Module – 1
Electrochemistry and Battery Technology

Course Objectives:

To provide students with knowledge of engineering chemistry for building technical competence in industries, research and development in the field of Electrochemical and Battery technology.

Course Outcome:

On completion of this module, students will have knowledge in Electrochemical and concentration cells. Classical and Modern batteries and fuel cells.

Introduction:

Electrochemistry is the branch of chemistry, which deals with the interaction of matter and electrical energy i.e., producing electrical energy from chemical reaction (spontaneous process) or bringing out chemical reactions by applying electrical energy (non spontaneous process). A device used for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell. It gives the relationship between electrical, chemical phenomenon and the laws of interaction of this phenomenon. The laws of electrochemistry form the basis of electrolysis and electro synthesis.

Single electrode potential:

It is defined as the potential developed when an electrode is in contact with a solution of its own ions. It is denoted as **E.**

Standard Electrode potential:

It is defined as the potential developed when an electrode is in contact with a solution of 1M concentration, at 298 K and 1 atm pressure. It is denoted as E^o.

Nernst equation:

Nernst derived an equation to establish relationship between electrode potential and concentration of metal ion.

Due to the power output from an electrochemical cell, the free energy decreases i.e.
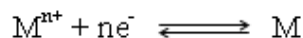
$$-\Delta G = nFE \quad (or) \quad \Delta G = -nFE$$

Under standard conditions the free energy ΔG is given by the equation

$$\Delta G^\circ = -nFE^\circ$$

E° is a constant called standard electrode potential.

Consider a reduction reaction:

$$M^{n+} + ne^- \rightleftharpoons M$$

For spontaneous reaction, the change in the free energy depends on the concentration of reacting species.

$$\Delta G = \Delta G^\circ + RT \ln K_c$$

$$\text{Where } K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Substituting the value of Kc in above equation, we get

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

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$$\Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

Substitute for ΔG and ΔG° in above equation

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^{n+}]}$$

Under standard conditions $[M] = 1$

$$-nFE = -nFE^0 + RT \ln \frac{1}{[M^{n+}]}$$

Dividing eq (5) by $-nF$ we get

$$E = E^\circ - \frac{RT \ln [1/M^{n+}]}{nF}$$

Converting ln to log we get

$$E = E^\circ - \frac{2.303RT \log [1/M^{n+}]}{nF}$$

Substituting for $R = 8.314$, $T = 298K$ and $F = 96500$ in eqn (6) we get

$$\boxed{E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}} \quad \text{or} \quad \boxed{E = E^0 + \frac{0.0591}{n} \log [M^{n+}]}$$

In general Nernst equation is,

$$E = E^\circ \quad \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

Reference electrode

Reference electrode is that whose potentials is known and used for determination of potential of other electrodes.

Note: Types of reference electrodes:

Beyond syllabus:

Primary reference electrode:

Whose potential is fixed as zero at all temperature and pressure. Example: Standard hydrogen electrode (SHE).

Secondary reference electrode:

Whose potential is known in connected with SHE. Secondary reference electrodes have several advantages over SHE. These electrodes are commonly used for determining the electrode potentials of other metals. The two commonly used secondary reference electrodes are *calomel electrode and silver-silver electrode*.

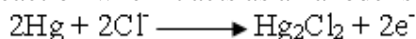**Calomel Electrode:**
Construction:

Calomel electrode consists of long glass tube with two side tubes. One at the top to fill sat KCl solution and the other side tube is connected to the salt bridge. Mercury is placed at the bottom which is covered with a layer of Hg and Hg_2Cl_2 (calomel) paste. The remaining portion is filled with saturated KCl solution. A platinum wire is dipped into the mercury and is used to provides external electrical contact. The calomel electrode is represented as,
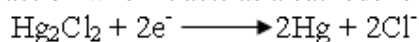
$$Cl^- / Hg_2Cl_2 / Hg$$

- Sat KCl solution
- Pt wire
- Hg + Calomel paste
- Hg
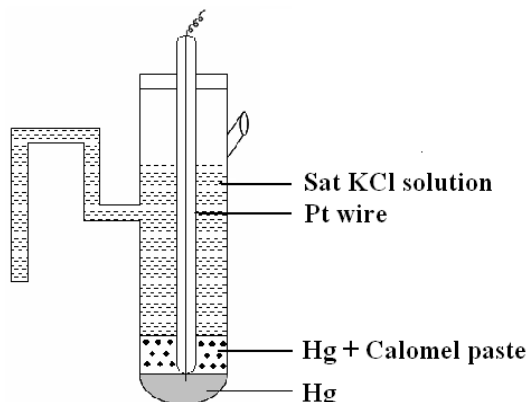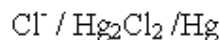
Working:

Calomel electrode behaves as anode or cathode depending upon the nature of other electrode.

The half-cell reaction when it acts as an anode is

$$2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$$

The half cell reaction when it acts as a cathode is

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

The electrode reaction is,

$$Hg_2Cl_2 + 2e^- \longleftrightarrow 2Hg + 2Cl^-$$
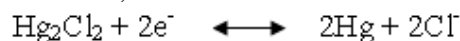
Applying Nernst equation,

$$E = E^o - \frac{0.0591}{n} log \frac{[Product]}{[Reactant]}$$

$$E = E^o - \frac{0.0591}{n} log \frac{[Hg]^2[Cl^-]^2}{[Hg_2Cl_2]}$$

$$E = E^o - \frac{0.0591}{2} log [Cl^-]$$

The calomel electrode potential is depends on the concentration of chloride ions in KCl. If the concentration of chloride ions increases, the potential decreases and vice versa. (The potential of calomel is inversely proportional to the concentration of chloride ions)

The potential of calomel electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

| Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.334V	0.281V	0.242V

Applications:
- Used to determine the potential of the other electrodes.

- It is commonly used as reference electrode in all potentiometric determinations.
- Electrode potential is reproducible.

**Silver - Silver Chloride Electrode:**
Construction:
It consists of a long glass tube in which saturated KCl solution is filled. A silver wire is coated with AgCl by electrolytic process and placed inside the tube and which provides external electrical contact. The electrode is represented as,
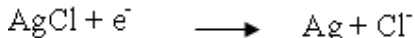
$Cl^-/AgCl/Ag.$
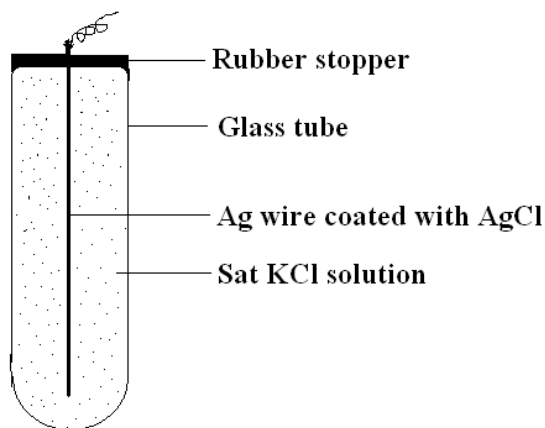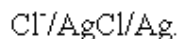
Working:
The electrode behaves as anode or cathode depending upon the nature of other electrode. The half-cell reaction when it acts as an anode is

$$Ag + Cl^- \longrightarrow AgCl + e^-$$

The half-cell reaction when it acts as a cathode is

$$AgCl + e^- \longrightarrow Ag + Cl^-$$
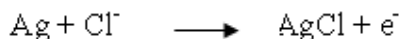
The electrode reaction is

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

Applying Nernst equation to the above equation,

$$E^\circ_{cell} - \frac{0.0591}{n} \log \frac{(product)}{(reactant)}$$

$$E_{cell} = E^\circ_{Cell} - \frac{0.0591}{1} \log \frac{[Ag][Cl^-]}{[AgCl]}$$

$$E_{cell} = E^\circ_{Cell} - \frac{0.0591}{1} \log [Cl^-]$$

The Ag – AgCl electrode potential is depends on the concentration of chloride ions in KCl. If the concentration of chloride ions increases, the potential decreases and vice versa. (the potential of Ag – AgCl is inversely proportional to the concentration of chloride ions)
The potential of Ag - AgCl electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

| Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.29V	0.22V	0.199V

Applications:
1. As a secondary reference electrode in ion selective electrodes.
2. In determining whether the potential distribution is uniform or not in ship hulls and old pipelines protected by cathodic protection.

Measurement of standard electrode potential using calomel electrode:

The electrode potential of unknown electrode is measured by connecting to a saturated calomel electrode through salt bridge. (The potential of saturated calomel electrode is fixed to 0.24V for sat KCl solution).

Ex: Zinc electrode coupled with saturated calomel electrode.

To measure the standard electrode potential of Zn, Zn electrode is dipped in Zinc chloride solution and coupled with saturated calomel electrode through voltmeter. Zinc electrode acts as anode and SCE acts as cathode. The emf of the cell is measured through voltmeter. Representation of the cell is
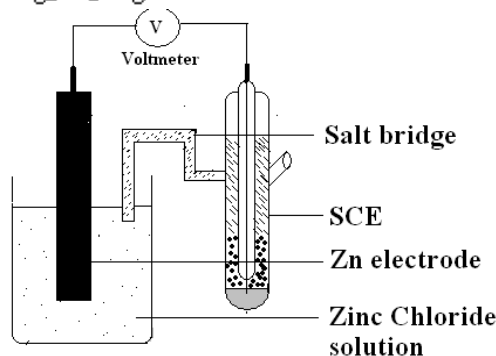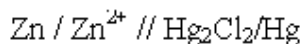
$$Zn / Zn^{2+} // Hg_2Cl_2/Hg$$

The two half-cell reactions are:

At anode, oxidation occurs, $Zn \longrightarrow Zn^{2+} + 2e^-$ (oxidation)

At cathode, reduction occurs, $Hg_2Cl_2 + 2e \longrightarrow 2Hg + 2Cl^-$

The standard electrode potential is calculated by substituting the potential values in the relation

$$E_{cell} = E_{SCE} - E_{Zn/Zn^{2+}}$$
$$E_{Zn/Zn^{2+}} = E_{SCE} - E_{cell}$$
$$= 0.24 - 1.0$$
$$E_{Zn/Zn^{2+}} = -0.76V$$

Ion-selective electrodes

The electrode, which responds to a specific ion in a mixture by ignoring other ion is known as ion selective electrode. It consists of a thin membrane in contact with ion solution.

Glass Electrode:

This electrode works on the principle that when a thin, low resistivity glass membrane is in contact with a solution containing H^+ ions, a potential develops across the membrane and the solution. Potential developed depends on the concentration of hydrogen ions in the solution.

Cell representation: Ag / AgCl / HCl (0.1M) / Glass/ unknown solution

Construction:

It consist of a long glass tube with a thin walled glass bulb contains 0.1 M HCl [C_1]. Ag/AgCl electrode placed in to the solution to provide electrical contact. The glass electrode is dipped in unknown solution of concentration C_2, the potential developed across the membrane by the exchange of ions with the composition of glass is known as the boundary potential E_b (E_1 & E_2). Even when $C_1=C_2$ a small potential is developed across the membrane is called as *asymmetric potential*.
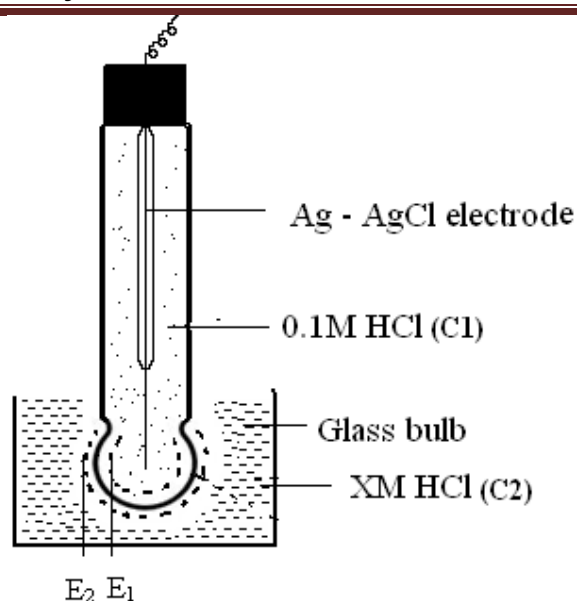
Working:

E_1 & E_2 is the potential developed at inner and outer membrane respectively

The boundary potential is,

$$E_b = E_2 - E_1$$

$$E_b = \frac{0.0591}{n} \log \frac{[C2]}{[C1]}$$

$$E = \frac{0.0591}{n} \log[C2] + \frac{0.0591}{n} \log[\frac{1}{C1}]$$

$$Where \quad \frac{0.0591}{n} \log[1/C_1] = L \ (constant)$$

$$E_b = L + \frac{0.0591}{n} \log[C_2]$$

Where n = 1

$$E_b = L + 0.0591 \log[C_2]$$

where $C_2 = [H^+]$ ions in outer membrane then,

$$E_b = L + 0.0591 \log[H^+]$$

$$E_b = L - 0.0591 \ pH \qquad (pH = -\log[H^+])$$

The glass electrode potential is ,

$$E_G = E_b + E_{Ag/AgCl} + E_{asy}$$

Substitute the value of E_b

$$E_G = L - 0.0591pH + E_{Ag/AgCl} + E_{asy}$$

Where $L + E_{Ag/AgCl} + E_{asy} = L_1$ (constant)

$$\boxed{E_G = L_1 - 0.0591pH}$$

Determination of pH of a Solution using Glass Electrode

The potential of a glass electrode depends on the concentration of H^+ ions. Hence, pH of a solution can be determined by using glass electrode and calomel electrode assembly. The cell assembly is represented as

$Hg/Hg_2Cl_2/Cl^-$ // solution of unknown pH / glass/0.1 M HCl / AgCl / Ag
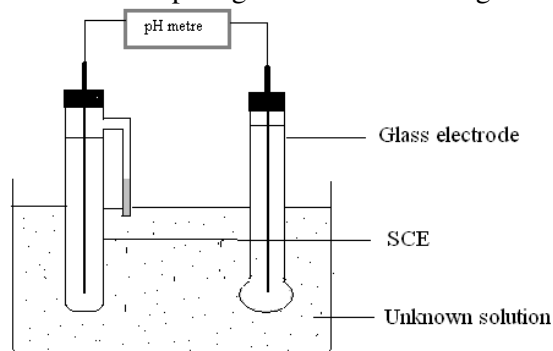
The emf of a cell is determined by using voltmeter.
E_{cell} is the difference b/w glass electrode potential E_G and the calomel electrode potential E_{SCE}

$$E_{cell} = E_G - E_{SCE}$$

$$= L_1 - 0.0591pH - E_{SCE}$$

$$pH = \frac{L_1 - E_{SCE} - E_{cell}}{0.0591} \quad [K = L_1 - E_{SCE}]$$

$$\boxed{pH = \frac{K - E_{cell}}{0.0591}}$$

Electrolyte Concentration Cells :

It is galvanic cell, which consists of two identical electrodes which are in contact with the same solution of electrolyte at different concentrations.
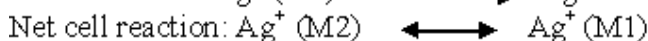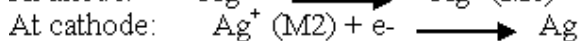Example:

Consider two silver electrodes that are in contact with the $AgNO_3$ solution of different concentrations (M_1 and M_2) connected through voltmeter. The electrolytes are connected through salt bridge.
The cell representation $Ag/ AgNO_3 (M1)// AgNO_3 (M2)/Ag$
Where M_1 and M_2 are the molar concentration of the Ag^+ ions in the two half-cells.

Electrode reaction:

At anode: $Ag \longrightarrow Ag^+ (M1) + e-$
At cathode: $Ag^+ (M2) + e- \longrightarrow Ag$
Net cell reaction: $Ag^+ (M2) \longleftrightarrow Ag^+ (M1)$
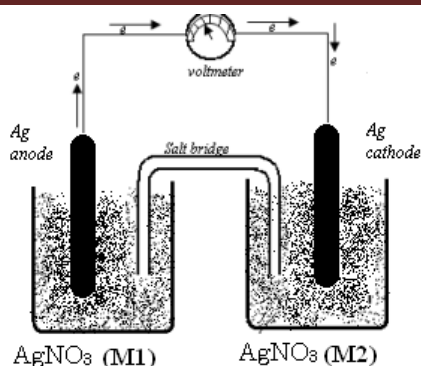
    The current produced in the cell due to migration of ions from higher concentration to lower concentration. This takes place until the concentration in the two Half -cells become equal(M1=M2) hence the production of current becomes zero.

Apply Nernst equation for the cell reaction,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{(product)}{(reactant)}$$

$$E_{cell} = E°_C - E°_A - \frac{0.0591}{n} \log \frac{(M1)}{(M2)}$$

$E°_C$ & $E°_A$ are of same metal so cancelled each other

$$E_{cell} = - \frac{0.0591}{n} \log \frac{(M1)}{(M2)} \quad (or) \quad E_{cell} = \frac{0.0591}{n} \log \frac{(M2)}{(M1)}$$

Battery Technology

Introduction

    A battery is a portable energy source with three basic components-an anode (the negative part), an cathode (the positive part), and an electrolyte. As current is drawn from the battery, electrons start to flow from the anode through the electrolyte, to the cathode. A device enables the energy liberated in a chemical reaction to be converted directly into electricity. The term battery originally implied a group of cells in a series or parallel arrangement, but now it is either a single cell or group of cells. Examples: It ranges from small button cells used in electric watches, lead acid batteries used for starting, lighting and ignition in vehicles with internal combustion engines. The batteries are of great importance based on the ability of some electrochemical systems to store electrical energy supplied by the external source. Such batteries may be used for emergency power supplies, for driving electric vehicles, etc. For the commercial exploitation, it is important that a battery should provide a higher energy, power density along with long shelf life, low cost and compatible rechargeable units.

Classification of Batteries:

    Batteries are classified as primary (non-rechargeable), secondary (rechargeable) and reserve (inactive until activated):

Primary battery:

The batteries, which produce electrical energy at the expense of free energy of active materials and produce energy only as long as active materials are present. These are not rechargeable batteries and are to be discarded after the use. These batteries are called as primary battery.

Example: Dry cell. $Zn-MnO_2$

Secondary battery:

The rechargeable batteries that produce electrical energy at the expense of free energy of active materials. These active materials are capable of restoring at respective electrodes on recharge and prepare for discharge once again. Such batteries are called secondary battery.

Example: Lead acid battery, NiMH battery, Ni-Cd battery

Reserve battery:

The high current batteries in which active materials are isolated from electrolyte due to their reactivity and are brought into contact whenever high potential is required for application are called reserve battery.

Example: Magnesium-water activated batteries, zinc-silver oxide batteries, etc.

Characteristics of a battery:

Cell potential / Voltage:

The cell potential or voltage of the battery is determined theoretically,

$$E_{cell} = (E_C - E_A) - \eta_A - \eta_C - iR_{cell}$$

Where E_C & E_A are reduction potential of cathode and anode, η_A & η_C are over potential at the anode and cathode and iR_{cell} is the internal resistance.

To attain the maximum cell potential or voltage from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Current:

"Is measure of the rate of flow of charges in a battery".

To attain the maximum current from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Capacity:

"The total amount of charge stored in a battery in Ampere hours."

The theoretical capacity may be calculated using faradays relation, $C = WnF/M$, where W and M is weight and mass of the active material respectively and n is the number of moles of the electro active material.

Electricity storage density:

"Amount of electrical energy stored per unit weight of the battery."

Energy efficiency:

The ratio of output energy to the input energy. Higher the efficiency, very good is the battery.

% Energy efficiency= $\dfrac{\text{Energy released during discharge}}{\text{Energy required during recharge}}$ x 100

Cycle life:

"The total number of discharge and recharge cycles that are possible before the failure of the battery". It is applicable only to secondary battery, higher the cycle life, better is the battery.

Shelf-life:

"The duration of storage of a battery without self discharge is known as shelf life of a battery". It referred to storage duration of battery. If shelf life is high, better is the battery.

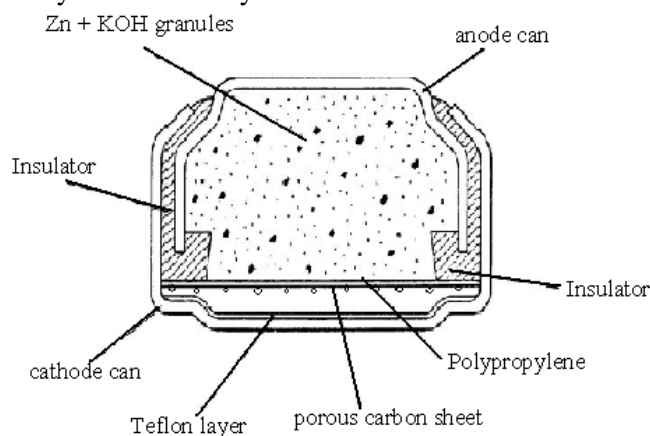**Zinc-air battery**
Reactive species at anode: Granulated Zn
Reactive species at cathode: pure oxygen from air
Electrolyte: KOH
Separator: polypropylene
Voltage: 1.45V

The **zinc-air,** electrochemical system can formally defined as **zinc/potassium hydroxide/oxygen** battery but commonly known as "zinc-air" cell.

