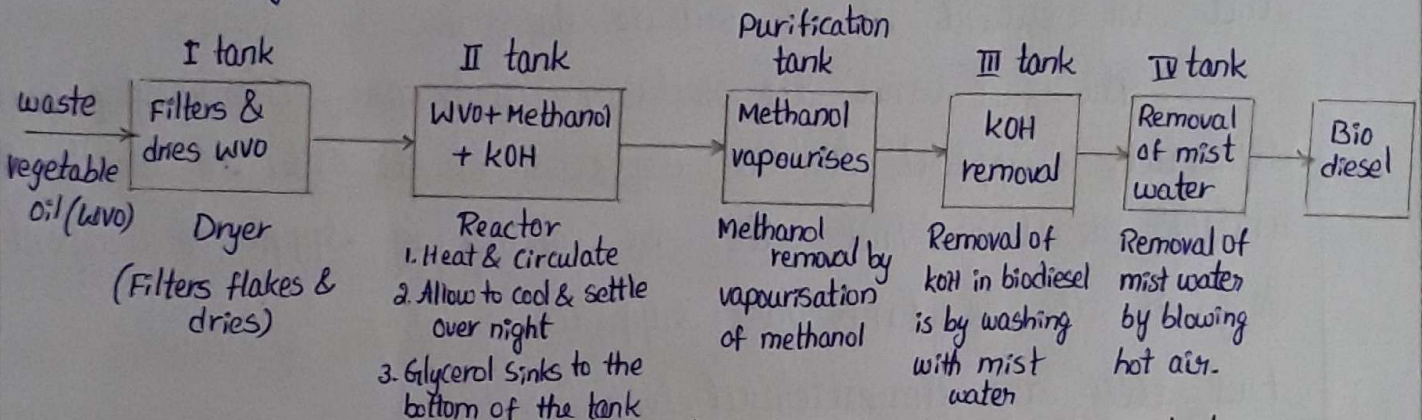
The amount of photogenerated current (I_L) increases slightly with increase in temperature.

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the vegetable oil, followed by transesterification in presence of catalyst and methanol in a reactor. Then the purification of biodiesel from the other chemicals present starting with glycerol biproduct which is mostly insolulble in biodiesel. The next step is to remove the left over methanol. In the third tank crude biodiesel is washed to remove catalyst and small amounts of glycerol that remained dissolved in the biodiesel. The fourth and final tank is for drying the product, yielding biodiesel that is free of impurities.

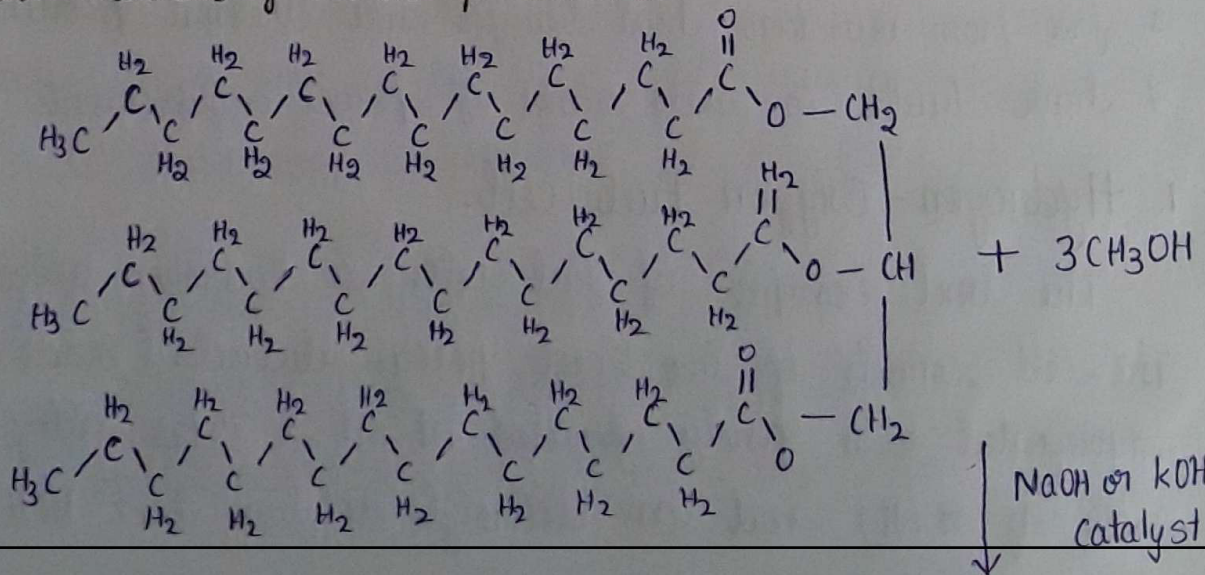
The biodiesel is a clear, light yellow liquid that looks like unused vegetable oil.