Construction:
It consists of nickel-plated steel cans acting as anode and cathode..
1. The anodic can contain the zinc powder and electrolyte in the form of granules with a gelling agent.
2. The cathode active material is carbon sheet impregnated with MnO_2 (to increase the conductivity of cathode) with multiple air holes punched at the bottom to provide air access to the cathode. The sheet is laminated with Teflon layer (to diffuse the oxygen faster to cathode side) on one side.
3. The anodic and cathodic compartments are separated by polypropylene
4. The alkaline electrolyte is potassium hydroxide.
5. The output voltage is 1.45 Volts.
Working:
When the battery discharge, the following reactions takes place at respective electrodes.

Reactions:

At anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$
At cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Net cell reaction $Zn + \frac{1}{2} O_2 \rightarrow ZnO$
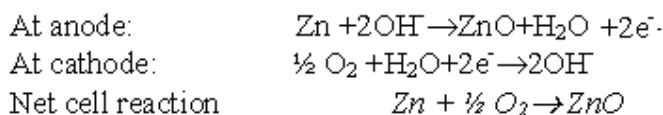
Application:
  • Used in hearing aids,

- In telecommunication devices such as pagers and wireless headsets
- In medical devices such as patient monitors, recorders, nerve & muscle stimulators and drug infusion pumps.

Nickel-metal hydride battery (Ni-MH)

Anodic active material: MH
Cathodic active material: NiO (OH)
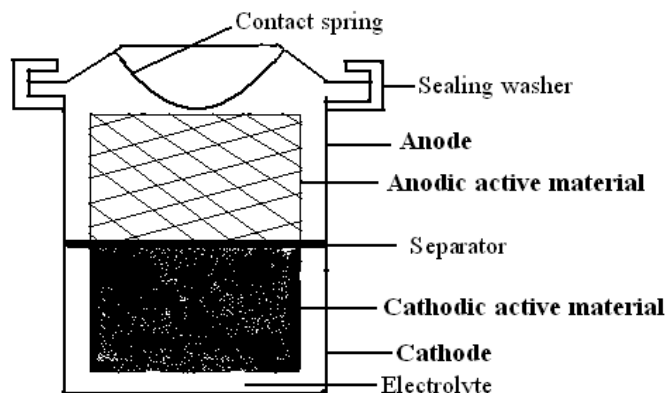Electrolyte: 6M KOH
Separator: polypropylene
Voltage: 1.35V

Construction:
1. In a Ni-MH cell, a hydrogen in the form of metal hydride (VH_2) acts as anodic active material and nickel oxy hydroxide as cathodic active material.
2. Both the anodic and cathodic compartments are made of Nickel grids and filled with its respective active materials.
3. The electrolyte used is potassium hydroxide solution.
4. Polypropylene used as a separator that separates the two electrodes and behaves as a medium for absorbing the electrolyte.
5. The output voltage is 1.35V.

Working:
When battery is discharging/charging, the following reactions takes place at respective electrodes.

Reactions:

At anode: $MH + OH^- \underset{C}{\overset{D}{\rightleftharpoons}} M + H_2O + e^-$

At cathode: $NiO(OH) + H_2O + e^- \underset{C}{\overset{D}{\rightleftharpoons}} Ni(OH)_2 + OH^-$

Cell reaction: $NiO(OH) + MH \underset{C}{\overset{D}{\rightleftharpoons}} Ni(OH)_2 + M$
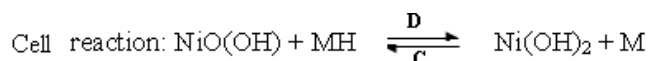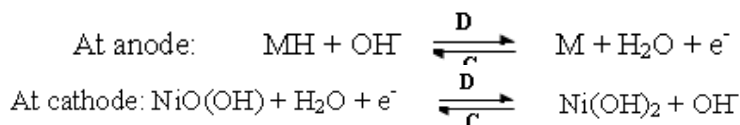
Applications:
- Used in Cellular phones and laptops
- In Emergency lights and Power tools
- In electric vehicles

Lithium battery:

Lithium is the lightest of metals and it can float on water. The electrochemical properties of lithium are excellent and it is a highly reactive material. These properties give Lithium the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power. Lithium batteries are primary batteries in which lithium metal (or) lithium compound acts as a Anode. A lithium cell can produce voltage from 1.5 V to about 3 V based on the types of materials used.

There are two types of lithium-based batteries available.

1.   Lithium batteries
2.   Lithium-ion batteries

In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable.

In lithium-ion batteries, lithium compounds are used as anode. These batteries are known as re-chargeable batteries. Therefore, Lithium ion batteries are considered as best than pure Lithium based batteries.

By comparison, lithium-ion batteries are rechargeable batteries in which lithium ions move between the anode and the cathode, using an intercalated lithium compound as the electrode material instead of the metallic lithium used in lithium batteries.

LiMnO$_2$ battery

Anodic active material: Lithium
Cathodic active material: MnO_2
Electrolyte: Lithium halide (LiCl, LiBr, LiClO$_4$ and LiAlCl$_4$)
Separator: polypropylene
Voltage: 3.0
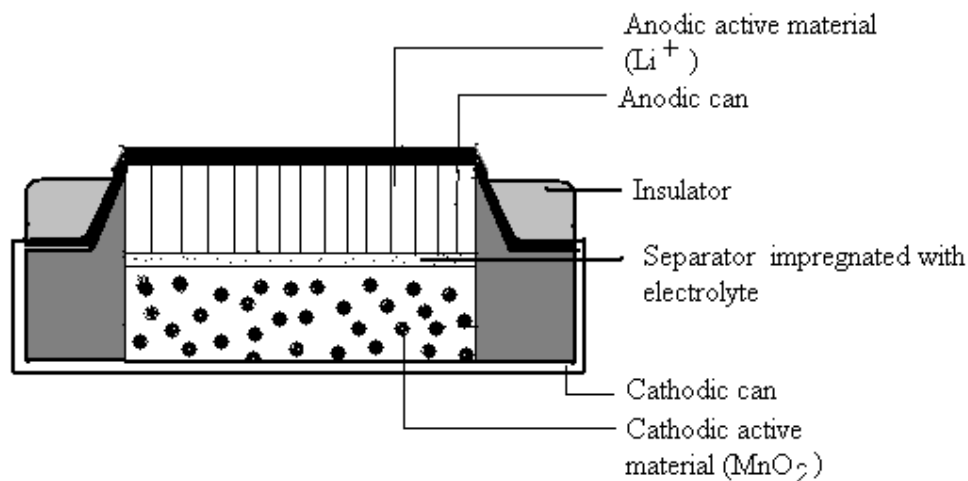
Construction:

1. Lithium Manganese Dioxide cell, is a primary battery. Anodic active material is Lithium metal (in the form of disc) and cathode is manganese dioxide (in the form of a pellet).
2. The electrolyte is lithium halide dissolved in organic solvent.
3. Separator is polypropylene impregnated with the electrolyte. It provides an electrical contact between the two electrodes.
4. The output voltage is 3.0V.

Working:

When battery is discharging, the following reactions take place at respective electrodes.

Reactions:

$$At\ anode: \quad Li \rightarrow Li^+ + e^-$$
$$At\ cathode: \quad MnO_2 + Li^+ + e^- \rightarrow LiMnO_2$$
$$Net\ cell\ reaction: \quad Li + MnO_2 \rightarrow LiMnO_2$$
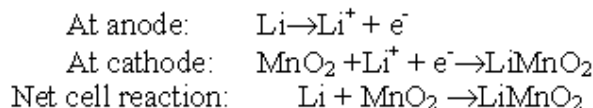
Application:
- Outdoor use (requiring a low temperature range)
- In high-discharge devices, which include digital cameras, electric watches, hearing aids, walkie-talkies, portable televisions, handheld video games, etc

Lithium-ion battery:

Anodic active material: Li^+ / graphite
Cathodic active material: $LiCoO_2$
Electrolyte: Lithium salt
Separator: polypropylene
Voltage: 3.6V
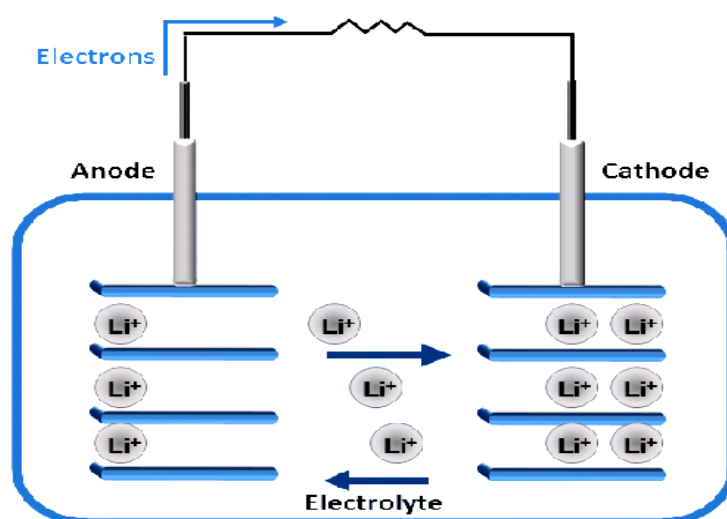
Construction:
1. In lithium-ion battery (Li-ion battery or LIB), the lithium ions (electrons) move from the negative electrode (anode) to the positive electrode (cathode) during discharge and back when charging.
2. Anode is made of carbon material with a high energy density and large doping capacity of lithium ion. Cathodes are metal oxide material containing lithium with capable of dedoping lithium ion during charging and undergo lithium doping during discharging.
3. Electrolyte is made of lithium salts in an organic solvent ($LiPF_6$, $LiBF_4$ or $LiClO_4$ in an organic solvent, such as ether,). Lithium ion migrates between the two electrolytes via an organic solvent.
4. Separator used is polypropylene.
5. The output voltage of this battery is 3.6V.

Working:

During charging lithium ion in cathodic side (positive electrode) is migrated and move towards anodic side (negative electrode) and during charging lithium ions move from anode to cathode.

Reactions:

At cathode: $LiCoO_2 \underset{D}{\overset{C}{\rightleftarrows}} Li_{(1-x)}CoO2 + xLi^+ + xe^-$

At anode: $xLi^+ + xe^- + xC \underset{D}{\overset{C}{\rightleftarrows}} xLiC$

Net cell reaction $LiCoO_2 + xC \underset{B}{\overset{C}{\rightleftarrows}} Li_{(1-x)}CoO2 + xLiC$
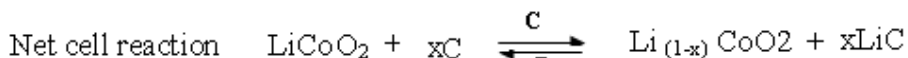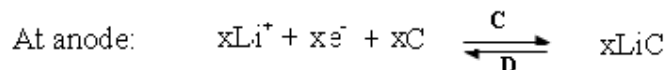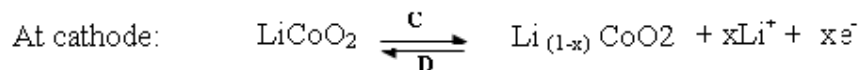
Application:
- The Li-ion batteries are used in mobile phones, cameras, calculators, LCD TVs, pagers, to operate laptop computers and aerospace application

FUEL CELLS

Fuel cell is a device, which converts chemical energy of the fuel, and oxidant into electrical energy.Electrical energy is obtained by the combustion of fuels in these galvanic cells. Here, the fuels are supplied from outside and do not form integral part of the cell. These do not store energy. Electrical energy can be obtained continuously as long as the fuels are supplied and the products are removed simultaneously. In these aspects, fuel cells differ from conventional electrochemical cells.

"Fuel cells are galvanic cells which converts chemical energy of the fuels into electrical energy through catalyzed redox reactions with elimination of minimum harmful biproducts".

Fuel is represented as

Fuel / electrode / electrolyte / electrode / oxidant

At anode, fuel undergoes oxidation, when battery discharge potential, the following reactions takes place at respective electrodes.

Fuel $\longrightarrow$ oxidized product + ne

At cathode, oxidant is reduced, oxidant + ne $\longrightarrow$ reduced product

Limitation of Fuel cell

1. Power output is moderate.
2. Fuels are to be stored in tanks under very high pressure in tanks.
3. The refueling and the starting time of fuel cell vehicles are longer and the driving range is shorter than in a "normal" car.
4. It generates only DC and should be converted to AC.

Advantages of fuel cells:
1. Do not pollute the atmosphere
2. Electrical energy can be obtained continuously.
3. Fuel cell provides high quality of DC power.
4. Fuel cells have a higher efficiency than diesel or gas engines.

Difference between conventional cell and fuel cell

S. No	Conventional battery	Fuel cells

DR.PRASHANTH.P.A/Mr.RAVEENDRA.R.S/Mrs.S.SATHYANARAYANI/Mrs.BHAGYA.N.P

1	Battery makes electricity from the energy it has stored inside the battery	Fuel cell makes its electricity from fuel in an external fuel tank
2	Battery may run dead	Fuel cell will make electricity as long as fuel is supplied
3	Store chemical energy	Do not store chemical energy
4	Reactants are not supplied and the products are not removed	Reactants are supplied continuously and the products are removed simultaneously
5	Construction cost is high	Construction cost is low
6	Life time is less	Life time is higher than battery
7	Battery produce electricity depends on concentration of the electrolyte	fuel cell will produce electricity as long as it has a fuel supply
8	Recharge of the cell is required.	Recharge of the fuel cell is not required.

Methanol – oxygen fuel cell

Fuel: CH_3OH
Oxidant: Oxygen
Electrolyte: H_2SO_4
Voltage: 1.2V
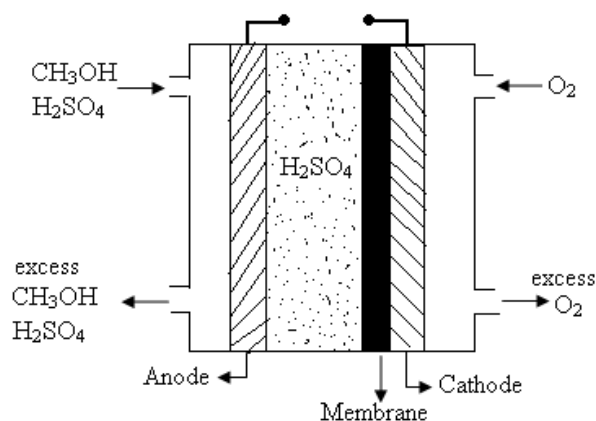
Construction:

1. It consists of anodic and cathodic compartments. Both the compartments contain platinum electrode.
2. Methanol containing H_2SO_4 is passed through anodic compartment. Oxygen is passed through cathodic compartment.
3. Electrolyte used is of sulphuric acid.
4. A membrane made of cellulose is provided which prevents the diffusion of methanol into the cathode.
5. The output voltage is 1.2V.

Working:

Reactions:

At anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$

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

Net cell reaction $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$
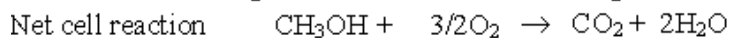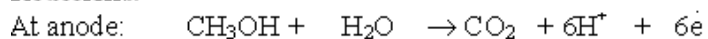
Application:
- Used in military applications
- Large-scale power productions.

Note:
1. *KOH is not used as electrolyte as it reacts with CO_2 and gets converted into carbonate. Thus, conductivity of the electrolyte decreases as well as the efficiency.*
2. *The advantage of acid electrolyte is that the CO_2, a product of the reaction can be easily removed.*

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Module-2
Corrosion Science and Metal Finishing

Corrosion Science

Introduction:

The term corrosion is used to denote a change. A metal changes from its elementary state to the combined state when it comes in contact with liquid medium. This is actually due to the chemical interaction between the metal and the environment.

Definition: *"The spontaneous deterioration and consequent loss of a metal/alloy due to chemical/electrochemical attack by the environment".*

Example: When iron metal is exposed to the moist environment, the metal forms a hydrated ferric oxide called rust which is relatively non-protective.

Most of the corrosion cases are electrochemical in nature taking place by an electrochemical attack on the metal in the presence of air and moisture (H_2O) called ***wet corrosion.*** The mechanism of the wet corrosion is explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion:

According to this theory,
1. When a metal is in contact with moist air or when dissimilar metals are contact with each other in a solution, large numbers of galvanic cells are formed with the existence of anodic and cathodic area on the metal.
2. In this corrosion, oxidation of the metal and reduction of species present in solution takes place.
3. The anodic part of the metal undergo oxidation and suffers from corrosion, cathodic part undergo reduction and protected from corrosion.
4. The electrons are transferred through the metal from anode to cathode.
5. During corrosion the following reactions takes place.

At anode (oxidation reaction) : $M \rightarrow M^{n+} + ne^-$

   The reaction at cathode (reduction reaction) depends on the nature of the environment:

   If the medium is acidic,

   In the presence of dissolved oxygen: $2H+ + \frac{1}{2}O2 + 2e- \rightarrow H_2O$

   In the absence of dissolved oxygen: $2H+ + 2e- \rightarrow H2\uparrow$

   If the medium is alkaline/neutral,

   In the presence of dissolved oxygen: $H_2O + \frac{1}{2} O_2 + 2e- \rightarrow 2OH^-$

   In the absence of dissolved oxygen: $2H_2O + 2e- \rightarrow 2OH^- + H_2\uparrow$

Example: Rusting of an Iron in the presence of moist air

   Anodic reaction : $Fe \rightarrow Fe^{2+} + 2e^-$

   Cathodic reaction : $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2\,OH^-$

   Products of anode & cathode : $Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2$

In the presence of oxygen : $2\,Fe(OH)_2 + \frac{1}{2} O_2 \rightarrow Fe_2O_3.2H_2O$

(Rust)

Galvanic Series:

In electrochemical series metals are arranged in the increasing order of their reduction potential but does not clear picture of corrosion of metals. In order to overcome the limitations of electrochemical series in corrosion studies, galvanic series was introduced. In galvanic series metals are arranged in the order of their corrosion resistance.

According to the electrochemical series Aluminium undergoes corrosion faster than Zinc. But in practice, in Zn-Al couple Zn is corroded while Al acts as cathode.

electro-chemical series

Potassium	-2.92
Calcium	-2.87
Sodium	-2.71
Magnesium	-2.37
Aluminium	-1.66
Zinc	-0.76
Iron	-0.44
Tin	-0.14
Lead	-0.13
Hydrogen	0.00
Copper	+0.34
Silver	+0.80
Mercury	+0.85
Gold	+1.68

metal activity increasing

metal oxide activity increasing
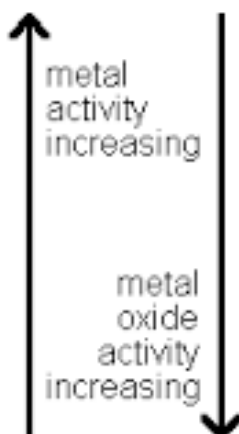
Galvanic Series

Magnesium	Active (Anode)	
Zinc	▲	
Galvanized Steel		
Aluminum		
Mild Steel		
Cast Iron		
Lead		
Brass		
Copper		
Bronze		
Monel		
Nickel (passive)		
Stainless Steel 304 (passive)		
Stainless Steel 316 (passive)		
Silver		
Titanium		
Gold		
Graphite		
Platinum	Noble (Cathode)	

Electrochemical series

Galvanic series

The arrangement of metals and non-metals in increasing order their standard reduction potential is known as electrochemical series

It contains metals and non-metals

It is an ideal series

ECS is based upon the electrode potential which is determined by using Nernst equation

Position of metals is fixed in ECS Galvanic

It gives no idea about the position of alloys

It gives information about the displacement tendencies

The arrangement of metals and alloys in decreasing order of their corroding tendency in an unpolluted sea water is known as galvanic series.

It contains metals and alloys.

It is a practical series

This series is based on actual corrosion rate

Position of a given metal in

series may change

It gives clear idea about the position of alloys

It gives information about the relative corrosion tendencies

Factors affecting the rate of corrosion

Nature of the metal:

1) Position of the metal/alloy in the galvanic series decides the rate of corrosion.
2) The metal top in the series is more anodic and undergoes corrosion faster than the metal below it.
3) The rate of corrosion depends upon the difference in the position of the metals in the galvanic series. Greater the difference faster is the corrosion at anode.

Nature of the corrosion product:

1) In a moist atmosphere almost all metals get covered with a thin surface film of metal oxide as the corrosion product.
2) If the corrosion product is nonporous protective in nature prevents the further corrosion. The layer acts as a barrier between the fresh metal surface and corrosive environment.
3) If the corrosion product is porous, it continues the corrosion processes.

pH of the medium:

1) The rate of corrosion increases with decrease in pH of the medium.
2) Acidic media are generally more corrosive than alkaline/neutral media. This is due to evolution of hydrogen at cathode.
3) When the pH < 4, the rate of corrosion increases due to higher concentration of H^+ ions. When pH > 10, the rate of corrosion decrease due to formation of insoluble metal hydroxides on the surface of metal.

Temperature:

1) Generally rate of corrosion increases with increase in temperature.
2) As the temperature increases conductance of the ions in the medium increases which reduces the polarization. Therefore the rate of corrosion increases.
3) A passive metal become active at high temperature and increases the rate of corrosion.

Area effect:

1) The rate of corrosion (x) is directly proportional to the ratio of area of cathode to the area of anode. i.e., x = area of cathode/ area of anode
2) Higher the value of x, greater is the rate of corrosion.
3) When anode is small and cathode is large, all the electrons liberated at anode and are consumed at the cathode. Therefore the rate of anodic reaction is greater and increases the extent of corrosion.

Conductivity:

1) The rate of corrosion increases with increase in the conductance of the medium.
2) As the conductance of the medium increases, ions can move easily trough the medium.
3) This decreases the polarization potential and due to this rate of corrosion increases.

Types of corrosion: Corrosion can be classified into 3 types as follows
1) Differential metal corrosion (Galvanic corrosion)
2) Differential aeration corrosion
3) Stress corrosion

Differential metal corrosion (Galvanic corrosion)

1) When two dissimilar metals are in direct contact with one another and exposed to a corrosive medium, the metal with lower electrode potential becomes anode and suffers from corrosion, whereas the metal with higher electrode potential becomes cathode and protected from corrosion. This type of corrosion is known as differential metal corrosion or galvanic corrosion.
2) The rate of corrosion depends mainly on the difference in the position of the two metals in galvanic series.
3) Higher the difference, faster is the rate of corrosion.

Example: Electrode potential of iron (-0.44 V) is less than that of copper (0.34 V). Therefore when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and protected from the corrosion.


Iron metal   Copper metal

$Fe \Rightarrow Fe^{2+} + 2\,e^-$ $1/2\,O_2 + H_2O + 2e^- \Rightarrow 2OH^-$

Anodic area   Cathodic area

Differential aeration corrosion

1) When a metal is exposed to different concentration of air (O_2), part of the metal exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
2) Other part of the metal exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
3) The difference in O_2 concentration produces a potential difference and causes corrosion. This type of corrosion is called differential aeration corrosion.

Example: 1 Water line corrosion

1) It is observed in steel or iron water tank partially filled with water. Part of the tank just below water level is exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
2) Part of the tank above the water line which is exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
3) More corrosion is observed just below the water line; hence this type is called water line corrosion.

Cathodic area
Anodic area
Water line
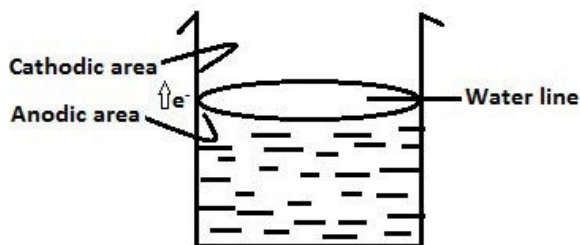
Example: 2 pitting corrosion

1. Pitting corrosion is observed when dust particles get deposited over the metal surface.
2. The portion of the metal covered by dust which is less aerated becomes anodic and suffers from corrosion.
3. Thus, metal is lost below the surface of dust particle forming a deep and narrow pit.
4. The adjaucent area of the metal which is exposed to higher concentration of O_2 becomes cathodic and protected from corrosion.
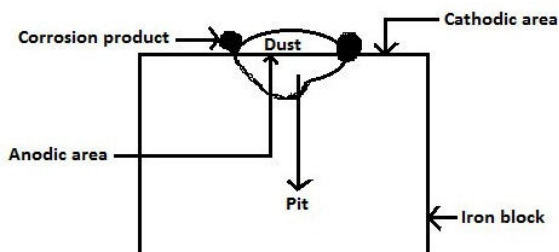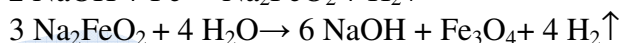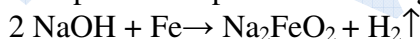
Stress corrosion

1) This corrosion occurs when some part of the metal is under stress and exposed to specific corrosive environment.
2) Stress may be produced on the metal during fabrication like bending or welding or servicing etc.

Example: Caustic Embrittlement

It is a stress corrosion occurring in mild steel when exposed to alkaline solutions at high temperature and stress. The boiler water usually contains a certain proportion of sodium carbonate added for water softening purposes. In high pressure boilers the carbonate breaks up to give respective hydroxide and carbon dioxide and make boiler water alkaline.

$$Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2\uparrow$$
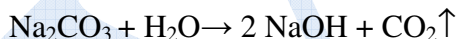
This alkaline water flows into the minute hairline cracks by capillary action. The water evaporates and increases the concentration of the alkali. This concentrated alkali reacts with iron and forms sodium ferroate in cracks. The sodium ferroate decomposes into magnetite and alkali which is regenerated in the process as per the following reactions.

$$2\ NaOH + Fe \rightarrow Na_2FeO_2 + H_2\uparrow$$
$$3\ Na_2FeO_2 + 4\ H_2O \rightarrow 6\ NaOH + Fe_3O_4 + 4\ H_2\uparrow$$

This type of stress corrosion in boilers in the presence of alkaline medium is called caustic embrittlement.

Corrosion control

Inorganic coatings (Chemical conversion coatings)

These coatings are produced at the surface of the metal by chemical/electrochemical reactions.
Examples: Anodizing and Phosphating

Anodizing: Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as protective layer.

Anode	: Aluminium
Cathode	: Steel or Copper
Electrolyte	: 5-10% chromic acid
Temperature	: 30-40 $^{\circ}$C

Applied potential   : 0-40 V

Aluminum is made as anode and copper or steel is used as cathode. The electrodes are immersed in an electrolyte consisting of 5-10% chromic acid. The temperature is maintained at 30-40 $^{\circ}$C. Potential of 0-40 V is applied which oxidizes outer layer of Al to Al_2O_3 and that get deposited over the metal.

The anodized coatings are thicker than the natural oxide film and possess improved corrosion resistance as well as resistance to mechanical injury.

Phosphating: Coating of metal with metal phosphate by oxidizing its outer layer in phosphoric acid medium is called Phosphating.

Anode   : Metal (Steel/Iron) to be phosphated
Cathode   : Graphite
Electrolyte   : Phosphoric acid (H_3PO_4)
Accelerators   : NO_3^- (added to speed up the reaction)
pH   : 1.8 - 3.2
Temperature   : 35 $^{\circ}$C

The metal which is to be phosphated is made as anode and inert metal as cathode. On maintaining the pH between 1.8 to 3.2 and by passing DC current the metal atoms on the surface, convert into metal ions and combine with phosphate ions in bath solution and deposits on the surface of the metal as metal phosphate. These coatings are applied by immersion or spraying or brushing. These are used as a primer coat for paints, enamels, etc.

Metal coatings

Metal coatings can be applied on the base metal by hot dipping process. This method is used for producing a coating of low melting metals such as Zn, Al, Sn etc, on iron/steel metals which have relatively high melting point. Example: Galvanizing and Tinning

Galvanization: Coating of zinc on iron or steel by hot dipping process is called galvanizing. (M.P of Zn=419 $^{\circ}$C) It is carried out as follows,
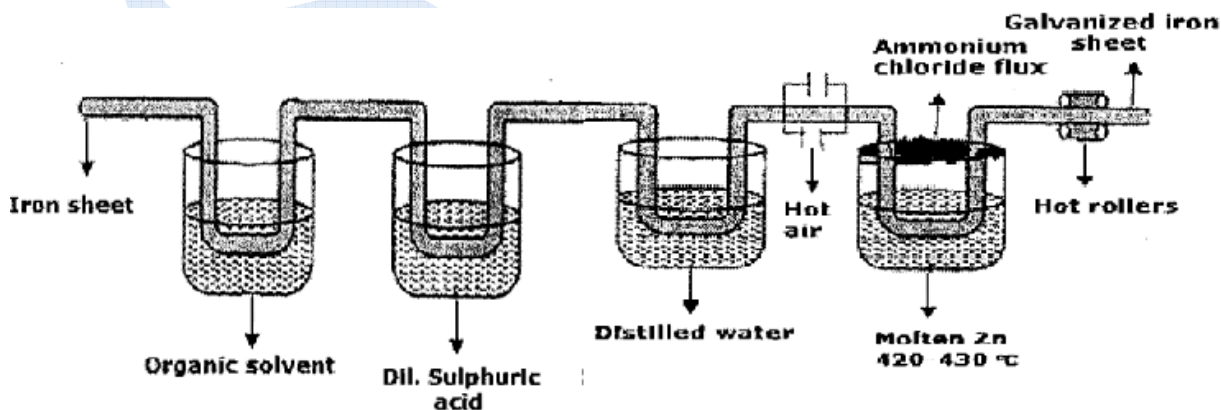
1) The iron sheet is subjected to pretreatment by degreasing with organic solvent.
2) The sheet is passed through dilute H_2SO_4 to remove any rust.
3) Washed with distilled water and dried by supplying hot air.

4) Then iron sheet is dipped in molten bath of Zn at $419^{°}C$ and surface is covered with NH_4Cl flux which prevents the oxidation of Zn metal.
5) The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.

**Tinning:** Coating of tin on iron or steel by hot dipping process is called tinning. (M.P of Sn = $232^{°}C$). It is carried out as follows
1) The iron sheet is subjected to pretreatment by degreasing with organic solvent.
2) The sheet is passed through dilute H_2SO_4 to remove any rust.
3) Washed with distilled water and dried by supplying hot air.
4) The sheet is treated with $ZnCl_2$ which acts as flux and helps the metal to adhere to the metal surface.
5) Then iron sheet is dipped in a molten bath of Tin (Sn) at $232^{°}C$ and surface is covered with palm oil to prevent oxidation of Tin.
5) The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.
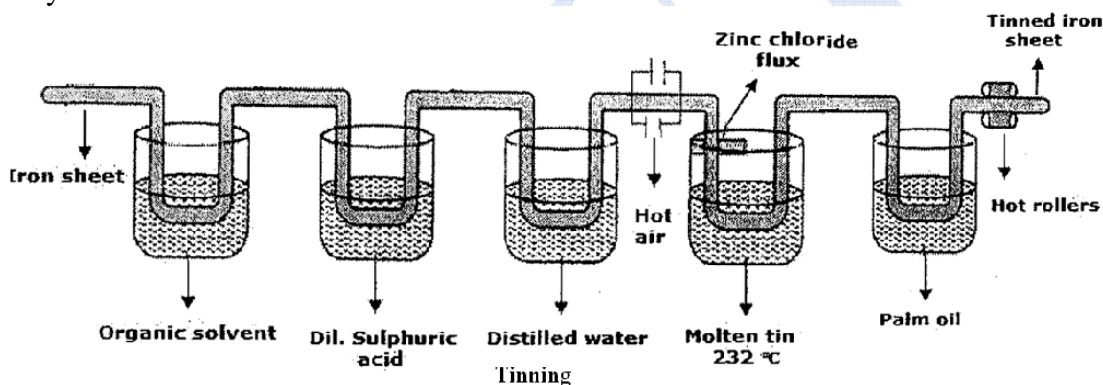
Cathodic Protection: The principle is to force the metal to be protected to behave as cathode**.** There are two types of cathodic protections namely,

1) Sacrificial anodic protection.
2) Impressed current cathodic protection.

Sacrificial anodic protection:

1) The metal to be protected is connected to a more anodic metal using a metallic wire.
2) The more active metal gets corroded while the parent structure is protected from corrosion.
3) The more active metal so employed is called sacrificial anode.
4) The sacrificial anodes to be replaced by fresh ones as and when it is required.
5) Commonly used sacrificial anodes are: Mg, Zn, Al etc.
Example: steel pipe is protected by connecting it to a block of Zn. In such cases steel acts as a cathode and is unaffected or protected from corrosion and Zn act as anode and undergoes sacrificial corrosion.

SOIL

Zn block
Sacrificial anode

Steel pipe
cathode
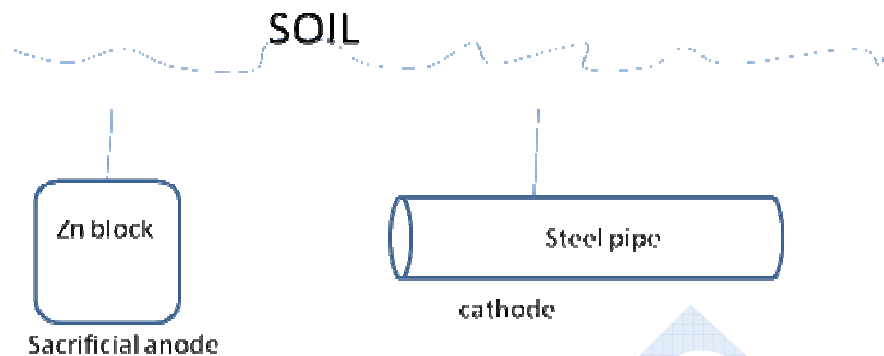
Impressed current protection:

1) In this method, electrons are supplied from a source of direct current.
2) Metal structure to be protected acts as cathode and connected to –ve terminal of battery.
3) The inert metal like graphite act as anode and connected to + ve terminal of battery.
4) When DC current is applied in a reverse direction to nullify the corrosion reaction.
5) Since anode is inert metal no reaction takes place at anode therefore the cathodic metal is protected from corrosion.

Graphite rod
inert anode

cathode
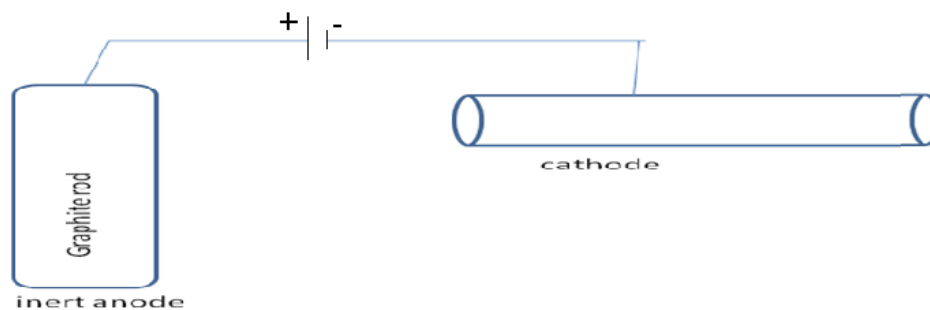
Impressed current protection

Metal Finishing

Introduction: Metal finishing covers the wide range of processes carried out in order to modify the surface properties of a metal. These processes involve deposition of a layer of another metal or a polymer, conversion of a surface layer of atoms into oxide films which ultimately modify the surface of the metal.

Definition: "It is a process of modifying surface properties of metals by the deposition of a layer of another metal or polymer on its surface or by the formation of an oxide film".

Technological importance of metal finishing:

The main technological importance of metal finishing include

[1] Imparting the metal surface to higher corrosion resistance.

[2] Providing electrical and thermal conducting surface.

[3] Imparting thermal resistance and hardness.

[4] In the manufacture of electrical and electronic components such as PCB's, capacitors contacts, etc.

[5] To increase the decorativeness of metal surface.

Principles of electroplating

1) Polarization:

The polarization is an electrode phenomenon. The electrode potential is determined by the Nernst equation,

$$E = E^o + \frac{0.0591}{n} \log [M^{n+}]$$

M^{n+} is the concentration of the metal ions surrounding the electrode surface at equilibrium. When there is a passage of current, the metal ion concentration near the electrode surface decreases due to the reduction of some of the metal ions into metal atoms. There exist a concentration gradient between electrode surface and bulk concentration. Therefore there is a shift in the equilibrium and a change in electrode potential. However equilibrium is re-established due to the diffusion of metal ions towards the electrode.

$$M^{n+} + n\ e^- \longrightarrow M$$

Therefore polarization can be defined as the process where there is a variation of electrode potential due to the inadequate supply of species from the bulk of the solution to the electrode is known as "*polarization*".

2) Decomposition potential:
It is defined as "The minimum voltage that must be applied in order to bring about continuous electrolysis of an electrolyte". The decomposition potential is represented as

$$E_D = E_{cathode} - E_{anode}$$

This can be determined by an electrolytic cell.

Determination of decomposition potential:

The decomposition potential is determined using an electrolytic cell as shown in the fig.1
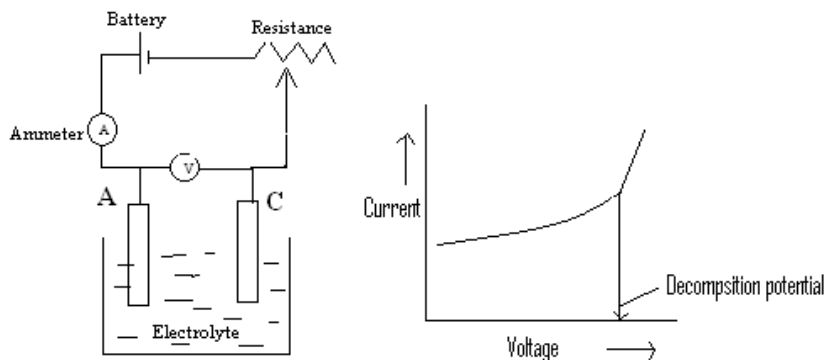
The cell consists of two platinum electrodes immersed in a dilute solution of an acid or a base. The voltage is varied along the wire and the current passing through the cell is measured using an ammeter. At low voltage no reaction occurs and there is a very slight increase in the current &

small amount of hydrogen & oxygen are liberated at the cathode & anode respectively. On increasing the voltage to slightly above 1.7V, there is an abrupt increase in the current and process of electrolysis begins. A plot of the current against the applied voltage is shown the fig.2.

3) Over voltage: It is defined as "The excess voltage that has to be applied above theoretical decomposition potential to bring the continuous electrolysis of an electrolyte is known as over voltage". For example theoretical potential of oxygen at platinum electrode is 1.23V. But the actual discharge potential of oxygen is 1.68V. The excess 0.45V is the over voltage of oxygen on platinum electrode surface.

Over voltage = (Experimental decomposition potential – Theoretical decomposition potential)

Factors (plating variables) influencing nature of electrodeposits

The nature of the electrodeposits is affected by numbers of factors which are discussed below.
[1] Metal ion concentration
[2] Electrolyte concentration
[3] Organic additives
[4] Current density
[5] p^H
[6] Temperature
[7] Throwing power of plating bath

1) Metal ion concentration: A higher concentration of metal ion increases the mass transfer leading to poor deposit. For a good adherent deposit, the metal ion concentration should be low; it is normally 1-3 mol dm^{-3}. The low metal ion concentration can be achieved by adding compounds having common ions or by the formation of complex compounds and ions. In general a decrease in metal ion concentration decreases the crystal size and result in a fine adherent coating films.

Example: In the electrodeposition of copper, the concentration of Cu^{2+} ion is maintained low by adding H_2SO_4. SO_4^{2-} ion acts as common ion and prevents the dissociation of $CuSO_4$, thus maintain low Cu^{2+} ion concentration.

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$
$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$
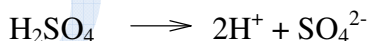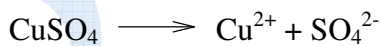
2) Electrolyte concentration: A good adherent deposition can be obtained with higher electrolyte concentration. The electrolytes used do not participate in the electrode reactions but increases the conductivity of the plating bath and cathode efficiency. It also controls the change in pH.

3) Organic additives: These are added to improve the nature of electrodeposits. They modify the structure, morphology and properties of the electrodeposits. The different organic additives used are as follows:

a) Brighteners   b) Levelers   c) Structure modifiers   d) Wetting agents

a) Brighteners: These are added to obtain a bright and microscopically fine deposit. The brighteners are adsorbed on the nuclei of the metal and forms new nuclei, i.e., large number of smaller crystals resulting in the formation of good deposit. Ex: Aromatic sulphones.

b) Levelers: Levelers are added to produce an even (level) deposit by getting adsorbed at regions where rapid deposition takes place. The levelers reduce the rate of deposition at those points. Ex: Sodium alkyl sulphonates.

c) Structure modifiers or Stress relievers: These additives modify the structure of the deposit and orientation in such a way as to alter the deposit properties. These substances avoid the development of internal stress in the deposits. Ex: Saccharin.

d) Wetting agents: Wetting agents are used to release hydrogen gas bubbles from the surface. The wetting agents also improve the uniformity of the deposit.
 Ex: Sodium lauryl sulphate.

4) Current density: Current density is the current per unit area expressed in amperes per m^2. At low current density, a bright, crystalline deposit is produced but the rate of deposition is slow. At higher current density, hydrogen evolution occurs and deposits are spongy, irregular and loosely held. Deposits may have a burnt appearance.

For good deposit the current density should be optimum. $(10\text{-}70 \text{ A m}^{-2}.)$

5) P^H: The nature and appearance of the electrodeposits depends on p^H of the plating solution. If p^H of the medium is low H_2 gas is evolved at the cathode causing brittle and burnt deposit. At higher p^H values, deposits of metallic oxides or hydroxides may form. Hence an optimum p^H (4-8) is employed.

6) Temperature: A good deposit is formed at slightly higher temperature ($35\text{-}60^{\circ}C$). At very low temperature hydrogen evolution takes place at the cathode forming a burnt deposit. Therefore moderate temperature is used to get good deposit.

7) Throwing Power of a plating bath: The ability of a plating bath to give a uniform and even deposit on the entire surface of the object irrespective of its shape is known as *"throwing power"*. Throwing power of plating bath can be determined by using *"Haring Blum Cell"*. Haring Blum cell consists of one anode and two cathode electrodes. Anode is placed at the centre and two cathodes are placed on the either side of the anode at a distance x_1 and x_2.