Flow diagram of biodiesel production

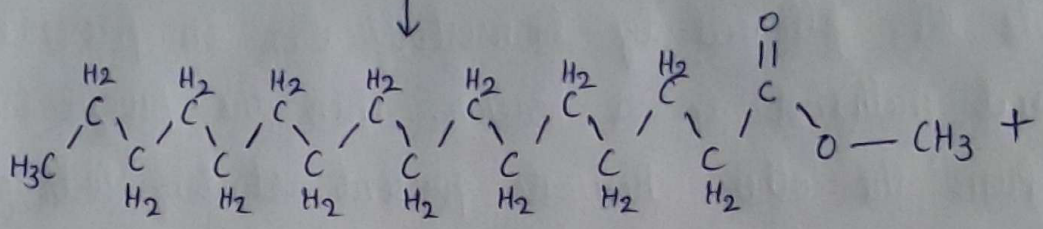
Application: Fuel in internal combustion engines.

* Chemical reactions of biodiesel productions:

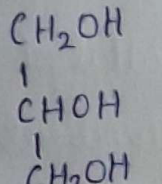


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Biodiesel



(glycerol)

* Fuel Cells

A fuel cell is an electrochemical cell which converts chemical energy contained in an easily available fuel oxidant system into electrical energy. The basic principles of fuel cells are identical to those of the well known electrochemical cells, the only difference is that in fuel cell the chemical energy is provided by a fuel and an oxidant stored outside the cell.

The fuel and the oxidising agents are continuously and separately supplied to the electrodes of the cell, at which they undergo reactions. Fuel cells are capable of supplying current as long as the reactants are supplied.

Fuel cells are characterised by:

1. High efficiency
2. low noise levels
3. free from vibration, heat transfer and thermal pollution and
4. have built in wide range of power requirements.

1. Hydrogen-Oxygen Fuel cell.

The best example of fuel cells is hydrogen-oxygen fuel cell. The cell consists of two inert porous electrodes (made of graphite impregnated with finely divided Pt or a 75/25 alloy of Pb with Ag or Ni) and an electrolyte solution 25% KOH. Through

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storage system for space applications.

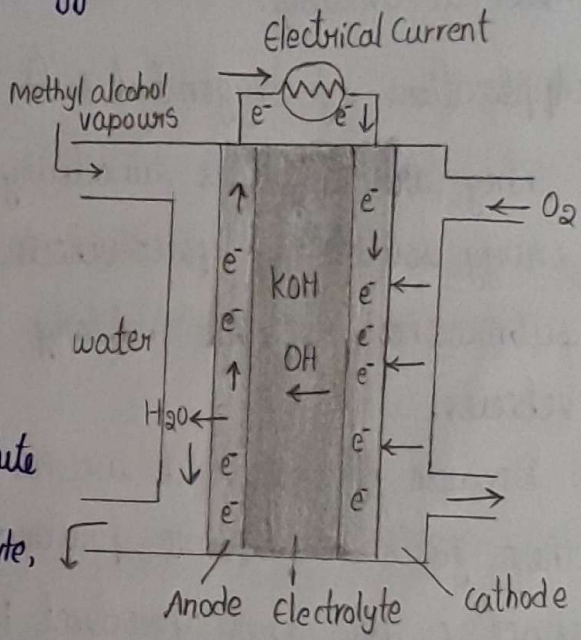
Limitations:

1. The life time of fuel cells is not accurately known.
2. Their initial cost is high.
3. The distribution of hydrogen is not proper.

2 * Methyl Alcohol - Oxygen Alkaline Fuel cell.

In this fuel cell, CH_3OH is used as a fuel and O_2 as oxidant to generate electrical energy.

The methyl alcohol-oxygen fuel cell has two electrodes. The anode consists of porous nickel electrode impregnated with Pt/Cd catalyst. Porous nickel electrode coated with silver catalyst constitute a cathode of the cell. The electrolyte, KOH, is taken in between the two electrodes. CH_3OH and O_2 are sent continuously into their respective electrodes as shown in Fig. and the electrical energy is produced with the continuous replenishment of the fuel, CH_3OH at the anode.