Haring - Blum Cell
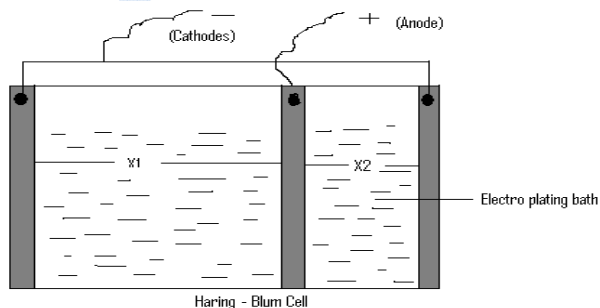
Electroplating is carried out and weight of electro deposit on the two cathodes is weighed. The weight of electro deposit (w_1) on x_1 which is placed far from anode is less than another x_2, which is very nearer to the anode. Then throwing of plating bath is calculated from the equation.
Then throwing of plating bath is calculated from the equation.

$$\% \text{ throwing power} = \left(\frac{K-M}{(K+M)-2}\right) \times 100$$

Where $K = x_1 / x_2$ (when $x_1 > x_2$); $M = w_2 / w_1$. Throwing power is said to be very good (100%) when $w_1 = w_2$.

Electroplating

Definition: "It is a process of deposition of a metal by electrolysis, over the surface of substrate. The substrate may be another metal, polymer, ceramic, or a composite".

Electroplating of Nickel (Watts bath):

The majority of the nickel plating solution used for decorative applications is based on Watts formulations developed by Oliver p. watts in 1916.

Pretreatment: Before the application of the electroplated coatings, it is essential to clean the surface of the base metal. The impurities present on the surface like grease, oil, oxide layer, dust etc are removed by solvent cleaning or alkali cleaning or mechanical cleaning.

Bath composition	: $NiSO_4.6H_2O$ (240-300 g/L) + $NiCl_2.6H_2O$ (30-90 g/L)
Current density	: 2-7 A m^{-2}
Temperature	: 40-60 °C.
Buffer	: Boric acid (H_3BO_3, 30-45 g/L)
P^H	: 3.5 - 4.5
Anode	: Nickel
Cathode	: Object to be electroplated.

Mode of plating: The nickel sulphate is source of nickel and nickel chloride is an accelerating agent which increases the conductivity thereby reducing voltage requirement. Boric acid is a buffer which control the pH. During the electroplating nickel metal undergoes oxidation and forms Ni^{2+} ion. Ni^{2+} ion undergoes reduction and forms Ni which gets deposited on the surface cathode. The reactions are as follows,

At anode: $Ni \longrightarrow Ni^{2+} + 2e^-$

At cathode: $Ni^{2+} + 2e^- \longrightarrow Ni$
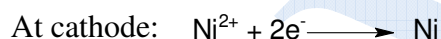
Applications: 1. It offers a high luster finish, corrosion protection and wear resistance.
2. Used in the manufacture of hand tools and household items such as lighting and Plumbing fixtures.
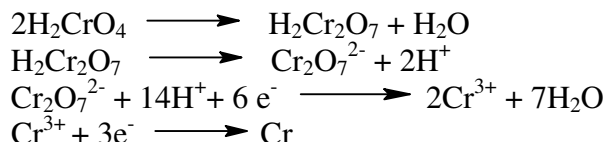
Electroplating of chromium

Chromium is one of widely used metal in electroplating industries. In the field of electroplating two types of Chromium are employed, decorative Chromium and hard Chromium.

Pretreatment: Before the application of the electroplated coatings, it is essential to clean the surface of the base metal. The impurities present on the surface like grease, oil, oxide layer, dust etc are removed by solvent cleaning or alkali cleaning or mechanical cleaning.

Decorative / hard chromium:

Bath composition	: 250g Chromic acid + 2.5g H_2SO_4 proportion/dm^3
Temperature	: 45-60°C. / 45-55°C
Current Density	: 145- 430 A m^{-2} / 290-580 A m^{-2}
Anode	: Insoluble anodes like pb-sb
Cathode	: Object to be electroplated.

Mode of plating: The plating bath contains CrO_3 in which Cr is in +6 oxidation state. This is reduced to +3 oxidation state in the presence of SO_4^{2-} furnished by H_2SO_4. Cr^{3+} ions are reduced to elemental Cr which gets deposited on the surface of cathode. The reactions taking place are given below.

$$2H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O$$
$$H_2Cr_2O_7 \longrightarrow Cr_2O_7^{2-} + 2H^+$$
$$Cr_2O_7^{2-} + 14H^+ + 6\,e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$Cr^{3+} + 3e^- \longrightarrow Cr$$

Applications:
1. Decorative chromium provides a durable finish on cycles, automobiles, furniture's, household fittings, air craft, surgical instruments etc.
2. Hard chromium is used in the manufacture of cutting tools, piston rings, cylindrical liners etc.

Note: Chromium anodes are not used in Chromium plating because
1. Chromium metal deactivates strongly in acid medium.

Electroless plating (Auto catalytic redox reaction)

Definition: "The process of depositing a metal over substrate by controlled chemical reduction of metal ion by a reducing agent without using electric current is called electroless plating"

$$\text{Metal ions + reducing agent} \longrightarrow \text{Metal + oxidized product}$$
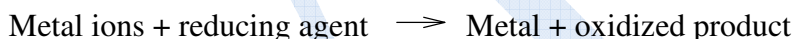
Differences between electroplating and electrolessplating:

Property	Electro plating	Electroless plating
1) Driving force	Passage of current	Auto catalytic redox reaction
2) Anode	A separate anode is used	Catalytic surface of the substrate acts as anode
3) Reducing agent	Electrons bring about reduction	Chemical reagents bring about reduction
4) Applicability	Applicable only to conductors	Applicable to both conductors and nonconductors

Electroless plating of copper over PCB

Electroless plating of copper involves the following features.
1) **Pretreatment and activation of the surface:**
   The surface to be plated is first degreased by using organic solvents followed by acid treatment.
2) PCBs are activated by first dipping in $SnCl_2$ solution containing HCl followed by dipping in palladium chloride solution.
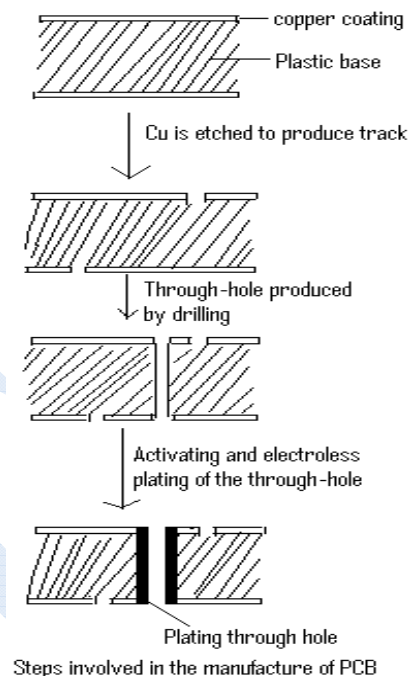
Composition of the bath:
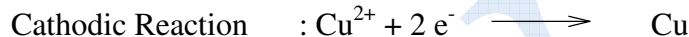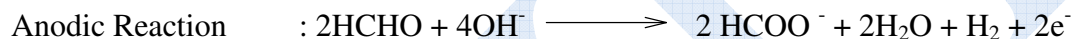
Coating solution   : $CuSO_4.5H_2O$ (15g/L)

Reducing Agent	: Formaldehyde (8g/L)
Buffer	: NaOH (15g/L) + Rochelle salt (14g/L)
Complexing agent	: EDTA solution (20g/L)
P^H	: 11
Temperature	: 25 °c

Procedure:

A thin layer of copper is first electroplated over the PCB. Then selected areas are protected by employing electroplated image and the remainder of the plated copper is etched away so as to get required type of circuit pattern. Usually double sided tracks are made in order to pack more number of components in a small space. Finally, the connection between 2 sides of PCB is made by drilling holes. The holes are activated and followed by electroless copper plating through holes.

Chemical Reactions:

Anodic Reaction : $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

Cathodic Reaction : $Cu^{2+} + 2e^- \longrightarrow Cu$

Net reaction : $Cu^{2+} + 2HCHO + 4OH^- \xrightarrow{Catalyic\ surface} Cu + 2HCOO^- + 2H_2O + H_2$

Note: Buffer is added because; above redox reaction involves the consumption of OH^- ions, so the p^H of the solution decreases as the reaction proceeds.

Application:

[1] Widely used for metalizing printed circuit boards.
[2] For plating on non-conductors.
[3] As an undercoat for electroplating.
[4] For decorative plating on plastics.

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Module-3

Fuels and Solar Energy

Fuel: Fuel is defined as naturally occurring or an artificially manufactured carbonaceous substance which serves as a source of heat and light.

Classification of fuels

1) Primary fuels: They are naturally occurring fuels

Ex: Solid   –   coal, wood, lignite, peat

    Liquid   –   crude oil

    Gas   –   biogas

2) Secondary fuels: They are derived from primary fuels

Ex: Solid   –   charcoal, coke, etc

    Liquid   –   kerosene, diesel, synthetic petrol, benzene, etc

    Gas   –   water gas, producer gas, LPG etc

Calorific value

         "The amount of heat liberated by burning a known mass of fuel in presence of air" is called *calorific value*.

Gross calorific value or High calorific value (GCV or HCV):

         The amount of heat liberated when a unit mass of a fuel is burnt in excess air & the products of combustion are cooled to room temperature" is called *Gross Calorific Value*.

Net calorific value or Less calorific value (NCV or LCV):

         The amount of heat liberated when a unit mass of a fuel is burnt in excess air and the product of combustion is allowed to escape in the atmosphere is called *Net Calorific Value*.

         Net calorific value = Gross calorific value – Latent heat of steam of H_2O.

Determination of Calorific Value of fuel using Bomb Calorimeter

Construction: A bomb calorimeter consists of a cylindrical vessel fixed with inlet valve for pumping of O_2. A Ceramic or platinum crucible is placed at the bottom of the vessel connected with iron wire, the end of the wire is connected to battery. The bomb is than placed in known weight of H_2O taken in a copper calorimeter and enclosed in air & water jacket to prevent heat exchange with the surrounding. Electrical stirrer is placed one side to maintain uniform temperature and thermometer on the other side.
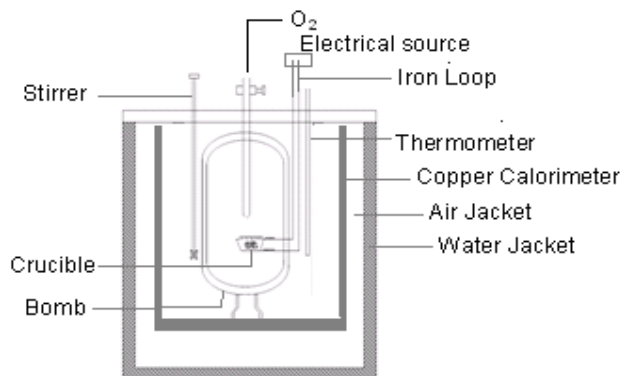
Working: A known weight of a fuel is taken in crucible Oxygen is pumped into a bomb at a pressure of 25-30 atm. Initial temperature of H_2O is noted. The fuel is ignited through spark produced by iron wire. The heat liberated is absorbed by surrounding water and calorimeter. The water in a jacket is continuously stirred. The maximum temperature attained by water is noted.

Principle: The amount of heat liberated by the fuel is equal to amount of heat absorbed by water and calorimeter.

Observation and calculation:

Let weight of fuel taken   = 'm' kg

Initial temperature of water   = $T1°$ c

Final temperature of water   = $T2°$ c

Change in temperature   = (T2-T1) = ΔT °c

Weight of water taken in calorimeter   = 'W' kg

Water equivalent of calorimeter   = 'w' kg

Specific heat of H2O $\qquad\qquad$ = 'S' J kg^{-1} c^{-1}

$$GCV = \frac{(W + w)\, kg \times SJ\, kg^{-1}\, c^{-1} \times \Delta T^{\circ}c}{m\, kg}$$

$$GCV = \frac{(W + w)\, S\Delta T}{m}\ J\, kg^{-1}$$

Cracking: "*Cracking* is a process of splitting long chain or heavy molecular weight hydrocarbon into smaller fragments.

$$Ex: C_{10}H_{22} \longrightarrow C_8H_{18} + C_2H_4$$

Fluidized bed catalytic cracking
Conditions:
Feed stalk: heavy oil
Catalyst: $Al_2O_3 + SiO_2$ (Alumina silicate)
Cracking Temperature: 530ºC
Regenerator temperature: 600ºC
Pressure: Little above the normal pressure

$\qquad$ In this process, the heavy oil is initially preheated to 300ºC. The oil is sent into reactor through riser column which containing finely powdered catalyst temperature maintained at 700ºC. Cracking occurs in a contact time of three seconds and temperature falls to 530ºC. The products obtained are subjected to fractionation to separate them to light oil and middle oil fractions.
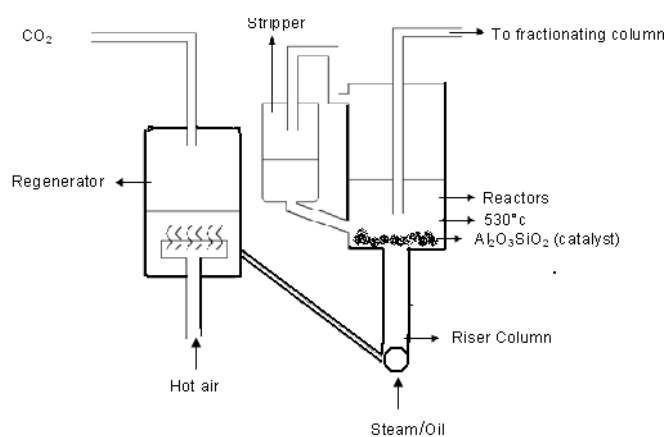
$\qquad$ The catalyst present in the reactor column becomes inactivate due to the deposition of carbon over it. The carbon is removed as carbondioxide by passing hot air into the regenerator chamber at 600^{0}C. The activated catalyst is again fed into reactor for further cracking processes. Due to high contact between oil and catalyst the cracking takes place at higher rate and the yield obtained is 99.99%.

Synthesis of petrol by Fishcher-Tropsch process
Synthetic petrol is a mixture of saturated and unsaturated hydrocarbons with composition resembling that of petrol.
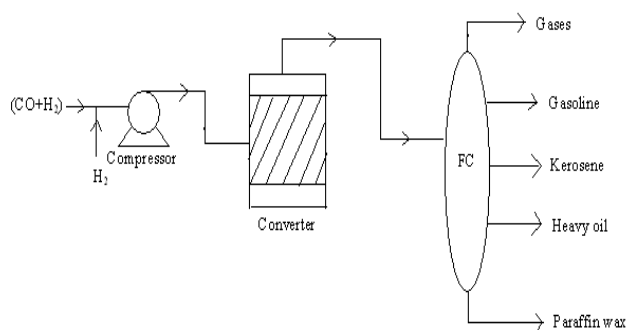Temperature: 200 - 300°C
Pressure: 5-25 atm pressure
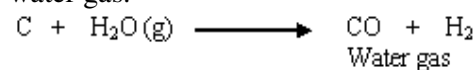Catalyst: mixture of cobalt oxide, thorium oxide and magnesium oxide.
Starting material: water gas
Production of water gas ($CO+H_2$)
Coke is treated with steam at 1200°C to produce water gas.

$$C + H_2O\,(g) \longrightarrow CO + H_2$$
$$\text{Water gas}$$

The synthesized gas is passed over mixture of Fe_2O_3 and Na_2CO_3 to remove dust, H_2S and organic compounds.

Hydrogenation of water gas: The purified water gas is compressed between 5-25 atm pressures and passed into converter containing mixture of cobalt oxide, thorium oxide and magnesium oxide hydrogenating catalyst the reaction products are saturated and unsaturated hydrocarbons formed between temperature 200-300ºC. The nature of the products formed depends on the temperature, pressure and catalyst used.

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$
$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$
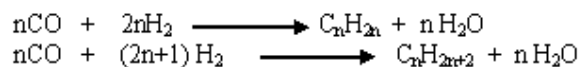
The products are subjected to fractional distillation to obtain petrol.

Reforming: It is the process of modifying structure of hydrocarbon to form new compound without change in the number of carbon in parent chain. The process is carried out by passing petroleum fraction over platinum coated alumina catalyst at 500ºC. The main reaction taking places are:

1) Isomerisation: It is the conversion of straight chain hydrocarbon into branched chain.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$
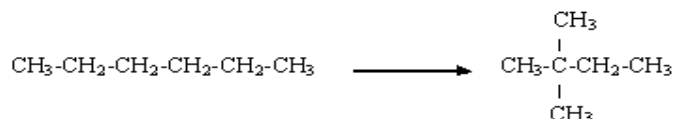
2) Cyclization: It is the conversion of straight chain hydrocarbon into cycloalkanes.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow \bigcirc$$

$$C_6H_{12}$$
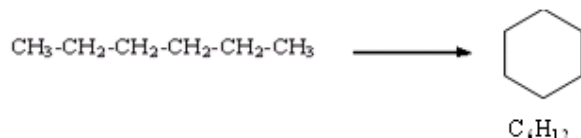
3) Aromatization: It is the conversion of straight chain hydrocarbon into aromatic.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow \bigcirc \xrightarrow{-3H_2} \bigcirc$$

$$C_6H_{12} \qquad C_6H_6$$
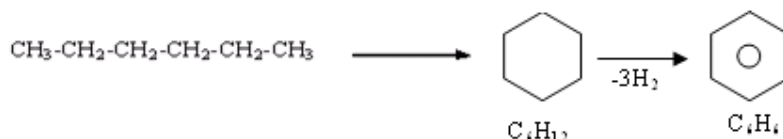
4) Hydro cracking: It is the cracking of a petrol sample in the presence of hydrogen.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 + H_2 \xrightarrow{Pt} CH_3-CH_2-CH_3 + CH_3-CH_2-CH_2-CH_3$$

Octane numbers: Octane numbers is the percentage by volume of Isooctane present in the standard mixture of isooctane and n-heptane, which has knocking characteristics as like petrol under test.

Eg: a petrol sample is said to have octane value 80 when it's knocking characteristics matches with 80% of iso octane and 20% of n-heptane.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \quad \underline{\qquad} \quad \text{Iso- octane having low knocking tendency, its octane number is 100}$$

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \quad \underline{\qquad} \quad \text{n heptane having high knocking tendency, its octane number is 0}$$
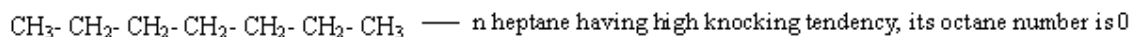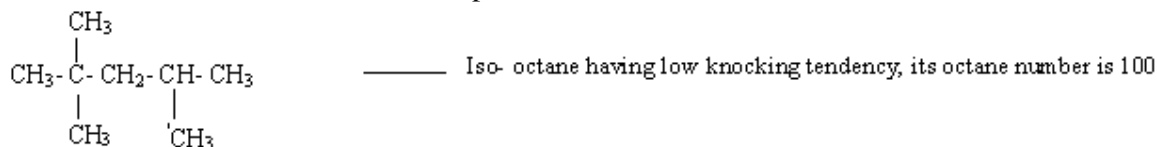
Cetane Number: Cetane number is percentage by volume of n-cetane present in mixture of n-cetane and α-methyl naphthalene which gives the same ignition delay as that of the diesel (fuel) sample under test.
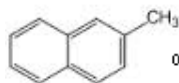
α-Methyl naphthalene (α-Methyl naphthalene having high knocking tendency, cetane no is zero)

$CH_3-(CH_2)_{14}-CH_3$ - n-Cetane (n-Cetane having low knocking tendency, cetane no = 100)

Knocking and its mechanism

It is the rattling sound being produced in an internal combustion engine due to the explosive combustion of fuel.
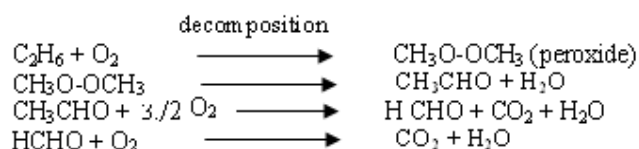
The efficiency of an IC engine depends on the *Compression ratio.*

$$Compression\ ratio\ =\ \frac{Volume\ of\ cylinder\ at\ end\ of\ suction\ stroke}{Volume\ of\ cylinder\ at\ end\ of\ compression\ stroke}$$

The petrol-air mixture drawn in the cylinder is compressed and ignited. Under ideal conditions (eg, CR-5 to10) the hydrocarbons undergo combustion and the flame propagates smoothly to produce power.

$$C_2H_4 + 7/2\ O_2 \longrightarrow 2CO_2 + 3H_2O$$

But, if the hydrocarbon present is unable to withstand pressure at high compression ratio (CR > 10), then hydrocarbons of the fuel combine directly with oxygen to form unstable peroxides which decompose and burst suddenly into flames by pre ignition producing shock waves. The shock wave hits the walls of the engine part producing sound. This is called as knocking. The knocking mechanism is as follows.

$$
\begin{aligned}
C_2H_6 + O_2 &\xrightarrow{\text{decomposition}} CH_3O\text{-}OCH_3\ (peroxide) \\
CH_3O\text{-}OCH_3 &\longrightarrow CH_3CHO + H_2O \\
CH_3CHO + 3/2\ O_2 &\longrightarrow H\ CHO + CO_2 + H_2O \\
HCHO + O_2 &\longrightarrow CO_2 + H_2O
\end{aligned}
$$

Knocking of Diesel engine

In diesel engine first air is draw into the cylinder and compressed at high pressure. At this stage fuel is injected into the cylinder. Heat produced (above 500 ^{o}C) from the compressed air ignites the diesel fuel and releases gases which push the piston and cycle is completed by removal of hot gases from the cylinder.

The interval between the start of fuel injection and its ignition is called ignition delay or ignition lag. If the fuel has long ignition lag, then injected fuel accumulate in the cylinder when ignition take place, it burnt violently at high temperature and pressure. This produces a rattling sound, is known as knocking of diesel engine.

Ill effects of knocking: Decreases in life of engine, causes mechanical damage to engine parts such as spark plug, piston and engine walls, more consumption of fuel and power output decreases

Anti-knocking agents

The substances that are added to gasoline in order to decrease the knocking tendency is called *"anti-knocking agents".*

The commonly used anti-knocking agent is Tetra ethyl lead (TEL), usually 1-1.5 ml of TEL is added to petrol along with ethylene dichloride or ethylene di-bromide.

Additional information
Leaded petrol: The Petrol containing Tetra ethyl lead (TEL). Tetraethyl Lead decomposes the peroxides formed and prevents knocking. In the process, lead gets deposited on the inner walls of the engines and at spark plugs. Hence ethylene di-chloride or ethylene di-bromide is added along with tetraethyl lead. These convert the lead into $PbCl_2$ or $PbBr_2$, which are volatile and escape with exhaust gases. The release of lead compounds pollutes the atmosphere.

TEL cannot be used as anti knocking agent in IC engines with catalytic converter.

Unleaded Petrol: The gasoline in which the antiknocking properties are increased without addition of lead substance is called unleaded petrol. In orders to improve the octane number of unleaded petrol some compounds like methyl tertiary butyl ether (MTBE) is added.

Addition of MTBE: Methyl tertiary butyl ether (MTBE) added to petrol (unleaded petrol) provides oxygen for combustion, thereby reduces the formation of peroxy compounds. MTBE can be used as anti knocking agent in IC engines with catalytic converter.

Advantages of Unleaded petrol
1) It increases the efficiency of the engine.

It permits the attachment of catalytic converters to the exhaust pipe of automobiles. The catalytic converters convert toxic gases like carbon monoxide and nitric oxide to CO_2 and N_2.

Power alcohol

Power alcohol is alcohol petrol blend containing 25% of alcohol and 75% of petrol. It is used as fuel in internal combustion engine.
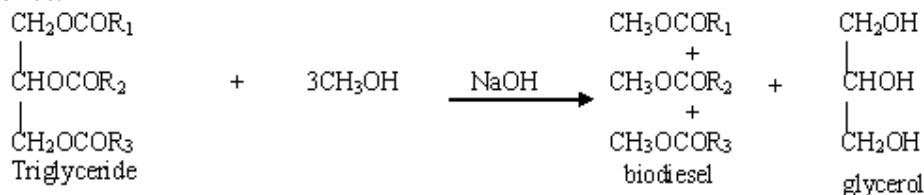
Advantages:
- Alcohol petrol blend processes better anti-knocking properties.
- Alcohol petrol blend can be used in an engine with higher compression ratio.
- There is no starting difficulty with alcohol petrol blend.
- Air required for the complete combustion is less.

Disadvantages
a) Alcohol lowers the calorific value of petrol
b) Alcohol easily oxidizes to acids. Hence alcohol may cause corrosion.
c) Alcohol absorbs moisture. As a result, separation of alcohol petrol layers takes place. To avoid these blending agents such as benzene or toluene are used.

Biodiesel: It is a mixture of mono alkyl esters of long chain fatty acids which can be produced by transesterification of the vegetable oil. The vegetable oils like soya bean oil, palm oil, sunflower oil etc..,

Preparation: It is a mixture of esters produced by the process of transesterification of vegetable oil with excess of methanol in presence of NaOH as catalyst. The resultant mixture containing glycerol is removed by gravity separation method; the esters are used as an alternative fuel to diesel in automobiles.

$$CH_2OCOR_1 \atop CHOCOR_2 \atop CH_2OCOR_3 \ (Triglyceride) \ + \ 3CH_3OH \ \xrightarrow{NaOH} \ CH_3OCOR_1 + CH_3OCOR_2 + CH_3OCOR_3 \ (biodiesel) \ + \ CH_2OH \atop CHOH \atop CH_2OH \ (glycerol)$$

Where R1, R2 and R3 are long chain fatty acids in oil.

Advantages: It has higher cetane number (48-60) compared to diesel (40-55), non toxic and eco friendly products are formed.

Disadvantages: Cost of production is high, Release nitrogen oxide which can lead to the formation of smog and As Biodiesel cleans the dirt from the engine, this dirt can then get collected in the fuel filter, thus clogging it. So, filters have to be changed after the first several hours of biodiesel use.

Solar Energy

Utilization of solar energy
- To provide electricity to satellites
- It is used in watches, calculators and other electronic devices as power supply source.
- It meets the energy requirements for lighting, irrigation and other essential in remote places.
- It is directly used for cooking, heating water and other various domestic use.

Conversion of solar energy

Solar energy can be converted into more useful forms of energies in two different ways thermal and photo conversion.

Thermal conversion involves the conversion of solar energy into heat energy the energy so produced used for domestic purpose.

Photo conversion involves the conversion of solar energy into electricity by photoelectric effect. In this photons of light strike the electrons on the metal surface. The electrons exist from the metal surface and pass through external circuit producing electrical energy.

Photovoltaic cells: (Solar cells)
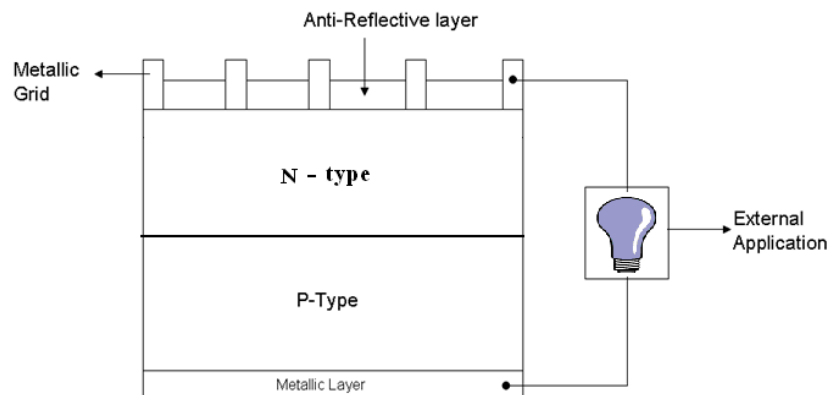
The device which converts solar energy into electrical energy is called photovoltaic cell and the phenomenon is called photovoltaic effect.

Principle: The principle involved is the ejection of electrons from metal surface by striking with photons of solar radiation.

Construction: The device consists of p-n junction diode coated with anti reflective layer (TiO_2). Two electrical contacts is provided, one in the form of metallic grid at the top of the junction and the other is a layer silver on the bottom of the cell. The antireflective layer coated in between the metallic grids allows light to fall on the semiconductor.

Working: The photons of solar radiations enters n-type semiconductor breaks barrier potential and moves to p-type semiconductor where photons knocks the electrons in p type to form electron hole pair. The free electrons so formed will travels through the circuit from n-type and recombines with holes again in p-region. The movement of electrons from n type to p type generates electric current. The electrical energy produced from the solar cell is used for various applications.

Advantages of PV cells: Eco friendly energy conversion devices do not undergo corrode and no moving parts in PV cell, hence no wear and tear

Disadvantages of PV cells: Installation cost is high, produced only during the day time and generates only DC current

Importance of photovoltaic cells: PV cell directly convert sunlight into electricity, do not pollute the nature, to improve remote area communication systems and in transportation systems, milling, sawing etc..,

PV: modules, panels & arrays

Photovoltaic module: A number of solar cells electrically connected to each other and mounted in a support frame are called as **photovoltaic module**. Modules are designed to supply electricity of 12 V,

Photovoltaic panels: PV panels include two or more PV modules assembled in series; it generates and supply electricity in commercial and residential applications.

Photovoltaic Arrays: The solar panels are linked together to get an array, the modules are usually first connected in series to obtain the desired voltage, the individual strings are then connected in parallel to allow the system to produce more current.

PV Panel / PV cell / PV Module / PV Arrays
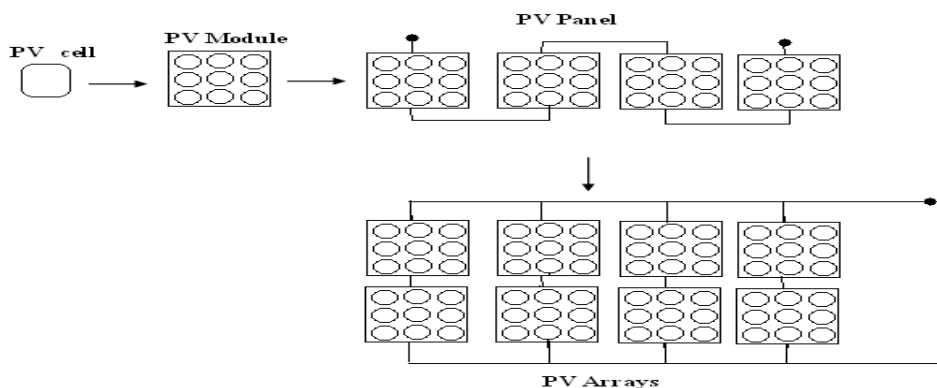
Production of solar grade silicon (union carbide process)

The production of solar cell grade silicon is carried out in different stages:
In this process SiO_2 is treated with carbon in electric arc furnace at 1500-2000°C to produce Silicon.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$
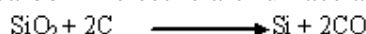
The molten silicon obtained is treated with O_2 and fresh silica as flux to remove impurities Al, Ca and Mg.

Metallurgical grade silicon is treated with HCl at 300°C to form trichlorosilane

$$Si + 3HCl \xrightarrow{300^oc} HSiCl_3 + H_2$$

Trichlorosilane is then passed through fixed bed columns containing ammonium ion exchange resin catalyst where trichlorosilane converts to silicon hydride.

$$6HSiCl_3 \xrightarrow{Ammonium\ ion\ exchange\ resin} 3H_2SiCl_2 + 3SiCl_4$$

$$3H_2SiCl_2 \xrightarrow{Ammonium\ ion\ exchange\ resin} SiH_4 + 2HSiCl_3$$
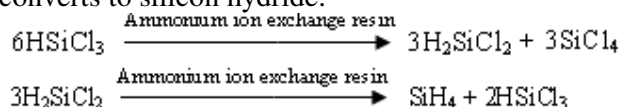
The products are separated by distillation and trichlorosilane are recycled. The poly silicon is obtained through pyrolysis of SiH_4 in silicon seed rods mounted in a metal bell jar reactor..

$$SiH_4 \longrightarrow 2H_2 + Si$$

Doping: The doping is a process of adding of impurity/atoms to pure semiconductor material to produce n or p type semiconductor.

Diffusion technique (n&p types): The doping of silicon is effectively done by diffusion method. When silicon wafer is heated just below melting point in an atmosphere of penta valent (P or As) or tri valent impurities (Boron) it become soft, the impurity atom condenses on the surface and slowly diffuse into crystal lattice and occupy the position to form either n-type or p–type semiconductor.

Purification of silicon (zone refining)

In this process a silicon rod is clamped vertically and heated by RF coil (Radio frequency) to its melting temperature. part of solid is heated to melt, the impurities concentrates in molten zone. The molten zone is carefully moved to end of solid material by moving RF coil from top to bottom. When the process is repeated all the impurities concentrate at bottom portion of the rod, finally rod is removed by cutting. The pure silicon is cut into thin wafers and doped suitably to get p-n junction.

RF heating coil
Molten zone
Inert atmosphere
Silicon rod
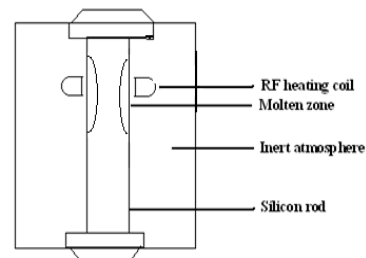
At the interference of the solid and the melt, there will be distribution of impurities. The distribution can be represented by distribution coefficient (Kd), Smaller Kd value gives better purification.

$$Kd = \frac{Concentration\ of\ impurity\ in\ solid\ phase}{Concentration\ of\ impurity\ in\ molten\ phase}$$

Module-4
POLYMERS
(*"Better thing for better living – through polymers"*)

Definition: "Polymers are macro sized molecules of high molecular mass formed by the combination of a large number of simple molecules by covalent bonds".

Ex: Polyethylene, polyacetylene, polystyrene, polyvinyl chloride, natural and synthetic rubbers etc.

**Polymerization:** "The process by which the monomers are converted into polymers is called Polymerization".

Types of Polymerization:
Polymerization is of two types.

1) Addition polymerization (chain polymerization):

It is a process in which number of simple monomers joining together by chain reaction without the elimination of any byproducts.
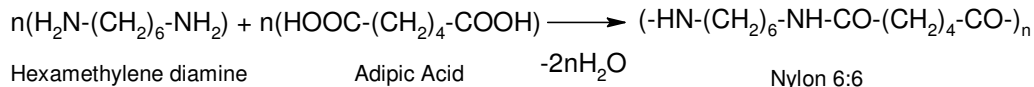
Ex: a) Preparation of polyethylene from ethylene

$$n(CH_2=CH_2) \longrightarrow (-CH_2-CH_2-)_n$$

Ethylene   Polyethylene
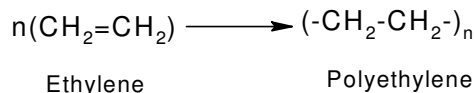
2) Condensation polymerization (step polymerization):

A polymerization reaction in which bi-functional monomers undergoes condensation with continuous elimination of byproducts such as H_2O, NH_3, HCl, etc is called condensation polymerization.

Ex: a) Preparation of nylon 6:6 from hexamethylene diamine and Adipic acid.

$$n(H_2N-(CH_2)_6-NH_2) + n(HOOC-(CH_2)_4-COOH) \longrightarrow (-HN-(CH_2)_6-NH-CO-(CH_2)_4-CO-)_n$$

Hexamethylene diamine   Adipic Acid $-2nH_2O$ Nylon 6:6

Difference between addition and condensation polymerization

Addition polymerization	Condensation polymerization
It is a process in which number of simple monomers joining together by chain reaction	polymerization reaction in which bi-functional monomers undergoes condensation
It requires two like molecules.	It requires two unlike molecules.
Kinetic long linear chain reaction.	Intermolecular reaction.

|	
Very fast reaction	Slow reaction takes hours and days to complete.
No by products	By product it produced.
Polymer produced thermoplastic.	Chemo setting plastic produced.
Example: PVC, Teflon, Poly ethylene.	Example: Bakelite, Silicon, GRP, Polystyrene.

Mechanism of polymerization:

Free radical mechanism of addition polymerization:

Free radical mechanism of polymerization of polyvinyl chloride involves three steps
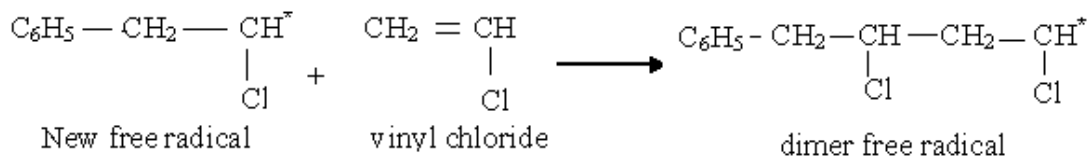**1)** Chain initiation 2) Chain propagation and 3) Chain termination
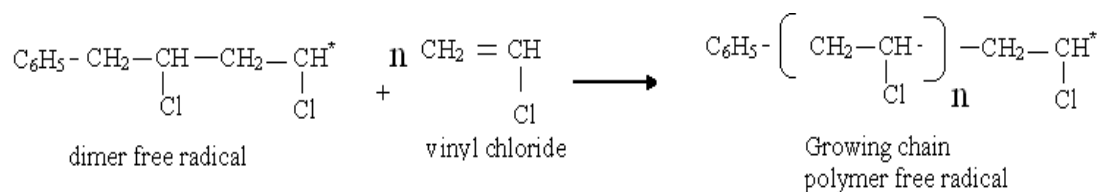
1) Chain initiation:

The polymerization is initiated by the free radicals generated from initiators. I.e. initiators homolytically dissociated into free radicals. The free radicals initiate the chain process by attacking the monomer molecule (vinyl chloride) at the double bond generating new free radicals.
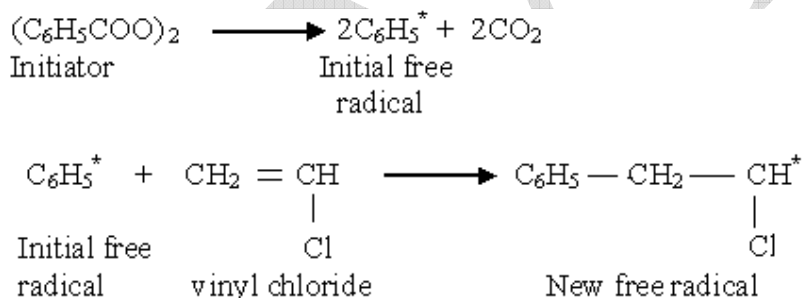
2) Chain Propagation:

The new free radical or chain initiating species capable of further interaction with initial monomer (vinyl chloride) molecule leading to chain propagation.
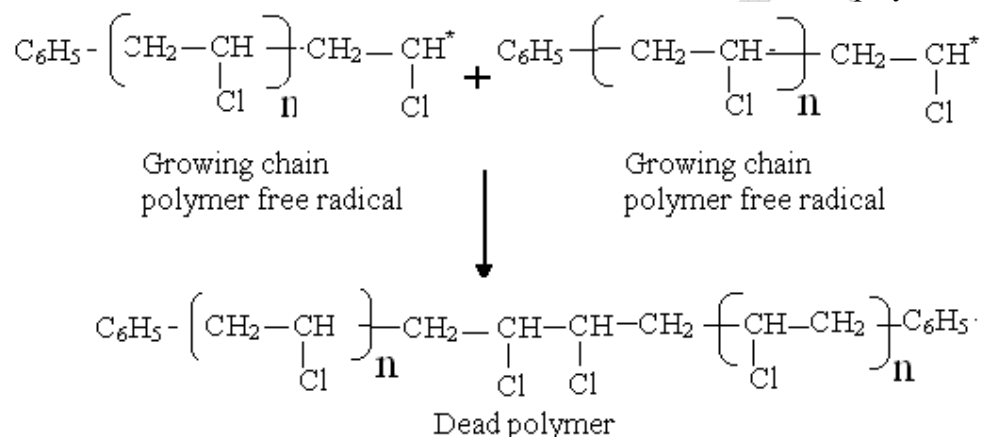
$$C_6H_5 - CH_2 - CH - CH_2 - \overset{*}{CH} \quad + \quad n\ CH_2 = CH \longrightarrow C_6H_5 - \left[CH_2 - CH \cdot \right]_n - CH_2 - \overset{*}{CH}$$

dimer free radical   vinyl chloride   Growing chain polymer free radical
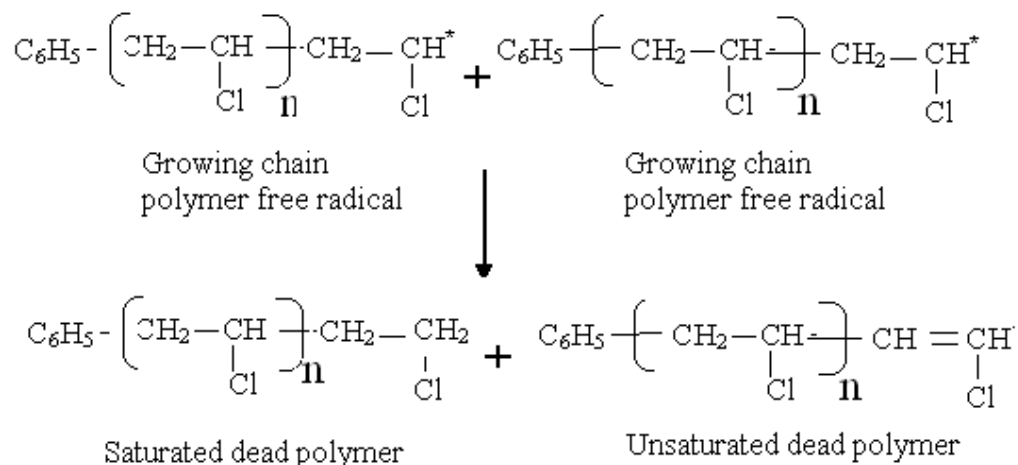
3) Chain termination:

In the termination process the growing polymer chain is transformed into a dead polymer molecule in any one of the following modes.

a) Chain termination by coupling of two new free radicals: When two growing polymer free radical reacts with each other it results in the formation of a dead polymer.

$$C_6H_5 - \left[CH_2 - CH \right]_n \cdot CH_2 - \overset{*}{CH} \quad + \quad C_6H_5 - \left[CH_2 - CH \cdot \right]_n CH_2 - \overset{*}{CH}$$

Growing chain polymer free radical   Growing chain polymer free radical

$$C_6H_5 - \left[CH_2 - CH \right]_n CH_2 - CH - CH - CH_2 \left[CH - CH_2 \right]_n C_6H_5$$

Dead polymer

c) Chain termination by disproportionation:

In this process a hydrogen atom of one growing chain is transferred to another growing chain resulting in the formation of saturated and unsaturated dead polymer.

$$C_6H_5 - \left[CH_2 - CH \right]_n \cdot CH_2 - \overset{*}{CH} \quad + \quad C_6H_5 - \left[CH_2 - CH \cdot \right]_n CH_2 - \overset{*}{CH}$$

Growing chain polymer free radical   Growing chain polymer free radical

$$C_6H_5 - \left[CH_2 - CH \right]_n \cdot CH_2 - CH_2 \quad + \quad C_6H_5 - \left[CH_2 - CH \cdot \right]_n CH = CH$$

Saturated dead polymer   Unsaturated dead polymer

Molecular weight of polymers:

Due to the varying chain lengths, a polymer is considered to have average molecular mass. 2 types of average molecular masses have been recognized namely, number average and weight average molecular masses.