A typical CH_3OH-O_2 fuel cell

At anode: $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$

At cathode: $3/2\,O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$

Overall reaction: $CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2H_2O$

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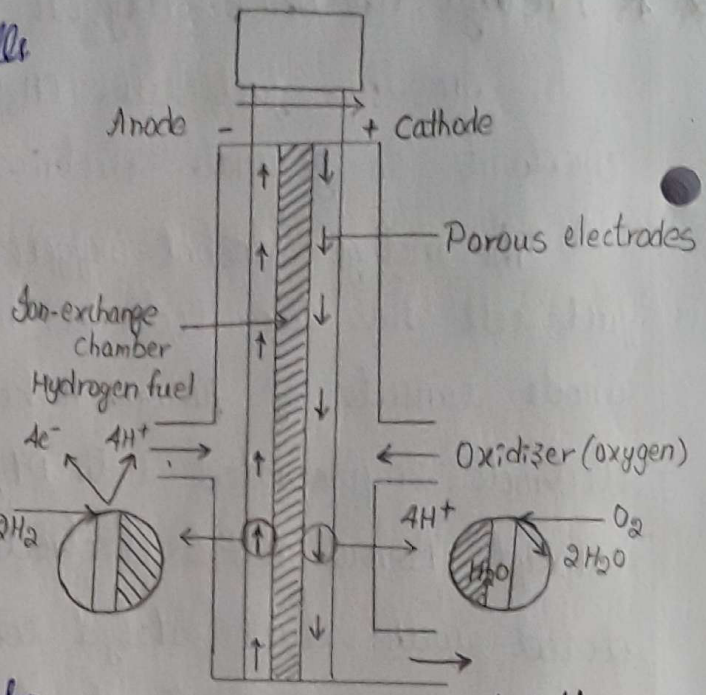
the anode hydrogen gas is bubbled and through cathode oxygen gas is bubbled. The following cell reactions take place.

at anode: $2H_{2(g)} + 4OH^- \longrightarrow 4H_2O_{(l)} + 4e^-$

at cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Net reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

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



Hydrogen Oxygen fuel Cell.

Applications of oxygen fuel cells

1. They are used as auxiliary energy source in space vehicle, submarines or other military vehicles.
2. Because of the light weight these fuels cells are preferred for space crafts and product H_2O is a valuable fresh water source for astronauts.

Advantages of Fuel cells.

The following are the advantages of fuel cells:

1. The energy conversion is very high (75-82%).
2. The product H_2O is a drinking water source for astronauts.
3. Noise and thermal pollution are low.
4. Fuel cells offer an excellent method for use of fossil fuels.
5. The maintenance cost is low for these fuels.
6. The regenerative hydrogen - oxygen fuel cell is an energy

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Advantages :

1. Methanol fuel cells are reasonably stable at all environmental conditions.
2. Easy to transport.
3. Do not require complex steam reforming operations.
4. These fuel cells are targeted to portable applications.
5. Because of high hydrogen concentration in methanol it is an excellent fuel.
6. Methanol poses less risk to aquatic plants, animals and human beings than gasoline.
7. Because methanol possess lower inflamability limit than gasoline it poses less fire risk than gasoline.
8. There is zero emission by the cells hence the fuel cells are eco friendly.

Applications :

1. The major application of methyl alcohol-oxygen fuel cells is a fuel cell motor vehicles like NECAR-5 in Japan, USA etc.

3 * Phosphoric Acid Fuel cells (PAFC)

Phosphoric acid fuel cell is a type of fuel cell developed in mid 1960s and makes use of liquid phosphoric acid as an electrolyte.

The electrolyte is highly concentrated, pure phosphoric acid (H_3PO_4) in silicon carbide matrix. The electrodes are made of carbon paper coated with a finely dispersed platinum catalyst.