Number average molecular mass: It is obtained by dividing the total weight of the monomers with the number of monomer molecules present in polymer i.e.,

$$\overline{M_n} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

Where n_1, n_2, n_3 are the number of molecules having masses M_1, M_2, M_3 respectively. The above equation can also be written as, $\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$

Where M_i is the masses of monomers and n_i is the number of monomers.

Weight average molecular mass: It gives the representation to different molecular species in proportion to their weight in the given polymer molecule.

$$\overline{M_w} = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3}{w_1 + w_2 + w_3}$$

Where w and M represent the weight and molecular masses of each species present in polymers. Since w= nM,

$$\overline{M_w} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Glass Transition Temperature (Tg)

Definition: "The temperature below which a polymer is hard, brittle, above which it becomes soft, flexible". It is denoted by Tg.

Eg: If an ordinary rubber ball is cooled, it becomes harder and harder and becomes so harder. When it reaches -70 $^{\circ}$C that it will break into pieces like a glass ball. When warmed the ball regains its rubbery state.

The hard brittle state of a polymer is called glassy state and soft, flexible state of a polymer is called rubbery state.

Significance of Tg:

1. Tg value is a measure of flexibility of polymers.
2. The use of any polymer at any temperature is decided by its Tg value.
3. Gives an idea of the thermal expansion, heat capacity, electrical and mechanical property of polymers.

Factors influencing Tg: There are several factors which influence the Tg. The important factors are:

1. Chain flexibility
2. Inter molecular forces
3. Molecular Mass
4. Branching and cross linking

5. Stereo regularity

1) Chain flexibility: Polymers with greater chain flexibility have low Tg value. Chain flexibility is due to rotation around chain bonds. Polymer chains consisting of linear sequence with no restrictions for free rotation around chain bonds have low Tg value. Substitution of bulky group to polymer prevents the free rotation around chain bonds and increases Tg.

Example, poly ethylene (linear) is having Tg,-110 $^{\circ}$C, poly propylene (-CH$_3$ bulky group) is having Tg,-20 $^{\circ}$C and poly styrene (bulky benzene group) is having Tg 100 $^{\circ}$C.

2) Intermolecular forces: Intermolecular forces of attraction between polymer chains are Vander Waal's force, dipole force and hydrogen bond. If a polymer has low intermolecular forces, polymer chains are relatively flexible, and possess low Tg value.

3) Molecular Mass: Tg of a polymer is also influenced by its molecular mass. Generally the Tg of a polymer increases with increase in the molecular mass up to 20,000 and beyond this there is no change.

4) Branching and Cross linking: A small amount of branching will tend to lower the Tg. Increase in chain ends in branched chain polymers increase free volume thus decreasing the Tg. Cross linking of polymer chains decreases the flexibility of a polymer and therefore as the extent of cross linking increases the Tg value increases.

5) Stereo regularity: In syndiotactic polymers, substituent groups attached to polymer chain lie alternatively above and below the plane of polymer chain. In isotactic polymers, substituent groups lie above or below the plane of the polymer chain. Random sequence of position of substituent group gives atactic polymers. Tg of sydiotactic polymer is higher than isotactic which has higher Tg than atactic polymers.

<center>**Structure – property Relationship:**</center>

1) Crystallinity of polymers: A polymer is said to be crystalline if all the molecules are arranged in an orderly manner, with symmetrical orientation, with higher force of attraction between the two chains. Crystalline regions are formed when individual chains are linear or contain no bulky groups and are closely arranged parallel to each other. The chains of a polymer are held together by secondary forces like hydrogen bonding, vanderwaals forces, polar interaction etc. Such type of close packing imparts high degree of crystallinity. Polymers like HDPE, PVC exhibit high crystallinity.

2) Chemical Resistivity: The resistance to chemical attack of a polymer depends on number of structural factors such as
1. The presence of polar groups or non polar groups
2. Degree of crystallinity and Molecular mass
3. The degree of cross linking

The presence of polar groups or non polar groups: A polymer having polar groups (-OH or -COOH group) are usually dissolved by polar solvents such as water or alcohols. Polymers with non polar groups like –CH$_3$, C$_6$H$_5$ dissolved in non polar solvents such as benzene, CCl$_4$, etc. Polymers with large number of aromatic group dissolved in aromatic solvents such as benzene toluene etc. Polymers containing ester group (polyester) undergo hydrolysis with

strong alkalies at high temperature. Polyalkanes, PVC, Fluorocarbons are the some polymers which have a high degree of chemical resistivity.

Degree of crystallinity and Molecular mass: For polymers having the same chemical character, the chemical resistance increases with increase in the degree of crystallinity. This is due to dense packing of the chain and the crystalline regions which makes the penetration of the solvent more difficult.

The degree of cross linking: Greater the degree of cross linking lesser is the solubility.

3) Tensile strength: The tensile strength of a polymer is an important mechanical property. This property is directly dependent on the molecular mass. High molecular mass polymers are tougher and more heat resistant. These polymers accounts for high tensile strength. Tensile strength increases with molecular mass up to 20,000 and thereafter the increase is negligible. The useful range is 200 to 20,000.

4) Elasticity: The elastomers are characterized by the high degree of elasticity. The elastic deformation in polymers arises from the typical coiled structure of the polymer chains in the normal unscratched state. The polymers chains are in a random arrangement. When stretched the coiled chains begin to straighten out. As a result the force of attraction between different chains increases thereby causing stiffening of the material. When the strain is released, they return to their original coiled form. Natural rubber and all synthetic rubbers exhibit this property.

Synthesis, properties and applications of some polymers:

1) Poly (methyl methacrylate): (PMMA, plexiglass)

Synthesis: It is synthesized by bulk or suspension polymerization of methyl methacrylate at 60-70°c in the presence of H_2O_2 as initiator.
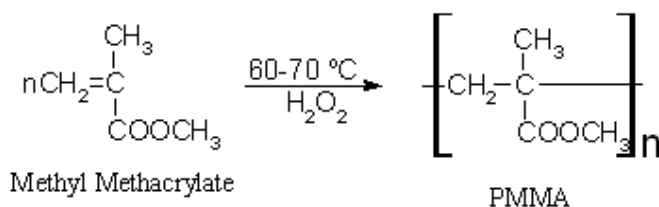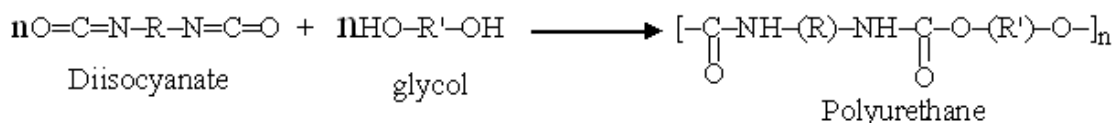

Properties:

1. It is a white transparent thermoplastic.
2. It has high optical clarity.
3. It is soluble in many organic solvents.

Applications:

1. It is used for making lenses; sign boards chemical instruments, etc.
2. It is used for making aircraft window, artificial eyes, etc.

1) Polyurethanes:

Synthesis: It can be synthesized by the polymerization of di-isocyanate with glycol.

$$nO=C=N-R-N=C=O + nHO-R'-OH \longrightarrow [-\underset{O}{\underset{\|}{C}}-NH-(R)-NH-\underset{O}{\underset{\|}{C}}-O-(R')-O-]_n$$

Diisocyanate   glycol   Polyurethane

Properties:

1. It is a spongy, transparent, polymer.
2. It has high degree of flexibility.
3. It is resistance to water, oil and corrosive chemicals.

Applications:

1. It is used for tyre retreading and industrial wheels.
2. It is used for making light weight garments, swim suits, etc.
3. It is used as cushions for furniture & automobiles.

2) Polycarbonate:

Synthesis: It is synthesized by the reaction between Bisphenol-A and phosgene.

Bisphenol-A   Phosgene   Polycarbonate
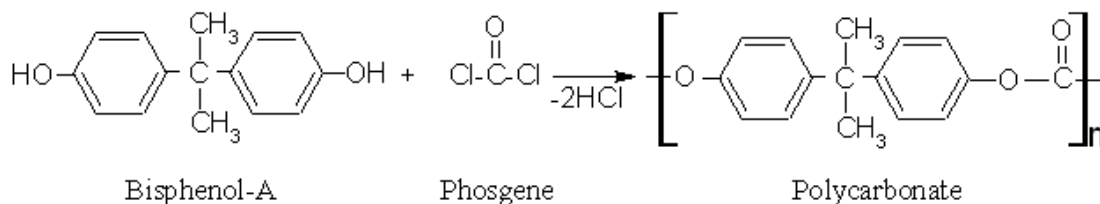
Properties:

1. It is a partially crystalline and transparent.
2. It has high impact strength and resistant to water.
3. It is thermally stable
4. It has good electrical insulation properties.

Applications:

1. It is used for making laboratory safety shields, bullet-proof windows and safety helmets.
2. It is used for making automobile parts, table wares, food containers etc.
3. It is used for making food processor bowls, microwave cookware's etc.

ELASTOMERS

Definition: Elastomers are high polymers which undergo very large elongation under stress but readily regain their original shape when the stress is removed. This property of elastomers is called "*elasticity*".

Elasticity arises from the fact that, in an unstreched condition, an elastomer molecule is not straight chained, <u>but it is in the form of coil</u>.
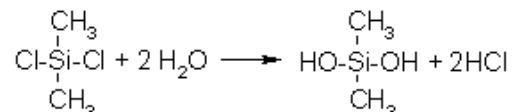
Synthesis and applications of Silicone rubber:

Synthesis: Silicon tetrachloride on treatment with methyl magnesium chloride (Grignard reagent) gives dimethyldichlorosilane.
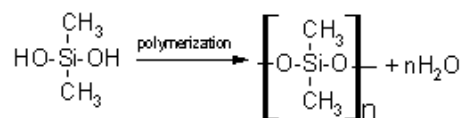
$$SiCl_4 + 2CH_3MgI \longrightarrow (CH_3)_2SiCl_2 + 2MgICl_2$$
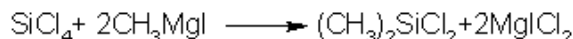
Grignard reagent   Dimethyldichorosilane

Dimethyldichorosilane undergo hydrolysis to give dimethylsilanol

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl-Si-Cl}} + 2H_2O \longrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HO-Si-OH}} + 2HCl$$

Dimethylsilanol is unstable & immediately undergo intermolecular condensation to give Silicone rubber.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HO-Si-OH}} \xrightarrow{polymerization} \left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O-Si-O}} \right]_n + nH_2O$$

Properties:
1. It has very low tensile strength.
2. It offers good resistance to temperature from -55 °C to +300 °C.
3. Highly inert material and does not react with most of the chemicals.

Applications:

1. Silicone rubber can be moulded into custom shapes and design.
2. It is used in making variety of cooking, baking and food storage products.
3. It is used in undergarments, sportswear and footwear.

ADHESIVES
Definition: "An adhesive is a polymeric substance used to bind together two or more materials by surface attachment".

Epoxy resins (araldite): Synthesis: Epoxy resins are manufactured by the condensation polymerization of Bisphenol-A with Epichlorohydrin in the presence of alkaline catalyst.

Bisphenol-A   Epichlorohydrin   Epoxy resins
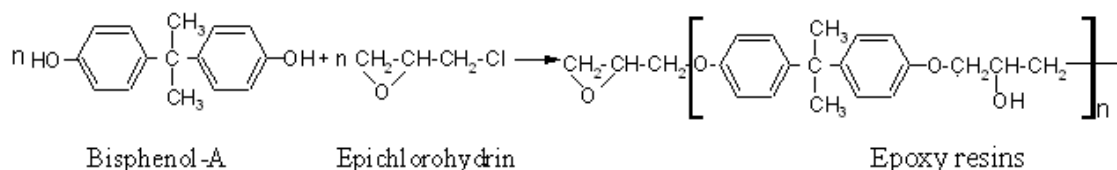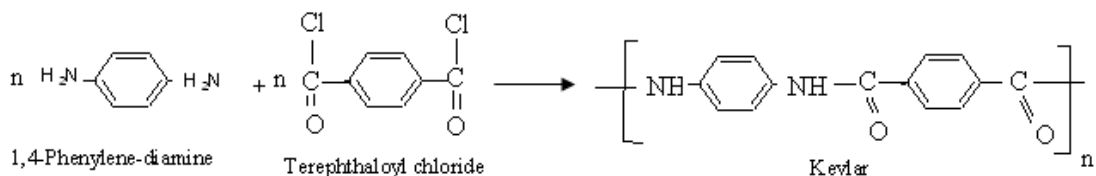
Properties:

1. These are linear, low molecular weight polymers.
2. Soluble in organic solvents.
3. After adhesion these are highly resistant to water, solvents, alkalies, acids.

Applications: Used as adhesives to bind the two materials. Used as laminating materials in electrical equipments. Used for skid resistant surface for highways.

POLYMER COMPOSITES

The combination of two or more distinct components to form a new class of material suitable for structural applications is referred to as composite materials. When one of the components is a polymer, resulting composite called as polymer composite.

Kevlar: Kevlar is synthesized in solution of N-methyl-pyrrolidone & calcium chloride from the monomers 1, 4-phenylene-diamine (para-phenylenediamine) & terephthaloyl chloride through a condensation reaction with liberation of HCl as a byproduct.

Properties:

1. It has very light weight.
2. It has high tensile strength and stiffness.
3. It has very good corrosion resistance.

Applications of Kevlar:

1. It is used to make light weight boat hulls
2. aircraft fuselage panels, pressure vassals, high performance race car, bullet proof vests,
3. Used in puncture resistance bicycle tyres etc.

CONDUCTING POLYMERS

Definition: "An organic polymer with highly delocalized pi-electron system having electrical conductance is called conducting polymer".
Ex: Polyacetylene, polypyrrole, polythiophene, polyphenylene, polyaniline, etc.

Mechanism of conduction in polyaniline:

Mechanism follows protonic acid doping. In this type current carrying charged species are created by the protonation of imine N_2. The mechanism steps are as follows.
1. Polyaniline is first partially oxidized using suitable oxidizing agent into base form of polyanilne.
2. This base form of polyaniline when treated with aqueous 1 M HCl, undergo protonation of imineN_2 creating current carrying positive charges in polyaniline.
3. The positive charges are compensated by anions of doping agent, resulting in corresponding salt.
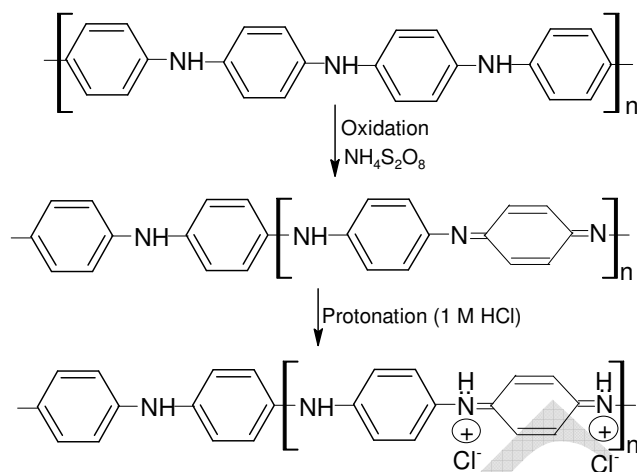
Applications of polyaniline:

1. It is used in packing electronics products.
2. It is used in sensors and biosensors in glucose sensing for medical applications.
3. It is used in electronic devices like batteries, capacitors etc.

Most probable Questions

1. What are polymers? Explain the free radical mechanism of polymerization taking vinyl chloride as example.
2. Explain the types of polymerizations with an example.
3. Define glass transition temperature of a polymer?
4. Explain number average and weight average molecular mass of polymers.
5. How the following factors affect the glass transition temperature
     (i) Cross linking (ii) Presence of intermolecular forces
6. How the following factors influence the properties?
     (i) Crystallinity   (ii) Tensile strength   (iii) Chemical resistance.
7. How are the following manufactured?
      (i) Polyurethane (ii) PMMA iii) polycarbonate. Mention few properties & application of each of them.
8. How the Silicone rubber is prepared? Mention two uses.
9. How epoxy resins are obtained? Mention the applications.
10. What are conducting polymers? Give applications of conducting polymers.
11. Explain the mechanism of conduction in polyaniline.
12. Explain the synthesis & applications of Kevlar.

MODULE 5
WATER CHEMISTRY

Water Technology: Introduction**,** boiler troubles with disadvantages & prevention methods-scale and sludge formation, priming and foaming, boiler corrosion (due to dissolved O2, CO2 and MgCl2). Determination of DO, BOD and COD, numerical problems on COD. Sewage treatment: Primary, secondary (activated sludge method) and tertiary methods. Softening of water by ion exchange process. Desalination of sea water by reverse osmosis & electro dialysis (ion selective).

COURSE OUTCOME: Boiler troubles; sewage treatment and desalination of sea water.
INTRODUCTION:
Water is one of the most basic and essential component of all life. It covers nearly 72% of the earth's surface. It is the second most important substance required to sustain human, animal, and plant lives. Water is essential resource for living system, industrial processes, agricultural production, and domestic use.

Pure water is a clear, colorless, and odorless liquid that is made up of one oxygen and two hydrogen atoms. The chemical formula of the water molecule, H_2O, was defined in 1860 by the Italian scientist **Stanislao Cannizzarro.** Water is a very powerful substance that acts as a medium for many reactions, which is why it is often referred to as the "universal solvent." Although pure water is a poor conductor of electricity, impurities that occur naturally in water transform it into a relatively good conductor. Water has unusually high boiling (100° C/212° F) and freezing (0° C/32° F) points. It also shows unusual volume changes with temperature. As water cools, it contracts to a maximum density of 1 grain per cubic centimeter at 4° C (39° F). Further cooling actually causes it to expand, especially when it reaches the freezing point. The fact that water is denser in the liquid form than the solid form explains why an ice cube floats in a beverage, or why a body of water freezes from the top down. While the density property of water is of little importance to the beverage example, it has a tremendous impact on the survival of aquatic life inhabiting a body of water.   Water exists in many forms in the nature. i.e. in the form of clouds, rain, snow, ice and fog. The distribution of water on the earth is as follows.

Boiler feed water
        The boilers are used in industries to generate steam. This steam is used in power production, sterilization etc. The water used to generate steam in boiler s called boiler feed water.

Boiler Troubles:
     Water used to generate steam is contaminated; it brings problem to boiler and reduces its efficiency. The major boiler troubles are
1. Scale and sludge formation
2. Priming and foaming
3. Boiler corrosion

1. Scale formation:
        During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is hard and strongly adhering on the inner walls of the boiler is known as scale.
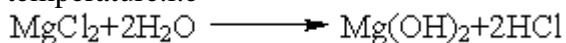**Causes for scale formation:**

The various dissolved salts of water are responsible for scale formation

1. Decomposition of bicarbonates: bicarbonates undergo decomposition and forms insoluble carbonates. i.e.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + CO_2 + H_2O$$
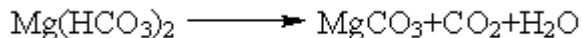
2. Presence of silica: Impurities like calcium silicates, magnesium silicates are highly insoluble in hot water, they precipitate and deposit as scale

3. Hydrolysis of salts of magnesium: Magnesium salts are precipitated as their hydroxides at high temperature.i.e

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

Prevention of scale formation:

The scale formation in boilers can be controlled by two methods.

1. By feeding soft water (external treatment): Water used in boilers is purified by removing suspended and hardness impurities. Suspended impurities are removed by sedimentation and filtration process and hardness is removed by lime soda or ion exchange methods.

Prevention of sludge formation:

2. By internal treatment: Process of adding chemicals directly to water in boilers to remove the scale forming impurities which were not removed during external treatment methods is known as internal treatment. In this process, an ion is prohibited to exhibit its original character by complexing or by converting into more soluble salt by adding appropriate reagent.

Example: colloidal conditioning, phosphate conditioning, carbonate conditioning.

Disadvantages of Scale:

1. Wastage of fuel: Scales have a poor conductor of heat, so the rate of heat transfer from boiler to water is greatly reduced.

2. Reduces boiler efficiency: Decomposition of scales in the valves and condensers of the boiler, choke them partially.

3. Increase in cleaning expenses: Scales must be removed regularly and this cleaning process is very expensive.

4. Lowering of boiler safety: The overheating of the boiler tube makes the boiler material softer and weaker.

5. Danger of explosion: The scale formation also leads to uneven expansion of boiler material.

Sludge formation:

During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is soft, loose and suspended in boiler feed water is called as sludge.

Causes for sludge formation:

The impurities of water which causes sludge formation are $MgCO_3$, $MgSO_4$, and MgCl2 etc. If the sludge is not removed periodically, then it will form scale.

Prevention of sludge formation:

Sludge formation can be prevented by using softened water, more over sludge can be removed by flowing off technique ie. by drawing off some of the concentrated water from the bottom of the boiler through a tap.

Disadvantages of scale and sludge formation:

1. The sludge is bad conductor of heat. So it requires more heating of boiler to produce steam which results in wastage of fuel.

2. Because of more and more heating of boiler, there is a chance of explosion of the boiler

3. It reduces the efficiency of boiler.
4. Sludge's need to be removed regularly and this cleaning process is expensive.

2. Priming: The process of carrying water droplets along with steam is called priming.
Causes for Priming:
1. Formation of steam of high velocity
2. Sudden boiling
3. Maintaining very high water levels in boiler
4. Presence of dissolved impurities in boiler feed water
Prevention of priming:
1. Filtration of the boiler feed water by fitting mechanical purifiers.
2. By supplying soft water by changing boiler water from time to time.
3. By avoiding rapid change in steaming velocity.
4. Maintain low water level.
Disadvantages of priming
1. Due to priming , it reduces the heating ability of steam
2. Priming causes corrosion of blades and pipelines
3. It reduces the life of engine.
4. A sudden boiling
5. An improper design of boiler

Foaming: The process of formation of persistent boubles on the surface of boiler water is called foaming.
Causes for Foaming:
1. The difference in the concentration of dissolved salts between surface layer and bulk of the water in boiler.
2. Due to the presence of impurities like oils, fats etc.forms foaming
Prevention of foaming:
1. The addition of anti foaming agents like caster oil.
2. The removal of foaming from boiler water by adding aluminium compounds like sodium aluminates and aluminium sulphate.
Disadvantages of foaming:
1. It is difficult to maintain boiler pressure
2. Decreases the boiler efficiency

3. Boiler corrosion
The decay of boiler material due to the presence of impurities in boiler feed water is called boiler corrosion.
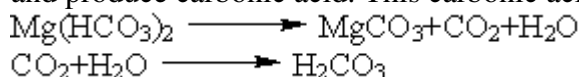**Causes for Boiler corrosion:**
1. Corrosion due to dissolved Oxygen:
When water containing dissolved oxygen is heated in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler material and forms the rust.
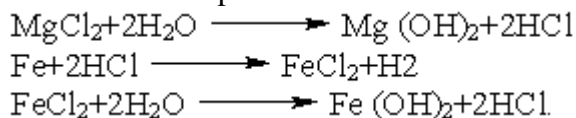
$$4Fe + 4H_2O + 2O_2 \longrightarrow 4Fe(OH)_2$$
$$4Fe(OH)_2 + O_2 \longrightarrow 2Fe_2O_3.2H_2O$$
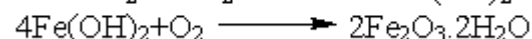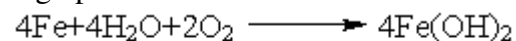
2. Corrosion due to dissolved carbon dioxide:

The CO_2 is obtained from the decomposition of bicarbonates. So formed CO_2 is react with H_2O and produce carbonic acid. This carbonic acid is slightly acid and corrosive in nature.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + CO_2 + H_2O$$
$$CO_2 + H_2O \longrightarrow H_2CO_3$$

3. Corrosion due to $MgCl_2$:

The salts like $MgCl_2$ in boiler feed water forms hydroxides and acid. The acid so formed will attack the boiler parts and causes corrosion.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
$$Fe + 2HCl \longrightarrow FeCl_2 + H2$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

Prevention of boiler corrosion:

Boiler corrosion can be controlled by reducing the quantities of O_2, CO_2 and any acid from the feed water.

1. By removing oxygen: Dissolved oxygen can be removed by treating boiler feed water with sodium sulphite or hydrazine.

2. By removing carbon dioxide: Lime stone easily removes carbondioxide or by adding ammonium hydroxide.

3. Finally acidic impurities if there any can be removed by treating with alkaline agents like ammonium hydroxide.

DETERMINATION OF DISSOLVED OXYGEN (DO): (WINKLER'S METHOD)

The dissolved oxygen can be determined either by the Winkler (iodometric) method or by the use of dissolved oxygen electrodes. The results are either expressed as a simple concentration (mg/l) or as a percentage of full saturation.

Principle: The dissolved oxygen is not capable of oxidizing KI. Therefore oxygen carrier like $Mn(OH)_2$ is produced in water to liberate I_2 from KI. The liberated Iodine is titrated against $Na_2S_2O_3$ by using starch as indicator.
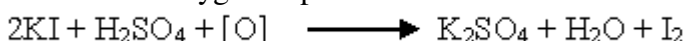
$$MnSO4 + 2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

The $Mn(OH)_2$ is reacted with DO to form oxygen carrier ie manganic oxide.

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

The manganic oxide is treated with H_2SO_4 to liberate nascent oxygen.

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$$
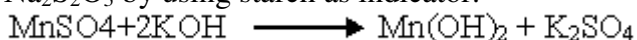
The nascent oxygen in presence of acid react with KI to liberate equivalent amount of iodine.

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + H_2O + I_2$$

The liberated iodine is titrated against $Na_2S_2O_3$ using starch indicator

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Procedure:

1. Pipette out 300 ml of water sample into a clean glass stoppered bottle.

2. Add 3 ml $MnSO_4$ solution and 3 ml alkaline KI solution. The bottle is closed immediately and shakes well to get brown precipitate. Allow the precipitate to settle down at the bottom.

3. Add 1 ml of concentrated H_2SO_4 slowly and mix well. Precipitate dissolves completely liberating iodine.

4. Pipette out 100 ml of this solution into a clean conical flask.

5. Titrate against 0.02N $Na_2S_2O_3$ using freshly prepared starch as indicator.

6. Record the volume of the $Na_2S_2O_3$ solution used.

Calculations:

$$Normality \times Volume\ of\ oxygen = Normality \times Volume\ of\ Na_2S_2O_3$$

$$Therefore\ Normality\ of\ oxygen = \frac{Normality \times Volume\ of\ Na_2S_2O_3}{Volume\ of\ oxygen\ solution}$$

$$= \frac{N \times V}{100}$$

$$= a$$

$$Mass\ of\ dissolved\ oxygen/dm^3 = N \times Equivalent\ mass\ oxygen$$

$$= a \times 8.0 \times 1000\ mg/L$$

DETERMINATION OF BOD BY WINKLER'S METHOD:

Definition of BOD: Biological Oxygen Demand is an important measure of water quality. BOD is defined as "The amount of oxygen required by microorganism to oxidize the organic matter in a water sample over a period of 5 days under aerobic condition at 20 ^{0}C".

Characteristics of BOD:

1) The unit of BOD is mg/dm^3 or ppm.
2) Determination is slow and time consuming method.
3) It represents only biodegradable organic matter under aerobic condition.

Principle: The dissolved oxygen is not capable of oxidizing KI. Therefore oxygen carrier like Mn (OH)$_2$ is produced in water to liberate I$_2$ from KI. The liberated Iodine is titrated against Na$_2$S$_2$O$_3$ by using starch as indicator.

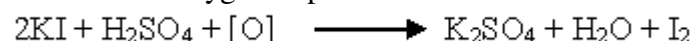The oxygen carrier is produced by the reaction of MnSO$_4$ and KOH.
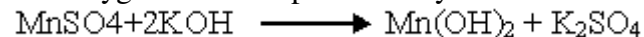
$$MnSO4 + 2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

The Mn(OH)$_2$ is reacted with DO to form oxygen carrier ie manganic oxide.

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

The manganic oxide is treated with H$_2$SO$_4$ to liberate nascent oxygen.

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$$

The nascent oxygen in presence of acid reacts with KI to liberate equivalent amount of iodine.

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + H_2O + I_2$$

The liberated iodine is titrated against Na$_2$S$_2$O$_3$ using starch indicator

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
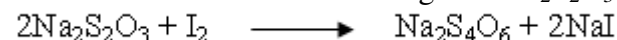
Procedure: A known volume of sewage sample is diluted to definite volume with water which contains nutrients for bacterial growth and sufficient oxygen. The diluted sample is separated in two bottle of equal volume.

DO at zero time (D$_1$): DO content in one of the BOD bottle is determined immediately.

Procedure:

1. Pipette out 300 ml of water sample into a clean glass stoppered bottle.
2. Add 3 ml MnSO$_4$ solution and 3 ml alkaline KI solution. The bottle is closed immediately and shakes well to get brown precipitate. Allow the precipitate to settle down at the bottom.
3. Add 1 ml of concentrated H$_2$SO$_4$ slowly and mix well. Precipitate dissolves completely liberating iodine.
4. Pipette out 100 ml of this solution into a clean conical flask.
5. Titrate against 0.02N Na$_2$S$_2$O$_3$ using freshly prepared starch as indicator until blue colour disappears.
6. Record the volume of the Na$_2$S$_2$O$_3$ solution used.

Do after 5 days (D$_2$): The second bottle is incubated for 5 days at 20 ^{0}C. After 5 days DO is measured as described above. (D$_2$). Then BOD is calculated from the formula

Calculation:

$$Normality \times Volume\ of\ oxygen = Normality \times Volume\ of\ Na_2S_2O_3$$

$$Therefore\ Normality\ of\ oxygen = \frac{Normality \times Volume\ of\ Na_2S_2O_3}{Volume\ of\ oxygen\ solution}$$

$$= \frac{N \times V}{100}$$

$$= a$$

$$Mass\ of\ dissolved\ oxygen/dm^3 = N \times Equivalent\ mass\ oxygen$$

$$= a \times 8.0 \times 1000\ mg/L$$

Mass of dissolved oxygen is D$_1$ similarly calculate for second bottle ie D$_2$.

$$BOD = \frac{D_1 - D_2}{A} \times B\ mg/dm^3$$

Where D$_1$ is the DO in the solution at start, D$_2$ is the DO in the solution after 5 days, 'A' is the volume of the sample before dilution and 'B' is the volume of the sample after dilution.

DETERMINATION OF COD OF WASTE WATER:

Definition of COD: It is defined as "The amount of oxygen required for the complete oxidation of both organic & inorganic matter present in 1 litre of waste water using strong oxidizing agent".

Characteristics of COD:

1)   The unit of COD is mg/dm^3 or ppm.

2)   In general COD > BOD since both biodegradable and non biodegradable organic load are completely oxidized.

Principle: In this method, the given samples of water containing organic and inorganic impurities are oxidized by $K_2Cr_2O_7$ in acidic media in the presence of catalyst Ag_2SO_4 and $HgSO_4$.(Added to prevent the interference the chloride and silver ions). The unreacted $K_2Cr_2O_7$ is titrated against FAS solution in the presence of a redox indicator, ferroin which shows its color change in the oxidized (bluish green) and reduced states (reddish brown).

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + 3(O)$$

$$3(O) + 2CHO \longrightarrow 2CO_2 + H_2O$$
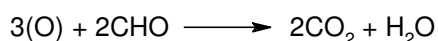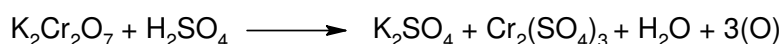
Procedure: **Preparation of standard solution:** Standard FAS solution is prepared by adding dilute H_2SO_4 (Added to prevent hydrolysis of FAS) to a known weight of FAS salt.

1.   Pipette out known amount of the waste water into a clean conical flask.
2.   Add 10 ml of $K_2Cr_2O_7$ and 10 ml 1:1 H_2SO_4 into a conical flask.
3.   Add 1 g of Ag_2SO_4 followed by 1 g of $HgSO_4$ and warm if necessary.
4.   Titrate with standard FAS using ferroin as indicator till color changes from bluish green to reddish brown.
5.   Note down the volume of FAS consumed as 'V$_1$' ml.

Perform the blank titration without waste water sample. Note down the volume as 'V$_2$' ml.

Calculations:

Normality of FAS = 'A' N

Volume of FAS consumed during blank titration = B cm^3

Volume of FAS consumed during Back titration = C cm^3

Volume of FAS consumed for the titration = (B − C) cm^3

Volume of water sample = V cm^3

1 ml of 1N FAS = 8 mg of oxygen

(B-C) cm^3 of 'A'N FAS = A*(B-C)*8 mg of oxygen

V cm^3 of water sample = $\dfrac{A*(B-C)*8}{V}$ mg of oxygen

Therefore 1000cm3 of water sample = $\dfrac{A*(B-C)*8*1000}{V}$ mg/dm^3 of oxygen

SEWAGE: Water containing any one of the waste is called as **effluent or sewage**.

SEWAGE TREATMENT: The water containing heavy load of BOD, pathogenic bacteria, colour and annoying smell can't be directly discharged into the rivers as they mainly affect the aquatic life and causes many water borne diseases. The domestic sewage therefore needs proper treatment which is carried out in 3 stages

- Primary treatment
- Secondary treatment
- Tertiary treatment

Primary treatment: It involves

Screening: Removal of large suspended or floating matter in sewage using mesh screens.

Silt and Grit removal: Removal of heavy particles like sand, glass pieces etc. using grit chambers.

Removal of oil and grease: is mainly done using skimming tanks by blowing air through the sewage and oils are lifted to the surface as foams (soapy mixture)which is then skimmed off.

Sedimentation process: involves addition of coagulants like alum, ferrous salts etc. and there by ppt. out the suspended particles by sedimentation process.

Secondary treatment:

It involves aerobic biological oxidation of sewage water. The sewage water after sedimentation is subjected to aerobic oxidation during which the organic matter is converted into H_2O and CO_2 and N_2 to NH_3 and finally to nitrates and nitrites.

Activated Sludge Method (Biological treatment): Activated sludge is a thick greasy mud containing aerobic bacteria.

This method involves extensive aeration of the sewage water after primary treatment is mixed with activated sludge and allowed to enter in a large aeration tank for biological treatment. Air is continuously passed into tank to maintain the aerobic condition. Under these condition microorganisms present in activated sludge attack on organic matter of sewage and decomposes them into CO_2 and H_2O. The effluent after this treatment is passed to sedimentation tank where sludge will settle down. The clear effluent is sent to tertiary treatment. A part of sludge is used for further treatment and rest is disposed off and used as manure.

Activated sludge treatment process
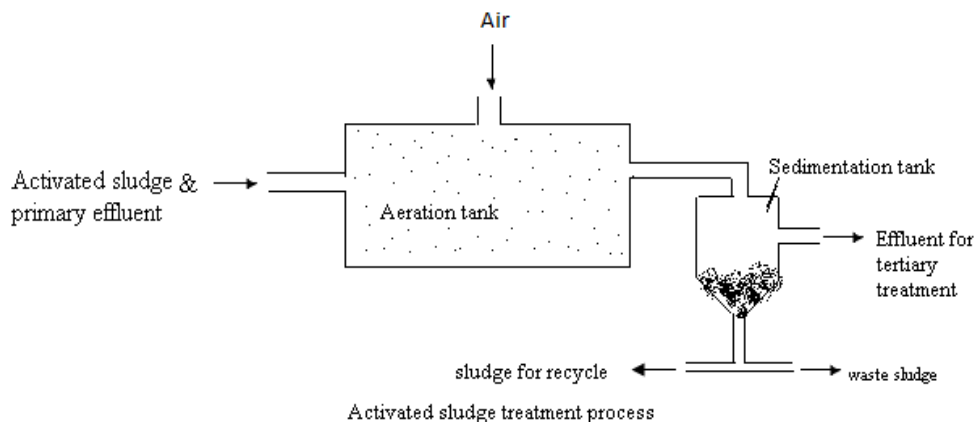
Tertiary treatment: It involves

Removal of phosphate using lime

$$PO_4^{3-} + Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2$$
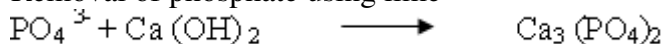
Removal of heavy metals by sulphides.

$$Hg + S \longrightarrow HgS$$

Degasification of NH_3, H_2S, and CO_2 by stripping hot water.

Disinfection of microorganisms by chlorine. Acid kills microorganisms.

$$Cl_2 + H_2O \longrightarrow HOCl \text{ (hypochlorous acid)}$$

Softening of water by Ion exchange process:

In this method all the ions present in water are removed. In this insoluble ion exchange resins are used. Resins means it is a long chain organic polymer with functional groups. Depending upon the functional groups attached to resins they are classified into

1. Cation Exchange Resin:

These resins exchange its H^+ ions with cations of water sample. Generally it is expressed as RH^+

2. Anion Exchange Resin:

These resins exchange its OH^- ions with anions of water sample. Generally it is expressed as ROH^-

Working:

The ion exchange resin contains two compartments. One is cation exchange resin and another is anion exchange resin. For the regeneration of respective resins, acid and alkali regeneration units are connected to compartments. The schematic diagram of ion exchange unit as shown in fig.

The water sample containing high minerals are first allowed to pass through cation exchange resins, which exchanges its H^+ ions with Ca^{2+} ions of water .i.e

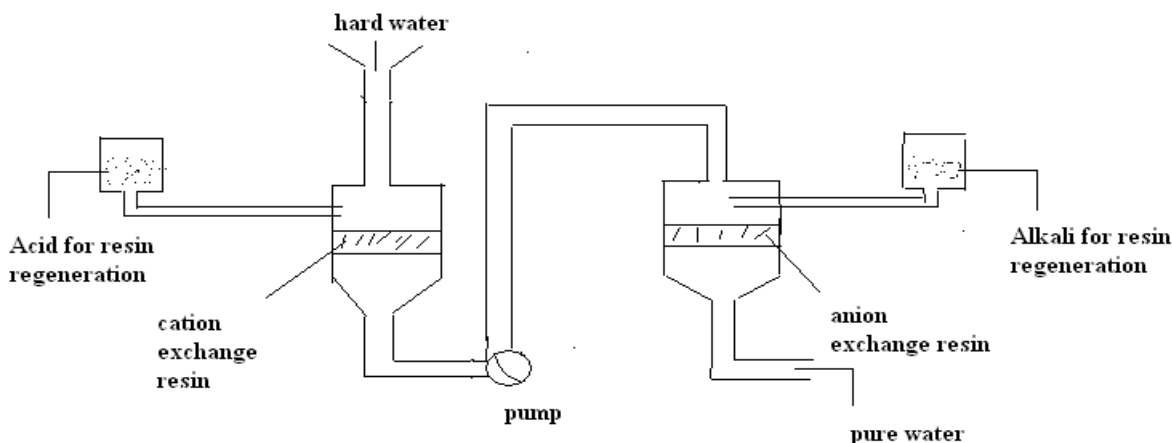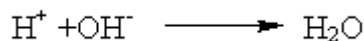$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$
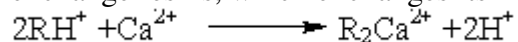
Now the water sample is free from cations.

The same water is further allowed to pass through anion exchange resin, which exchanges its OH- ions with Cl- of water. i.e.

$$ROH^- + Cl^- \longrightarrow RCl^- + OH^-$$

Now the water is totally free from all the ions.

Now H^+ ions formed at cation exchange resin and OH^- ions formed at anion exchange resin will combine to form pure water.

$$H^+ + OH^- \longrightarrow H_2O$$

Advantages:
1. The ion exchange apparatus, once set up, is easy to operate and control.
2. Both acidic and alkaline water can be softened.
3. Water of very low hardness is produced.
4. Water produced by this method is used as boiler feed water.

Disadvantages:
1. Equipment and process is costly.
2. Turbid water needs to be filtered first before softening.

POTABLE WATER-Water that is fit for human consumption and free from pathogenic bacteria and toxic chemicals is called potable water.

DESALINATION-The process of removal of dissolved salts from sea water to the extent that water becomes usable is described as desalination. The important methods of desalination are a) Reverse Osmosis.   B) Electrodialysis.

REVERSE OSMOSIS:
Principle: - The principle of osmosis is that water flows from lower concentration to higher concentration side through semi permeable membrane. If the pressure is applied on solution side, the solvent will flow in the reverse direction. This is called reverse osmosis.
It is studied that sea water exerts an osmotic pressure of about 4500-5500 KPa. In reverse osmosis, hydrostatic pressure which is greater than osmotic pressure is applied on the salt solution side then water flows from salt solution to fresh water side. This water can be used for human consumption.

Reverse Osmosis
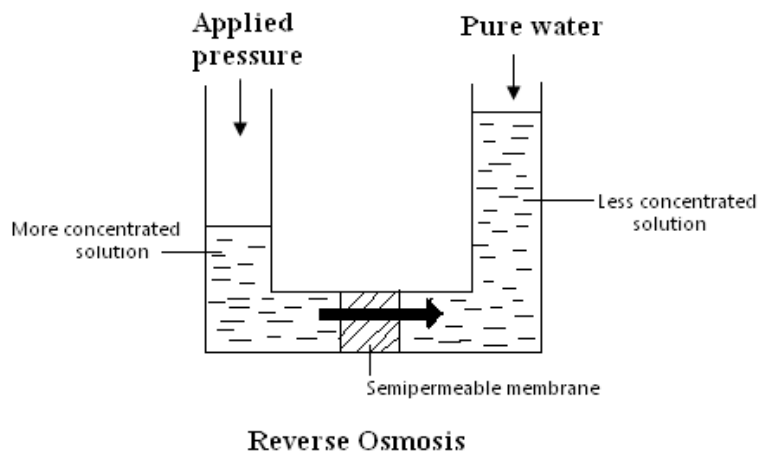
Application:
1. It is economical, simple and continuous.
2. The process needs extremely low energy.
3. It has long life and membrane is easily replaceable.

ELECTRODIALYSIS: The process of migration of ions present in the solution towards the oppositely charged electrodes under the influence of applied emf is known as electrodialysis.