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The electrode reactions are:

Anode reaction:

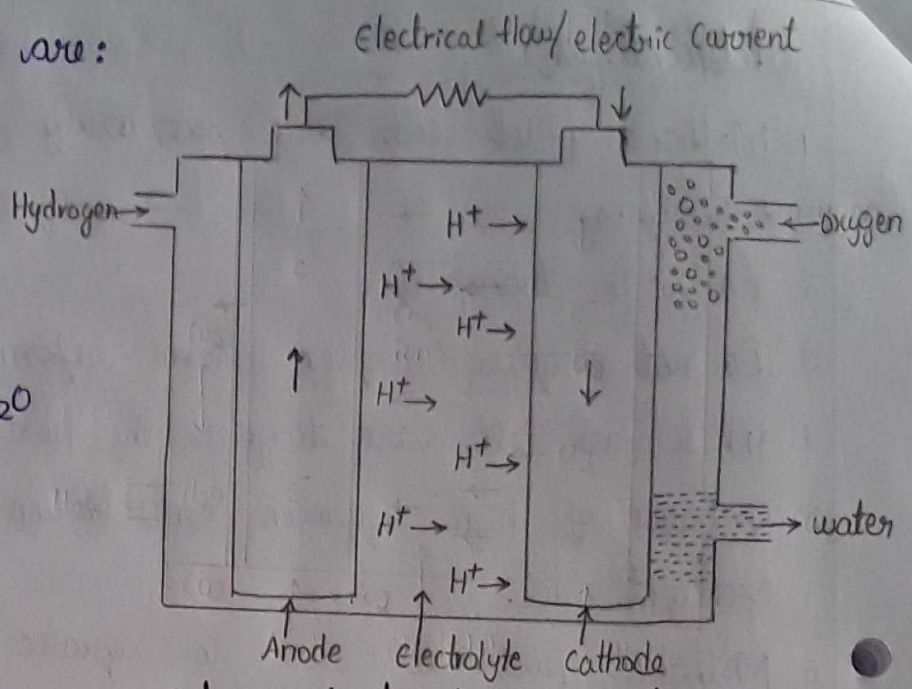
$$2H_{2(g)} \longrightarrow 4H^+ + 4e^-$$

Cathode reaction:

$$O_{2(g)} + 4H^+ + 4e^- \longrightarrow 2H_2O$$

Over all reaction:

$$2H_2 + O_2 \longrightarrow 2H_2O$$



Scheme of phosphoric acid fuel cell

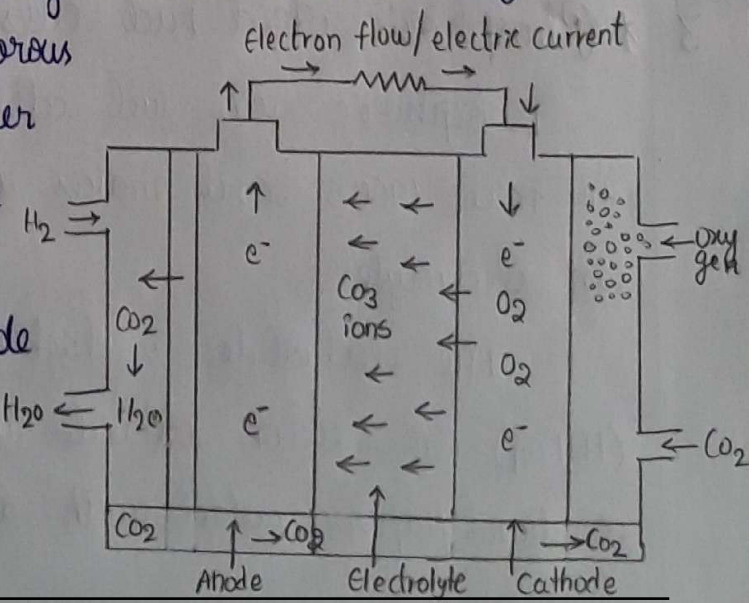
Applications:

1. Phosphoric acid fuel cells are used for stationary power generations with output 100 kW to 400 kW.
2. Used for large vehicles such as buses.
3. In India DRDO has developed PAFC for air independent propulsion for integration into submarines.

4 * Molten carbonate fuel cells (MCFC):

The utilization of electricity in natural gas, bio gas and coal based power plants is by molten carbonate fuel cells.

The anode consists of porous Ni based alloy with 2% of either chromium or aluminium. The materials are creep resistant and prevents sintering of anode at high temperature. The cathode consists of porous Ni. That is converted lithinated



Molten Carbonate fuel cell

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nickel oxide. The electrolyte consists of sodium potassium carbonate, supported by a ceramic ($LiAlO_2$) matrix to maintain liquid between cathode and anode.

Cell reactions:

Anode: $H_2 + CO_3^{2-} \longrightarrow H_2O + CO_2 + 2e^-$

Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-}$

Cell reaction: $H_2 + \frac{1}{2}O_2 + CO_2 \longrightarrow H_2O + CO_2$

Applications:

1. Molten carbonate fuel cells are used in many industrial purposes.
2. To produce electric power via steam turbines.

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