It consists of two electrodes and ion selective membranes which are permeable to either cation or anion. The anode is placed near anion selective membrane, while the cathode is placed near to the cation selective membrane. The anion selective membrane has positively charged functional groups and allows negatively charged ions to pass through them similarly cation allows only negatively charged ions. When emf is applied between the two electrodes, the cation of salt move towards cathode ie Na^+ and anion move towards anode ie Cl^- through selective membrane. As a result the concentration of the ions in alternate compartment decreases ie 2, 4, 6 etc., and on other compartment increases ie 1, 3, 5, 7 etc., of ions. Thus water in even compartment becomes pure and is collected from the bottom. The water in odd compartment becomes rich in the salts and it is rejected.
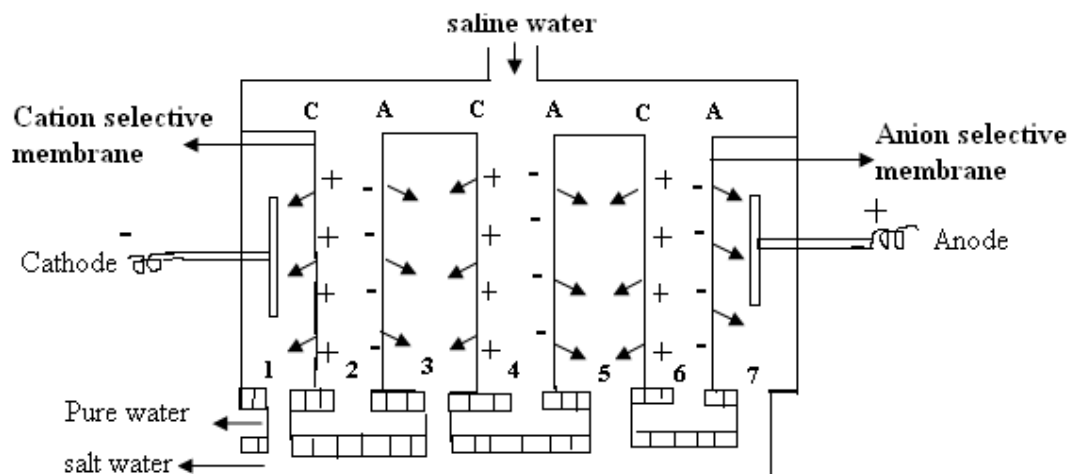
NANO MATERIALS

Nano Materials: Introduction, properties (size dependent). Synthesis-bottom up approach (sol-gel, precipitation, gas condensation & chemical vapour condensation processes). Nano scale materials- carbon nano tubes, nano wires, fullerenes, dendrimers, nano rods, & nano composites.

COURSE OUTCOME: **Over viewing of synthesis, properties and applications of nanomaterials Program.**

INTRODUCTION: Nanotechnology is a multidisciplinary science and technology and encompasses physical, chemical, biological, engineering and electronic processes. It is the study deals with various structures of matter having dimensions of the order of billionth of a meter. These materials or particles are called as nano particle. Nano technology is the making of usage and technique, in order to solve a problem to perform specific functions. The particles which are smaller than about 100nm give rise to enhance properties of nano structures built from them. Matter arranged by exercising control over length of one to hundred nanometers and the formulating structures exhibit characteristics that are specific to their size and dimensions, the resulting materials are called nano materials.

SIZE DEPENDENT PROPERTIES

a) **Surface area**: Nanomaterials have a significant proportion of atoms existing at the surface. Properties like catalytic activity, gas adsorption and chemical reactivity depend on the surface area. Therefore nanomaterials can show specific related properties that are not observed in bulk materials.

b) **Electrical properties:** the electronic bands in bulk materials are continuous due to overlapping of orbitals of billion of atoms. But in the nanomaterials, very few atoms or molecules are present so the electric band becomes separate and the separation between different electric stated varies with the size of the nanomaterials. Hence, some metals which are good conductors in bulk semiconductors and insulator as their size is decreased to nano level.

c) **Optical properties:** Nanomaterials have particular optical properties as a result of the way light intersects with their fine nanostructures. The discrete electronic states of nanomaterials allow absorption and emission of light at specific wavelength. Hence, nanomaterials exhibit unique color different from bulk materials.

d) **Magnetic properties:** Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. The large surface area to volume ration results in a substantial proportion o f atoms having different magnetic coupling with neighboring atoms leading to different magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Gold nano particles become ferromagnetic when they are capped with appropriate molecules such as thiol.

e) **Mechanical properties:** Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of the bulk materials. For

example, the bending of bulk solution(wire, ribbon etc..,) occurs readily with the movement of copper atoms/clusters at about 50nm scale. Copper nanoparticles smaller than 50nm are considered super hard materials that do to exhibit the same malleability and ductility as bulk copper.

SYNTHESIS OF NANOMATERIALS

There are two methods of preparing nanomaterials. One is top-down approach & the other is bottom-up approach.

- In top-down approach, the material is reduced from bulk size to nano scale.
Examples for top-down approach are ball milling method & nanolithography.
- In bottom-up approach, matter in atomic or molecular level gets assembled to form tiny clusters which grow to reach nano-size.
Examples for bottom-up approach are arc discharge method, chemical vapor deposition, physical vapor deposition & sol gel method.

SOL – GEL PROCESSES

Sol gel processes principle is conversion of precursor solution into gel via hydrolysis and condensation reactions.

Sol gel processes allow to synthesis of nano materials of high purity.

This process involves five steps

1. Preparation of sol: sol is prepared by suspended particles in water during suspension hydrolysis reaction takes place.

$$M\text{-}OR + H2O \longrightarrow M\text{-}OH + R\text{-}OH$$
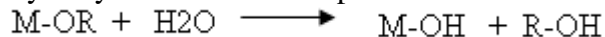
2. Conversion of sol into gel: sol is converted into gel by condensation reaction forming network between oxides. When networking takes place, the viscosity of the solution increases.

$$M - OH + M - OH \rightarrow M - O - M + H_2O$$

3. Aging of gel: during which poly condensation reaction continue until the gel is transformed into solid mass.

4. Removal of solvent: Further the solid mass is isolated from the solvent by thermal evaporation. The product formed is xerogel.

5. Heat treatment: solid mass (xerogel) obtained is dried at nearly to 800C to get fine nano particle powder.
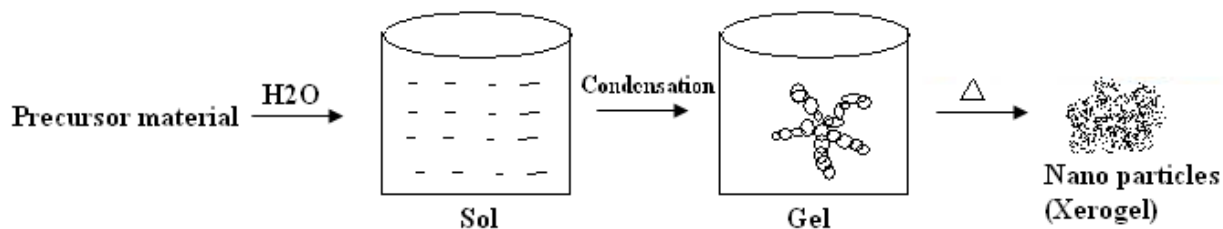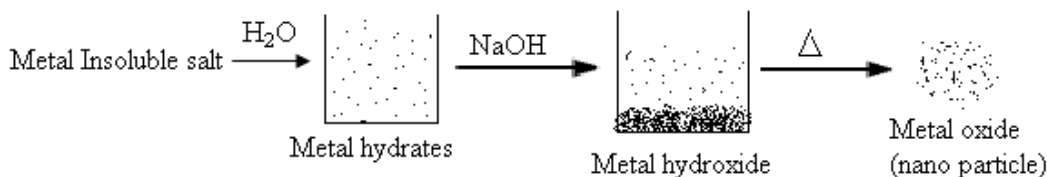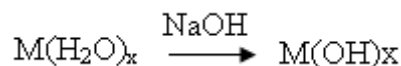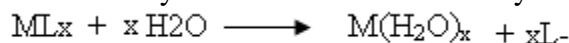
Advantages:

- ➢ Nano materials of high purity with good homogeneity can be obtained.
- ➢ Samples can be prepared at low temperature.
- ➢ Easy to control the synthesis parameters like shape and size of resulting material

PRECIPITATION METHOD

Principle: The principle involved in the precipitation of precursor materials at constant pH via condensation.

Processes: In this method inorganic metal salt such as chloride, sulphate, nitrate ions etc.., are used as precursor. Precursor materials is dissolved in water and undergo hydrolysis where metal ions exist in metal hydrates form. On adding base like NaOH/NH$_4$OH, pH of the solution changes and reaches super saturation level leading to condensation of precursor to form metal hydroxide precipitate. The precipitate is washed with water, filtered and finally calcinated at higher temperature to convert metal hydroxide into metal oxide by dehydrogenation takes place.

$$ML_x + x\,H2O \longrightarrow M(H_2O)_x + {}_xL\text{-}$$

$$M(H_2O)_x \xrightarrow{NaOH} M(OH)x$$

$$M(OH)x \rightarrow MOx + H_2O$$

Advantages: The process is relatively economical.

- ➢ The wide range of single and multi components to oxide nano powders can be synthesized.

GAS CONDENSATION

Principle: the principle of this method is to heat the bulk material to vaporize. Vapours are carried by inert gas and allow collecting in cold surface.

Process: The precursor material taken in crucible and heated to high temperature, precursor material vaporizes and that mean time inert gas is passed from bottom. Condensation reaction takes place between them.

Gas condensation
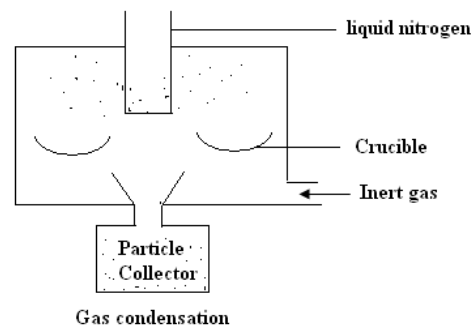
The product formed is passed onto cold surface (cool area is created on passing liquid nitrogen on to the rod). The vapors condenses on cold surface and grow, later the particles are collected in receiver plate and removed by scraping.

Advantages:

➢   Used to control the particle size and uniform size.
➢   Better suited for larger scale synthesis of nano powders.
➢   The products formed are free from impurities.

CHEMICAL VAPOUR CONDENSATION

Principle: the process involved is conversion of precursor (metal organic compound) into vapors in reduced pressure atmosphere.

Processes: the precursor (starting material) is vaporized in a bubble and mixed with inert gas like helium to carry vapors into heating furnace. Condensation reaction takes place in heating furnace at a particular temperature. The product formed after the condensation process is in the form of clusters. The clusters are then condensed into nano particles in a cold finger which are removed by scraping.

Advantages:

➢   Simple technique and does not require high vacuum
➢   It is possible to deposit nano materials with almost any shape and size.

The byproducts are removed to gas phase. Therefore the product obtained is pure.
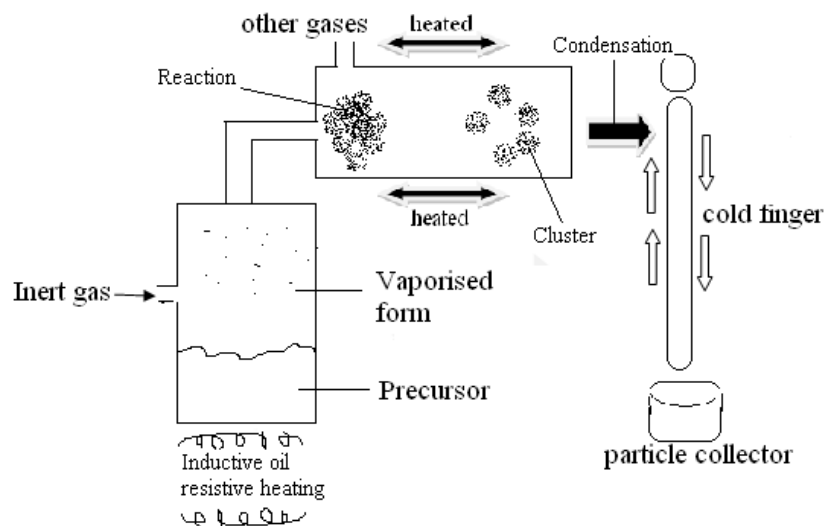
NANO SCALE MATERIAL

Nano scale materials are defined as a set of substances where atleast one dimension is less than approximately 100nm. A nanometer is one millionth of a millimeter. Nano materials are of interest because of this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine and other fields.

FULLERENES: Fullerenes are class of molecules made of only carbon atoms having closed cage like structure. Many number of fullerene molecules with different carbon atoms like C_{60}, C_{70}, C_{74}, C_{76} etc.., have been prepared but C_{60} is more stable. The C_{60} molecule had spherical

shape resembling a soccer ball (foot ball). It is also commonly called as Bucky ball. The C_{60} molecule consist of 12 pentagons and 20 hexagons and each pentagon is surrounded by five hexagons and each hexagon is surrounded by three hexagons and three pentagons placed next to each other alternately fold in the form of ball. Each carbon atom on the cage surface is bonded to three carbon neighbors therefore is sp2 hybridized. The chemical formula for fullerene is C_{20+2n}.

Fullerene

In fullerenes, 12 pentagonal rings are necessary and sufficient to form the cage closure. It is quite stable, breaking the balls requires temperature of about 1000C. Fullerene has high tensile strength and high packing density.

Applications:

➢ It is used in electrographic imaging, solar cells, non linear optical thin films etc..,
➢ Used to make carbon films, diodes, double layer capacitor and storage devices.
➢ Used for the conversion of diamond
➢ Used as gas sensors, temperature sensors, particle sensors and detection of organic vapors.

CARBON NANO TUBES: Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure having diameter of 1nm and longer than a micrometer. It is one dimensional material like nano wires. CNT is made up of graphite sheet. When the graphite sheet is rolled up hexagonally, it forms a tube like structure is called as CNT.

Types of CNT:

1. Single walled nanotubes (SWCNT): These are formed by rolling up of single graphite layer. Diameter is 1.4nm and length upto few micrometers.

graphene sheet   Roll-up   SWNT   MWCNT
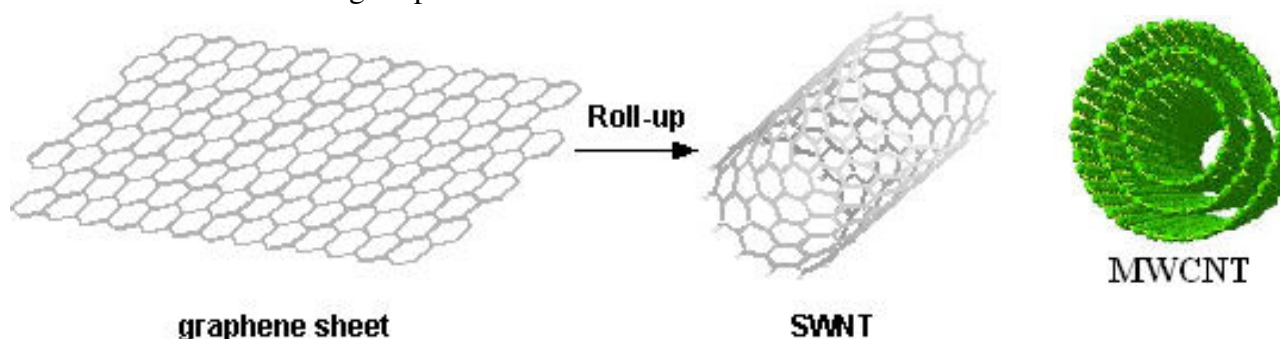
2. Multi walled nanotubes (MWCNT): These are formed by rolling up of two or more graphite layers. Diameter is from 30 to 50nm and length upto few micrometers.

Properties:

➢ CNTs have High Electrical Conductivity, Tensile Strength, Thermal Conductivity
        And flexibility and elasticity.

Applications: It can be used in

➢ Conductive plastics ,Structural composite materials, Flat-panel displays, Gas storage
Micro- and nano-electronics, Radar-absorbing coating, Batteries with improved lifetime,
Biosensors for harmful gases

NANO WIRES: Nanowires are one dimensional structure because one dimension is in micro scale and the rest two are in nano scale. The width of the nanowire is in the range of 1-100nm

whereas length can be more than nanoscale. Nano wires will be able to reduce the size of electronic devices in order to increase the efficiency.

Silicon Nanowires

Applications:
1.   Used in bio molecular nano sensors
2.   Used for metallic interconnections in nano quantum devices
3.   Used as additives for nano composites
4.   Used as photocatalysis to decompose organic molecules in polluted water

NANO RODS: Any elongated crystal structure is considered as nanorods. Nano rods are one dimensional nano structured. The aspect ratio of nano rods is less than 10. The aspect ratio is defined as the ratio of length of a particle to width of a particle. The length and width usually vary from 10 to 100nm.. Nano rods are very useful to study about the effect of size and shape on the magnetic, electronic, optical and chemical properties of materials at nano scale range.

Nano rod
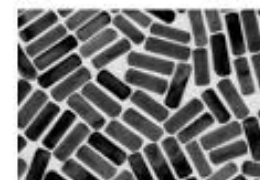
Applications:
1.   Nano rods of metal oxides like TiO_2, V_2O_5, CuO and MnO_2 are used in catalysis.
2.   They are used in gas sensors, video displays, and computer components.
3.   Nano rods absorb in the near IR and generate heat when excited with IR light. This property is used as cancer treatment to selectively kill cancer cells without affecting nearby healthy tissues.
4.   It is used as light emitting devices based on semi conducting material used.
5.   In display technologies, the reflectivity of the rods can be changed by changing their orientation with an applied electric field.

DENDRIMERS: Dendrimers are repetitively branched molecules. They have a central core with more than two functional groups to which branched molecules are added repeatedly step by step. Each addition of branches to a dendrimers is called as generation. A dendrimers can grow upto 10 -15 generations with size ranging from 1 to 25nm.

Dendrimers of lower generation posses more open structures as compared to higher generation dendrimers. The repetitive addition of branches leads to globular structure and becomes densely packed. Further growth is restricted due to lack of space.

Dendrimer generations

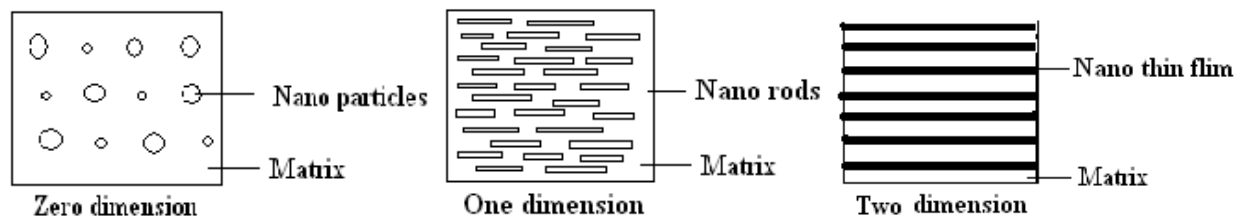G = 0   →   G = 1   →   G = 2   →   G = 3   →   G = 4
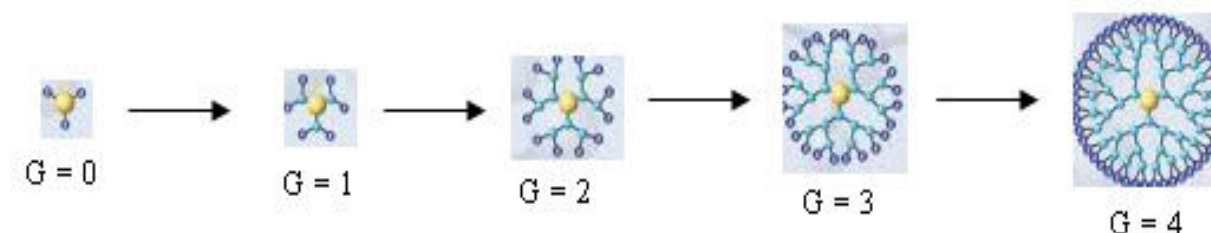
Applications:
1.   Dendrimers have less dense central core and large number of functional groups or outer surface. Both these sites can be used to accommodate drug of any size and for any type of delivery. Their surface can be further modified with addition of other bio responsive elements like lipids and fatty acids.

2.   They have nano scale spherical shape, which can move and diffuse easily through the human body. They are very quickly cleared by kidneys after the drug delivery.

3.   It is used as medical imaging agents in magnetic resonance imaging (MPI scan) of human body.

4.   Dendrimers themselves are biologically active and used as antiviral and anti microbial agents.

5.   It is used as coating agent to protect drug deliver it to specific sites in the body.

NANO COMPOSITE: Composite is a combination of two or more different materials that are mixed in an effort to blend the best properties of both. Nano composite material is obtained by inserting nano material into the matrix layer. Such material will have the properties of both nano particle and matrix. This allows the combination of properties in one material that would never exist together in nature. In nano composite particles are distributed in such a way that they do not touch each other. Nano composite materials are of three types, depending on the dimension and distribution of nano materials on to matrix

1.   Zero dimensions: In which isolated nano particles are distributed in matrix. Interaction between different particles is minimized by maintaining sufficient distance between particles.

2.   One dimension composites: In which nano tubes and nano rods are distributed in a matrix.

3.   Two dimension composites: In which thin nano films are placed between the two matrix layers.

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